Versatile Zirconium Reductants and Carbon–Carbon Coupling Agents Selectively Accessible from the 2:1 Molar Aggregate of *n*-Butyllithium and Zirconium(IV) Salts^[‡]

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In previous studies of transition metal alkyls the 2:1 molar aggregate of *n*-butyllithium and zirconium(IV) salts has been found to react both with benzylic hydrocarbons and aromatic carbonyl derivatives in diverse and useful ways. In the present study the reactions of the aggregates, $2nBuLi\cdot ZrE_4$ (E = Cl, OEt), with benzaldehyde have involved carbometallation, hydrometallation and reductive dimerization (paths 1-3) in THF and were selectively achievable by temperature control alone. First, at -78 °C benzaldehyde underwent carbolithiation to give upon hydrolysis 1-phenyl-1-pentanol. However, short-term reaction times and prompt D₂O quenching revealed that with Zr(OEt)₄ both benzaldehyde and 1-phenyl-1-pentanol were deuteriated, consistent with the presence of a phenyl(lithioxy)carbene intermediate. The observed dimerization of benzaldehyde to benzyl benzoate by lithium 2,2,6,6-tetramethylpiperidide is also consistent with such a

Introduction

To the dismay but the ultimate delight of the research chemist, admixing a given set of starting reagents can often lead to two or more different products, whose formation is individually dependent on the experimental variables of temperature, time, concentration and ratio of reactants. We have encountered such an instructive and versatile competition of kinetic and thermodynamic processes with zirconium(IV) chloride (1) or zirconium(IV) ethoxide (2) and *n*-butyllithium (3) in a 1:2 equiv. ratio in THF. In previous studies we have observed that such a combination of reagents can lead to the various important transformations depicted in Scheme 1. On the right side are shown the three reactions (paths 1-3) applicable to the typical aromatic carbonyl derivative, benzaldehyde (4); on the left side in paths 4–6 are shown reactions found with benzylic hydrocarbons,

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[b] Chemistry Department, Drake University, 207 University Avenue, Des Moines, Iowa 50311, USA E-mail: john.gitua@drake.edu phenyl(lithioxy)carbene intermediate. Second, at 25 °C the $2nBuLi\cdotZrE_4$ aggregate reduced benzaldehyde exclusively to benzyl alcohol, which observation is consistent with the formation of the hydrozirconating agent, H_2ZrE_2 . Third, heating the aggregate at reflux and subsequent reaction with benzal-dehyde produced solely the reduced dimer, 1,2-diphenyl-1,2-ethanediol with high stereoselectivity: E = Cl, *rac/meso* of 93:7 and E = OEt, *rac/meso* of 100:0. The proposed mechanism involves the formation of ZrE₂, the epizirconation of benzaldehyde and the insertion of the second benzaldehyde into the zirconaoxacyclopropane under steric control. Finally, the high selectivity in hydrozirconation and reductive dimerization shown by $2nBuLi\cdotZrE_4$ appears at this time to be superior to that attainable with analogous titanium or hafnium aggregates.

such as toluene (9), diphenylmethane (10) and 1,1,2,2-tetraphenylethane (14).^[2]

Finally, because the 2:1 aggregate of *n*-butyllithium (**3**) with $Zr(OEt)_2$ (**2**) in THF can lithiate benzylic hydrocarbons, such as toluene at 0 °C (path 4 in Scheme 1), we have been prompted to search for the possible involvement of lithiation at the carbonyl group in the reaction of benzaldehyde (**4**) at low temperatures. In such a possible lithiation (path 7 in Scheme 1) the initially formed lithium derivative **15a** would be more stable as phenyl(lithioxy)carbene **15b**, with the anionic charge on oxygen.^[3]Such carbenes are known to be immediately trapped by ambient RLi or carbonyl reagents.^[4] As part of the quest for likely routes to carbenes like **15b**, we have also explored the behavior of benzaldehyde (**4**) toward hindered bases, such as lithium 2,2,6,6-tetramethylpiperidide (LTMP).^[5]

