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Communications

Carbon−Carbon Bond Formation in the Surprising Rearrangement of Diorganylzirconium Dialkoxides: Linear Dimerization of Terminal Olefins[1]

John J. Eisch* and Somnath Dutta

Department of Chemistry, P.O. Box 6000, The State University of New York at Binghamton, Binghamton, New York 13902-6000

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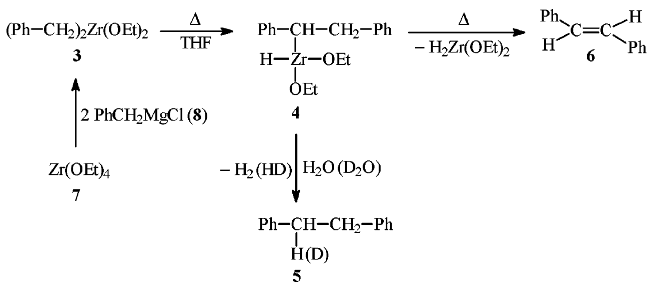
Summary: The mechanism of the rearrangement of diorganylzirconium dialkoxides, such as $R_1(R_2CH_2)Zr(OEt)_2$*, into organylzirconium hydride alkoxides of the type* $R_1R_2CHZr(OEt)_2H$*, has been investigated as a function of the* R_1 *and* R_2 *substituents and been found to involve optimally an intramolecular migration of* R_1 *to an* sp^3*-hybridized C−H center. A remarkably rapid transfer hydrozirconation between* $Bu^n{}_2Zr(OEt)_2$ *and the olefin* $RCH{=}CH_2$ *now permits the synthesis of* $(RCH_2CH_2)_2Zr(OEt)_2$*, whose rearrangement offers a route to the linear olefin dimer* $R(CH_2)_4R$*.*

Recently we have reported that dialkylzirconium dialkoxides, $R_2Zr(OR')_2$, are able to effect the ready benzylic zirconation of hydrocarbons, such as toluene (**1**) and other arylalkanes, as exemplified in eq 1.[2]

$$\underset{\mathbf{1}}{2PhCH_3} + \underset{\mathbf{2}}{Bu^n{}_2Zr(OEt)_2} \xrightarrow[\text{THF, LiOEt catalyst}]{25\ ^\circ C} \underset{\mathbf{3}}{(PhCH_2)_2Zr(OEt)_2} + 2Bu^nH \quad (1)$$

Scheme 1



Although this facile and useful zirconation was unexpected, even more surprising and exciting was the observed thermal behavior of the resulting benzylic derivatives such as **3**. In refluxing THF **3** underwent C−C bond formation, as was demonstrated by the hydrolysis of such reaction mixtures, during which hydrogen gas was evolved and varying proportions of dimeric hydrocarbons were then shown to be present. In the case of toluene, either bibenzyl (**5**) or *trans*-stilbene had formed in good overall yield, depending upon the length of heating[2] (Scheme 1).

Significant insight into the mechanism of this unusual C−C bond formation was obtained by synthesizing the key intermediate **3** unambiguously by another route, namely the treatment of $Zr(OEt)_4$ (**7**) with 2 equiv of benzylmagnesium chloride (**8**) in THF. Here again, as in Scheme 1, heating **3** in THF for short periods gave

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* To whom correspondence should be addressed. Fax: 607-777-4865. E-mail: jjeisch@binghamton.edu.

(1) Part 35 of the series Organic Chemistry of Subvalent Transition Metal Complexes. Part 34: Eisch, J. J.; Owuor, F. A.; Shi, X. *Polyhedron*, in press (Symposium-in-Print).

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

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Table 1. Thermal Rearrangement with C−C Bond Formation of Diorganylzirconium Dialkoxides and the Hydrocarbons Resulting from Subsequent Hydrolysis

