The Decomposition of Transition Metal Alkyls Revisited: Surprising Wellspring of Novel Reagents for Organic Synthesis[‡]

John J. Eisch,*[a] Adetenu A. Adeosun,[a] Somnath Dutta,[a] and Paul O. Fregene[a]

Dedicated to Professor Dr. Dr. h.c. mult. Günther Wilke on the occasion of his 80th birthday[‡‡]

Keywords: Transition metals / Hydride and methyl derivatives / Direct and transfer epimetallation / Alkylidenes in C–C bond formation / Ziegler–Natta and ROMP catalysts

A broad survey of both the simple and double decomposition modes of transition metal alkyls has been undertaken. From the two main processes of C–M bond rupture, homolysis, and β-metal hydride elimination, the following modes of decomposition and types of useful reagents generated can be distinguished: 1) reductive decomposition of R_nME_{m-n} to yield subvalent, carbene- or free-radical-like ME_{m-n}, which can cleave π- or σ-bonds by direct epimetallation; 2) β-metal hydride elimination to produce hydrometallating agents; 3) combined reductive and β-metal hydride eliminations to produce anionic, and hence more nucleophilic, epimetallating agents; 4) α-metal hydride elimination thought to be involved in the transition state leading to C–C bond coupling from $(RR'HC)_2ME_2$ derivatives; 5) α,μ-elimination from lithiated $RHC(Li)\text{–}ME_{n-1}$, which produces alkylidenes, $RHC{=}ME_{n-2}$, capable of ROMP catalysis; 6) metal–hydrogen metathesis, whereby sufficiently acidic C–H bonds become C–M bonds; 7) metal–metal metathesis, whereby $RR'ME_2$ undergoes an equilibrating redistribution reaction to form R_2ME_2 and R'_2ME_2; 8) transfer epimetallation, in which epimetallation (point 1) is achieved with R_2ME_2 in one step by transfer of ME_2 to the substrate with the concomitant loss of R groups; and 9) transfer epimetallation of olefins by R_2TiE_2 in hydrocarbons to produce titana(IV)cyclopropanes, which serve as active sites in Ziegler–Natta polymerization. In each situation, the reaction-mechanistic features are analyzed in terms of existing experimental data and evidence.

Introduction

Elemental Metals and Organic Radicals

The interaction of free metals with organic radicals has commanded the attention of chemists ever since the pioneering attempts of Bunsen[2] and of Frankland[3] to capture the elusive cacodyl radical, Me_2As, and the simple methyl and ethyl radicals, respectively. In Frankland's studies his attempt to remove just the iodine from R–I (path a) was confounded by the stable R–Zn bonding formed instead (path b) [Equation (1)].

$$2\,R + ZnI_2 \xleftarrow[\text{path a}]{\not\quad} 2\,R\text{–}I + Zn \xrightarrow[\text{path b}]{} R_2Zn + ZnI_2 \qquad (1)$$

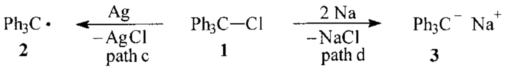
Subsequent research by Gomberg[4] demonstrated that an organic halide like triphenylmethyl chloride (**1**) could react by either path c or path d depending upon the reducing potential of the metal [Equation (2)]. The enhanced stability of the trityl free radical **2** permitted this type of selective dehalogenation, while the comparably increased stabilization of anion **3** permitted the rapid electron transfer from Na.

[‡] Organic Chemistry of Subvalent Transition Metal Complexes, 33. Part 32: Ref.[1]

[a] State University of New York at Binghamton, Department of Chemistry,
P. O. Box 6000, Binghamton, NY 13902-6000, USA
Fax: +1-607-777-4865
E-mail: jjeisch@binghamton.edu

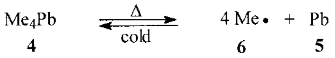
[‡‡] Master of transition-metal catalysis and a great inspiration to the research of our group.

DOI: 10.1002/ejoc.200500088



$$\underset{\mathbf{2}}{Ph_3C\bullet} \xleftarrow[-AgCl \text{ path c}]{Ag} \underset{\mathbf{1}}{Ph_3C{-}Cl} \xrightarrow[-NaCl \text{ path d}]{2\,Na} \underset{\mathbf{3}}{Ph_3C^-\ Na^+} \quad (2)$$

That such carbon–metal bonding or its homolytic reversal can be controlled by temperature change alone was demonstrated by Paneth and Hofeditz.[5] In passing a stream of Me_4Pb vapor (**4**) past a heated zone in a glass tube they were able to observe the deposition of a lead metal ring. Now if a second lead ring (**5**) had been placed a short, predetermined distance downstream in a cold zone of the tube, that lead ring was removed with the reformation of Me_4Pb (radioactive labeling). The reaction depicted in Equation (3) to the right is clearly reversed at lower temperatures, if the methyl free radicals **6** have not yet decomposed.



$$\underset{\mathbf{4}}{Me_4Pb} \underset{cold}{\overset{\Delta}{\rightleftarrows}} \underset{\mathbf{6}}{4\,Me\bullet} + \underset{\mathbf{5}}{Pb} \quad (3)$$

With similar methodology the methyl radicals thus generated were shown to remove other metallic mirrors of zinc, antimony, arsenic, bismuth, and mercury to form Me_2Zn, Me_3Sb and $Me_2SbSbMe_2$, Me_3As and $Me_2AsAsMe_2$, Me_3Bi, and Me_2Hg, respectively.[6] Especially relevant to this review is the reaction of methyl radicals with a lanthanum mirror,[7] although no such rare earth Me_3M could be isolated. In fact, no such rare earth or transition metal alkyl appears to have been isolated by the Paneth radical-capture technique.