In the present study we have focused on the individual reactions of benzaldehyde (4), given in paths 1, 2, 3 and 7, in order to determine the specific lithium or zirconium reagent responsible for each transformation and to achieve, if possible, each individual transformation in high yield and with great selectivity. We have chosen to defer further study of the reactions of the 2:1 *n*-butyllithium-ZrCl₄ and -Zr(OEt)₄ aggregates with benzylic hydrocarbons **9**, **10** and **14** in paths 5–7, because such reactions are complex, involv-

^[‡] Organic Chemistry of Subvalent Transition Metal Complexes, 47. Part 46: Ref.^[1]



Scheme 1. All reactions were worked up with H_2O or D_2O . The individual products shown from paths 1–6 were in fact found but in widely varying yields, which were not optimized (cf. text).

ing thermal, photochemical and/or iron-promoted reaction steps and often causing unusual side products to dominate.^[6]

Results and Discussion

General Observations on Reactions of the 2:1 Aggregate of *n*-Butyllithium (3) and Zirconium(IV) Chloride (1) or Zirconium(IV) Ethoxide (2) with Benzaldehyde (4)

After preliminary reaction runs with the 2:1 aggregates of 3 with 1 or with 2 in THF at various temperatures, it was determined that path 1 was solely followed at -78 °C, path 2 was completely selective at 25–30 °C, and path 3 was the only reaction course after the reaction mixture was preheated at reflux (Scheme 1).

The 2:1 aggregates of 3 with 1 or with 2 in THF existed as a suspension or solution, which was pale yellow at -78 °C, orange at 25 °C and dark brown after several hours at reflux. As individual reactions of these three with benzaldehyde (4) have shown, the benzaldehyde samples were quantitatively transformed under these individual conditions into 1-phenyl-1-pentanol (5), benzyl alcohol (6) and the 1,2-diphenyl-1,2-ethanediols, respectively, which diols were preponderantly the rac-isomer (7) over the meso-isomer (8). Unless otherwise stated, the 2:1 aggregates of 3 with 1 or with 2 in THF gave very similar results when admixed with benzaldehyde (4) under the stated conditions and at the given temperature. Therefore, the observed reactions will be depicted and discussed with the 2:1 n-butyllith $ium-Zr(OEt)_4$ aggregate. Where there were any significant differences between 1 and 2, a word of explanation will be offered.

Formation of the 2:1 Aggregate of *n*-Butyllithium (3) and Zirconium(IV) Ethoxide (2) at -78 °C and Reaction with Benzaldehyde (4)

Admixing *n*-butyllithium (3) with $Zr(OEt)_4$ (1) in THF at -78 °C seems to cause no profound chemical change. Al-

though some complexation between 3 and 2 may have occurred (cf. *infra*), the aggregate still underwent the same chemical reaction of reagent 3 alone and added quantitatively to benzaldehyde (4) to yield upon hydrolysis the expected 1-phenyl-1-pentanol (5) [Equation (1)].^[8,9] The 2:1 aggregate of 3 and 1 gave identical results.

$$Ph-C \underset{O}{\overset{H}{\underset{}}} H + nBuLi \longrightarrow Ph-C \underset{I}{\overset{H}{\underset{}}} OLi \xrightarrow{H_2O} Ph-C \underset{I}{\overset{H}{\underset{}}} OH (1)$$

$$4 \qquad 5a \qquad 5$$

Possible Role of the Phenyl(lithioxy)carbene (15b) in the Reaction of *n*-Butyllithium (3) and Zirconium(IV) Ethoxide with Benzaldehyde in THF at -78 °C

Since two equivalents of *n*-butyllithium are involved in the reaction with benzaldehyde, it is possible that competing with straightforward carbolithiation $[4 \rightarrow 5a, \text{Equation (1)}]$, known for over 80 years,^[8,9] might be the lithiation of 4 at the carbonyl group (15b) (Scheme 2). There is rich pre-



Scheme 2.

cedent for the *alpha*-addition of organolithium reagents to carbenes, as shown by the transformation of **15b** to **5b**.^[4] One such example is illustrated in Scheme 3.^[10]



Scheme 3.