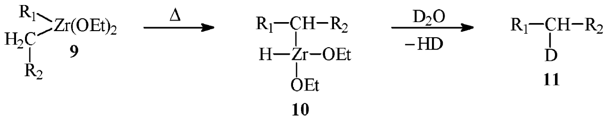
	substrate RR′Zr(OEt)$_2$[a]				
run	R	R′	solvent (reflux time, h)	hydrocarbon R−R′ [b]	conversion[j] (yield, %)
1	*n*-butyl	*n*-butyl (**2**)	hexane (8)	*n*-octane	>50[c]
2	benzyl	benzyl (**3**)	THF (8)	1,2-diphenylethane	79
3	benzyl	ethoxy (**11**)	THF (8)		
4	2-phenylethyl	2-phenylethyl (**12**)	THF (8)	1,4-diphenylbutane	22[d]
5	diphenylmethyl	diphenylmethyl	THF (8)	tetraphenylethylene	74
6	1,1-diphenylethyl	1,1-diphenylethyl	THF (8)		
7	phenyl	benzyl	THF (8)	diphenylmethane	29
8	phenyl	2-phenylethyl	THF (8)	1,2-diphenylethane	20
9	phenyl	2,2,2-triphenylethyl (**13**)	THF (8)	triphenylmethane + toluene	40[e]
10	*n*-hexyl	*n*-hexyl	hexane (6)	n-dodecane	88[f]
11	methyl	methyl	hexane (8)	ethyl iodide	+[g]
12	*p*-tolyl	*p*-tolyl (**14**)	THF (8)	3,4′-bitolyl (59) 4,4′-bitolyl (41)	60[h,i]

[a] The substrates RR′Zr(OEt)$_2$ were generally prepared on a 3 mmol scale in 35 mL of THF or hexane by treating at −78 °C a suspension of 3.0 mmol of Zr(OEt)$_4$ with 6.0 mmol of the appropriate organolithium reagent in hexane or Grignard reagent in THF, where R = R′ (as in runs 1, 2, 4, 11, and 12), or by adding first 3.0 mmol of RMgX and then after 15 min 3.0 mmol of R′MgCl, where R ≠ R′, as in runs 7−9. [b] The rearrangements of RR′Zr(OEt)$_2$ themselves were conducted by first bringing the substrates prepared as in footnote *a* to room temperature. After 6−12 h at this temperature and hydrolytic workup, little or no R−R′ was found. Hence, the rearrangements generally required 8 h of reflux to take place in noticeable conversion and with significant H$_2$ evolution upon hydrolysis. [c] Due to losses in separating octane from the hexane solvent, the actual yield is likely higher than the observed 50%. [d] In addition to a 72% recovery of ethylbenzene, 6% of a 1:1 mixture of "anomalous products", toluene and *n*-propylbenzene, were observed (cf. run 9). [e] These "anomalous products" were detected even at 25 °C. None of the expected product, 1,1,1,2-tetraphenylethane, was detected even at reflux. [f] The *n*-dodecane contained 12% of decane (cf. Scheme 5). [g] The rearrangement product, CH$_3$CH$_2$Zr(H)(OEt$_2$)$_2$, was trapped in this case by adding I$_2$ and detecting CH$_3$CH$_2$I by NMR spectroscopy. [h] The finding of a mixture of 3,4′ bitolyl and 4,4′-bitolyl establishes the intermediacy of an aryne−zirconium complex (**15** in Scheme 3). [i] Analogous to run 12, diphenylzirconium diethoxide was prepared in THF from Zr(OEt)$_4$ and 2 molar equiv of PhMgBr. Refluxing in THF and workup with D$_2$O gave a 38% yield of 2-deuteriobiphenyl. [j] Complete experimental details for each preparation of R$_2$Zr(OEt)$_2$ or RR′Zr(OEt)$_2$ and their thermal rearrangement are given in the Supporting Information.

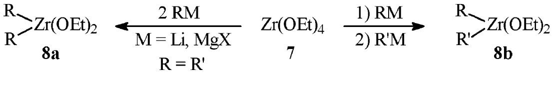
principally bibenzyl (**5**) and dihydrogen gas upon hydrolysis, whereas prolonged heating produced principally *trans*-stilbene (**6**) and a more copious H$_2$ evolution.[3] Clearly the H$_2$ gas stemmed from the Zr−H bonds eliminated from **3** in forming **5** and **6**. This type of coupling of carbon centers with metal−hydride bond elimination accordingly has been termed *oxidative dimerization*.[2] The chemical opposite of such dimerizations would be the famous Fittig pinacol coupling[4] and the more recently discovered McMurry−Mukaiyama−Tyrlik coupling processes,[5−7] which are formally *reductive dimerizations*.[5−7] However, the most unforeseen insight gained into the mechanism of the oxidative dimerization of **3** to form **5** came from treatment of the reaction mixture with D$_2$O. The isolated bibenzyl was found to be about 90% monodeuterated on one of the four benzylic C−H positions (**5**, α-deuterio). The detection of such α-deuteriobibenzyl as well as the evolution of HD gas presupposes the presence of zirconium precursor **4**. It should be noted here that dibenzylzirconium dichloride undergoes an analogous rearrangement in refluxing THF and again α-deuteriobibenzyl (**5**, α-deuterio) is isolated upon workup with D$_2$O. This observation shows that the LiOEt present in **3** plays no essential role in the rearrangement.

