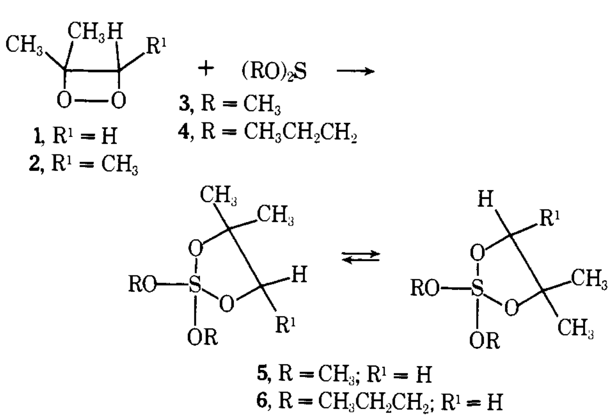

age. The reason for the difference in modes of decomposition of **5** and **6** is not clear. It appears that **5** decomposes by some sort of chain reaction whereas **6** decomposes by an intramolecular path. It does not seem reasonable that electronic effects can account for this difference, and steric interactions may be responsible for the change in reaction course.

Reactions of diphenyl sulfide, **7**, with **1** at low temperature led to the production of diphenyl sulfoxide and isobutylene oxide. These products could arise from a sulfurane or a zwitterion(s). Reaction of **7** with **2** yielded trimethylethylene oxide, diphenyl sulfoxide, and diphenyl sulfone. In a separate experiment it was shown that diphenyl sulfoxide reacts with **2** to give diphenyl sulfone and trimethylethylene oxide. The dioxetane **2**, is considerably more stable than **1** and thus it survives long enough under the reaction conditions to react with diphenyl sulfoxide.

When dimethyl sulfide, tetrahydrothiophene, and trimethylene sulfide were allowed to react with **1** at −78°, exothermic reactions occurred which led to the destruction of **1** and with the production of nonvolatile residues. Virtually none of the sulfides were consumed in this process.

Dimethyl sulfide and tetrahydrothiophene reacted with **2** to give 3-hydroxy-3-methyl-2-butanone. This process is similar to that observed by Kornblum[8] for the base catalyzed decomposition of peroxides and hydroperoxides bearing α-hydrogens. Wasserman and Saito[6] have investigated the decomposition of dioxetanes by diphenyl sulfide.

The results of this study show that there is a multiplicity of reaction paths for the reactions of divalent sulfur compounds with dioxetanes. The inherent instability of **5** and **6** suggests that more electronegative groups will have to be introduced to achieve greater stabilization.

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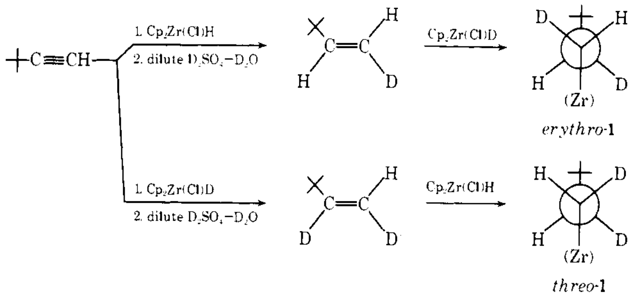
Electrophilic Cleavage of the Carbon–Zirconium(IV) Bond. Comparison and Contrast with Other Transition Metal Alkyl Systems

Sir:

Mechanisms for electrophilic cleavage of the carbon–metal bond in transition metal alkyls can be elucidated by observing the stereochemical consequences, at carbon, of the cleavage process.[1] A point of recurrent interest in this area deals with the mechanism that leads to *inversion* of configuration at carbon in the electrophilic cleavage by halogen of alkyliron[1] and -cobalt[2] complexes. In these cases, there is evidence that oxidation of the complex followed by backside nucleophilic attack by halide ion[3,4] occurs, rather than backside electrophilic attack by the halogen molecule (S_E2 (open) mechanism). We have previously observed that bromination of di(η^5-cyclopentadienyl)(chloro)alkylzirconium(IV) complexes yields alkyl bromides.[5] It appeared worthwhile to examine the stereochemistry, at carbon, of certain electrophilic cleavage reactions, since, for these d^0 species, routes involving oxidation are unlikely. Indeed, we find that the stereochemical course at carbon for cleavage reactions involving Zr(IV) alkyls differs from that observed for other transition metal alkyls in several key instances.

The alkyl group which has proved to be most useful for the study of cleavage reactions of metal alkyls is (*erythro*- or *threo*-)$(CH_3)_3CCHDCHD$, since the stereochemistry at carbon of the process can be monitored directly by NMR.[1] The Zr(IV) complexes of this moiety can be easily prepared by addition of a suitably deuterated olefin to the hydride (or deuteride) $(\eta^5\text{-}C_5H_5)_2Zr(Cl)X$ (X = H or D).[5,6] Interestingly, the deuterated olefin is also prepared using the same hydride (reaction 1). This route to diastereomeric transition metal alkyls is much faster and more convenient than those previously employed.[1] The ^{1}H NMR spectral parameters[7] of **1** are shown in Table I.[8]



$$Cp = \eta^5\text{—}C_5H_5;\ (Zr) = (\eta^5\text{—}C_5H_5)_2Zr(Cl)\text{—} \quad (1)$$

Table I. NMR parameters[7] of $(CH_3)_3CCH_BDCH_AD(X)Zr(Cl)Cp_2$

X	δ_{H_A}	δ_{H_B}	$\delta_{(CH_3)_3}$	δ_{Cp}	$J_{H_1H_2}$ (Hz) (erythro)	$J_{H_1H_2}$ (Hz) (threo)
...	*a*	1.38	0.85	5.88	12.9	4.2
CO	2.85	1.66	0.92	5.71	11.7	5.0
SO_2	2.37	1.50	0.74	6.10	12.5	4.8
O	3.90	1.30	0.82	6.01	8.8	6.0

[a] Hidden by $(CH_3)_3$ peak.

