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Unexpected Benzylic Carbon−Carbon Bond Cleavage by Transfer Epizirconation: Indications of an SET Pathway and Implications for Alkane Metathesis[1]

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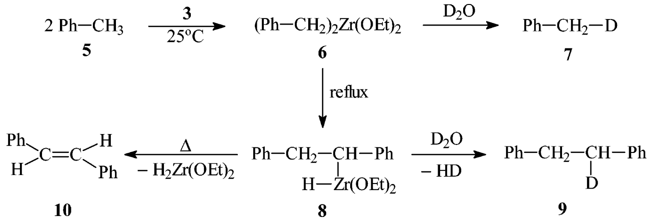
Summary: In addition to the zirconation of benzylic hydrocarbons, Ar−CH$_3$, by di-n-butylzirconium diethoxide and the ensuing C−C bond formation from (Ar−CH$_2$)$_2$Zr(OEt)$_2$ to yield Ar−CH$_2$−CH(ZrH(OEt)$_2$)−Ar, it has now been found that Bu$_2$Zr(OEt)$_2$ in ethers can also cleave the C−C bond in bibenzylic hydrocarbons, Ar−CH$_2$−CH$_2$−Ar′, into benzylic zirconium fragments, (Ar−CH$_2$)(Ar′−CH$_2$)Zr(OEt)$_2$, as fostered by LiOEt and donor solvents. The role of SET processes in such C−C bond cleavages and the potential relevance to practical alkane metathesis are considered.

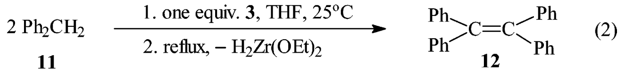
During ongoing studies of the chemical reactivity of early-transition-metal alkyls,[2−8] we have made the valuable observation that group 4 metal alkyls of the type $R_2Zr(OR')_2$ can readily zirconate weaker carbon acids such as toluene and diphenylmethane at the benzylic carbon in THF at 25 °C.[9] The requisite di-*n*-butylzirconium diethoxide ($Bu_2Zr(OEt)_2$, **3**) is readily accessible by treating $Zr(OEt)_4$ (**1**) in THF at −78 °C with 2 equiv of *n*-butyllithium (**2**) (eq 1). The lithium ethoxide byproduct (**4**) has been shown to be a cocatalyst in such zirconations.[10] Thus, a 2:1 molar mixture of toluene (**5**) and **3** reacts at 25 °C to produce principally dibenzylzirconium diethoxide (**6**), as evidenced by workup of a reaction aliquot and the isolation of α-deuteriotoluene (**7**) in >90% purity (Scheme 1).

$$\underset{\mathbf{1}}{Zr(OEt)_4} + \underset{\mathbf{2}}{2BuLi} \xrightarrow[-78\ ^\circ C]{THF} \underset{\mathbf{3}}{Bu_2Zr(OEt)_2} + \underset{\mathbf{4}}{2LiOEt} \quad (1)$$

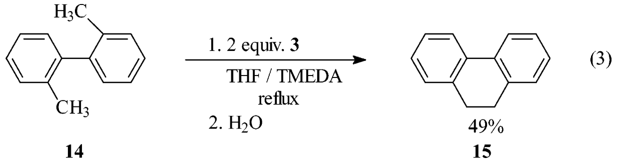
However, a more surprising observation was that made when zirconated intermediate **6** was heated at reflux in THF or higher boiling ethers. The organic groups bonded to zirconium became coupled to each other with the formation of the organylzirconium diethoxide hydride **8**, whose structure follows from its treatment with D$_2$O to produce both H−D and α-deuteriobibenzyl (**9**) in 75% overall yield.[11] Prolonged heating of **6** then led to *trans*-stilbene (**10**), a finding consistent with the dehydrozirconation of **8**. In a completely analogous process diphenylmethane (**11**) and **3** underwent consecutive zirconation at 25 °C, C−C bond formation at reflux, and complete dehydrozirconation to provide a 74% yield of only tetraphenylethylene (**12**) (eq 2).[9]

Scheme 1





When such C−C bond formation occurs intermolecularly (R$_1$ and R$_2$ unlinked, as with **5** and **3** to produce **8**), the process may be properly termed an *oxidative dimerization*. When R$_1$ and R$_2$ are bonded, then the reaction becomes an *oxidative cyclization*. An intramolecular cyclization of 2,2′-dimethylbiphenyl (**14**) to give 9,10-dihydrophenanthrene (**15**) is offered in eq 3. The scope and mechanism of this novel C−C bond-forming process have recently been scrutinized by preparing diorganylzirconium diethoxides (**16**) and studying their thermal rearrangement to **18**.[12a] A central unifying feature in such a process is the transition state **17**,



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(1) Organic Chemistry of Subvalent Transition Metal Complexes. 37. Part 36: Eisch, J. J.; Otieno, P. O.; Gitua, J. N.; Adeosun, A. A. *Eur. J. Org. Chem.* **2005**, 4364.