Hence, the intriguing question now arises as to the mechanism of C−C bond formation on passing from **3** to **4** in this oxidative dimerization. Therefore, we now wish to present our recent studies on the scope and mechanism of this unusual C−C bond-forming rearrangement and to show how such mechanistic understanding can be applied in a novel method for the linear dimerization of terminal olefins.[8]

Scheme 2



A deeper understanding of the unprecedented rearrangement of **9** into **10**, as depicted in Scheme 2, has been obtained by examining the thermal behavior of an array of diorganylzirconium derivatives (**9**) in refluxing THF or hexane, as generalized in Scheme 2 and summarized in Table 1. The requisite RR′Zr(OEt)$_2$ substrates for runs 2 and 5 were obtained by the zirconation of toluene or diphenylmethane, respectively, by reagent **2** according to eq 1. The zirconium derivatives **8a** and **8b** in runs 1, 3, 4, 7, 8, 9, 11, and 12 resulted from treating Zr(OEt)$_4$ (**7**) with 1 or 2 equiv of the same or different RLi or RMgX reagent, respectively, according to eq 2.[9] (The unique and significant source of the hexyl derivative (run 10) is discussed below.)

 (2)

Scrutiny of the results of these thermal rearrangements permits several important observations concerning the scope of this novel reaction. First of all, there is no exchange or crossover of organyl groups on different zirconium centers during rearrangement; hence, the

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(3) The amount of hydrogen gas arising here from the hydrolysis of zirconium hydrides cannot be monitored accurately, since some of the Zr−H bonds generated are consumed by cleavage of the THF solvent, as is indicated by the 1-butanol obtained upon hydrolysis.

(4) Fittig, R. *Liebigs Ann. Chem.* **1859**, *110*, 17.

(5) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708.

(6) Mukaiyama, T.; Sato, T.; Hanna, J. J. *Chem. Lett.* **1973**, 1041.

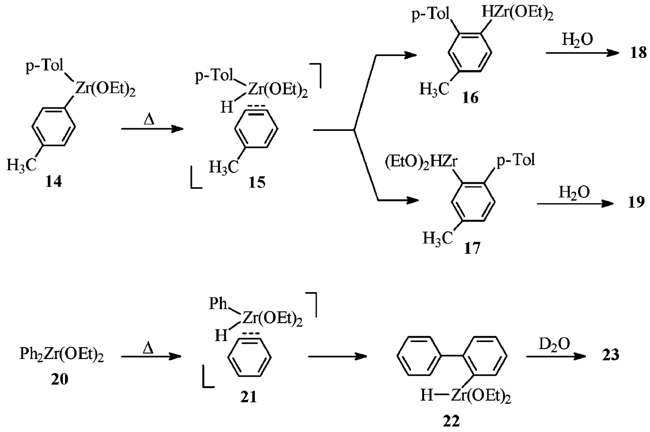
(7) Tyrlik, S.; Wolochowicz, I. *Bull. Soc. Chim. Fr.* **1973**, 2147.

(8) By the linear dimerization of terminal olefins we mean the direct bonding of the two terminal carbon atoms, as in 2RCH═CH$_2$ → RCH$_2$CH$_2$CH$_2$CH$_2$R, rather than C$_1$−C$_2$′ and C$_2$−C$_2$′ coupling, which would produce the branched chains RCH$_2$CH$_2$CH(CH$_3$)R and RCH(CH$_3$)CH(CH$_3$)R, respectively.

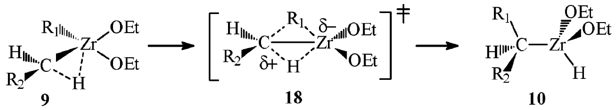
reaction is intramolecular. This conclusion follows from examining runs 2 and 3. The failure of $(PhCH_2)Zr(OEt)_3$ (**11**) to yield bibenzyl means that no benzyl group exchange occurs between molecules of **11** to produce $(PhCH_2)_2Zr(OEt)_2$ (**3**). Second, as a corollary, only the two organyl groups attached to the same zirconium center can undergo C−C bond coupling. Note the hydrocarbons formed in runs 7 and 8, where the alternative coupling products, biphenyl and bibenzyl for run 7 and biphenyl and 1,4-diphenylbutane for run 8, are not found. Third, the C−C bond coupling occurs more slowly when R is phenyl and not at all in a straightforward manner when R and R′ are aryl groups (run 12).[10] Examination of the extent of C−C bond coupling further indicates that migration from Zr to C (e.g., **3** to **4**) is faster when C−Zr bond rupture involves sp^3-hybridized carbon (runs 1, 2, 5, and 10). Fourth, for rearrangement and C−C bond formation to occur, either R or R′ must have a C−H bond at the α sp^3-hybridized C−Zr bond. Consider runs 1, 2, 4, 5, and 7−11, which do couple to provide R−R′ upon hydrolysis, and runs 6 and 12, which do not. Finally, in all cases the newly formed carbon chain in R−R′ is linear rather than branched.[8]