Transition Metal Alkyls

The extensive literature prior to 1954 on the purported claims and abortive attempts to prepare either alkyls or aryls of transition metals has been thoroughly surveyed and assessed by Cotton.[8] It is equally clear from the much more extensive but somewhat older review of Krause and von Grosse published in 1937[9] that as a class such alkyls have a markedly lower kinetic stability than their main-group metal counterparts. Transition metal alkyls sufficiently stable at room temperature, *without coordinating ligands*, were found to be rare: $[Me_3PtCl]_4$ (originally thought to be Me_4Pt), MeCu (explodes on drying at room temp.), $MeTiCl_3$, Me_2TiCl_2, and Me_2Mn (stable under 75 °C) may be taken as representative of such isolable derivatives. When the more recent techniques of low-temperature mixing of reagents (–80 °C to –100 °C) and the use of coordinating

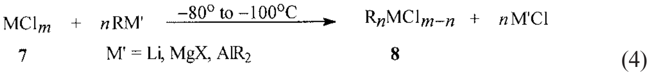
John Joseph Eisch (second from left) is Distinguished Professor of Chemistry in the State University of New York at Binghamton, where he has been engaged in teaching and research since his arrival as Chemistry Department chairperson in 1972. Previous professorial appointments starting in 1957 were with St. Louis University, University of Michigan and the Catholic University of America. His research has focused on the fundamental organometallic chemistry of both main-group and transition-metal compounds, with attention given to their efficient preparation, their underlying reaction mechanisms and their significant utility in organic synthesis. Such investigations have furnished the research topics for over 70 graduate students pursuing the MS or Ph.D. degree under his direction. In addition, some 60 postdoctoral research associates have carried out specific organometallic studies funded by governmental or industrial agencies both at home and abroad. The results of such experimental inquiries have been reported in over 350 scientific publications including reviews and patents, in some 200 invited lectures and in 5 monographs. One of the last-named monographs, "The Chemistry of Organometallic Compounds" (Macmillan, 1967), is currently undergoing revision with considerable expansion.

Adetenu Adebisi Adeosun (far right) was born in Ibadan, Nigeria in 1968. He received the B.S. degree in chemistry with honors from the University of Ibadan in 1991. Subsequently, he taught science in high school and worked as a factory supervisor in a hair products company in Nigeria. In 1997 he came to the United States to begin graduate studies at Binghamton University under the direction of Professor Eisch. He has pursued research on the use of Group 4 metal alkyls in organic chemistry and in 2004 successfully defended a doctoral dissertation entitled, "Novel Alkylidenation, Epimetallation and Hydrometallation Reactions of Group 4 Metal Alkyls". Thus far, he is a co-author of 3 scientific publications. Presently he is a postdoctoral fellow with Professor Helena Malinakova at the University of Kansas and is engaged in the study of palladium(IV) complexes in asymmetric organic transformations.

Somnath Dutta (far left) was born in 1972 in the holy city of Varanasi, India. He was awarded both the B.S. degree in chemistry in 1994 and the MS degree in biochemistry in 1996 from the University of Calcutta. After some postgraduate study on drug design at the University of Calcutta, he began graduate studies in chemistry at Binghamton University in 1997 under the supervision of Professor Eisch. He has completed the requisite experimental work and now is preparing his doctoral dissertation entitled, "Alkylzirconium(IV) Alkoxide Reagents in Organic Chemistry: Reactions with sigma- and pi-Bonded Substrates". He is a co-author of two scientific publications thus far.

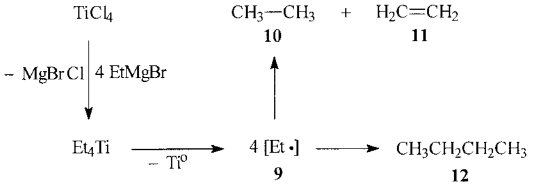
Paul Oritseweyimi Fregene (second from right) was born in New Bussa, Niger State, Nigeria in 1968. He was awarded the B.S. degree in chemistry in 1990 from the University of Ibadan. After an interim year as a high school teacher of science, he also earned the MS degree in analytical chemistry from the University of Ibadan. Appointment to several technical positions followed: project administrator in Warri, Nigeria; research assistant in biotechnology at the Centro Internacionale Agricultura Tropica, Cali, Columbia; and Hogeschool in the School of Environmental Studies, IJselland, The Netherlands. Thereafter, he began graduate studies in chemistry at Binghamton University in 1998 under the supervision of Professor Eisch. With his experimental studies complete, he is currently composing his doctoral dissertation on the theme, "Low-Valent Vanadium Reagents in Organic Chemistry: Reaction Mechanisms and Applications in Synthesis". He is a co-author of two publications that will appear shortly.

solvents or ancillary ligands are applied to such metal–metal metatheses as in Equation (4), the general opinion prevails that the partly or fully substituted transition metal alkyl **8** is formed from MCl_m (**7**) and persists for some time before decomposition or bimolecular reaction.



