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Synthesis and Structure of Moderately Stable Metallaoxetanes: $(\eta^5\text{-}C_5Me_5)_2(CH_3)\overline{TaOCHRC}H_2$ (R = H, C_6H_5). Investigations of Their Decomposition to Olefin and $(\eta^5\text{-}C_5Me_5)_2Ta(=O)CH_3$ and Evidence Revealing That They Are *Not* Intermediates in the Deoxygenation of Epoxides by $[(\eta^5\text{-}C_5Me_5)_2\dot{T}a(CH_3)]$

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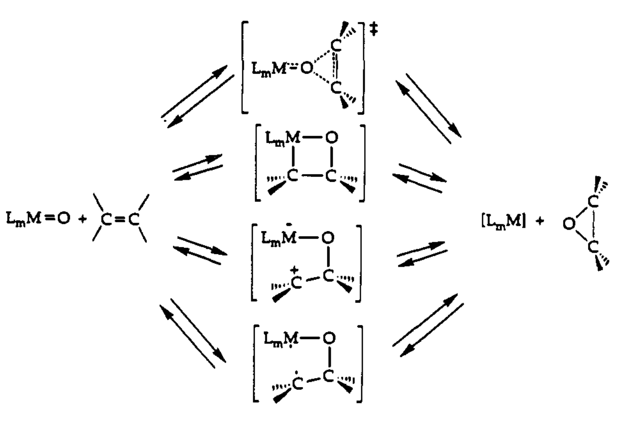
Abstract: Metallaoxetanes $Cp^*_2(CH_3)\overline{TaOCHRC}H_2$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$; R = H, $p\text{-}C_6H_4X$; X = H, Cl, CF_3, CN, NO_2) have been prepared by reaction of $Cp^*_2Ta({=}CH_2)CH_3$ with the appropriate aldehyde RCHO. The kinetic products of the 2 + 2 reaction between the benzaldehydes with $Cp^*_2Ta({=}CH_2)CH_3$ are *O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH(p\text{-}C_6H_4X)O}$, which rearrange in benzene solution at 25 °C to the more stable *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(p\text{-}C_6H_4X)C}H_2$. An X-ray crystal structure determination for *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$ has been carried out (space group $P2_1/c$ (No. 14) with cell parameters $a = 15.677$ (10) Å, $b = 9.502$ (4) Å, $c = 18.315$ (18) Å, $\beta = 110.81$ (7)°, $V = 2550.3$ (32) Å^3, and $Z = 4$), revealing a slightly puckered four-membered ring. The distortion from planarity likely arises from close contacts between a pentamethylcyclopentadienyl ligand and the phenyl ring. Decomposition of *O-anti*-$Cp^*_2(CH_3)\overline{TaOCHRC}H_2$ proceeds smoothly at 80 °C to afford $Cp^*_2Ta({=}O)CH_3$ and $RCH{=}CH_2$. The rates for styrene formation depend only slightly on the para substituent and do not correlate with σ or σ^+. In a related transformation, $Cp^*_2Ta({=}CH_2)H$ reacts with epoxides in THF even at −50 °C to yield $Cp^*_2Ta({=}O)CH_3$ and olefin. Significantly, neither *O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH_2O}$ nor *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH_2C}H_2$ is observed as an intermediate for the deoxygenation of ethylene oxide, and deoxygenation of *trans*-styrene-d_1 oxide, *trans*-ethylene-d_2 oxide and *cis*-ethylene-d_2 oxide proceed with >95% retention of stereochemistry. These results strongly implicate a concerted process and indicate that epoxide deoxygenation and (more importantly) olefin epoxidation with transition-metal oxo derivatives *need not* involve metallaoxetane intermediates.

The mechanisms of olefin epoxidation by transition-metal oxo compounds and its microscopic reverse, deoxygenation of epoxides by unsaturated metal complexes, have been debated extensively over the past several years.[1] Metallaoxetane intermediates commonly have been proposed, but a concerted mechanism or one mediated by a 1,4-biradical has been suggested for this process (eq 1). Polar intermediates have also been discussed.[1e,r,v–x]

2 + 2 cycloaddition of olefin to [M=O] to afford a metallaoxetane is certainly appealing by analogy to a common reaction pathway for olefins with transition-metal alkylidenes. Sharpless[1a] first proposed metallaoxetanes as possible intermediates in olefin epoxidation by chromyl chloride and subsequently considered them likely intermediates in olefin deoxygenation by W^{IV} and in olefin dihydroxylation by OsO_4. It should be noted, however, that in Sharpless' original paper in which he first suggests the intermediacy of metallaoxetane he cautions "...we have as yet no evidence which cannot also be rationalized by direct attack of olefin on the (oxo) ligands".[1a] Using theoretical methods, Rappé and Goddard[2] examined olefin epoxidation by chromyl chloride, and



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they concluded that a chromaoxetane is a likely intermediate. In an elegant series of experiments Groves and co-workers have shown that metallaoxetanes are unlikely intermediates in the epoxidation of olefins by oxo/porphyrin derivatives of iron and manganese[1b-e] and in the isomerization of chiral epoxides by ruthenium porphyrin complexes, although in the latter study facile homolysis of a Ru–C bond of the putative ruthenaoxetane was not ruled out.[11] Spurred by these recent experimental results, Drago and Cundari theoretically examined epoxidation by a model six-coordinate Ru^{IV} oxo complex and concluded that metallaoxetanes are probably *not* intermediates.[3] With regard to the microscopic reverse process, deoxygenation of epoxides, Mayer and co-workers recently concluded that a tungstenaoxetane is unlikely to mediate the deoxygenation of ethylene oxide by $WCl_2(CH_2{=}CH_2)_2(PMe_2Ph)_2$, since reaction with ethylene-d_4 oxide yields ethylene-d_4 in solution (only), not in the $W(O)Cl_2(CH_2{=}CH_2)(PMe_2Ph)_2$ coproduct.[4] Thus, metallaoxetanes appear to be gradually falling into disfavor. Jørgensen and Schiøtt have recently published an excellent review of this developing area of research.[5]

Whereas all attempts at direct observation of a metallaoxetane in these systems have failed, several stable metallaoxetanes have been reported, e.g., $L_2\overline{PtOC(CN)_2C}(CN)_2$ and $L_2(CO)X\overline{IrOC(CN)_2C}(CN)_2$[6,7] (L = PR_3, AsR_3; X = halogen), $Cp^*(PMe_3)\overline{IrOC(CH_3)_2C}H_2$,[8] and $(PMe_3)_4\overline{RuOC(CH_3)(C_6H_5)C}H_2$.[9] A route involving addition of diphenylketene to sources of reactive methylenetitanocene, $[(\eta^5\text{-}C_5H_5)_2Ti{=}CH_2]$, has been used successfully by Grubbs and co-workers to obtain $(\eta^5\text{-}C_5H_5)_2\overline{TiOC(=CPh_2)C}H_2$,[10] and very recently this same Wittig-like method has been shown to yield moderately stable molybdenaoxetanes and tungstenaoxetanes, $(Me_3CO)_2(ArN)\overline{MCH(CMe_3)CH(C_6F_5)O}$ (Ar = 2,6-$(CHMe_2)_2C_6H_3$; M = Mo, W).[11] The stability of these metallaoxetanes of Ti, Mo, and W is due, at least in part, to the relatively high energy C=C double bond generated should the Wittig-like reaction go to completion. Perhaps most relevant to the issue of metallaoxetanes and olefin oxidation is the iridaoxetane $[(\overline{C_8H_{12}O)Ir}(P_3O_9)]^{2-}$ recently reported as a product of the reaction between a cyclooctadiene complex and dioxygen.[12]

The permethyltantalocene $[Cp^*_2Ta]$ (Cp^* = $(\eta^5\text{-}C_5Me_5)$) moiety has proven to be a versatile framework for stabilizing normally reactive intermediates and for studying migratory insertion processes.[13-17] The methylene derivatives $Cp^*_2Ta({=}CH_2)H$ and $Cp^*_2Ta({=}CH_2)CH_3$ provided us a logical synthetic entry to tantalaoxetanes using the Wittig-like route, which proved successful with the titanium, molybdenum, and tungsten alkylidenes (vide supra). Herein we report the synthesis of moderately stable representatives, *O-syn-* and *O-anti-*$Cp^*_2(CH_3)\overline{TaOCHRC}H_2$ (R = H, *p*-C_6H_4X; X = H, Cl, CF_3, CN, NO_2), along with the results of an X-ray crystal structure determination for *O-anti-*$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$. We have also investigated the reactions of $[Cp^*_2Ta{-}CH_3]$ (in equilibrium with $Cp^*_2Ta({=}CH_2)H$) with epoxides to yield $Cp^*_2Ta({=}O)CH_3$ and olefin. Our results indicate that this deoxygenation reaction is mediated *neither* by the tantalaoxetane *nor* by the 1,4-biradical $[Cp^*_2(CH_3)Ta^{\bullet}{-}OCH_2CHR^{\bullet}]$. Thus, an important implication from our work is that olefin epoxidation may proceed by a concerted mechanism.

