ORGANOZIRCONIUM COMPOUNDS IN ORGANIC SYNTHESIS: CLEAVAGE REACTIONS OF CARBON-ZIRCONIUM BONDS

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Abstract - Methods for synthesis of bis(cyclopentadienyl) organozirconium compounds are described. Cleavage mechanisms for these compounds are discussed and a unifying mechanism to account for a variety of cleavage processes is presented.

INTRODUCTION

Organozirconium compounds have been found to be useful intermediates in organic synthesis and to undergo intriguing reactions with ramifications for several aspects of catalysis. We describe herein methods for preparing bis-(cyclopentadienyl) organozirconium compounds; we also discuss in detail several typical cleavage reactions of these organozirconium compounds which make them useful in organic synthesis or as models for intermediates in catalytic processes.

HYDROZIRCONATION OF OLEFINS OR ACETYLENES

Several years ago we found that Cp₂Zr(H)Cl (Cp = η⁵-C₅H₅) would react with olefins or acetylenes under mild conditions to give the corresponding organozirconium c-bonded complex (Cp₂Zr(R)Cl, R = alkyl or alkenyl) in high yield (1). If acyclic olefins were employed, then the terminal zirconium alkyl was obtained regardless of the position of the double bond in the starting material (2); if acetylenes were used, then hydrozirconation was found to proceed stereospecifically cis with high regioselectivity for attachment of the zirconium-containing species to the sterically least hindered side of the triple bond (3).

C-Zr CLEAVAGE USING COMMON ELECTROPHILIC REAGENTS

It was observed that several types of electrophilic reagents (for example, Br₂, NBS, tert-C₅H₉OOH) reacted rapidly with Cp₂Zr(R)Cl to give an organic product (bromide or alcohol, respectively) in high yield. By this route it was possible to readily form carbon-heteroatom but not carbon-carbon bonds(1). An examination of the stereochemical course of this electrophilic cleavage reaction revealed this process to occur with retention of configuration at carbon (4). To account for this observation, a closed transition state was proposed. It is important to note that Cp₂Zr(R)Cl is a 16-electron,
coordinatively unsaturated species. It was suggested, by analogy with electrophilic cleavage processes described for organomercurials (5), that the cleavage reagent X-Y interacts with the zirconium atom via its sole low-lying valence orbital (6). Polarization of coordinated X-Y followed by a closed transition state generates the cleavage products. It may be that a closed transition state, which would lead to retention of configuration at carbon, is required to avoid build-up of positive charge on the Zr(IV) center.

\[
\text{Cp}_2\text{Zr}\text{Cl} \rightleftharpoons \text{Cp}_2\text{Zr}^+\text{Cl}^-
\]

**Retention**

**TRANSMETALATION: CLEAVAGE USING METALLIC ELECTROPHILES**

To circumvent the low tendency of \(\text{Cp}_2\text{Zr(R)Cl}\) to participate directly in carbon-carbon bond formation processes, the reaction between them and Lewis acidic metal halides was investigated. It was proposed that it should be possible to transfer an organic group from zirconium to a second metal center via a closed transition state analogous to the one described above for electrophilic cleavage. If this newly derived organometallic compound were able to undergo carbon-carbon bond forming processes, then through the sequence of hydridozirconation-transmetalation it would be possible to functionalize an olefin or an acetylene using a zirconium reagent, transfer the organic group to a second metallic species, and form a carbon-carbon bond using this second organometallic reagent. It has been found that such transmetalations occur when halides of Al (6), Hg(II) (8,9), Cu(I) (10), Pd(II) (10,11), Ni(II) (12,13), and Sn(IV) (14) are employed.