If **5b** is sufficiently stable in THF, it might persist until workup with D_2O and dideuterio **5c** might be isolable. But deprotonation of THF, producing ethylene and the lithium enolate of acetaldehyde,^[11] might instead produce *O*-deuterio-**5d**. In the following section an attempt has been described for generating carbene **15b** in a straightforward manner.

In order to trap intermediates, such as **5b** and **15b**, reaction mixtures of a 2:1 ratio of *n*-butyllithium and $Zr(OEt)_4$ with subsequently added benzaldehyde were quenched with D₂O (98%) at different stages: a) the reaction mixture warmed finally to 25 °C gave only **5d** and no **5c**; b) the reaction mixture promptly brought to 25 °C likewise gave only **5d**; and c) the reaction mixture mixed for 15 min at -78 °C and promptly quenched with D₂O gave 95% of **5** and 5% of benzaldehyde (4). Alcohol **5** contained about 13% of **5c** and the benzaldehyde had about 2% of **4** as C₆H₅–CD=O (**4a**). Thus about 15% of **4** was lithiated to **15b** (Scheme 2) and most of **15b** converted to **5b**.

It is noteworthy that the 2:1 aggregate of *n*-butyllithium (3) and zirconium(IV) chloride (1) showed no sign of lithiating benzaldehyde. This is consistent with the similar failure of this aggregate to lithiate toluene or diphenylmethane between -78 and 0 °C (path 4, Scheme 1), a reaction achieved by 2 in the *n*BuLi–Zr(OEt)₄ aggregate.^[12]

For this reason, we suggest that the 2:1 $nBuLi-Zr(OEt)_4$ aggregate at -78 °C has not yet undergone the intermetallic ligand exchange depicted in Scheme 5. Rather the C-Li bond in 3 is further polarized by a chelating coordination of 2 with 3 as proposed in complex 2-3 of Equation (2).



Such alkoxide coordination may also be operative in enhancing the lithiating activity of organolithium reagents by potassium alkoxides.^[13]

Lithiation of Benzaldehyde (4) at the Carbonyl Group by Lithium 2,2,6,6-Tetramethylpiperidide (LTMP)

The acidity of the aldehydic H-C bond of 4 can be estimated by the following polarographic measurements of pK_a values: benzene, 37; ethylene 36 and the formyl proton of methyl formate, 35.^[14a] Accordingly, the p K_a of benzaldehyde (4) should be certainly smaller than that of benzene, whose H-C bonds can be lithiated in THF and especially in TMEDA. Hence, deprotonation of benzaldehyde was attempted with LTMP, a strong deprotonating base with little nucleophilic tendency to attack the carbonyl group because of steric hindrance. Indeed, when benzaldehyde is treated with LTMP in hexane, it is dimerized readily and upon hydrolysis yields benzyl benzoate. This process can be satisfactorily explained by the lithiation of benzaldehyde (4) by LTMP to produce carbene 15b and its carbene-like addition to a second molecule of 4. Opening of the cyclic intermediate would provide the lithium derivative (16a) of benzyl benzoate (16) (Scheme 4).^[14b,14c]



Scheme 4.

Formation of the 2:1 Aggregate of *n*-Butyllithium (3) and Zirconium(IV) Chloride (1) at 25 °C and Subsequent Reaction with Benzaldehyde (3)