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(6) Eisch, J. J.; Adeosun, A. A. *Eur. J. Org. Chem.* **2005**, 993.

(7) Eisch, J. J.; Adeosun, A. A.; Dutta, S.; Fregene, P. O. *Eur. J. Org. Chem.* **2005**, 2657.

(8) Eisch, J. J.; Owuor, F. A.; Shi, X. *Polyhedron* **2005**, *24*, 1325 (Symposium-in-Print).

(9) Eisch, J. J.; Dutta, S. *Organometallics* **2004**, *23*, 4181.

(10) Since di-*n*-butylzirconium dichloride, which is prepared from ZrCl$_4$ and 2 equiv of *n*-butyllithium in THF, has been shown not to zirconate toluene or diphenylmethane, we assume that the LiCl byproduct cannot catalyze zirconation. Therefore, the LiOEt byproduct from the reaction of Zr(OEt)$_4$ with 2 equiv of *n*-butyllithium must catalyze benzylic C−H zirconation.

(11) The course of the rearrangement of **6** into **8** was also followed by preparing **6** from the treatment of Zr(OEt)$_4$ with 2 equiv of benzylmagnesium chloride in THF at 25 °C. Subsequent heating of **6** in refluxing THF caused the rearrangement to **8**. Workup with D$_2$O led to the evolution of H−D and the isolation of **9**.[9]

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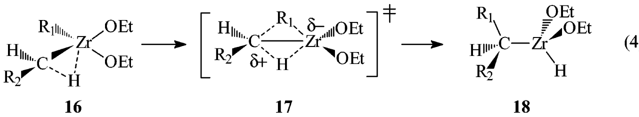
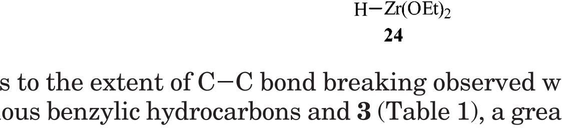
having a carbene-like α-carbon to which a carbanionic group migrates from the hydridic zirconium center[12b] (eq 4).



16 **17** **18** (4)

In our further exploration of the scope of such zirconations of benzylic hydrocarbons and the carbon−carbon bond-forming reactivity of such intermediates, we have treated bibenzyl (**19**), diphenylmethane (**11**), [2,2]-paracyclophane (**20**), and other hydrocarbons with **3** in THF at 25 °C (Table 1). From such experiments we have now been astonished to learn that the principal reaction, in 50% or greater extent, is *neither zirconation* of a benzylic C−H bond (Scheme 1, **5** → **6**) *nor oxidative dimerization* (Scheme 1, **6** → **8** or **9**) but, rather, a third novel process: namely, what may be considered as an overall metalative cleavage of the *σ* carbon−carbon benzylic bond (Scheme 2). The presence of carbon−metal bonds in the cleavage adducts (**21**−**23**) was established by workup with D_2O and by identifying the appropriately deuterated fragments in the deuteriolysate, such as $PhCH_2D$ from **21** and Ph_2CHD from **22**.[13] A variety of other hydrocarbons bearing at least two or more benzylic-substituted C−C bonds have been subjected to the action of 1 equiv of $Bu^n{}_2Zr(OEt)_2$ (**3**) in THF for 24 h at room temperature (25 ± 5 °C) and then hydrolyzed. The products and their yields arising from such reactions are summarized in Table 1. These findings verify the surprising and seemingly contradictory conclusion that the very reagent, **3** in THF, which is able to form C−C bonds from benzylic hydrocarbons at reflux in an *oxidative dimerization*, can as well effect the *reductive cleavage* of similar benzylic C−C bonds at room temperature.