**CLEAVAGE USING METAL HYDRIDES: MIXED Zr-Al POLYHYDRIDES AND THE REDUCTION OF CO**

In contrast to the reaction between \(\text{Cp}_2\text{ZrCl}_2\) and \(\text{LiAlH}_4\) (which gives rise to \(\text{Cp}_2\text{ZrHCl}\)), treatment of \(\text{Cp}_2\text{ZrCl}_2\) with the electron-deficient species \(\text{i-Bu}_2\text{AlH}\) gives rise to a new type of hydridozirconium species, \(\text{Cp}_2\text{ZrH}_2\text{Al}_2\text{Cl}(\text{i-Bu}_2)_2\). In this compound two hydride ligands bridge the Zr and the two Al centers (15). It was also found (15) that the analogous compound \(\text{Cp}_2\text{ZrH}_2\text{Al}_2\text{R'}(\text{i-Bu}_2)_2\) could be prepared by reaction between the dialkyl complex \(\text{Cp}_2\text{ZrR}_2\) \((\text{R'} = \text{alkyl})\) and \(\text{i-Bu}_2\text{AlH}\). It was believed (16) that such polyhydrido mixed metal complexes might demonstrate reducing ability different from that displayed by \(\text{Cp}_2\text{ZrHCl}\) by virtue of the presence of two different metal centers in the cluster. Because of current interest in CO reduction, reaction between small molecule and mixed Zr-Al polyhydridic clusters was studied. It was observed that two equiv CO was taken up by \(\text{Cp}_2\text{ZrH}_2\text{Al}_2\text{Cl}(\text{i-Bu}_2)_2\), followed by quantitative precipitation of the starting material \(\text{Cp}_2\text{ZrCl}_2\). On hydrolysis a distribution of linear aliphatic alcohols was
obtained. Therefore, in this sequence \( \text{Cp}_2\text{ZrCl}_2 \) catalyzes the reduction of carbon monoxide by \( \text{i-Bu}_2\text{AlH} \) to give species which, on hydrolysis, yield aliphatic alcohols. Although \( \text{H}_2 \) could not be utilized (at 1 atm) in this CO reduction scheme, the observation of products derived from reductive polymerization of CO in a sequence which proceeded at room temperature and 1 atm CO encouraged us to examine this reaction in greater detail.

Although \( \text{Cp}_2\text{ZrCl}_2 \) did catalyze reduction of CO by \( \text{i-Bu}_2\text{AlH} \), the presence of a large excess of the aluminum hydride inhibited the rate of CO uptake. Increasing CO pressure enabled reduction to occur in the presence of a large excess of the aluminum hydride. These observations suggest that CO and \( \text{i-Bu}_2\text{AlH} \) compete for a vacant coordination site on Zr. Through the reduction sequence shown below, coordinated CO is postulated to be reduced first to a formyl species and then to an alkoxyalkyl. This critical intermediate then, through transmetalation with \( \text{i-Bu}_2\text{AlH} \), can give an organoaluminum compound plus a zirconium hydride (analogous to the reaction described above for the preparation of \( \text{Cp}_2\text{ZrH}_3\text{Al}_2\text{R}'(\text{i-Bu})_2 \)). Alternatively, reduction of the C-O bond by \( \text{i-Bu}_2\text{AlH} \) would give a Zr alkyl. This upon insertion of CO and reduction by additional \( \text{i-Bu}_2\text{AlH} \), would yield a homologated alkoxyalkyl Zr species. The ultimate products of these reactions would be the aluminum alkoxyalkyls which, upon hydrolysis, would give the observed alcohols (16,17).

A possible analogue for the above-described sequences exists in the chemistry of iron acyls: Reaction with BH₃ gives a mixture containing an iron hydride and an iron alkyl (18).

CLEAVAGE USING \( \text{H}_2 \)