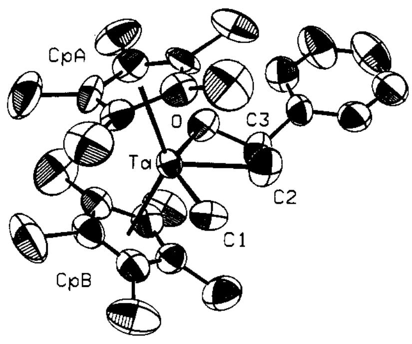

Figure 1. ORTEP drawing of *O-anti-*$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$.

Results and Discussion

Synthesis and Characterization of Tantalaoxetanes. We first attempted to prepare a tantalaoxetane via the Wittig-like pathway[18] utilizing $Cp^*_2Ta({=}CH_2)H$;[14] however, facile α migratory insertion, which generates 16-electron $[Cp^*_2Ta{-}CH_3]$, presents a complication. The products obtained from reaction with formaldehyde or benzaldehyde appear to be simple aldehyde adducts of the methyl derivative, $Cp^*_2Ta(CH_3)(\eta^2\text{-}OCHR)$ (R = H, C_6H_5).[19] In order to encourage the desired 2 + 2 addition of the carbonyl to the $[Ta{=}CH_2]$ group, we switched to $Cp^*_2Ta({=}CH_2)CH_3$, since for this system we had shown that methyl α migratory insertion is a factor of 10^{10} slower than hydride.[13] Indeed, reaction of $Cp^*_2Ta({=}CH_2)CH_3$ with paraformaldehyde, benzaldehyde, and para-substituted benzaldehydes proceeds smoothly at room temperature in benzene or toluene solution to yield *O-syn-*$Cp^*_2(CH_3)\overline{TaCH_2CHRO}$ (eq 2).[20] It soon became apparent that rearrangement of this kinetic isomer to a more stable tantalaoxetane occurs readily in solution over the period of several hours at room temperature (eq 3).

The assignment of the positional isomerism for these two products (Table I) was possible only after an X-ray crystal structure determination for the thermodynamically more stable tantalaoxetane derived from $Cp^*_2Ta({=}CH_2)CH_3$ and benzaldehyde. The pentamethylcyclopentadienyl– and methyl–tantalum bonding are unexceptional (Figure 1 and Table II), and the tantalaoxetane ring is slightly puckered (deviations of the four atoms from coplanarity is ±0.16 Å; sum of internal angles is 354.0°). Slight puckering of the titanaoxetane and molybdenaoxetane rings has been ascribed to oxygen lone-pair donation to Ti in the former[8] and a distortion characteristic of square-pyramidal group 6 metallacyclobutanes for the latter.[9] We attribute the puckering of the tantalaoxetane ring to unfavorable steric interactions between the β-phenyl substituent and a $(\eta^5\text{-}C_5Me_5)$

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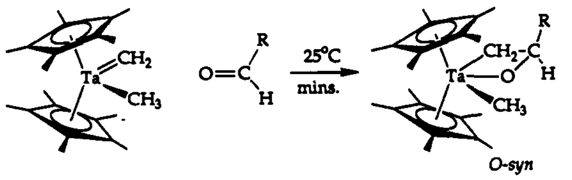
(19) $Cp^*_2Ta(CH_3)(\eta^2\text{-}OCH_2)$. ^1H NMR (benzene-d_6): δ 1.54 (s), $(C_5(CH_3)_5)_2$; 1.90 (s), $Ta(OCH_2)$; –0.07 (s), $TaCH_3$. $Cp^*_2Ta(CH_3)(\eta^2\text{-}OCHC_6H_5)$. ^1H NMR (benzene-d_6): δ 1.40 (s), $C_5(CH_3)_5$; 1.57 (s), $C_5(CH_3)_5$; 1.90 (s), $Ta(OCHC_6H_5)$; 6.5–7.5 (m), $Ta(OCHC_6H_5)$; 0.07 (s), $TaCH_3$.

(20) Reaction of $Cp^*_2Ta({=}CH_2)CH_3$ with acetaldehyde is not as clean as for paraformaldehyde or benzaldehydes; however, ^1H NMR spectra do suggest a tantalaoxetane is the major product. Reactions with ketones are not clean, and a multitude of uncharacterized products are formed. Another possible route to tantalaoxetanes was also explored briefly: reaction of $Cp^*_2Ta({=}CH_2)H$ with phenethyl alcohol does yield methane as expected (see ref 14); however, the 16-electron alkoxide $[Cp^*_2Ta{-}OCH_2CH_2C_6H_5]$ appears to undergo preferential β-H elimination to the aldehyde/hydride, $Cp^*_2Ta(H)(\eta^2\text{-}CHOCH_2C_6H_5)$, rather than the desired γ-H elimination to afford $[Cp^*_2(H)\overline{TaOCH_2C}H(C_6H_5)]$. *sec*-Phenethyl alcohol reacts to yield what appears to be the benzotantalaoxacyclopentene complex, $Cp^*_2(H)\overline{TaOCH(CH_3)C}_6H_4$, presumably via ortho metalation from the intermediate alkoxide $[Cp^*_2Ta{-}OCH(CH_3)(C_6H_5)]$. When the β-hydrogen and ortho phenyl hydrogens are completely eliminated, for example, by reaction of $Cp^*_2Ta({=}CH_2)H$ with *tert*-butyl alcohol, no reaction is observed.



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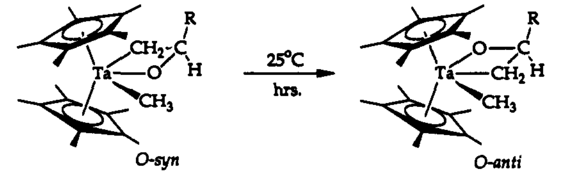


(3)

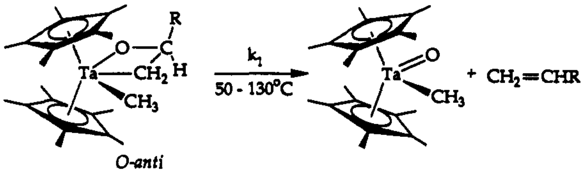
(R = H, p-C_6H_4X; X = H, Cl, CF_3, CN, NO_2)

ligand. In accord with this suggestion, both *O-syn*-$Cp^*_2(CH_3)TaCH_2CH_2O$ and *O-anti*-$Cp^*_2(CH_3)TaOCH_2CH_2$ display ^1H NMR spectra indicative of planar tantalaoxetane rings, even at −50 °C.

Isomerization of *O-syn*- to *O-anti*-Tantalaoxetanes. The mechanism for the process shown in eq 3 has been studied, albeit thus far in only a rather cursory way. Interestingly, the O-syn ⇄ O-anti isomerization proceeds spontaneously in the direction opposite of that observed for group 4 metallocene acyls.[21] Unfortunately, the measured rates for this process are not reproducible, being very sensitive to impurities,[22] so that a kinetic analysis was not undertaken. A retro 2 + 2 process involving reversible loss of olefin is excluded, since olefin loss is found to be totally irreversible (vide infra). The possibility of reverse 2 + 2 to regenerate aldehyde and $Cp^*_2Ta({=}CH_2)CH_3$ was examined by carrying out the isomerization of *O-syn*-$Cp^*_2(CH_3)TaCH_2CH(C_6H_5)O$ in the presence of either p-NCC_6H_4CHO or p-$CH_3C_6H_4CHO$. No incorporation of para-substituted aldehyde (or release of free C_6H_5CHO) is observed after conversion to *O-anti*-$Cp^*_2(CH_3)TaOCH(C_6H_5)CH_2$ (Scheme I).

Although we have been unable to elucidate the details of this mechanism, the most likely sequence appears to be heterolysis of the Ta–O bond[22] and reassociation of oxygen in the lateral position while the Ta–CH_2, CH_2–CHR and O–CHR bonds remain intact.

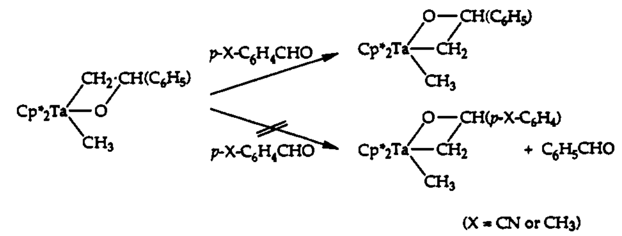
Thermal Decomposition of *O-anti*-$Cp^*_2(CH_3)TaOCHRCH_2$. When these tantalaoxetanes are heated in a variety of solvents (vide infra), they smoothly release olefin to generate the previously reported oxo methyl derivative $Cp^*_2Ta({=}O)CH_3$[14] (eq 4).