When the 2:1 aggregate of nBuLi (3) and $ZrCl_4$ (1) was brought to 25 °C, stirred and recooled to -78 °C (path 2), addition of benzaldehyde (4) and subsequent workup now gave a quantitative yield of only benzyl alcohol (6), indicative that transmetallation had in fact taken place to produce di-*n*-butylzirconium(IV) dichloride (17) and what is typical of transition metal alkyls, 17 was in equilibrium with zirconium(IV) dichloride dihydride 17a and 1-butene. The zirconium reagent 17a had then performed a monomeric hydrozirconation of benzaldehyde (4) to yield 19 and only benzyl alcohol (6) upon hydrolysis (Scheme 5). The generation of the hydrozirconating agent H_2ZrCl_2 (17a) in this way thus proves to be more convenient and less costly than the preparation of the commercially available Cp2ZrHCl or Schwartz reagent.^[15] Zirconium(IV) dichloride dihydride (17a) has been successfully used thus far for the hydrozirconation of 1-alkenes, alkynes, carbonyl derivatives, imines, nitriles and epoxides.^[16,17] The 2:1 aggregate of 3 and 2 gave identical results.

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Scheme 5.

Heating the 2:1 Aggregate of *n*-Butyllithium (3) and Zirconium(IV) Chloride (1) at Reflux in THF and Reaction Thereafter with Benzaldehyde (4)

Finally, when the foregoing solution of nBu_2ZrCl_2 (17) in THF is allowed to reflux for several hours and benzaldehyde then added (path 3), the only products obtained upon hydrolysis were the 1,2-diphenyl-1,2-ethanediols, in essentially quantitative yield and as a 93:7 ratio of the racemic and *meso* isomers, 7, and 8. When the solution of $nBu_2Zr(OEt)_2$ (18) was treated in an analogous way, *only* the *rac*-isomer was formed. Thus in this overall reaction the reductive dimerization of benzaldehyde was achieved with very high (nBu_2ZrCl_2 , 17) to exclusive [$nBu_2Zr(OEt)_2$, 18] stereoselectivity (Scheme 6). The most likely steps in path 3 are the reductive elimination of butyl groups from *n*-BuZrE₂ to zirconium salt ZrE₂ (19), the epizirconation of benzaldehyde by ZrE₂ to form 20 and the insertion of the



Scheme 6.



meso-(8, after hydrolysis) meso-+racemic-(8 and 7, after hydrolysis)

Scheme 7.

second benzaldehyde into the sterically more accessible side of the C–Zr bond of **20** to yield **21**.^[18] An alternative reaction involving the coupling of zirconium radical intermediates (**20a**) seems less satisfactory. Slow coupling of **20a** radicals would favor the formation of the *meso*-dimer for steric reasons, while rapid coupling would tend to favor comparable amounts of *rac*- and *meso*-dimers (Scheme 7).

Status of Reductions of Organic Compounds by Low-Valent Titanium Reagents

The pioneering and revolutionary studies of Karl Ziegler and co-workers with early transition metal salts (TiCl₄, ZrCl₄ and VCl₄) in combination with aluminum alkyls in the 1950s led to the discovery of highly active catalysts for the oligomerization and/or polymerization of olefins and diolefins.^[19–21] Thereafter, early transition metals were intensively studied as reagents for organic transformations, with the result that in 1973 three research groups reported independently on the novel reductive dimerization of carbonyl derivatives to olefins by various subvalent titanium reagents^[22–24] [Equation (3)].

$$2 \underset{R}{\overset{R}{>}} C = 0 \qquad \xrightarrow{\text{Ti}(?)} \qquad \underset{R}{\overset{R}{>}} C = C \overset{R}{\underset{R}{\overset{(3)}{\sim}}} \qquad (3)$$

The transformation depicted in Equation (3), which has come to be termed the McMurry reaction after one of its discoverers, is a most impressive and versatile method for the construction of a wide variety of open-chain and ring carbon skeletons in high yields.^[25,26] Unfortunately, the nature of various subvalent titanium reductants used for the McMurry reaction have largely remained shrouded in uncertainty: in almost all applications, neither the exact oxidation state(s) of the titanium reductants in solution nor their mechanism(s) of reaction can be confidently specified, even after almost 40 years. Problems in formulating a molecular interpretation of this reaction are not difficult to identify: (1) the titanium reductant is generated in a heterogeneous medium; (2) the presence of more than one subvalent state [Ti⁰ and Ti^{II}] often cannot be ruled out; (3) residual reductant used to generate subvalent titanium (LiAlH₄, Mg, Al, Zn) may play a role; and (4) the Lewis acid formed from generating subvalent titanium (LiCl, MgCl₂, AlCl₃, ZnCl₂) can and almost surely does influence the reducing character of the titanium reagent.

