

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

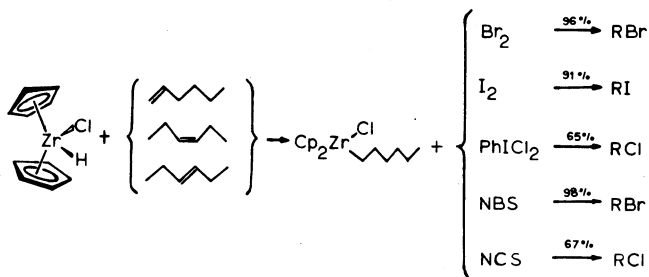
Organozirconium compounds have been found to be useful intermediates in organic synthesis and to undergo intriguing reactions with ramifications for several aspects of catalysis. We describe herein methods for preparing bis-(cyclopentadienyl) organozirconium compounds; we also discuss in detail several 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

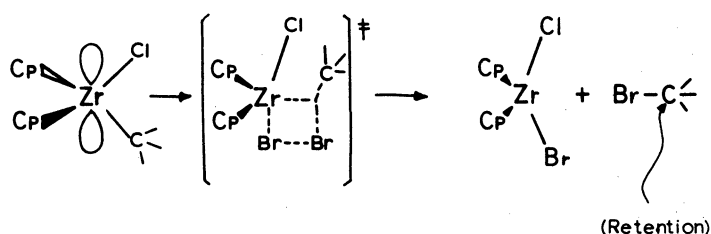
Several years ago we found that $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) would react with olefins or acetylenes under mild conditions to give the corresponding organozirconium σ -bonded complex ($\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$, $\text{R} = \text{alkyl or alkenyl}$) 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, Br_2 , NBS, *tert*- $\text{C}_4\text{H}_9\text{OOH}$) reacted rapidly with $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ 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 $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ is a 16-electron,

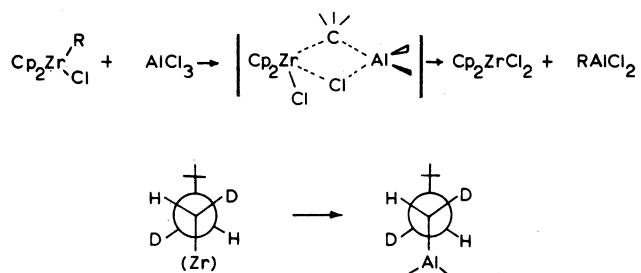


coordinatively unsaturated species. It was suggested, by analogy with electrophilic cleavage processes described for organomercurials (5), that the cleavage reagent X-Y interacts with the zirconium atom via its sole low-lying valence orbital (6). Polarization of coordinated X-Y followed by a closed transition 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.



TRANSMETALATION: CLEAVAGE USING METALLIC ELECTROPHILES

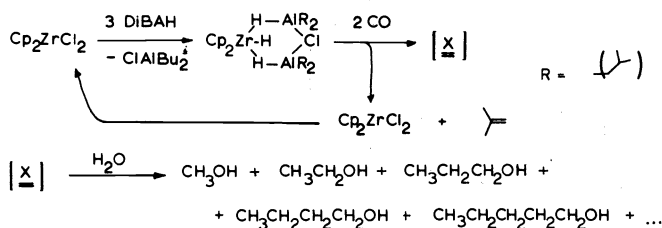
To circumvent the low tendency of $\text{Cp}_2\text{Zr}(\text{R})\text{Cl}$ to participate directly in carbon-carbon bond formation processes, the reaction between them and Lewis acidic metal halides was investigated. It was proposed that it should be possible to transfer an organic group from zirconium 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 hydrozirconation-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.