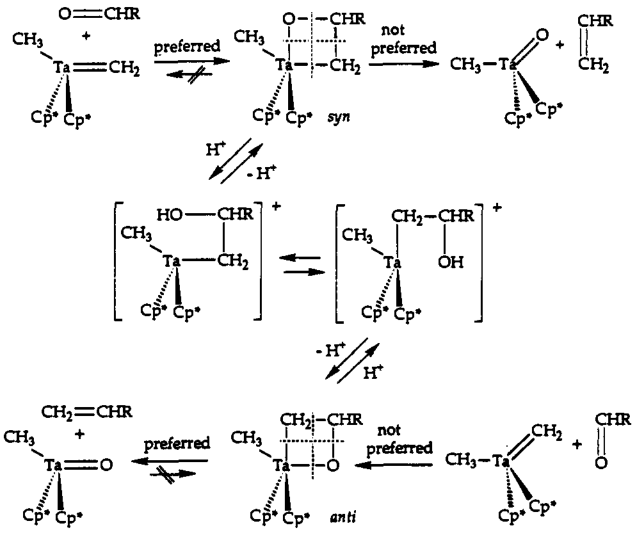
(4)

Since this process is the microscopic reverse for formation of the tantalaoxetane by reaction of an olefin with the [Ta=O] moiety of $Cp^*_2Ta({=}O)CH_3$, we have addressed the mechanism of this transformation, particularly for the variously para-substituted β-phenyl derivatives. As noted above, the rate of the O-syn → O-anti isomerization proved to be rather irreproducible and very sensitive to impurities. Thus, we first examined the effects of added acids and bases on the rate of reaction 4. As can be seen from the data of Table III, little effect is observed and no trend is apparent. Thus, acid or base catalysis does not appear to present a complication, and we proceeded with a kinetic study.

Scheme I

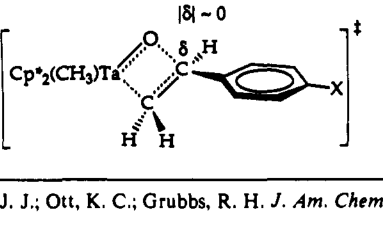


Scheme II



The decomposition of *O-anti*-$Cp^*_2(CH_3)TaOCH(C_6H_5)CH_2$ in toluene-d_8 exhibits well-behaved first-order kinetics over 3–4 half-lives, and activation parameters derived from rates measured over the range 53–131 °C are $\Delta H^\ddagger = 27.8\ (2)$ kcal·mol^{-1} and $\Delta S^\ddagger = 0\ (0.5)$ eu. The small value for $\Delta S^\ddagger$ compares favorably with that measured for 2 + 2 cleavage of $Cp_2TiCH_2CH(CMe_3)CH_2$ ($\Delta S^\ddagger$ = 9 eu),[23] $(Me_3CO)_2(ArN)MoCH(CMe_3)CH(C_6F_5)O$ (−16 eu), and $(Me_3CO)_2(ArN)WCH(CMe_3)CH(C_6F_5)O$ (−7 eu).[9] Although our study of the effect of solvent polarity was limited somewhat by the reactivity of these compounds, over the range of dielectric constants (ε = 2.21, 2.28, 20.7, and 36.2 at 25 °C) for benzene-d_6, dioxane-d_8, acetone-d_6, and acetonitrile-d_3, respectively, essentially no effect is observed (Table IV). Curiously, although their dielectric constants fall in this same range (ε = 9.1 and 4.8 at 25 °C), methylene-d_2 chloride and chloroform-d_1 promote much faster rates. The nature of this rate acceleration is not clear; however, it is noteworthy that addition of the radical trap, nitrosobenzene, slows considerably the rate for reaction 4 in chloroform, suggesting that a radical chain may be initiated in chlorinated solvents. Nonetheless, the small variation in k_1 observed in benzene, dioxane, acetone, and acetonitrile indicates little polarity in the transition state.

Little charge development in the transition state for reaction 4 is also indicated by the very small dependence of k_1 on the nature of the para substituent for the tantalaoxetanes *O-syn*-$Cp^*_2(CH_3)TaCH_2CH(p\text{-}C_6H_4X)O$ (X = H, Cl, CF_3, CN, NO_2) (Table V). As can be seen, the change in rate does not correlate linearly with σ_{para} or with σ^+, and the slowest and fastest rates differ by less than a factor of 7.



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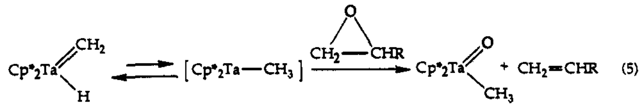
[22] Added weak acids (e.g., methanol or benzoic acid) or bases (e.g., 2,6-lutidine) greatly accelerate this isomerization. Whereas acid catalysis is easily envisioned, proceeding through the cation, $[Cp^*_2Ta(CH_3)(\eta^1\text{-}CH_2CHROH)]^+$, we presently do not have a viable suggestion for the mechanism of base catalysis.

[23] Lee, J. J.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

An interesting feature of the reaction sequence involving addition of aldehydes to the [Ta$=$CH$_2$] moiety of $\mathrm{Cp^*_2Ta({=}CH_2)CH_3}$, isomerization of the kinetic tantalaoxetane *O-syn*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CHRO}}$ to *O-anti*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCHRCH_2}}$, and final decomposition to olefin and $\mathrm{Cp^*_2Ta({=}O)CH_3}$ is the strongly preferred direction for the 2 + 2 addition of aldehyde and retro 2 + 2 elimination of olefin within the wedge of the permethyltantalocene. As illustrated in Scheme II, the preferred direction for 2 + 2 addition of aldehyde is from the center of the wedge. The principle of microscopic reversibility thus dictates the retro 2 + 2 elimination of aldehyde will proceed preferentially from the center of the wedge. Whereas this preference does not apply to the retro 2 + 2 loss of olefin, the similarity of the two processes is suggestive that the latter would also prefer to proceed from the center, rather than lateral, position of the permethyltantalocene unit. Hence, we may rationalize the tortuous pathway followed: addition of aldehyde to $\mathrm{Cp^*_2Ta(CH_3)({=}CH_2)}$ to afford the kinetic isomer, *O-syn*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CH(C_6H_5)O}}$, then rearrangement to *O-anti*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)CH_2}}$, and finally retro 2 + 2 loss of olefin from the central position. Similar observations concerning the preferred geometries for retro 2 + 2 loss of olefin from tungstenacyclobutanes have recently been reported by Schrock and co-workers.[24]

Deoxygenation of Epoxides by $\mathrm{Cp^*_2Ta({=}CH_2)H}$. The exothermic decomposition of *O-anti*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)CH_2}}$ to $\mathrm{Cp^*_2Ta({=}O)CH_3}$ and olefin is, of course, an indication that the tantalaoxetanes are not accessible from reaction of $\mathrm{Cp^*_2Ta({=}O)CH_3}$ with olefins, nor is it likely that olefin epoxidation could be effected with this system. The very high Ta$=$O bond energy is undoubtedly the main contributing factor for these thermodynamic preferences. On the other hand, deoxygenation of epoxides by 16-electron [$\mathrm{Cp^*_2Ta{-}CH_3}$] did appear feasible. It occurred to us that should this reaction proceed cleanly, we could probe olefin epoxidation via the microscopic reverse process. Thus, we have investigated the reactions of $\mathrm{Cp^*_2Ta({=}CH_2)H}$, a precursor to [$\mathrm{Cp^*_2Ta{-}CH_3}$], with epoxides.

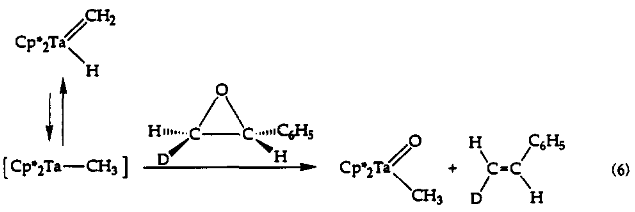
Indeed, reaction of ethylene oxide or styrene oxide with $\mathrm{Cp^*_2Ta({=}CH_2)H}$ cleanly affords ethylene or styrene and $\mathrm{Cp^*_2Ta({=}O)CH_3}$ (eq 5). These reactions are very rapid, and no intermediates are observed when the reaction with ethylene oxide is monitored by ^{1}H NMR spectroscopy at room temperature in benzene-d_6, or at −50 °C in THF-d_8. Significantly, whereas the tantalaoxetanes *O-syn*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CH_2O}}$ and *O-anti*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH_2CH_2}}$ are stable under the reaction temperatures for deoxygenation of ethylene oxide, neither is observed as an intermediate.[25] In order to ensure that ethylene oxide was not somehow catalyzing the decomposition of *O-syn*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CH_2O}}$ or *O-anti*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH_2CH_2}}$, the isomerization and decomposition (79 °C) of *O-syn*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CH_2O}}$ was carried out in the presence of 15 equiv of ethylene oxide, and the rate was found within experimental error to be the same as that without ethylene oxide. Thus, we conclude that tantaloxetanes do not mediate the deoxygenation of epoxides by [$\mathrm{Cp^*_2Ta{-}CH_3}$].