Therefore, if greater mechanistic insight into the course of the McMurry reaction was to be achieved or if superior reagents were to be found for carrying out such reductive couplings on a wider variety of C=O, C=N, C=S and C=N derivatives, low-valent transition metal complexes of Ti and other early transition metals were required that would have the following attributes: (1) a soluble metal reagent; (2) the metal present in one well-defined oxidation state; (3) the absence of any residual, secondary reductant (main group metal or metal hydride); and (4) absence of any possibly disturbing Lewis acid (main group metal halide).



Because of investigations undertaken by our research group in the 1990s, reductants of low-valent early transition metal salts, largely fulfilling the aforementioned criteria, were found to be readily accessible by the reductive alkylation of high-valent starting metal salts with organolithium, -magnesium or -aluminum reagents in a variety of nonprotic polar or nonpolar media. Such a reductive alkylation can best be exemplified by the prototypical generation of titanium(II) chloride reported in $1995^{[27]}$ (Scheme 8). This convenient, high-yielding preparation provided TiCl₂ in a form most useful for exploring the reduction of many organic substrates.^[2,18,28]



Scheme 8.

Exploring the possible scope of this reaction has led to successful preparation of analogous complexes of ZrCl₂, HfCl₂, VCl and CrCl. In addition, the use of an excess of *n*-butyllithium with VCl_n (n = 3 or 4) or CrCl₃ in THF has led to the stoichiometric formation of low-valent hydridic anionic salts of V(I) or Cr(I), as depicted in Scheme 9.^[30,31]



Scheme 9.

Evaluation of the relative reducing powers of these neutral and anionic reagents has been the ongoing focus of our investigations and the role of zirconium reductants are addressed in this present report.

It should be noted that empirical combinations of lowvalent transition metal salts and a second component, either as reductant or as Lewis base, continue to appear in the literature but no decisive evidence is presented concerning the oxidation state of the transition metal actually operative in such reductions.^[32]

Summary and Conclusions

Careful investigation of the reactions between benzaldehyde (4) and the 2:1 molar aggregates of *n*-butyllithium (3) with either zirconium(IV) chloride (1) or zirconium(IV) ethloxide (2) in THF as a function of temperature has established the following selectivities in reaction. First, at -78 °C the aggregates react with benzaldehyde, followed by hydrolysis, to give quantitatively the same product produced by *n*-butyllithium alone, namely 1-phenyl-1-pentanol (5). But in the case of the 2:1 aggregate of 3 and 2 the reaction with benzaldehyde, followed by prompt quench with D₂O, revealed that the unreacted benzaldehyde was partially deuteriated at the carbonyl as C_6H_5 -CD=O and that the alcohol 5 contained some deuterium as in 5c. This is clear evidence that the $Zr(OEt)_4$ in the 2 *n*BuLi·Zr(OEt)₄ aggregate had accelerated the lithiation of benzaldehyde.

Second, the reaction of either aggregate, **1** and **3** or **2** and **3**, with benzaldehyde at 25 °C was identical: after hydrolysis a quantitative yield of benzyl alcohol was obtained. This outcome is perfectly consistent with transmetallation occurring within the original aggregate to yield nBu_2ZrE_2 and 2 LiE (E = Cl, OEt) and the facile *beta*-elimination of the former to provide the useful hydrozirconating agent, H₂ZrE₂.