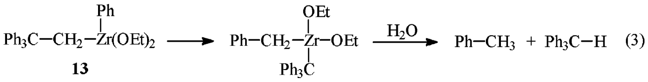
Before the foregoing observations made on this unusual rearrangement are reconciled in a proposed mechanism, the two anomalous rearrangements encountered in runs 9 and 12 should be considered. First, the heating of di-*p*-tolylzirconium diethoxide (**14**) and subsequent hydrolysis did not produce solely 4,4′-bitolyl (**19**), as might be expected, but rather comparable amounts of 3,4′-bitolyl (**18**) as well. In a companion observation, heating diphenylzirconium diethoxide (**20**) and then treating with D_2O yielded 2-deuteriobiphenyl (**23**).[10] Both observations are clear indications of a *β*-hydride-elimination route to aryne intermediates, namely **15** and **21** (Scheme 3). Hydrolysis or deuteriolysis of **16**, **17** and **22** would nicely account for the isolated products.[11] Second, the hydrolysis products observed in run 9 reveal that **13** has undergone an alternative rearrangement as well (eq 3). Such a rearrangement seems also to have occurred in run 4 to a minor extent (Table 1).

Scheme 3



Scheme 4





$$Ph_3C-CH_2-\overset{\displaystyle Ph}{\overset{|}{Zr}}(OEt)_2 \longrightarrow Ph-CH_2-\underset{\displaystyle Ph_3C}{\underset{|}{\overset{\displaystyle OEt}{\overset{|}{Zr}}}}-OEt \xrightarrow{H_2O} Ph-CH_3 + Ph_3C-H \quad (3)$$

13

A transition state for this principal C−C bond-forming rearrangement which accommodates all of the foregoing structural prerequisites is **18**, which is depicted in Scheme 4.[12] In what may be considered to be an accentuated agostic H-interaction possibly already present in **9**, the α-C−H bond would be polarized in a

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(9) Treatment of a group 4 tetrachloride $[MCl_4]$ or tetraalkoxide $[M(OR)_4]$ with the appropriate stoichiometric quantity of Grignard or lithium reagent has been widely employed to prepare in situ the individual heteroleptic complexes, such as $PhZrCl_3$ (Clarke, J. F.; Fowles, G. W. A.; Rice, D. A. *J. Organomet. Chem.* **1974**, *76*, 349), $Bu^n_2TiCl_2$, and $Bu^n_2ZrCl_2$ (Eisch, J. J.; Owuor, F. A.; Shi, X. *Polyhedron*, in press (Symposium-in-Print)) and $Pr^i_2Ti(OPr^i)_2$ (Kulinkovich, O. G.; Sviridov, S. V.; Vasilevski, D. A.; Prityckaja, T. S. *Zh. Org. Khim.* **1989**, *25*, 2245). However, such metal−metal metatheses must be conducted below 0 °C, because the R_nME_{4-n} products (E = X, OR) are thermally unstable at 20 °C or higher, due both to reductive elimination (path **a**) and to *β*-hydride elimination (path **b**). Hence, the isolation of R_nME_{4-n} from the solvent and byproduct salts and the performance of elemental analyses or molecular weight measurements are generally precluded. In fact, to the best of our knowledge, no homoleptic (R_4Zr) or heteroleptic (R_nZrE_{4-n}, E = X, OR′) alkylzirconium derivative, whose alkyl group bears a *β*-hydrogen with respect to the Zr center, has ever proved to be isolable above 0 °C and to be sufficiently stable for molecular mass or structure determination (Cardin, D. J.; Lappert, M. F.; Reston, C. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, pp 635−642.