(5)

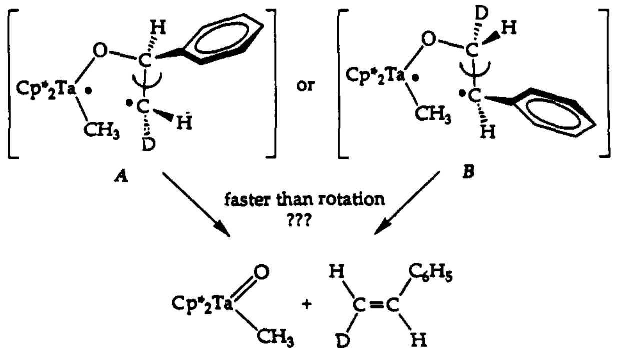
Having ruled out a mechanism involving a tantalaoxetane intermediate, we considered two alternatives most likely: (1) a concerted abstraction of oxygen from the epoxide, and (2) a mechanism proceeding via a 1,4-biradical of the type [$\mathrm{Cp^*_2(CH_3)Ta^{\cdot}{-}OCH_2CH_2^{\cdot}}$].[26] A restriction is placed on the second option: decomposition of the biradical must yield $\mathrm{Cp^*_2Ta({=}O)CH_3}$ *without collapse to tantalaoxetane*. Nonetheless, this alternative is attractive by analogy to the mechanism proposed for the deoxygenation of epoxides by titanocene. Grubbs and Wheeler[27] found that reaction of [$(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Ti}$], generated by low-temperature photolysis of $(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{\overline{TiCH_2CH(CMe_3)CH_2}}$, reacts with either *cis*- or *trans*-styrene-d_1 oxide to yield (in both cases) a 1:1 mixture of *cis*- and *trans*-styrene-d_1. Schobert reported that titanocene, generated in situ from $(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{TiCl_2}$ and magnesium in THF at 25 °C, affords olefins with some loss of stereochemistry in the deoxygenation of *cis*-epoxides.[28] A radical process similar to that suggested above was suggested to account for loss of stereochemistry.

Treatment of *trans*-styrene-d_1 oxide with $\mathrm{Cp^*_2Ta({=}CH_2)H}$ produces only $\mathrm{Cp^*_2Ta({=}O)CH_3}$ and *trans*-styrene-d_1 (>95% ^{1}H NMR) (eq 6).



(6)

Thus, if a 1,4-biradical mediates the deoxygenation of styrene oxide, there is an additional restriction: not only must the biradical decompose to $\mathrm{Cp^*_2Ta({=}O)CH_3}$ without collapse to tantalaoxetane, but its decomposition must also occur more rapidly than rotation about the C–C bond of the intermediate. Should homolysis of the [O–CHD] bond of *trans*-styrene-d_1 oxide occur preferentially (to yield intermediate A), the barrier for rotation is expected to be very low, since a simple twirl of [$^{\cdot}$CHD] group around the C–C bond is all that is required. The observed retention of trans geometry would thus imply a concerted mechanism. On the other hand, the benzylic C–O bond is weaker, and hence it is more likely that the 1,4-biradical generated would be B. In the crowded wedge of the permethyltantalocene moiety there could, in fact, be a moderately large steric barrier for rotation of the benzylic radical center about the C–C bond. Thus, this complication resembles the situation for aliphatic 1,4-biradicals, for which alkyl substitution introduces a steric barrier sufficiently



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[24] Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.

[25] There are *four* possible isomers for the phenyl-substituted tantalaoxetane: *O-endo*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH_2CH(C_6H_5)O}}$, *O-exo*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)CH_2}}$, *O-endo*-$\mathrm{Cp^*_2(CH_3)\overline{TaCH(C_6H_5)CH_2O}}$, and *O-exo*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH_2CH(C_6H_5)}}$. Thus, it could be argued that one of the latter two possible tantalaoxetanes is an intermediate in the deoxygenation of styrene oxide. This ambiguity is not present, of course, for the putative tantalaoxetanes derived from ethylene oxide and $\mathrm{Cp^*_2Ta({=}CH_2)H}$.

[26] Stepwise mechanisms involving polar intermediates are considered less likely. As noted in the previous section, the decomposition of the tantalaoxetane *O-exo*-$\mathrm{Cp^*_2(CH_3)\overline{TaOCH(C_6H_4X)CH_2}}$ proceeds without charge development at the β-carbon.

[27] Wheeler, D. R. Ph.D. Thesis, California Institute of Technology, June 1990.

[28] Schobert, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 855. Nearly complete retention of stereochemistry was observed for *trans*-epoxides; however, direct deoxygenation by active Mg could be occurring in these reaction mixtures.