Third, refluxing the former hydrozirconating agent in THF led to the complete elimination of its butyl groups and the formation of $ZrCl_2$ or $Zr(OEt)_2$, respectively. Reaction with benzaldehyde and subsequent hydrolysis now led exclusively to the 1,2-diphenyl-1,2-ethanediol system. Moreover, the stereoselectivity for the racemic diol 7 over the *meso*-diol **8** was most gratifying: $ZrCl_2$ produced a *rac/meso* ratio of 93:7 and $Zr(OEt)_2$ yielded solely the *rac*-diol **7**. Therefore, by careful temperature control alone the 2:1 aggregate 2BuLi·ZrE₂ can function as a highly selective hydrozirconating agent or reductive coupling reagent toward benzaldehyde. As previous work has already shown, such reductions are readily applicable to other carbonyl, epoxide and acetylenic and olefinic systems.^[16,17]

Given the demonstrated versatility of the zirconium reagents discussed here, one might wonder how the titanium and hafnium derivatives compare with those of zirconium. Current studies indicate that pure samples of nBu_2TiE_2 are difficult to prepare, because such samples tend to decompose into TiCl₂ rapidly above 0 °C.^[16b] Secondly, samples of TiCl₂ in THF can readily bring about the reductive coupling of benzaldehyde at 25 °C but with distinctly less stereoselectivity: a typical rac/meso ratio observed is 70:30.^[33] On the other hand, the nBu_2HfE_2 can be readily generated at 25 °C but it has proved to be mostly thermally stable to decomposition. Thus, in reactions of such a reagent with ketones, reduction to the monomeric alcohol predominates and little coupling to the diol occurs.^[16b] Thus it appears that in terms of reactivity and selectivity in such reductions, zirconium reagents will remain superior to those of titanium and hafnium.

Experimental Section

Instrumentation, Analysis and Starting Reagents: The *n*-butyllithium (1.6 M in hexane), and the zirconium(IV) chloride and zirconium(IV) ethoxide (both anhydrous and of 97% purity) were used as received from Aldrich Chemical Company. All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal-benzophenone ketyl mixture prior to use.^[34] The IR spectra were recorded with a Perkin–Elmer instrument (model 457), and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (¹H and ¹³C) were recorded with a Bruker spectrometer (model EM-360) and

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tetramethylsilane (Me₄Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me₄Si reference signal. The GC/MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett–Packard 5970 mass-selective detector instrument. The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-30 capillary column. Melting points were determined on a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected.

Reaction of Lithium 2,2,6,6-Tetramethylpiperidide (LTMP) with Benzaldehyde (4)

Generation of Lithium 2,2,6,6-Tetramethylpiperidide (LTMP): To 10 mL of anhydrous, deoxygenated hexane at -78 °C were introduced 1.00 mL (5.8 mmol) of 2,2,6,6-tetramethylpiperidine ($\geq 99\%$) and then 3.60 mL (5.8 mmol) of 1.6 M *n*-butyllithium in hexane. The resulting orange solution became a yellow suspension of LTMP and was kept at 0 °C for 3 h.

Reaction of LTMP in Hexane with Benzaldehyde: To a solution of 6.00 mL (60 mmol) of benzaldehyde (freshly distilled under argon) in 50 mL of toluene and kept at 0 °C was added the previously prepared hexane solution of LTMP. The resulting orange solution was left overnight at 25 °C and then hydrolyzed with water and ether. The separated organic layer was dried with anhydrous Na₂SO₄ and all volatiles removed by evaporation under reduced pressure to yield 5.3 g of an orange liquid. The ¹H NMR spectral analysis of this liquid showed the presence of 52% (13 mmol) of benzyl benzoate (16) (¹H peak at 5.34 ppm), 7% (3.4 mmol) of benzyl alcohol (6) (¹H peak at 4.6 ppm) and 41% of benzaldehyde. The identity of 6 and 16 were confirmed by individual separation by column chromatographic on silica gel with hexane elution and comparison with the ¹H and ¹³C NMR spectra of authentic samples.^[35]

The original aqueous layer from the reaction workup was evaporated to about one-half its volume and then acidified with 1 N aqueous HCl. Cooling of the solution led to the deposition of 310 mg (2.5 mmol.) of benzoic acid (IR and mp). The conclusion is that the benzyl alcohol and benzoic acid most likely arose from the saponification of **16** in the strongly alkaline aqueous solution prior to workup.