Resolution of these striking findings must be sought in differing mechanistic pathways for the C−C bond-making and the C−C bond-breaking processes. The overall transformation clearly involves the breaking of the benzylic C−C bond, as for example in the conversion of **19** into **22** (Scheme 2). However, the new benzylic C−C bond formed by the thermal rearrangement of **22** into **24** is that of a hydridozirconium derivative of bibenzyl (**24**) and not of bibenzyl itself (**19**). Thus the conversion shown in eq 5 of first C−C bond-breaking and then C−C bond-making is an irreversible process, leading to the more stable product (**19** → **22** → **24**).



$$\underset{\mathbf{19}}{Ph{-}CH_2{-}CH_2{-}Ph} \xrightarrow[-\,2\,Bu\bullet]{\mathbf{3}} \underset{\mathbf{22}}{(Ph{-}CH_2)_2Zr(OEt)_2} \xrightarrow{\Delta} \underset{\mathbf{24}}{\underset{H-Zr(OEt)_2}{Ph{-}\underset{|}{C}H{-}CH_2{-}Ph}} \quad (5)$$

As to the extent of C−C bond breaking observed with various benzylic hydrocarbons and **3** (Table 1), a greater extent of the C−C bond cleavage was generally observed where both carbons were benzylic (run 5 versus run 8). Further experimental factors significantly influencing the rate of C−C bond cleavage of *sym*-tetraphenylethane (**11**) by Bu_2ZrE_2 are the following: (1) cleavage by $Bu_2Zr(OEt)_2$ (**3**) containing LiOEt occurs readily in THF but *not at all* in hexane (runs 1 versus 2); (2) cleavage by

Table 1. Cleavage of Benzylic C−C Bonds by Di-*n*-Butylzirconium Diethoxide (3) in Tetrahydrofuran at 25 °C and the Hydrocarbons Resulting from Subsequent Hydrolysis[a,j]

run	hydrocarbon substrate	hydrocarbon product(s)	conversn[c] (yield, %)
1	1,1,2,2-tetraphenylethane	diphenylmethane	80
2	1,1,2,2-tetraphenylethane[b]		0
3	1,1,2,2-tetraphenylethane[d]	diphenylmethane	65
4	1,1,2,2-tetraphenylethane[e]		0
5	1,2-diphenylethane	toluene	55
6	1,2-di-*p*-tolylethane	*p*-xylene	75
7	[2.2]paracyclophane	1,2-di-*p*-tolylethane	90
8	1,1-diphenylethane	diphenylmethane methane[f]	25
9	1,3-diphenylpropane	toluene ethylbenzene	20[g] 25
10	2,2-diphenylpropane		
11	1,1,1-triphenylethane	triphenylmethane methane[f]	30
12	ethylbenzene		
13	isopropylbenzene		
14	*tert*-butylbenzene[h]		
15	tetrahydrofuran (solvent)[i]	1-butanol 1,8-octanediol	25 75

[a] The standard conditions for generating $Bu_2Zr(OEt)_2$ (**3**) in THF and attempting cleavage of a benzylic C−C bond in the hydrocarbon substrate, unless otherwise specified, were as follows: to a white suspension of $Zr(OEt)_4$ (740 mg, 2.72 mmol) in 35 mL of anhydrous THF, cooled to −78 °C under an argon atmosphere, was added 3.40 mL of 2.5 M *n*-butyllithium (5.44 mmol) in hexane. After it was stirred for 2 h, the light yellow mixture was warmed to −60 °C, after which 1 molar equiv of the hydrocarbon substrate in 5 mL of THF was added. The reaction mixture was brought to room temperature over 2 h and stirred at 25 ± 5 °C for 24 h. The usual hydrolytic workup and analysis by GC and NMR techniques then ensued. [b] Dry hexane was substituted for THF as the medium for generating reagent **3**. Although the LiOEt byproduct was insoluble at low temperatures, the reaction mixture was almost a complete solution at room temperature. [c] The percentage of conversion was reproducible to within ±2%. [d] $Bu_2Zr(OEt)_2$ was prepared essentially free of LiOEt by the following sequence of reactions performed on $ZrCl_4$ in THF at −78°C: (1) addition of 2 equiv of BuLi to produce Bu_2ZrCl_2; (2) addition of 2 equiv of absolute ethanol to yield $(EtO)_2ZrCl_2$; (3) addition of 2 equiv of Bu^nLi to generate $Bu_2Zn(OEt)_2$ and LiCl as the byproduct. [e] In this run 1 equiv of Bu_2ZrCl_2 was used in place of $Bu_2Zr(OEt)_2$. $Bu^n{}_2ZrCl_2$ was generated in THF at −78 °C by treating $ZrCl_4$ with 2 equiv of BuLi. [f] Methane detected in the gas evolved upon hydrolysis by mass spectrometry. [g] Some of the more volatile toluene was possibly lost upon rotatory evaporation of the solvent. [h] Under similar conditions, the following substrates gave no sign of C−C bond cleavage: 1-hexylbenzene, cyclopropylbenzene, a mixture of *cis*- and *trans*-1,2-diphenylcyclopropane, and cyclohexylbenzene. [i] In this run $Bu_2Zr(OEt)_2$ (**3**) was prepared in THF, as described in footnote *a* and then without adding any hydrocarbon substrate brought to room temperature and held there for 24 h. After a terminal 3 h reflux period the reaction mixture was worked up in the usual manner. [j] Complete experimental details for the preparation of $Bu_2Zr(OEt)_2$ (**3**) and its use for the cleavage of benzylic C−C bonds in each of the hydrocarbon substrates (runs 1−14) or of THF (run 15) are given in the Supporting Information.