Table I. ^{1}H and ^{13}C NMR Data^a

assignment	^{1}H, ppm	^{13}C, ppm	$^1J_{CH}$, Hz
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH_2O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.67 (s)^b		
$\mathrm{TaCH_2C\mathit{H}_2O}$	5.56 (t), J_{ab} = 7 Hz		
$\mathrm{TaC\mathit{H}_2CH_2O}$	0.78 (t)		
$\mathrm{(C\mathit{H}_3)Ta}$	−0.19 (s)		
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH_2C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.64 (s)^b	11.0 (q)^c	127
$\mathrm{C_5(CH_3)_5}$		114.7 (s)	
$\mathrm{TaOCH_2C\mathit{H}_2}$	5.48 (t), J_{ab} = 7 Hz	20.3 (t)	132
$\mathrm{TaOC\mathit{H}_2CH_2}$	0.09 (t)	75.4	134
$\mathrm{(C\mathit{H}_3)Ta}$	−0.45 (s)	37.0 (q)	125
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH(C_6H_5)O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.64 (s)^b	11.9 (q)^{c,d}	127
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.55 (s)	11.3 (q)	127
$\mathrm{C_5(CH_3)_5}$		113.3 (s)	
$\mathrm{C_5(CH_3)_5}$		112.6 (s)	
$\mathrm{TaCH_2C\mathit{H}_a(C_6H_5)O}$	5.56 (dd)^e		
$\mathrm{TaC\mathit{H}_bH_cCH(C_6H_5)O}$	1.12 (dd), $^2J_{ab}$ = 9 Hz, $^2J_{ac}$ = 6 Hz, $^2J_{bc}$ = 12 Hz		
$\mathrm{TaCH_b\mathit{H}_cCH(C_6H_5)O}$	0.67 (dd)		
$\mathrm{TaCH_2CH(C_6H_5)O}$		f	
$\mathrm{TaCH_2CH(C_6H_5)O}$		81.7	138
$\mathrm{(C\mathit{H}_3)Ta}$	0.01 (s)	43.6	124
$\mathrm{TaCH_2CH(C_6\mathit{H}_{2o}H_3)O}$	7.77 (d)	127.3 (d)	158
$\mathrm{TaCH_2CH(C_6\mathit{H}_{2m}H_3)O}$	7.34 (t)	124.0 (d)	158
$\mathrm{TaCH_2CH(C_6\mathit{H}_pH_4)O}$	f	124.5 (d)	160
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH(C_6H_5)C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.61 (s)^b	11.8 (q)^{c,d}	127
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.57 (s)	10.3 (q)	127
$\mathrm{C_5(CH_3)_5}$		114.9 (s)	
$\mathrm{C_5(CH_3)_5}$		113.4 (s)	
$\mathrm{TaOC\mathit{H}_a(C_6H_5)CH_2}$	5.31 (dd)^e		
$\mathrm{TaOCH(C_6H_5)C\mathit{H}_bH_c}$	0.51 (dd), $^2J_{ab}$ = 9 Hz, $^2J_{ac}$ 6 Hz, $^2J_{bc}$ = 13 Hz		
$\mathrm{TaOCH(C_6H_5)CH_b\mathit{H}_c}$	0.17 (dd)		
$\mathrm{TaOCH(C_6H_5)CH_2}$		30.0	132
$\mathrm{TaOCH(C_6H_5)CH_2}$		81.2	138
$\mathrm{(C\mathit{H}_3)Ta}$	0.01 (s)	35.6	120
$\mathrm{TaOCH(C_6\mathit{H}_{2o}H_3)CH_2}$	7.70 (d)	127.5 (d)	157
$\mathrm{TaOCH(C_6\mathit{H}_{2m}H_3)CH_2}$	7.37 (t)	124.4 (d)	158
$\mathrm{TaOCH(C_6\mathit{H}_pH_4)CH_2}$	f	124.9 (d)	155
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH(\mathit{p}\text{-}C_6H_4Cl)O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.62 (s)		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.52 (s)		
$\mathrm{TaCH_2C\mathit{H}_a(C_6H_4Cl)O}$	5.45 (m)		
$\mathrm{TaC\mathit{H}_bH_cCH(C_6H_4Cl)O}$	1.00 (m)^e		
$\mathrm{TaCH_b\mathit{H}_cCH(C_6H_4Cl)O}$	0.59 (m)		
$\mathrm{(C\mathit{H}_3)Ta}$	0.00 (s)		
$\mathrm{TaCH_2CH(C_6\mathit{H}_4Cl)O}$	7.42 (d)		
$\mathrm{TaCH_2CH(C_6\mathit{H}_4Cl)O}$	7.29 (d)		
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH(\mathit{p}\text{-}C_6H_4Cl)C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.59 (s)^g		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.52 (s)		
$\mathrm{TaOC\mathit{H}_a(C_6H_4Cl)CH_2}$	5.17 (m)		
$\mathrm{TaOCH(C_6H_4Cl)C\mathit{H}_bH_c}$	h		
$\mathrm{TaOCH(C_6H_4Cl)CH_b\mathit{H}_c}$	h		
$\mathrm{(C\mathit{H}_3)Ta}$	−0.31 (s)		
$\mathrm{TaOCH(C_6\mathit{H}_4Cl)CH_2}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH(\mathit{p}\text{-}C_6H_4CF_3)O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.63 (s)^g		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.50 (s)		
$\mathrm{TaCH_2C\mathit{H}_a(C_6H_4CF_3)O}$	5.47 (m)		
$\mathrm{TaC\mathit{H}_bH_cCH(C_6H_4CF_3)O}$	h		
$\mathrm{TaCH_b\mathit{H}_cCH(C_6H_4CF_3)O}$	h		
$\mathrm{(C\mathit{H}_3)Ta}$	0.00 (s)		
$\mathrm{TaCH_2CH(C_6\mathit{H}_4CF_3)O}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH(\mathit{p}\text{-}C_6H_4CF_3)C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.63 (s)		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.55 (s)		
$\mathrm{TaOC\mathit{H}_a(C_6H_4CF_3)CH_2}$	5.20 (m)		
$\mathrm{TaOCH(C_6H_4CF_3)C\mathit{H}_bH_c}$	1.05 (m)		
$\mathrm{TaOCH(C_6H_4CF_3)CH_b\mathit{H}_c}$	0.27 (m)		
$\mathrm{(C\mathit{H}_3)Ta}$	0.00 (s)		
$\mathrm{TaOCH(C_6\mathit{H}_4CF_3)CH_2}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH(\mathit{p}\text{-}C_6H_4CN)O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.59 (s)		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.47 (s)		
$\mathrm{TaCH_2C\mathit{H}_a(C_6H_4CN)O}$	5.35 (m)		
$\mathrm{TaC\mathit{H}_bH_cCH(C_6H_4CN)O}$	0.88 (m)		
$\mathrm{TaCH_b\mathit{H}_cCH(C_6H_4CN)O}$	0.50 (m)		
$\mathrm{(C\mathit{H}_3)Ta}$	−0.04 (s)		
$\mathrm{TaCH_2CH(C_6\mathit{H}_4CN)O}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH(\mathit{p}\text{-}C_6H_4CN)C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.60 (s)g		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.50 (s)		
$\mathrm{TaOC\mathit{H}_a(C_6H_4CN)CH_2}$	h		
$\mathrm{TaOCH(C_6H_4CN)C\mathit{H}_bH_c}$	h		
$\mathrm{TaOCH(C_6H_4CN)CH_b\mathit{H}_c}$	h		
$\mathrm{(C\mathit{H}_3)Ta}$	−0.30 (s)		
$\mathrm{TaOCH(C_6\mathit{H}_4CN)CH_2}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{syn}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaCH_2CH(\mathit{p}\text{-}C_6H_4NO_2)O}}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.60 (s)		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.50 (s)		
$\mathrm{TaCH_2C\mathit{H}_a(C_6H_4NO_2)O}$	h		
$\mathrm{TaC\mathit{H}_bH_cCH(C_6H_4NO_2)O}$	h		
$\mathrm{TaCH_b\mathit{H}_cCH(C_6H_4NO_2)O}$	h		
$\mathrm{(C\mathit{H}_3)Ta}$	0.00 (s)		
$\mathrm{TaCH_2CH(C_6\mathit{H}_4NO_2)O}$	6.5–7.5 (m)^i		
$O\text{-}\mathit{anti}\text{-}\mathrm{Cp^*_2(CH_3)}\overline{\mathrm{TaOCH(\mathit{p}\text{-}C_6H_4NO_2)C}}\mathrm{H_2}$			
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.58 (s)		
$\mathrm{C_5(C\mathit{H}_3)_5}$	1.50 (s)		
$\mathrm{TaOC\mathit{H}_a(C_6H_4NO_2)CH_2}$	5.10 (dd)		
$\mathrm{TaOCH(C_6H_4NO_2)C\mathit{H}_bH_c}$	h		
$\mathrm{TaOCH(C_6H_4NO_2)CH_b\mathit{H}_c}$	h		
$\mathrm{(C\mathit{H}_3)Ta}$	−0.35 (s)		
$\mathrm{TaOCH(C_6\mathit{H}_4NO_2)CH_2}$	7.48 (d) 8.15 (d)		

^{a}Spectra were recorded on a JEOL GX400Q (^{1}H, 399.78 MHz; ^{13}C, 100.38 MHz) spectrometer in benzene-d_6 and referenced to the residual proton of benzene-d_5 at 7.15 ppm, unless otherwise noted. ^{b}Toluene-d_8. ^{c}THF-d_8. ^{d}−20 °C. ^{e}H$_b$ and H$_c$ assignments based on coupling to H$_a$. ^{f}Obscured by solvent. ^{g}Recorded on EM390 spectrometer. ^{h}Not assigned. ^{i}Complex.

large that rotation becomes slow relative to decomposition to olefin products.[29]

In order to eliminate the latter equivocation, we have undertaken a stereochemical study of the deoxygenation of *cis*- and *trans*-ethylene-d_2 oxide. For this substrate the putative 1,4-biradical should have a rotational barrier of no greater than 2–3 kcal·mol^{-1}.[30] Unfortunately, a convenient, high-yield synthesis of the stereochemically labeled compounds of the purity required for use with

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(29) Dervan, P. B.; Santilli, D. S. *J. Am. Chem. Soc.* **1980**, *102*, 3863–3870.

(30) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York.

Table II. Selected Distances and Angles from the X-ray Crystal Structure Determination for *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$

atoms	distance, Å	atoms	distance, Å	atoms	distance, Å
Ta–C1	2.271 (12)	Ta–CpA	2.198	O–C3	1.436 (17)
Ta–C2	2.236 (14)	Ta–CpB	2.220	C2–C3	1.506 (20)
Ta–O	2.053 (8)				
atoms	**angle, deg**	**atoms**	**angle, deg**	**atoms**	**angle, deg**
Ta–C2–C3	91.1 (9)	CpA–Ta–C1	99.2	CpB–Ta–C2	111.2
C2–C3–O	99.2 (11)	CpA–Ta–C2	113.0	CpB–Ta–O	100.1
C3–O–Ta	100.9 (7)	CpA–Ta–O	98.0	C1–Ta–C2	71.4 (5)
O–Ta–C2	62.8 (4)	CpB–Ta–C1	96.4	O–Ta–C1	134.2 (4)
CpA–Ta–CpB	135.8				

Table III. Effect of Acids or Bases on the Rate of Decomposition of *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$ at 79 °C (Benzene-d_6)

run	k_1, $\times 10^5$ s^{-1}	run	k_1, $\times 10^5$ s^{-1}
nothing added-1	3.33 (5)	1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU)	3.14 (5)
nothing added-2	3.50 (5)	10% MeOH	3.51 (5)
acid-washed NMR tube	1.85 (5)	10% 2,6-lutidine	5.52 (5)
base-washed NMR tube	2.16 (5)	10% $C_6H_5CO_2H$	5.72 (5)
1,8-bis(dimethylamino)-naphthalene (Proton Sponge)	2.93 (5)	Ph_3PCH_2	6.21 (5)

Table IV. Solvent Effects on the Rate of Decomposition for *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2$ at 79 °C

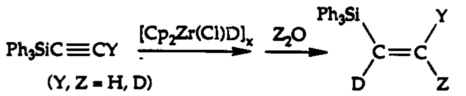
solvent	k_1, $\times 10^5$ s^{-1}	solvent	k_1, $\times 10^5$ s^{-1}
benzene-d_6	3.50	methylene-d_2 chloride	42.4
dioxane-d_8	3.67	chloroform-d_1	291
acetone-d_6	2.91	chloroform-d_1 + nitroso-benzene (ca. 0.1 equiv)	9.9
acetonitrile-d_3	3.07		