Reactions of the 2:1 Aggregate of Zirconium(IV) Ethoxide (2) with *n*-Butyllithium (3)

General Reaction Procedure and Hydrolytic Workup: All glassware and needles for the transfer and reaction of liquid samples were dried in an oven at 120 °C and while cooling were thoroughly flushed with argon. The standard reaction apparatus was a 125mL, two-necked Schlenk flask, provided with a Teflon®-coated stirbar and having the argon inlet on one neck and a rubber septum on the other neck. Then 30 mL of anhydrous, deoxygenated tetrahydrofuran (cf. supra) was introduced and cooled to -78 °C in a solid CO₂/acetone bath. Thereupon a tared 2.00 mmol sample (560 mg) of zirconium(IV) ethoxide (2) (± 0.10 mmol and corrected for its 97% purity) in a glass-stoppered vial under argon was emptied into the flask in the stream of emerging argon. To the reaction suspension stirred magnetically at -78 °C were added dropwise by gastight syringe 2.6 mL of 1.60 M n-butyllithium (3) in hexanes (4.10 mmol). The resulting white suspension was subjected to stirring at different temperatures for given times before the benzaldehyde (4) was introduced. All such reactions were conducted under the diffuse fluorescent lighting of the laboratory provided during the daytime.

1) Stirring for Two Hours at -78 °C Followed by Addition of Benzaldehyde (4) and Subsequent Workup with H₂O: After 2 h at -78 °C the white suspension was treated with 210 mg (0.20 mL, 2.0 mmol) of benzaldehyde (4) (freshly distilled under argon), whereupon the reaction mixture turned pale yellow. After stirring at -78 °C for an additional 2 h and warming to 25 °C over 24 h the orange reaction solution was quenched with 15 mL of water. Hydrolytic workup with ether extraction, drying the organic extract with anhydrous Na₂SO₄ and solvent removal by rotary evaporation gave 35 mg of liquid ($\approx 100\%$), which by ¹H and ¹³C NMR analysis proved to be solely 1-phenyl-1-pentanol (5). Such spectra were superimposable with the published spectrum in CDCl₃^[35] and lacked any trace of characteristic ¹H absorptions for benzyl alcohol (6), such as the peak at $\delta = 5.80$ ppm, or for *rac*- and *meso*-1,2-diphenyl-1,2-ethanediol (7 and 8) at $\delta = 4.57$ and 4.75 ppm, respectively.

2) Stirring for Two Hours at -78 °C, Followed by Addition of Benzaldehyde (4) and Subsequent Treatment with D2O: a) Normal procedure: Repetition of the procedure exactly as given in section 1), except that D₂O (98%) was substituted for H₂O in the workup, again gave solely 1-phenyl-1-pentanol (5) as the only product. But (5) contained a deuteron in the hydroxy group (¹H, ²H NNHR peaks) and none at the C_1 site (5a). b) Inverse addition: In this procedure the mixture of the specified amounts of zirconium(IV) ethoxide (2) and benzaldehyde in THF at -78 °C was treated with the two equivalents of *n*-butyllithium. After 15 min. of stirring at -78 °C the pale yellow suspension was warmed up to 25 °C over 2 h. The mixture then was treated with D₂O in THF. Subsequent workup showed the presence of only CH3CH2CH2CH2-CHPh-OD (5b). c) Inverse addition with prompt quench with D_2O at -78 °C: As in procedure 2b the same mixture of 2 and 4 in THF at -78 °C was treated with two equivalents of *n*-butyllithium. After the resulting vellow suspension was stirred for 15 min, it was promptly quenched at -78 °C with a solution of D₂O (98%) in THF. Usual hydrolytic workup led to a mixture of 1-phenyl-1-pentanol and 5% remaining benzaldehyde, as shown by integrating the C-H peaks at 10.0 and at 4.6 ppm in the ¹H NMR spectrum. Furthermore, integrating the methyne H of 5 vs. the methyl H of 5 gave a ratio of 0.87:3.0, compared with the expected 1.0:3.0 ratio of undeuteriated 5. These results are consistent with the presence of about 13% of deuterium on the methyne C, as in 5c: CH₃CH₂CH₂CH₂-CD(OH)-C₆H₅. Additional confirmation for the presence of 5c was obtained from the ²H NMR spectrum of the reaction mixture: a small but distinct peak was found at 4.6 ppm, where the methyne C-D peak would occur. Finally, the same ²H NMR spectrum displayed a further peak at $\delta = 10.0$ ppm, which observation shows that the unreacted 4 was also partially deuteriated on the carbonyl carbon (4a).