To incorporate \( \text{H}_2 \) into a CO reduction sequence requires that alkylzirconium intermediates such as those described above be able to react with \( \text{H}_2 \). Model compounds \( \text{Cp}_2\text{ZrH}(\text{alkyl}) \) were prepared and were studied with regard to the possibility for hydrogenolysis of the Zr-C bond. It was observed that \( \text{Cp}_2\text{ZrH}(\text{alkyl}) \) species react readily with \( \text{H}_2 \); with \( \text{D}_2 \) both exchange of hydride ligand with the atmosphere and cleavage of the C-Zr bond occurred. The
mechanism for hydrogenolysis of the C-Zr bond in Cp₂ZrH(alkyl) is of considerable interest since these organozirconium compounds are derivatives of Zr(IV), a d⁰ species. In conventional organometallic chemistry, activation of H₂ occurs by oxidative addition of that small molecule to a metal center possessing at least one pair of d-electrons. How then do Cp₂ZrH(alkyl) species undergo hydrogenolysis? One possibility to account for this observation involves a hydride shift process (19). Here a hydride ligand is transferred from Zr to a cyclopentadienyl ring with concomitant formal reduction of Zr(IV) to Zr(II). This latter species (d⁰) could then activate H₂ by oxidative addition. This mechanism, however, does not explain the observed facile exchange of hydride ligand with a D₂ atmosphere observed for Cp₂ZrH(alkyl). We have recently found (20) that alkylzirconium(IV) compounds not containing a terminal hydride ligand also undergo hydrogenolysis. The observed trend for hydrogenolysis of the C-Zr bond in a series of Zr(IV) complexes is: Cp₂ZrH(alkyl) > Cp₂ZrCl(alkyl) > Cp₂Zr(Cl)CH₂OX, X = Cp₂ZrCl⁻. We suggest (21) that alkylzirconium(IV) derivatives can react with H₂ directly through a pathway which is analogous to the ones described above to account for electrophilic cleavage and transmetalation. In this process the H₂ molecule reacts with the Zr(IV) center via the low-lying vacant orbital of this metallic species; a two-electron, three-center interaction is implied between the σ-bonding electrons of the H₂ molecule and this vacant orbital on Zr. A closed transition state leads to the observed products (22). Clearly for this direct attack mechanism to operate successfully, the availability of the vacant low-lying Zr orbital to interact with H₂ is prerequisite. In solution Cp₂ZrH(alkyl) exists as an appreciably dimerized species; for monomeric Cp₂ZrH(alkyl) the vacant orbital on Zr is available for interaction with H₂. For Cp₂ZrCl(alkyl), 2r-donation from the chloride ligand would compete with H₂ for this vacant orbital. In the alkoxyalkyl, σ-chelation (via the α-oxygen atom) would even more strongly compete for this orbital on the metal required for interaction with H₂. The observation of hydrogenolysis of Cp₂ZrH(alkyl), Cp₂ZrCl(alkyl), and Cp₂Zr(Cl)CH₂OX seems to rule out an H₂- activation mechanism which necessitates the presence of a hydride ligand on Zr, such as is required by the migration route noted above. Furthermore, the observation of rate trends for hydrogenolysis, suggesting competition for a single vacant orbital on the metal between the H₂ molecule and a filled orbital (if present) of another ligand on Zr, argue in favor of a direct attack mechanism.
REACTION OF Cp₂ZrH(ALKYL) WITH ADDED LIGANDS

As noted above, homologation of CO would likely involve the reaction between zirconium alkyls and CO. The reaction between Cp₂ZrH(alkyl) and CO was therefore studied to model this critical homologation step (23). Insertion of CO into the C-Zr bond of Cp₂ZrH(alkyl) resulted in the formation of acyl hydride species which gave rise to condensation products, hydrolysis of which yielded alcohols. To study this condensation reaction in detail, an acyl zirconocene chloride (24) was treated with Cp₂ZrHCl and the desired alkoxyalkyl zirconium compound was obtained (25). ¹H NMR analysis (20) of this alkoxyalkyl provided insight into an interesting structural feature of these organometallic compounds. Note that in the condensed product a chiral center has been generated at carbon. A low-temperature ¹H NMR survey of this compound demonstrated the diastereotopic nature of the cyclopentadienyl ligands on each type of zirconium species present. At room temperature the four peaks derived from the Cp ligands collapsed to a set of two (26). Thus, carbon and oxygen modes of attachment to Zr are interchangeable with low activation energy (in other words, the carbon unit can jump between the two metal atoms with facility). The fact that the set of four Cp peaks condenses to two indicates the intramolecular nondissociative nature of this fluxional process: In the requisite intermediate for C-Zr, O-Zr bond interchange, a single mirror plane is present; it is not possible to interconvert Cp with Cp'. Since the carbon unit must transverse this mirror plane in the course of the fluxional process, it undergoes a formal inversion of configuration during it. In other words, this complex experiences a continuous, degenerate S₅/₂ process at carbon (26).
It was found that in addition to anticipated insertion, CO reacted with Cp₂ZrH(alkyl) to induce reductive elimination of alkane to give Cp₂Zr(CO)₂, a compound which had been prepared previously through another route (27). Unfortunately, this compound does not display the high reactivity expected for a complex of Zr(II). It is possible that the π-acidity of the CO ligands is responsible for this fact. Therefore, ligand-induced reductive elimination of alkane from Cp₂ZrH(alkyl) was attempted using tertiary phosphines with the aim in mind of generating highly reactive Zr(II) complexes. The products obtained from this reaction, Cp₂ZrL₂ (L = tertiary phosphine) were indeed found to be highly reactive species from several points of view (28). For example, these species readily undergo ligand exchange reactions; an intriguing example of this involves the exchange reaction with a Wittig reagent. The ylide complex initially formed by ligand exchange undergoes loss of triphenylphosphine; a Zr(II) carbene exchange results (20). This is the first example of a carbene complex of Zr.