Table V. Para-Substituent Effects on the Rate of Decomposition for *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_4X)C}H_2$ at 79 °C (Benzene-d_6)

substituent	σ_{para}	σ^+	k_1, $\times 10^5$ s^{-1}
H	0.0	0.00	3.33; 3.51
p-Cl	0.23	0.11	4.19
p-CF_3	0.54		1.55
p-CN	0.66	0.66	0.66
p-NO_2	0.78	0.79	1.18

these sensitive permethyltantalocene derivatives was apparently lacking. Thus, the procedures outlined in eqs 7–11 were developed.

$$Ph_3SiC{\equiv}CH \xrightarrow{C_4H_9Li} \xrightarrow{D_2O} Ph_3SiC{\equiv}CD \qquad (7)$$



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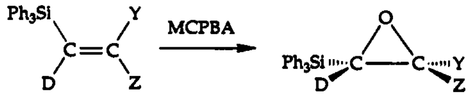

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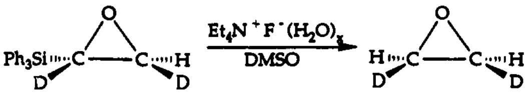
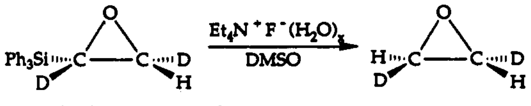


(10)



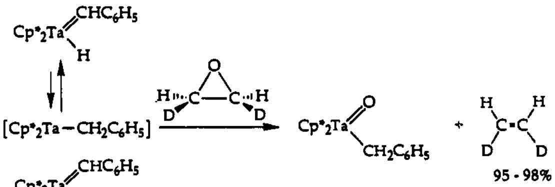
(11)

Deuteriozirconation of (triphenylsilyl)acetylene or (triphenylsilyl)acetylene-d_1, followed by treatment with either D_2O or H_2O, yields (*Z*)- or (*E*)-dideuterio(triphenylsilyl)ethylene, respectively.[31]

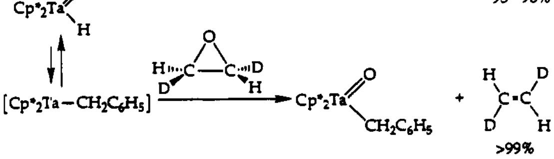
Oxidation of these with *m*-chloroperbenzoic acid[32] and fluoride cleavage of the triphenylsilyl group[33] proceed stereospecifically. It is important to use the triphenylsilyl rather than trimethylsilyl auxillary for two reasons: (1) the triphenylsilyl-substituted intermediates are white crystalline solids rather than high boiling oils, and (2) trimethylsilyl fluoride boils within 2 °C of ethylene oxide, making it very difficult to separate from product in the final step. The final products were passed through two traps at −78 °C and collected via a Toepler pump. This procedure affords *cis*- and *trans*-ethylene-d_2 oxide in high yields with isotopic and geometric purities in excess of 98% (MS, ^{1}H NMR, and IR).

Whereas infrared spectra for *cis*- and *trans*-ethylene-d_2 oxide in CCl_4 solution have been previously reported,[34] our spectra in the same solvent revealed several discrepancies.[35] Gas-phase infrared spectroscopy proved particularly informative, since there are regions in the spectra for each isomer that are clean and would easily reveal the presence of as little as 1–2% of the other isomer. Gas-phase IR spectra of the product ethylenes, *cis*- and *trans*-ethylene-d_2, were also diagnostic. Standard spectra were recorded from mixtures of commercially available samples.

Treatment of *cis*- or *trans*-ethylene-d_2 oxide with $Cp^*_2Ta({=}CHC_6H_5)$ yields $Cp^*_2Ta({=}O)CH_2C_6H_5$ and either *cis*-ethylene-d_2 (95–98%)[36] or *trans*-ethylene-d_2 (>99%) (eqs 12 and 13). These results strongly implicate a *concerted* mechanism for deoxygenation of epoxides by $[Cp^*_2Ta{-}R]$.



(12)



(13)

Conclusions

Metallaoxetanes may be sufficiently stabilized with the permethyltantalocene moiety to allow isolation and characterization. The Wittig-like route proved to be the most convenient synthetic entry. As expected for oxophilic tantalum, decomposition leads to olefin and the oxo derivative $Cp^*_2Ta({=}O)CH_3$, rather than to $R_2C{=}O$ and the alkylidene as is observed for late-transition

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[31] (a) Labinger, J. A. Hydrozirconation of C=C and C≡C, and Hydrometallation by Other Metals. In *Comprehensive Organic Synthesis*; Trost, B. M., Flemming, I., Eds.; Pergamon Press: London, in press. (b) Buchwald, S. L.; La Maire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

[32] Schwartz, N. N.; Blumbergs, J. H. *J. Org. Chem.* **1964**, *29*, 1976.

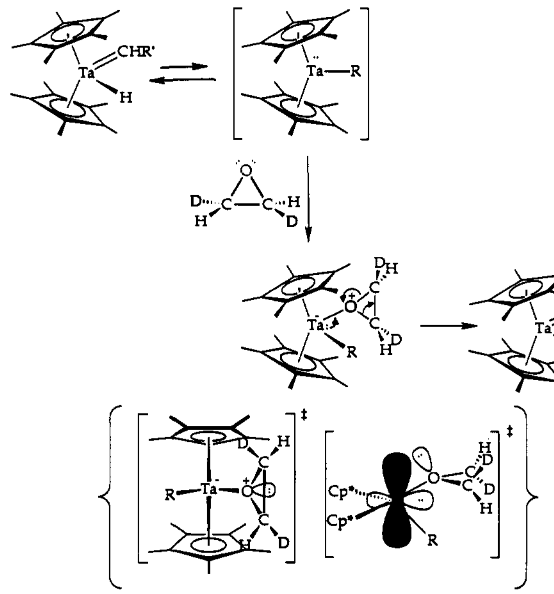
[33] Chan, T. H.; Lau, P. W. K.; Li, M. P. *Tetrahedron Lett.* **1976**, *31*, 2667.

[34] Price, C. C.; Spector, R. *J. Am. Chem. Soc.* **1966**, *88*, 4171.

[35] Some of the reported bands are absent in our spectra, and several of the reported bands should have been completely obscured by very strong solvent absorptions.

[36] The very small amount (1–5%) of *trans*-ethylene-d_2 is obtained in the reaction of *cis*-ethylene-d_2 oxide with $Cp^*_2Ta({=}CHC_6H_5)H$. Puzzling is our observation that in the complementary experiment <1% *cis*-ethylene-d_2 is formed in the reaction of *trans*-ethylene-d_2 oxide with $Cp^*_2Ta({=}CHC_6H_5)H$. There may be an impurity in the sample of *cis*-ethylene-d_2 oxide (but not in the sample of *trans*-ethylene-d_2 oxide) responsible for the small amount of isomerization.

Scheme III



metallaoxetanes.[8] Due to a strong preference for the 2 + 2 addition and elimination of the unsaturated group (aldehyde or olefin) to occur from the central rather than lateral position of the [$Cp^*_2Ta(=X)CH_3$] moiety (X = CH_2, O), isomerization of the kinetic isomer, *O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CHRO}$, to the more stable *O-anti*-$Cp^*_2(CH_3)\overline{TaOCHRCH_2}$ precedes elimination of olefin. Olefin loss occurs via a nonpolar transition state, very likely in a concerted manner.

The permethyltantalocene system not only permitted us to examine the structures and reactivity of these moderately stable metallaoxetanes, but also provided some important mechanistic information concerning epoxide deoxygenation, and hence, olefin epoxidation. The deoxygenation of epoxides by [Cp^*_2Ta–R] (R = CH_3, $CH_2C_6H_5$) proceeds rapidly, even at –50 °C, cleanly yielding the same two products obtained by thermolysis of the tantalaoxetanes: olefin and $Cp^*_2Ta(=O)CH_3$ or $Cp^*_2Ta(=O)CH_2C_6H_5$. Significantly, the latter process is not mediated by the tantalaoxetanes. The retention of cis or trans geometry, even for the dideuterioethylene oxides, strongly supports a concerted mechanism, i.e., formation of the [Ta=O] double bond simultaneously with breakage of the two C–O bonds of the epoxide. The d^2, 16-electron [Cp^*_2Ta–R] moiety appears ideally suited to such a concerted oxygen abstraction, since coordination to tantalum via an oxygen lone pair orients the complex for simultaneous Ta–O π bond formation and cleavage of both C–O bonds. The doubly occupied $1a_1$ orbital, the HOMO for [Cp^*_2Ta–R], is particularly well positioned for this concerted step (Scheme III). These results indicate that epoxide deoxygenation, and its microscopic reverse, olefin epoxidation, (1) need not proceed via a metallaoxetane intermediate, (2) need not proceed by a biradical pathway, and, thus, (3) may be concerted. Since the permethyltantalocene system appears ideally suited to carry out this process in a concerted manner, the implications as regards other systems are not yet clear. As has been shown by Groves and co-workers, biradicals *are* likely intermediates in olefin epoxidation and isomerization of chiral epoxides catalyzed by iron or ruthenium porphyrin complexes. Whereas there is still no direct evidence for the intermediacy of a metallaoxetane in olefin epoxidation or epoxide deoxygenation, we are reluctant to rule this pathway out in other systems, given that a variety of mechanisms often compete in reactions involving organotransition metal compounds.