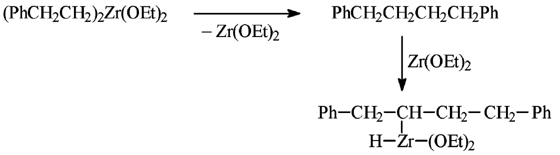
$$HME_3 \xleftarrow[-\,RCH=CH_2]{\mathbf{b}} R-CH_2-CH_2-ME_3 \xrightarrow[-\,RCH_2CH_2^{\bullet}]{\mathbf{a}} ME_3$$

For the key reagents in this study, $Bu^n_2ZrCl_2$ and $Bu^n_2Zr(OEt)_2$, as formed with their lithium salt byproducts, ^1H NMR spectral measurements at −60 °C support their presence in CH_2Cl_2 solution predominantly (>90%) as this specified heteroleptic complex with little trace of Bu^nZrE_3 or Bu^n_3ZrE (E = Cl, OEt). For further commentary, refer to the Supporting Information.

(10) Eisch, J. J.; Dutta, S.; Goldrich, A. Unpublished studies.

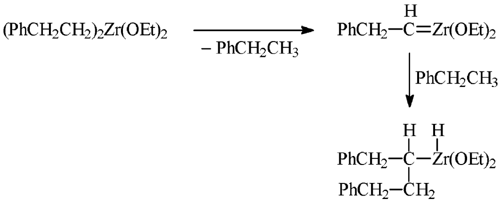
(11) As is depicted in Scheme 3, the tolyl group coupling observed in the heating of di-*p*-tolylzirconium diethoxide (**14**) and subsequent hydrolysis is clear evidence that aryne intermediates are involved. For previous precedents for the thermal generation of aryne−zirconocene complexes from di-*p*-tolylzirconocene, cf.: Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

(12) Other mechanistic paths for this most remarkable rearrangement have been given careful consideration but at this stage have been judged to be both of higher energy and of implausible selectivity. One such alternative pathway would be a standard reductive elimination, followed by an oxidative addition of $Zr(OEt)_2$ *only* into the α-C−H bond (here illustrated with $(PhCH_2CH_2)_2Zr(OEt)_2$):



$$\begin{array}{c} (PhCH_2CH_2)_2Zr(OEt)_2 \xrightarrow[-\,Zr(OEt)_2]{} PhCH_2CH_2CH_2CH_2Ph \\ \big\downarrow Zr(OEt)_2 \\ Ph-CH_2-\underset{\displaystyle H-Zr-(OEt)_2}{\underset{|}{CH}}-CH_2-CH_2-Ph \end{array}$$

Another scenario would be an α-elimination leading to an alkylidene complex followed by insertion of the C=Zr bond into the α-C−H bond of the hydrocarbon with a reversal of the C−H bond polarity, $C^{\delta+}-H^{\delta-}$:



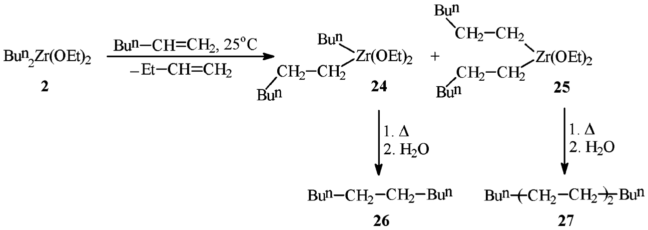
$$\begin{array}{c} (PhCH_2CH_2)_2Zr(OEt)_2 \xrightarrow[-\,PhCH_2CH_3]{} PhCH_2-\overset{\displaystyle H}{C}=Zr(OEt)_2 \\ \big\downarrow PhCH_2CH_3 \\ PhCH_2-\underset{\displaystyle PhCH_2-CH_2}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{Zr}}(OEt)_2 \end{array}$$

Both of the foregoing pathways would involve at the some stage a *complete* and thus prohibitive degree of *σ* bond breaking before new *σ* bond making could begin.

hydridic sense toward the Zr center in **18**. Such electron density buildup on Zr loosens the anionic R_1 group, which in turn migrates toward the positively polarized α-carbon center to consummate carbon−carbon bond formation in **10**. From a standpoint of minimizing the activation energy for this rearrangement, the most appealing aspect of this proposed pathway is the concerted bond breaking and bond making involved in attaining transition configuration **18**. Other potential pathways, such as those requiring reductive elimination to Zr(II) or α,*μ*-elimination to alkylidene−zirconium(IV) intermediates, would demand a higher investment of $\Delta G^{\ddagger}$.[12]