Treatment of a benzene solution of **1** with an equivalent amount of Br_2 at 10° yields, after work-up by treatment with aqueous $NaHCO_3$ followed immediately by rapid, reduced pressure distillation at room temperature, the alkyl bromide resulting from *retention* of configuration at carbon. The unavailability, therefore, of an oxidation mechanism changes the stereochemical course of the cleavage reaction from that found with other, oxidizable transition metal complexes. A closed transition state, such as that proposed for halogenation of organomercurials,[9] is a reasonable one to account for retention at carbon. The availability of a vacant, low-lying orbital on Zr in these "16-electron" complexes[10] may facilitate frontside attack[9] on the C-Zr bond. Reaction of **1** with *N*-bromosuccinimide, which also gives good yields of alkyl bromides,[5] and iodination with I_2, both proceed with retention at carbon.

Because halogenation of the C-Zr(IV) bond proved to be mechanistically different from that of other transition metal alkyls, several other cleavage reactions were examined for comparison with results reported for other metal alkyls. Insertion of CO to give the acyl complex[11] proceeds with retention as is the case for all other systems reported.[1] Reaction with SO_2 is complex; $(\eta^5\text{-}C_5H_5)_2Zr(Cl)CH_3$ has been reported to add 2 equiv of SO_2 to give a highly insoluble product formulated as $(C_5H_5)(C_5H_5SO_2)Zr(Cl)(O_2SCH_3)$.[12] We find that addition of less than 1 equiv of SO_2 to a benzene solution of **1** gives rise to a new set of ^1H NMR peaks (Table I) consistent with formulation as an SO_2 insertion product, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)(O_2SCHDCHDC(CH_3)_3)$.[13] The values for $^3J_{HH}$ indicate that SO_2 insertion here proceeds with *retention* at carbon, in contrast to the reaction with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHDCHDC(CH_3)_3)$ which goes with >95% *inversion.* These results are in agreement with the mechanistic proposal of Wojcicki[14] that coordinatively saturated complexes react by direct backside attack of SO_2 on the alkyl group followed by rearrangement, resulting in inversion at carbon, while coordinatively unsaturated complexes such as Cp_2MRX (M = Ti, Zr) can coordinate SO_2 to the metal, followed by frontside attack on the alkyl giving retention.

Alkylzirconium complexes $Cp_2Zr(Cl)R$ can be converted to alcohols, ROH, using a variety of reagents,[15] including dry oxygen followed by acid hydrolysis. Such treatment of **1** gives the alcohol $(CH_3)_3CCHDCHDOH$ resulting from approximately one-half racemization and one-half retention of configuration. Loss of stereochemistry does not occur during hydrolytic work-up, since the initial product $Cp_2Zr(Cl)(OCHDCHDC(CH_3)_3)$[16] (Table I) has the same stereochemical composition. Reaction of cobalt alkyls with O_2 to give alkylperoxycobalt complexes proceeds with complete racemization and is thought to involve alkyl radical intermediates;[17] some nonradical pathway must be operating, as well, for zirconium alkyls. For example, the following scheme could account for the observed results.

$$R^*(Zr) + O_2 \longrightarrow R\cdot + \cdot OO(Zr) \longrightarrow ROO(Zr)$$

$$ROO(Zr) + R^*(Zr) \longrightarrow RO(Zr) + R^*O(Zr)$$

R^* = chiral alkyl
R = racemized alkyl
(Zr) = $(\eta^5\text{—}C_5H_5)_2Zr(Cl)\text{—}$

The above results clearly demonstrate that d-electron configuration plays a significant role in determining the mechanistic paths followed in reactions of transition metal alkyls. Further work to extend the range of reactions studied and to elucidate details of the mechanisms involved, specifically those for oxygenation, is in progress.

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Electrocyclic Reaction of the Cyclodecatrienyl Anion

Sir:

The number of electrocyclic reactions of carbanions which have been reported is limited.[1] In many cases no stereochemical information is available, but most cases in which it is seem to fall within the predictions based on orbital topology. We now report the preparation and direct observation of the cyclodecatrienyl anion (**1**) and its facile electrocyclization to the *cis*-bicyclo[5.3.0]deca-3,5-dien-2-yl anion (**2**),[2] a process not anticipated by orbital topology considerations.

Treatment of *cis*-bicyclo[6.2.0]deca-2,4,6-triene[3] (**3**) with 4 g-atoms of potassium in liquid ammonia cleanly produced the cyclodecatrienyl anion (**1**). The bicyclo[6.2.0]deca-1,3,5,7-tetraene dianion[4] was sometimes pro-