Experimental Section

General Considerations. All manipulations of air-sensitive compounds were carried out with glovebox, high-vacuum, or Schlenk line techniques described earlier.[37] Solvents were dried over $LiAlH_4$ or sodium benzophenone and stored over "titanocene". Benzene-d_6 and toluene-d_8 were dried over activated 4-Å molecular sieves and stored over "titanocene". 1,4-Dioxane-d_8 and acetonitrile-d_3 were also dried over 4-Å molecular sieves but stored over sodium benzophenone. Acetone-d_6 was both dried and stored over activated 4-Å molecular sieves. Chloroform-d_1 and methylene-d_2 chloride were washed with an aqueous KOH solution, dried over anhydrous magnesium sulfate and activated 4-Å molecular sieves, and stored over sodium benzophenone. Argon was purified by passage over MnO on vermiculite and activated molecular sieves.

NMR spectra were recorded on Varian EM-390 (^1H, 90 MHz), JEOL FX90Q (^1H, 89.56 MHz; ^{13}C, 22.50 MHz), and JEOL GX400Q (^1H, 399.78 MHz; ^{13}C, 100.38 MHz) spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. All elemental analyses were conducted by either Lawrence Henling or Fenton Harvey of the Caltech Analytical Laboratory.

Paraformaldehyde, *p*-(dimethylamino)benzaldehyde, *p*-methylbenzaldehyde, *p*-chlorobenzaldehyde, *p*-methoxybenzaldehyde, *p*-cyanobenzaldehyde, potassium hydride, silver hexafluorophosphate, benzophenone, styrene oxide, benzylidenemethylamine, *sec*-phenethyl alcohol, phenethyl alcohol, α,α,α-trifluoro-*p*-tolualdehyde, (triphenylsilyl)acetylene, *n*-butyllithium, deuterium oxide, Cp_2ZrCl_2, tetraethylammonium fluoride, trimethylphosphine, and nitrosobenzene were used as obtained from Aldrich with further purification. Benzaldehyde (Spectrum or MC/B), *p*-nitrobenzaldehyde (Matheson), and acetaldehyde (Baker) were used as obtained from the companies indicated with further purification. Ethylene oxide (Matheson) was taken through at least two freeze/pump/thaw cycles directly prior to use. The *trans*-styrene-d_1 oxide was a generous gift from Dr. Dave Wheeler and was prepared from the reaction of *trans*-styrene-d_1 with *m*-chloroperbenzoic acid according to literature methods.[32] $Cp^*_2TaCl_2$,[13] $Cp^*_2Ta(=CH_2)H$,[14] $Cp^*_2Ta(=CH_2)CH_3$,[14] and $Cp^*_2Ta(=CHC_6H_5)H$[38] were prepared as described previously. To facilitate filtrations in the hydrozirconation procedures, $LiAlD_4$ was purified by dissolving the soluble part of the commercially available (Aldrich) gray powder in dry diethyl ether, filtering, and removing solvent under vacuum to yield a pure white powder. $Cp_2Zr(D)Cl$ was prepared by the modified procedure described by Buchwald.[31b] *cis*- and *trans*-ethylene-d_2 standards were obtained from Cambridge Isotope Laboratories. Mass spectra of *cis*- and *trans*-ethylene-d_2 oxide were measured at the U.C. Riverside Mass Spectroscopy Facility.

***O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH_2O}$ and *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH_2CH_2}$.** The thermal instability of these compounds makes their isolation difficult, and they were therefore characterized spectroscopically. Treatment of $Cp^*_2Ta(=CH_2)CH_3$ (15 mg, 0.03 mmol) with excess paraformaldehyde (40 mg, 1 mmol) in benzene-d_6 resulted in clean conversion to *O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH_2O}$ in approximately 10 min. The isomerization to *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH_2CH_2}$ was observed over a period of several hours at room temperature. (^1H NMR; see Table I).

***O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH(C_6H_5)O}$.** A slurry of $Cp^*_2Ta(=CH_2)CH_3$ (480 mg, 1 mmol) and 10 equiv of benzaldehyde (1 mL, 10 mmol) in ≈10 mL of toluene was stirred in a Schlenk tube at room temperature for 1 h. The solvent and excess benzaldehyde were removed under vacuum. Toluene was transferred onto the oily solid, stirred, and removed again under vacuum. This process was repeated twice more to help remove all of the benzaldehyde. The solid was dissolved in the minimum amount of toluene, and petroleum ether was added. Cooling the solution to –78 °C and removal of the mother liquor via cannula resulted in a light brown precipitate. The remaining volatiles were removed under vacuum, and the solid was washed several times with cold petroleum ether and dried in vacuo to yield 330 mg (56%, 1st crop) of *O-syn*-$Cp^*_2(CH_3)\overline{TaCH_2CH(C_6H_5)O}$. Anal. Calcd for $C_{29}H_{41}OTa$: C, 59.37; H, 7.06. Found: C, 59.63; H, 6.73.

***O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)CH_2}$.** Gentle warming (50 °C) of a Schlenk flask containing a solution of $Cp^*_2Ta(=CH_2)CH_3$ (250 mg, 0.5 mmol) and 10 equiv of benzaldehyde (0.5 mL, 5 mmol) in ≈10 mL of toluene for 4 h, followed by a workup similar to that described above for the syn isomer, resulted in isomerically pure *O-anti*-$Cp^*_2(CH_3)\overline{TaOCH(C_6H_5)CH_2}$ (115 mg first crop, 40% yield). Anal. Calcd. for $C_{29}H_{41}OTa$: C, 59.37; H, 7.06. Found: C, 59.15; H, 6.91. The para-substituted derivatives were prepared by procedures directly analogous to those above.

X-ray Crystal Structure Determination for *O-anti*-$Cp^*_2(CH_3)$-

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(37) *Organometallic Compounds*; Wayda, A. L.; Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(38) Trimmer, M. S. Ph.D. Thesis, California Institute of Technology, June 1989.

$\mathrm{\overline{TaOCH(C_6H_5)C}H_2}$. A colorless crystal was mounted in a greased capillary. Oscillation and Weissenberg photographs showed the crystal to be twinned, with a maximum difference in orientation of nearly 2°. The crystal was then centered on a CAD-4 diffractometer. Unit cell parameters and an orientation matrix were obtained by a least-squares calculation from the setting angles of 24 reflections with $10° < 2\theta < 25°$. One data set out to a 2θ of 40° was collected by an ω scan of $(1.8 + 0.35 \tan \theta)°$ width. The data were corrected for absorption and a slight decay and adjusted by Lorentz and polarization factors. Systematic absences in the diffractometer data led to the choice of space group $P2_1/c$. Coordinates of the tantalum atom were obtained from a Patterson map; locations of the other non-hydrogen atoms were determined from successive structure factor–Fourier calculations. Hydrogen atom positions were determined from difference maps for the methyl group coordinated to the metal atom and by calculation for the remaining atoms. The methyl groups with calculated positions were modeled by six half-weight hydrogen atoms. All hydrogen atoms were given isotropic B values 20% greater than that of the attached atom. No hydrogen parameters were refined. The complete least-squares full matrix, consisting of spatial and anisotropic and isotropic thermal parameters for the non-hydrogen atoms and a scale factor, contained 280 parameters. A final difference Fourier map showed deviations ranging from −0.94 to +1.96 eÅ^{-3}. The larger peaks are near the tantalum atom and indicate imperfectly applied absorption corrections. The refinement converged with an R factor of 0.0544 (0.0370 for $F_o^2 > 3\sigma(F_o^2)$) and a goodness of fit of 1.47 for all 2368 reflections. The final parameters are listed in the supplementary material.

Calculations were carried out with programs of the CRYM Crystallographic Computing System and ORTEP. Scattering factors and corrections for anomalous scattering were taken from a standard reference.[39] $R = \sum|F_o - |F_c|| / \sum F_o$, for only $F_o^2 > 0$, and goodness of fit $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of data and p the number of parameters refined. The function minimized in least squares was $\sum w(F_o^2 - F_o^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Variances of the individual reflections were assigned based on counting statistics plus an additional term, $(0.014I)^2$. Variances of the merged reflections were determined by standard propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. The absorption correction was done by Gaussian integration over an $8 \times 8 \times 8$ grid. Transmission factors varied from 0.240 to 0.486.