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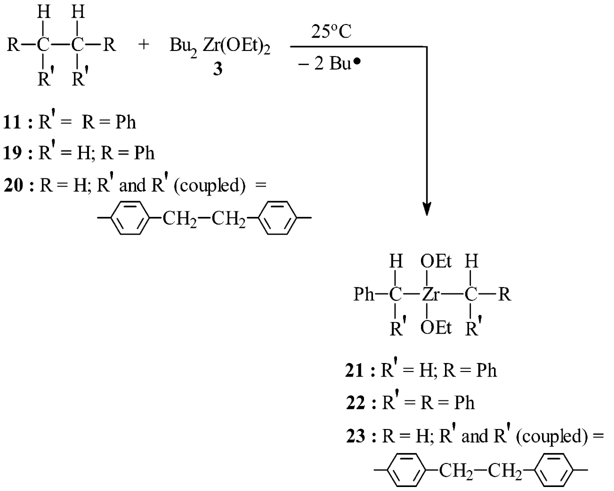
(12) (a) The agostic C- - -H- - -Zr interaction indicated in **16** is as yet only proposed as occurring in the ground state. Low-temperature NMR experiments with the unstable **3** have not been able to corroborate such bonding. (b) Eisch, J. J.; Dutta, S. *Organometallics* **2005**, *24*, 3355.

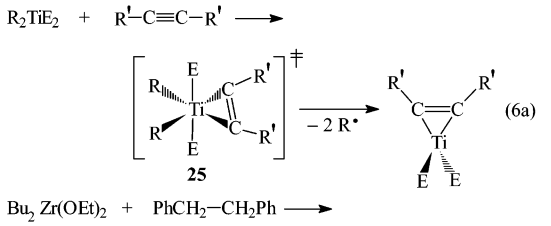
(13) As will be evident, the benzylic C−C bond cleavage products $RR'Zr(OEt)_2$ (e.g., **21**−**23**) may well complex with the LiOEt byproduct and establish the following complex equilibria: $RR'Zr(OEt)_2 + 2LiOEt \rightleftharpoons Li_2[RR'Zr(OEt)_4] \rightleftharpoons Zr(OEt)_4 + RLi + R'Li$. Hence, the carbon−metal bond actually being cleaved upon workup with D_2O may be either the C−Zr bond or the C−Li bond in mutual equilibrium. The deep colors (orange to wine red) would be consistent with the presence of delocalized anions of such organolithium compounds.