The linear carbon chains generated by the rearrangements of $Bu^n{}_2Zr(OEt)_2$ (**2**) and of $(PhCH_2CH_2)_2Zr(OEt)_2$ (**12**) awakened our hope of developing a general method of doubling the length of alkane chains by the analogous rearrangement of di-*n*-alkylzirconium diethoxides (**9**; R_1 and R_2CH_2 are the same *n*-alkyl). Up to the present, however, the difficulty of obtaining such di-*n*-alkylzirconium derivatives would have made such a synthesis impractical. Neither the zirconation of *n*-alkanes as depicted in eq 1 for arylalkanes nor the alkylation of $Zr(OEt)_4$ by *n*-alkylmetallics as in eq 2 would have proved feasible. In the latter approach, the laborious availability of the requisite *n*-alkyl halide would impose a severe limitation. Consequently, our finding of the facile hydrozirconation by transfer between α-olefins of the type $RCH{=}CH_2$, and $Bu^n{}_2Zr(OEt)_2$ (**2**) represents an important, indeed crucial, step in achieving the transformation given in Scheme 2, where $R_1 = R_2CH_2$. For example, stirring an excess of 1-hexene with **2** in hexane at 25 °C while slowly passing argon through the reaction vessel achieved almost the complete conversion of **2** into di-*n*-hexylzirconium diethoxide (**25**). Subsequent reflux and hydrolysis now provided an 88% yield of dodecane (**27**); the small content of decane (12%, **26**) is attributed to some residual *n*-butyl(*n*-hexyl)zirconium diethoxide (**24**), whose rearrangement would provide the precursor to the decane[13] (Scheme 5). Analogous transfer hydrozirconations between **2** and 1-octene or 1-decene have led to comparatively high yields of the corresponding linear dimeric alkanes (93% of hexadecane with 7% of dodecane from 1-octene and 84% of eicosane with 16% of tetradecane from 1-decene, respectively).[15] The further possibilities of achieving transfer hydrozirconations of α,*ω*-alkadienes leading to cycloalkanes or of *ω*-substituted α-olefins, $E(CH_2)_nCH{=}CH_2$ ($E = MeO, X, R_2N$), are receiving our earnest attention.[14]

Scheme 5



In summary, this study of the unprecedented rearrangement of diorganylzirconium diethoxides leading to C−C bond formation lends support to a transition state involving the reciprocal migration of an α-H to the Zr center with a countermigration of an R group from Zr to the α-carbon. This mechanistic understanding has led to the recognition of novel, important ways of making C−C bonds, such as the linear dimerization of α-olefins and the proposed cyclization of α,*ω*-alkadienes to cycloalkanes.[15]

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. Technical advice and assistance have been generously given by the former students Drs. Adetenu A. Adeosun and John N. Gitua.

Supporting Information Available: Text giving experimental details 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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[13] In a typical procedure for the linear dimerization of 1-hexene to dodecane, a suspension of 2.50 mmol of $Bu^n{}_2Zr(OEt)_2$ (containing the byproduct LiOEt) in 35 mL of hexane was treated with 1.6 mL (11 equiv) of freshly distilled 1-hexene and stirred for 12 h as a very slow stream of argon was passed over the reaction mixture, which had then turned brown. The mixture was heated at reflux for 2 h before all volatiles were removed in vacuo. Hydrolysis of the reaction mixture, now dissolved in ether, and the usual workup provided 0.38 g of product (88% of the theoretical 0.43 g of pure dodecane possible). By GC analysis this product was shown to consist of 94% dodecane and 6% decane. Adding authentic samples of these hydrocarbons to both the GC and the ^1H and ^{13}C NMR spectral samples gave no new peaks and thus corroborated their chemical identity.

[14] Eisch, J. J.; Dutta, S.; Gitua, J. N. Research in progress.

[15] Refer to the Supporting Information for complete experimental details on general laboratory manipulations for organometallic reagents, specific preparations of the individual $R_2Zr(OEt)_2$ and $RR'Zr(OEt)_2$ starting materials, and the specific thermal rearrangement of each of these substrates, including the identification and yield determination of each reaction product. Also included are experimental details for the reactions of di-*n*-butylzirconium diethoxide (**2**) individually with 1-hexene, 1-octene, and 1-decene, according to Scheme 5. Finally, the procedure followed for the recording and interpreting of the ^1H NMR spectra of $Bu^n{}_2ZrCl_2$ and $Bu^n{}_2Zr(OEt)_2$ in CH_2Cl_2 at −60 °C is described and discussed.