The permethylcyclopentadienyl rings are bound normally to the tantalum atom with the metal to ring centroid distances of 2.198 and 2.200 Å and a ring centroid–tantalum–ring centroid angle of 135.8°. In the wedge between these rings lie the methyl group and the tantalaoxetane ring. The Ta–O and Ta–C distances in the oxetane are 2.053 (8) and 2.236 (14) Å, respectively. The O–Ta–C angle is only 62.8 (4)°. The tantalaoxetane ring is slightly puckered; the four atoms are within ±0.16 Å of being coplanar and the sum of the internal angles is 354.0°. The methyl group, 2.271 (12) Å from the tantalum, is also in the wedge. It is nearest the carbon of the oxetane, with a C–Ta–C angle of 71.4 (5)°. The remaining distances and angles are normal. There are no significant interactions between molecules.

$\mathrm{Ph_3SiC{\equiv}CD}$. A 1.6 M solution of *n*-BuLi (37.5 mL, 60 mmol) was slowly added to a stirring ether solution (80 mL) of $\mathrm{Ph_3SiC{\equiv}CH}$ (15.5 g, 55 mmol) while under an argon atmosphere. After the reaction mixture was allowed to stir for 30 min at room temperature, $\mathrm{D_2O}$ (1.1 mL, 60 mmol) was slowly added dropwise. The reaction mixture was filtered in air and the solvent removed on a rotary evaporator. The ^{1}H NMR spectrum indicated that there was ≤1% residual proton in the final product (13.5 g, 87% yield).

***trans*-$\mathrm{Ph_3SiCD{=}CHD}$.** Cold (−78 °C) methylene chloride (300 mL) was transferred into a large Schlenk flask containing $\mathrm{Cp_2Zr(D)Cl}$ (15.5 g, 60 mmol) and $\mathrm{Ph_3SiC{\equiv}CD}$ (15.5 g 54 mmol). The reaction mixture became a clear orange solution upon warming to room temperature with stirring. Removal of the solvent under vacuum followed by several petroleum ether (500 mL total) washings resulted in a yellow powder, presumably *trans*-$\mathrm{Cp_2Zr(CD{=}CDSiPh_3)Cl}$. The yellow powder was dissolved in $\mathrm{Et_2O}$ (200 mL) and cooled to 0 °C, and 1.5 mL (80 mmol) of $\mathrm{H_2O}$ was slowly added. The reaction flask was vented through a mercury bubbler, and evolution of some gas was observed. The white $\mathrm{[Cp_2ZrCl]_2O}$ precipitate was filtered off in air and washed with $\mathrm{Et_2O}$. The $\mathrm{Et_2O}$ solution was dried over $\mathrm{MgSO_4}$ and the solvent removed under vacuum. The product was purified by addition of charcoal to a pentane solution of the crude off-white solid, followed by gravity filtration and flash chromatography on Florisil (pentane eluant). The fractions were concentrated and cooled to −10 °C to induce formation of beautiful white crystals (11 g, 71% yield) of *trans*-$\mathrm{Ph_3SiCD{=}CHD}$.

***cis*-$\mathrm{Ph_3SiCD{=}CDH}$.** The procedure followed was analogous to the that used to prepare the trans isomer with the following exceptions: $\mathrm{Cp_2Zr(D)Cl}$ (16 g, 62 mmol) was treated with $\mathrm{Ph_3Si\text{-}C{\equiv}CH}$ (17 g, 60 mmol), followed by addition of $\mathrm{D_2O}$ (1.5 mL), resulting in *cis*-$\mathrm{Ph_3CD{=}CDH}$ (16 g, 94% crude yield). Recrystallization from pentane gave 13 g (76% yield) of *cis*-$\mathrm{Ph_3CD{=}CDH}$.

***trans*-$\mathrm{Ph_3Si\overline{CDCHDO}}$.** *trans*-$\mathrm{Ph_3SiCD{=}CHD}$ (10 g, 35 mmol) was added as a solid to a slurry of 50% MCPBA (18 g, 52 mmol) in $\mathrm{CHCl_3}$ (75 mL) in air. The reaction mixture became very hot and was solid after 2 h. Chloroform was added to break up the solid, followed by filtration and generous washings with chloroform. The $\mathrm{CHCl_3}$ solution was extracted five times with 5% $\mathrm{NaHCO_3}$, two times with 5% $\mathrm{NaHSO_3}$ and two times with 5% $\mathrm{NaHCO_3}$. Drying over $\mathrm{MgSO_4}$ and removal of the solvent under vacuum gave a yellow oil. The ^{1}H NMR spectrum of this oil indicated 50% starting material and 50% desired product. Consequently, the oil was dissolved in petroleum ether and then pumped on to remove the $\mathrm{CHCl_3}$. This procedure was repeated several times, whereupon a white solid that is insoluble in petroleum ether (product) resulted together with a petroleum ether soluble portion (starting material). The crude product so obtained was dissolved in a minimum of $\mathrm{CHCl_3}$, loaded onto a flash column (Florisil), and eluted with generous quantities of petroleum ether and then with $\mathrm{CHCl_3}$. The petroleum ether fractions contained *trans*-$\mathrm{Ph_3SiCD{=}CHD}$, which could be easily recovered by reducing the volume of the solvent and inducing crystallization by cooling. The final product, *trans*-$\mathrm{Ph_3Si\overline{CDCHDO}}$, was obtained by removal of the $\mathrm{CHCl_3}$ solvent under vacuum, washed several times with petroleum ether, and finally recrystallized from hot petroleum ether.

***cis*-$\mathrm{Ph_3Si\text{-}\overline{CDCDHO}}$.** The procedure followed was analogous to the procedure described above for the trans isomer with the following modifications: solid *cis*-$\mathrm{Ph_3SiCD{=}CDH}$ (15 g, 52 mmol) was added to a stirring slurry of 50% MCPBA (38 g, 75 mmol) in 75 mL of $\mathrm{CHCl_3}$. Similar workup gave 8 g (90% yield based on starting material consumed) of *cis*-$\mathrm{Ph_3Si\overline{CDCDHO}}$.

***trans*-Ethylene-d_2 Oxide.** A 50-mL heavy-walled glass reaction vessel with Kontes valve was charged with *trans*-$\mathrm{Ph_3\overline{CDCHDO}}$ (1.3 g, 4 mmol), $\mathrm{Et_4NF{\cdot}}x\mathrm{H_2O}$ (0.7 g, 4 mmol), and DMSO (10 mL). After being stirred at room temperature for 2 h the reaction mixture was frozen by cooling with liquid nitrogen, and the flask was evacuated. The gaseous product (88% yield) was collected by Toepler pump (through two −78 °C cooled traps) as the reaction flask warmed to room temperature. Mass spectra and a gas-phase IR spectrum (10-cm path) recorded in a cell equipped with NaCl windows, together with those for the cis isomer, are included in the supplementary material.

***cis*-Ethylene-d_2 Oxide.** The same procedure as that described above for the trans isomer was followed. The product was collected via Toepler pump in 77% yield.

Deoxygenation of Labeled Ethylene Oxides. Approximately 5 mL of toluene was vacuum transferred to a 25-mL glass reaction vessel equipped with a Kontes valve and charged with $\mathrm{Cp^*{}_2Ta({=}CHC_6H_5)H}$ (500 mg, 1 mmol). *trans*-Ethylene-d_2 oxide (125 Torr, 0.7 mmol in a 104-mL gas bulb) was condensed into the reaction flask at −196 °C. To ensure complete reaction, the mixture was stirred at room temperature for 5 days. The reaction flask was cooled back to −196 °C, and the gaseous products were collected via Toepler pump, through two cold traps at −78 and −115 °C (10:1 EtOH/MeOH), as the reaction mixture warmed to room temperature. When transfer of the toluene into the −78 °C trap was complete, ≥99% (by IR, vide supra) *trans*-ethylene-d_2 (85% yield) had been collected by the Toepler pump. The same procedure was followed for the cis isomer and resulted in ≥95% (by IR) *cis*-ethylene-d_2 in approximately the same yield.

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Supplementary Material Available: An ORTEP drawing and tables of crystal structure parameters, final non-hydrogen parameters, anisotropic thermal displacement parameters, assigned hydrogen parameters, and complete distances and angles for *O-anti*-$\mathrm{Cp^*{}_2(CH_3)\overline{TaOCH(C_6H_5)C}H_2}$ and gas-phase infrared spectra and mass spectra for *trans*- and *cis*-ethylene-d_2 oxide (9 pages). Ordering information is given on any current masthead page.

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(39) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 71, 149.