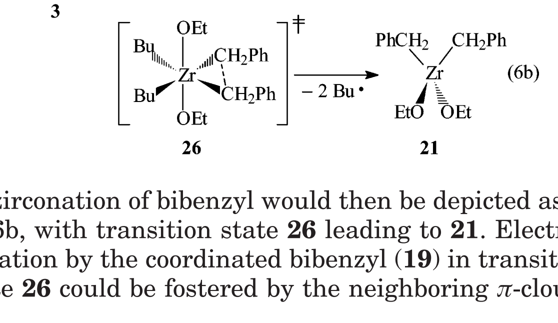
Scheme 2



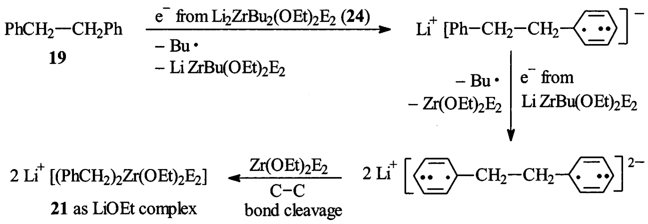
$Bu_2Zr(OEt)_2$ containing LiCl occurs less readily (run 3) but no cleavage at all is effected by Bu_2ZrCl_2 containing LiCl (run 4); (3) styrene is completely converted into atactic polystyrene under these conditions, an outcome consistent with the presence of some radical intermediate;[14] (4) competitive with the observed C−C bond cleavage in the substrate is C−O bond cleavage in THF, and this side reaction leads to the formation of both 1-butanol and 1,8-octanediol upon hydrolysis. The detection of 1-butanol from various solutions of metal hydrides or organometallics in THF is not unusual,[15] but the simultaneous formation of 1,8-octanediol from such THF ring cleavage is unprecedented. As will be seen, such an anomalous reaction provides a powerful clue as to the reaction mechanism of such σ-bond cleavages.

A possible mechanism for these unexpected C−C and C−O bond cleavages is the occurrence of a transfer epimetalation of the relatively labile benzylic C−C bonds by either $Bu_2Zr(OEt)_2$ itself (**3**) or its lithium complex, $Li_2ZrBu_2(OEt)_2E_2$ (**24**; E = OEt, Cl in runs 1 and 3, respectively). In previous investigations we have adduced evidence in support of the transfer epimetalation of π-bonds such as C═C, C≡C, C═O, C═N, and C≡N linkages by R_2TiE_2 reagents (E = X, OR′) as proceeding through octahedrally coordinated transition states such as **25** (eq 6a).[16] In an analogous fashion, transfer epizirconation of bibenzyl would then be depicted as in eq 6b, with transition state **26** leading to **21**. Electron donation by the coordinated bibenzyl (**19**) in transition state **26** could be fostered by the neighboring π-clouds of the aromatic rings. However, as an alternative or competing pathway the lithium zirconate salt **24** could mediate single-electron transfers to the antibonding π^*-orbitals of the hydrocarbon substrate (bibenzyl) with concomitant butyl radical loss to yield the zirconated cleavage product (Scheme 3).[17] This latter SET mechanism would be in better accord with the accelerating effect of a donor solvent and of the lithium salt complex on the bond cleavage reaction, as well as taking into account the evidence for a free-radical polymerization of styrene.

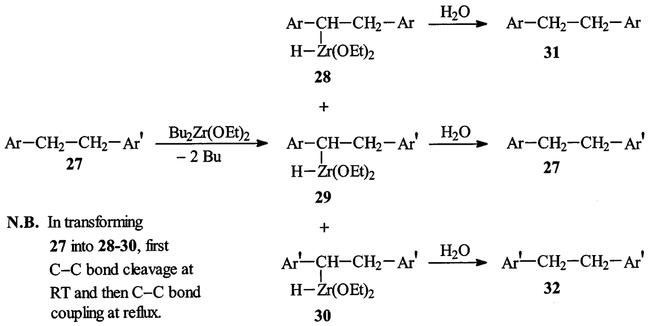




Scheme 3



Scheme 4



Since dibutylzirconium diethoxide (**3**) in THF has been shown capable of both the cleavage of benzylic C−C bonds at 25 °C and the formation of any sp^3-hybridized C−C bonds at reflux in THF, this zirconium reagent seems to have all the requisite reactivity necessary for the alkane metathesis of bibenzylic hydrocarbons,[18] as shown in Scheme 4. In the first step **27** and **3** would react at 25 °C to give benzylic C−C bond cleavage and then at reflux (cf. eq 5) C−C bond formation would produce **28**−**30**. Of course, the occurrence of σ-C−C bond metathesis with these arylethanes, such as that turning 2 mol of **27** ultimately into **31** and **32** is irreversible (see above and eq 5) and thus is unlike

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(14) Styrene is also known to polymerize via anionic intermediates, such as those possibly formed by the addition of butyllithium to the styrene monomer: $PhCH{=}CH_2 + BuLi \rightarrow [PhCH{-}CH_2{-}Bu]^-Li^+$. However, with other substrates known to add butyllithium, such as diphenylacetylene and 1,1-diphenylethylene, no such butylation by **3** has been observed by us.