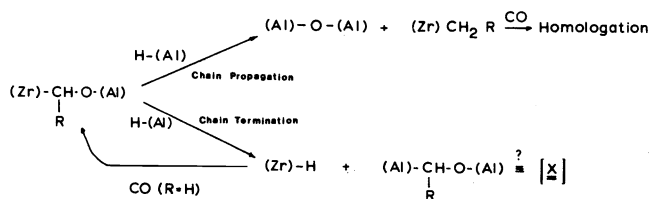
CLEAVAGE USING METAL HYDRIDES: MIXED Zr-Al POLYHYDRIDES AND THE REDUCTION OF CO

In contrast to the reaction between Cp_2ZrCl_2 and LiAlH_4 (which gives rise to Cp_2ZrHCl), treatment of Cp_2ZrCl_2 with the electron-deficient species $i\text{-Bu}_2\text{AlH}$ gives rise to a new type of hydrido-zirconium species, $\text{Cp}_2\text{ZrH}_3\text{Al}_2\text{Cl}$ ($i\text{-Bu}_2$)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 $\text{Cp}_2\text{ZrH}_3\text{Al}_2\text{R}'(i\text{-Bu}_2)_2$ could be prepared by reaction between the dialkyl complex $\text{Cp}_2\text{ZrR}'_2$ ($\text{R}' = \text{alkyl}$) and $i\text{-Bu}_2\text{AlH}$. It was believed (16) that such polyhydrido mixed metal complexes might demonstrate reducing ability different from that displayed by Cp_2ZrHCl by virtue of the presence of two different metal centers in the cluster. Because of current interest in CO reduction, reaction between that small molecule and mixed Zr-Al polyhydridic clusters was studied. It was observed that two equiv CO was taken up by $\text{Cp}_2\text{ZrH}_3\text{Al}_2\text{Cl}(i\text{-Bu}_2)_2$, followed by quantitative precipitation of the starting material Cp_2ZrCl_2 . On hydrolysis a distribution of linear aliphatic alcohols was

obtained. Therefore, in this sequence Cp_2ZrCl_2 catalyzes the reduction of carbon monoxide by $i\text{-Bu}_2\text{AlH}$ to give species which, on hydrolysis, yield aliphatic alcohols. Although 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.

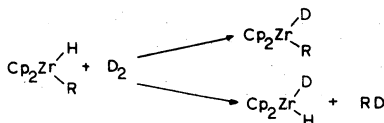


Although Cp_2ZrCl_2 did catalyze reduction of CO by $i\text{-Bu}_2\text{AlH}$, the presence of a large excess of the aluminum hydride inhibited the rate of CO uptake. Increasing CO pressure enabled reduction to occur in the presence of a large excess of the aluminum hydride. These observations suggest that CO and $i\text{-Bu}_2\text{AlH}$ 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 $i\text{-Bu}_2\text{AlH}$, can give an organoaluminum compound plus a zirconium hydride (analogous to the reaction described above for the preparation of $\text{Cp}_2\text{ZrH}_3\text{Al}_2\text{R}'(i\text{-Bu}_2)_2$). Alternatively, reduction of the C-O bond by $i\text{-Bu}_2\text{AlH}$ would give a Zr alkyl. This upon insertion of CO and reduction by additional $i\text{-Bu}_2\text{AlH}$, would yield a homologated alkoxyalkyl Zr species. The ultimate product 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 BH_3 gives a mixture containing an iron hydride and an iron alkyl (18).

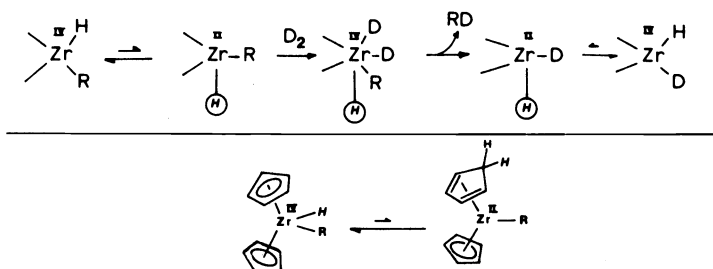


CLEAVAGE USING H_2

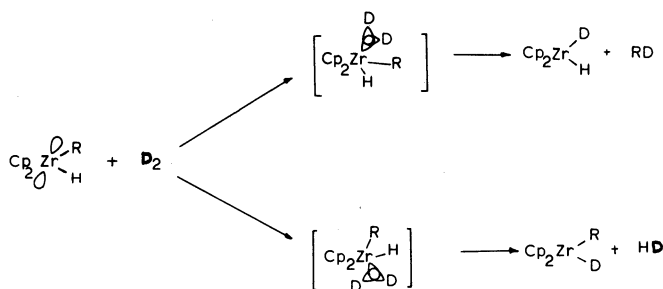
To incorporate H_2 into a CO reduction sequence requires that alkylzirconium intermediates such as those described above be able to react with H_2 . Model compounds $\text{Cp}_2\text{ZrH(alkyl)}$ were prepared and were studied with regard to the possibility for hydrogenolysis of the Zr-C bond. It was observed that $\text{Cp}_2\text{ZrH(alkyl)}$ species react readily with H_2 ; with D_2 both exchange of hydride ligand with the atmosphere and cleavage of the C-Zr bond occurred. The