Oxidative addition reactions were found to be facile for Zr(II) and to occur with a variety of substrates. Treating Cp₂ZrL₂ with acetylenes or olefins results in metallacycle formation. This occurs presumably through replacement of the phosphine ligands by the unsaturated organic molecules, followed by metallacyclization (29). Oxidative addition of C-H bonds has also been noted. Thermolysis of the bis(phosphine) complex yields a diamagnetic dimeric Zr(III) species obtained by oxidative addition of a cyclopentadienyl ring C-H bond followed by loss of H₂. The structure of this Zr(III) dimer is the same as that one obtained by treating "zirconocene" (formed by sodium amalgam reduction of Cp₂ZrCl₂) with tertiary alkyl phosphines. "Zirconocene" is thus believed to have the same carbon ligand skeleton as the Zr(III) dimer.

Oxidative addition of organic halides to Cp₂ZrL₂ occurs quite rapidly (28,30). In fact, Cp₂ZrL₂ reacts with simple alkyl halides (such as n-butyl bromide) approximately ten times faster than does the bis(DMG)Rh(I) derivative reported (32) to be one of the most reactive complexes known from the point of view of attack upon alkyl halides. For these reactions of Cp₂ZrL₂ initial phosphate
ligand dissociation has been demonstrated (30). An intriguing steric effect controls the course of the oxidation reaction when then ensues. Monophosphine complex \( \text{Cp}_2\text{ZrL} \) is presumed to attack the alkyl halide by halogen atom abstraction, yielding a halozirconium(III) monophosphine intermediate plus alkyl radical. If steric hindrance is small, the alkyl radical can react with this species to give \( \text{Cp}_2\text{ZrR(Hal)} \) (Hal = I, Br, Cl), the product of a formal oxidative addition. (In theory then, oxidative addition of R(Hal) to \( \text{Cp}_2\text{ZrL} \) provides a route to \( \text{Cp}_2\text{ZrR(Hal)} \) complexes not directly accessible by hydriodization.) However, if steric hindrance to C-Zr bond formation is significant, then attack of the Zr(III) intermediate upon a second equivalent of alkyl halide can occur competitively; this yields \( \text{Cp}_2\text{Zr(Hal)}_2 \). This partitioning is summarized below.

**CONCLUSIONS**

We have seen that the chemistry of bis(cyclopentadienyl)zirconium(IV) organic derivatives can be explained in large measure by means of a single mechanistic concept. This involves complexation between the unsaturated organozirconium starting material and the cleavage reagent to give a saturated organozirconium species. Polarization of the complex followed by cyclic collapse generates the observed products. Such a mechanism can be used to explain reactions of \( \text{Cp}_2\text{ZrRX} \) as apparently diverse as bromination, transmetalation to metal halides, transmetalation to aluminum hydrides, or hydrogenolysis. Ligand-induced reductive elimination may parallel this pattern: Reductive elimination is initiated by ligation which coordinatively saturates the Zr(IV) complex; this is followed by collapse to give the products observed.
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REFERENCES

25. It is interesting to contrast this with a comparable reaction of a permethylzirconocene compound which gives the enolate: J. M. Marquez, D. R. McAlister, R. D. Sanner, and J. E. Bercaw, J. Am. Chem. Soc. 100, 2716 (1978).
26. The collapse of Cp resonances to a singlet in Cp2Zr(Cl)CH2OZrCp2(Cl) had been noted (17). In the absence of the chiral center at C, little about this process could be elucidated.
29. Metallacycle formation by this pathway has been established for a number of metal complexes. For example, see: D. R. McAlister, J. E. Bercaw, and R. G. Bergman, J. Am. Chem. Soc. 99, 1666 (1977), and references therein.