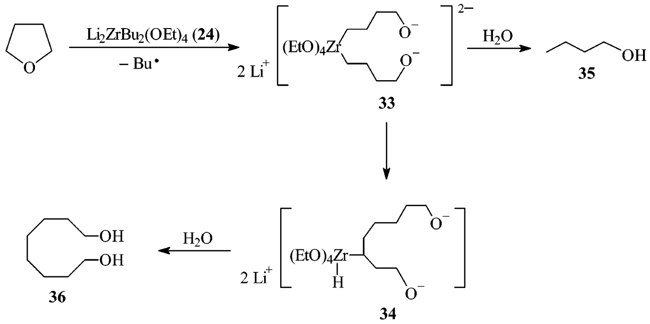
(15) For example, allowing solutions of the 2:1 lithium−biphenyl adduct in THF to come to reflux causes consumption of the reagent and cleavage of the THF ring. An equivalent amount of 1-butanol is produced upon hydrolysis. Cf.: Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.

(16) Eisch, J. J.; Gitua, J. N. *Organometallics* **2003**, *22*, 24.

(17) An unambiguous case of C−C bond cleavage of such bibenzylic hydrocarbons by SET processes is provided by the reactions of Ar_n-CH_{3-n}−$CH_{3-n}Ar_n$ substrates by Li, Na, or K in liquid ammonia or in ethers. For a leading reference, cf.: Gilman, H.; Gaj, B. J. *J. Org. Chem.* **1963**, *28*, 1725.

(18) For the seminal publication on alkane metathesis through the use of zirconium hydrides bonded on silica for the hydrogenolysis of simple alkanes at mild temperatures (150 °C), cf.: Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966.

Scheme 5



the alkene or alkane metathesis in current technical parlance, which is considered a priori as involving reversible equilibria, as for example in eq 7.[18] Nevertheless, these irreversible arylethane metatheses continue to receive our earnest attention.

$$2CH_3CH_2CH_3 \xrightleftharpoons{\text{catalyst}} CH_3CH_3 + CH_3CH_2CH_2CH_3 \tag{7}$$

However, even at this point in our studies, the cleavage behavior of THF by **3** observed here provides evidence for the operation of such a type of C−O bond metathesis. Although the origin of the 1-butanol from THF can be explained by a straightforward SET process initiated with **3** or **24**, the formation of 1,8-octanediol cannot. We suggest, therefore, an SET cleavage of THF by **3** to produce **33**, which undergoes the C−C bond-forming rearrangement generalized in eq 4 to yield **34**. Hydrolysis of **33** and **34** would produce **35** and **36**, respectively (Scheme 5). Thus, such a tandem C−O bond cleavage of THF and the C−C bond coupling of the open-chain oxybutylene fragments is tantamount to a σ-bond metathesis. The implications of these findings for the cleavage and coupling of both C−C and carbon−heteroatom bonds are most appealing and are under further scrutiny.

In summary, because the zirconations by $Bu_2Zr(OEt)_2$ of benzylic hydrocarbons lead to intermediates capable of forming C−C bonds in refluxing THF and since the same $Bu_2Zr(OEt)_2$ is now shown capable of cleaving benzylic C−C bonds at room temperature, conditions now appear to have been found under which $Bu_2Zr(OEt)_2$ in THF would be capable of promoting the irreversible alkane metathesis of bibenzylic hydrocarbons. Achieving such metatheses would be an important first step toward realizing reversible alkane metathesis in general.

Acknowledgment. Our research on reactions of group 4 metal alkyls over the past decade has been supported at various times by Akzo Corporate Research America, The Boulder Scientific Co., the U.S. National Science Foundation, and Solvay, SA, Brussels, Belgium. The present investigation has also been funded by the Alexander von Humboldt Stiftung, Bonn, Germany, which has provided the principal investigator with a Senior Scientist Award, first in 1993 and again in 2005 for investigations in the Laboratory of Professor Wolfgang A. Herrmann, Institute of Inorganic Chemistry, Munich Technical University. Technical advice and assistance have been generously given by the former students Drs. Adetenu A. Adeosun and Peter O. Otieno.

Supporting Information Available: Text giving experimental procedures and characterization data for the compounds discussed in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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