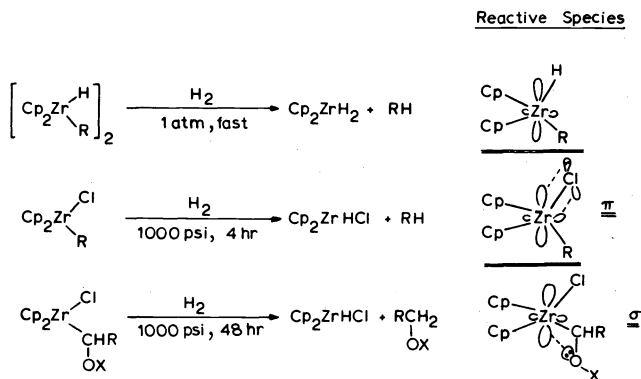
mechanism for hydrogenolysis of the C-Zr bond in $\text{Cp}_2\text{ZrH(alkyl)}$ is of considerable interest since these organozirconium compounds are derivatives of Zr(IV), a d^0 species: In conventional organometallic chemistry, activation of H_2 occurs by oxidative addition of that small molecule to a metal center possessing at least one pair of d-electrons. How then do $\text{Cp}_2\text{ZrH(alkyl)}$ 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 (d^2) could then activate H_2 by oxidative addition. This mechanism, however, does not explain the observed



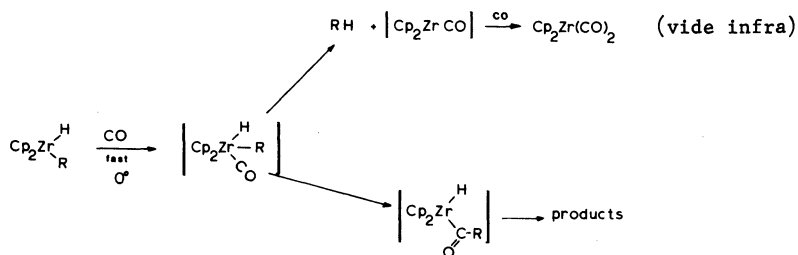
facile exchange of hydride ligand with a D_2 atmosphere observed for $\text{Cp}_2\text{ZrH(alkyl)}$. We have recently found (20) that alkylzirconium(IV) compounds not containing a terminal hydride ligand also undergo hydrogenolysis. The observed trend for hydrogenolysis of the C-Zr bond in a series of Zr(IV) complexes is: $\text{Cp}_2\text{ZrH(alkyl)} > \text{Cp}_2\text{ZrCl(alkyl)} > \text{Cp}_2\text{Zr(Cl)CH}_2\text{OX}$, $\text{X} = \text{Cp}_2\text{ZrCl-}$. We suggest (21) that alkylzirconium(IV) derivatives can react with H_2 directly through a pathway which is analogous to the ones described above to account for electrophilic cleavage and transmetalation. In this process the H_2 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 H_2 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



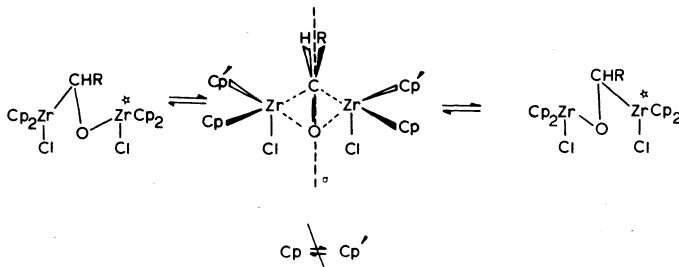
successfully, the availability of the vacant low-lying Zr orbital to interact with H_2 is prerequisite. In solution $\text{Cp}_2\text{ZrH(alkyl)}$ exists as an appreciably dimerized species; for monomeric $\text{Cp}_2\text{ZrH(alkyl)}$ the vacant orbital on Zr is available for interaction with H_2 . For $\text{Cp}_2\text{ZrCl(alkyl)}$, π -donation from the chloride ligand would compete with H_2 for this vacant orbital. In the alkoxyalkyl, σ -chelation (via the β -oxygen atom) would even more strongly compete for this orbital on the metal required for interaction with H_2 . The observation of hydrogenolysis of $\text{Cp}_2\text{ZrH(alkyl)}$, $\text{Cp}_2\text{ZrCl(alkyl)}$, and $\text{Cp}_2\text{Zr(Cl)CH}_2\text{OX}$ seems to rule out an H_2 -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 H_2 molecule and a filled orbital (if present) of another ligand on Zr, argue in favor of a direct attack mechanism.

REACTION OF $\text{Cp}_2\text{ZrH}(\text{ALKYL})$ WITH ADDED LIGANDS

As noted above, homologation of CO would likely involve the reaction between zirconium alkyls and CO. The reaction between $\text{Cp}_2\text{ZrH}(\text{alkyl})$ and CO was therefore studied to model this critical homologation step (23). Insertion of CO into the C-Zr bond of $\text{Cp}_2\text{ZrH}(\text{alkyl})$ 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