3) Stirring While Allowing to Warm to 25 °C, Followed by Addition of Benzaldehyde (4) at -78 °C: The white suspension, generated at -78 °C, was warmed to 25 °C and then stirred for 1 h. The suspension turned into a pale yellow solution. The reaction mixture was recooled to -78 °C and treated with 210 mg (0.20 mL, 2.0 mmol) of freshly distilled 4. After warming to 25 °C over 24 h the orange reaction mixture was hydrolyzed and worked up as in section1. The pale yellow organic residue (400 mg) consisted of solely benzyl alcohol (6) (100%) with some THF by ¹H and ¹³C NMR analyses. No characteristic absorptions for 1-phenyl-1-pentanol (5) or for *rac-* or *meso-*1,2-dihenyl-1,2-ethanediol (7 or 8) could be detected.

An identical reaction run to the foregoing was carried out, except that the workup quench employed D₂O (98%). Again benzyl alcohol (**6**) was the only product, containing a deuteron only in the hydroxy group and none at the C_{α} of **6** (PhCH₂–OD) (¹H and ²H NMR spectra).

4) Stirring While Allowing to Warm to 25 °C, Followed by Heating at Reflux and then Addition of Benzaldehyde (4) at 25 °C: A reaction run identical to that in section 3 and also brought to 25 °C for 1 h was then heated at reflux for 4 h. The resulting dark brown solution was cooled to 25 °C and treated with 1.95 mmol of freshly distilled **4**. After stirring for 24 h the brown mixture was hydrolyzed in the usual manner. The pale organic liquid (450 mg) was shown by ¹H and ¹³C NMR spectroscopy to consist of THF and solely of *rac*-1,2-diphenyl-1,2-ethanediol (7). No spectral absorptions characteristic of 1-phenyl-1-penatnol (**5**) or benzyl alcohol (**6**) or *meso*-1,2-diphenyl-1,2-ethanediol (**8**) were detectable.

Reactions of Zirconium(IV) Chloride (1) with *n***-Butyllithium (3):** Reaction runs were identical to the three sets of experimental conditions employed above for 2.00 mmol of zirconium(IV) ethoxide (2) with 4.10 mmol of *n*-butyllithium (3) in THF, except that 2.00 ± 0.10 mmol of zirconium(IV) chloride (1) was substituted for 2. Details of the individual procedure and the hydrolytic workup were exactly parallel to the corresponding numbered sections above.

1) Stirring for Two Hours at -78 °C, Followed by Addition of Benzaldehyde (4): The isolated organic residue consisted of essentially only 1-phenyl-1-pentanol with traces of THF.

An identical reaction run to the foregoing was carried out, except that the workup-quench employed D_2O (98%). As above, 1-phenyl-1-pentanol (**5**) was the sole product, which contained a deuteron only in the hydroxy group and none at the C₁ of **5** (¹H and ²H NMR spectra).

2) Stirring While Allowing to Warm to 25 °C, Followed by Addition of Benzaldehyde (4) at -78 °C: As carried out and worked up as in section 3 above, solely benzyl alcohol (6) was obtained in almost a quantitative yield.

3) Stirring While Allowing to Warm to 25 °C, Followed by Heating at Reflux and then Addition of Benzaldehyde (4) at 25 °C: As carried out and worked up as in section 4 above, the product consisted of THF and solely of a 93:7 mixture of racemic and *meso*-1,2-diphenyl-1,2-ethanediol (7 and 8).

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