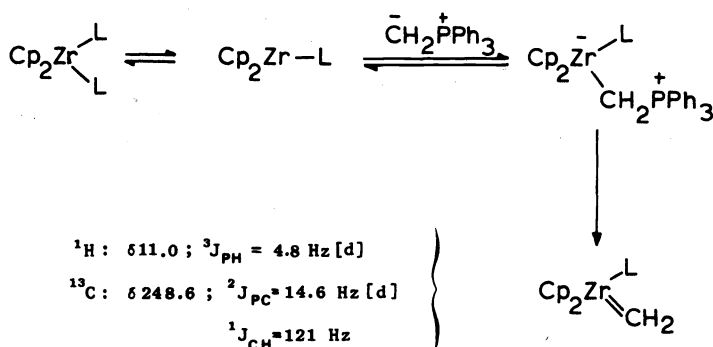


acyl zirconocene chloride (24) was treated with Cp_2ZrHCl and the desired alkoxyalkyl zirconium compound was obtained (25). ^1H NMR analysis (20) of this alkoxyalkyl provided insight into an interesting structural feature of these organometallic compounds. Note that in the condensed product a chiral 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 $\text{S}_{\text{N}}2$ process at carbon (26).

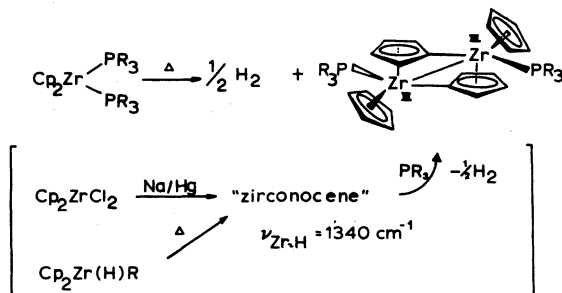


LIGAND-INDUCED REDUCTIVE ELIMINATION

It was found that in addition to anticipated insertion, CO reacted with $\text{Cp}_2\text{ZrH(alkyl)}$ to induce reductive elimination of alkane to give $\text{Cp}_2\text{Zr(CO)}_2$, 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 $\text{Cp}_2\text{ZrH(alkyl)}$ was attempted using tertiary phosphines with the aim in mind of generating highly reactive Zr(II) complexes. The products obtained from this reaction, Cp_2ZrL_2 (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 complex results (20). This is the first example of a carbene complex of Zr.

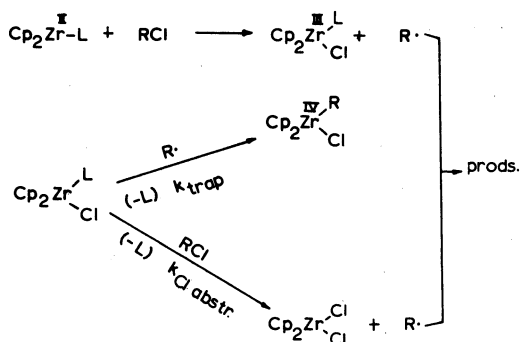


Oxidative addition reactions were found to be facile for Zr(II) and to occur with a variety of substrates. Treating Cp_2ZrL_2 with acetylenes or olefins results in metallacycle formation. This occurs presumed through replacement of the phosphine ligands by the unsaturated organic molecules, followed 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 H_2 . The structure of this Zr(III) dimer is the same as that one obtained by treating "zirconocene" (formed by sodium amalgam reduction of Cp_2ZrCl_2) with tertiary alkyl phosphines. "Zirconocene" is thus believed to have the same carbon ligand skeleton as the Zr(III) dimer.



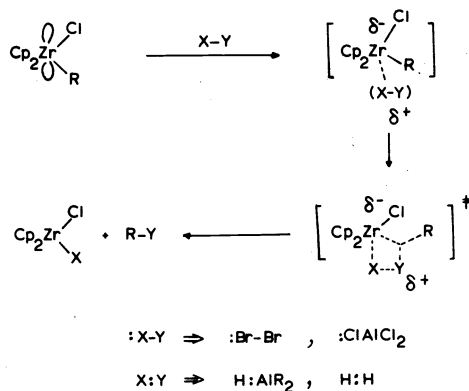
Oxidative addition of organic halides to Cp_2ZrL_2 occurs quite rapidly (28,30). In fact, Cp_2ZrL_2 reacts with simple alkyl halides (such as n-butyl bromide) approximately ten times faster than does the bis(DMG)Rh(I) derivative reported (32) to be one of the most reactive complexes known from the point of view of attack upon alkyl halides. For these reactions of Cp_2ZrL_2 initial phosphine

ligand dissociation has been demonstrated (30). An intriguing steric effect controls the course of the oxidation reaction when then ensues. Monophosphine complex Cp_2ZrL 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 $Cp_2ZrR(Hal)$ ($Hal = I, Br, Cl$), the product of a formal oxidative addition. (In theory then, oxidative addition of $R(Hal)$ to Cp_2ZrL_2 provides a route to $Cp_2ZrR(Hal)$ complexes not directly accessible by hydrozirconation.) 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 $Cp_2Zr(Hal)_2$. 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 Cp_2ZrRX 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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