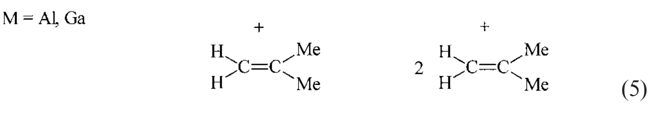
$$\underset{\mathbf{7}}{MCl_m} + \underset{M' = Li,\ MgX,\ AlR_2}{n\,RM'} \xrightarrow{-80^\circ \text{ to } -100^\circ C} \underset{\mathbf{8}}{R_nMCl_{m-n}} + n\,M'Cl \qquad (4)$$

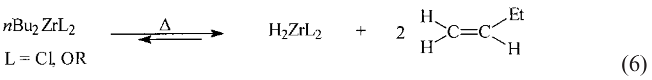
In the previous attempts to prepare transition metal alkyls in the temperature range of 0° to 35 °C, reduction of the metal salts and formation of hydrocarbon by-products almost invariably have been observed. Although any transitory C–M bond most likely decomposes in its primary step by homolysis through thermal promotion, the resulting organic radical appears not to become completely "free" of the metal. For example, in a detailed study by Gilman and Jones[10] it was found that treating either $TiCl_4$ or $ZrCl_4$ with 4 equiv. of EtMgBr in ether led to the evolution of chiefly ethane containing only 2% of ethylene. Were the ethyl radicals (**9**) completely ever "free", they should have undergone disproportionation to produce both ethane (**10**) and ethylene (**11**) or have coupled with the formation of butane (**12**) (Scheme 1). The trace or absence of **11** and **12** rules out the generation of the typically "free" ethyl radical **9**. In the discussion of the decomposition pathways of transition metal alkyls given herein, we shall demonstrate how this puzzling homolytic decomposition given in Scheme 1 has served as a useful clue for discovering novel chemical reactions of these alkyls (cf. Scheme 2 and relevant discussion).



Scheme 1.

However, for metal alkyls in general having a β-hydrogen an alternative primary step in their decomposition can be a metal–hydride bond elimination, as exemplified for alkyls of aluminum[11] and gallium[12] in Equation (5) and those of zirconium[13,14] in Equation (6).





The rate of such metal–hydride elimination usually is greater in hydrocarbon solvents and less in coordinating solvents.

In the following sections we undertake to consider the various discrete ways transition metals can undergo decomposition, thereby either effecting a valuable reaction of great use in organic synthesis or generating a transition metal reagent for subsequent organic reactions. In this discussion we wish to embrace the term *decomposition* in its broader sense. Naturally we are interested in the *simple decomposition* of individual transition metal alkyl molecules into fragments. But in addition we find it fitting to include various types of metatheses, formerly termed *double decompositions*, of such alkyls with an organic substrate. Where appropriate, we will exemplify such modes of simple decomposition and double decomposition by citing recent contributions of our group to the theme of "Organic Chemistry of Subvalent Transition Metal Complexes".[15]

Modes of Transition Metal Alkyl Decomposition

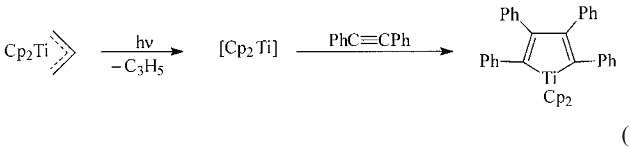
Simple Decompositions

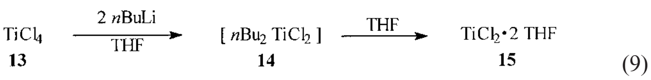
Although the primary decomposition steps of M–C bond homolysis and M–H bond elimination are centrally involved in such decompositions, these processes are often combined with subsequent reactions to result in useful reagents.

1. Reductive Elimination

Here the homolysis of M–C bonds leads to the loss of alkyl radicals and the reduction of the metal either to the finely divided native metal or to a lower valent alkyl or salt. The preparations of $(COD)_2Ni$,[16,17] unstable Cp_2Ti,[18] or $TiCl_2{\cdot}2THF$[19] illustrate the utility of reductive elimination [Equations (7), (8), and (9)]. Since in Equation (9) the initial $TiCl_4$ (**13**) is ultimately reduced to the solvated $TiCl_2$ (**15**) via the alkylated **14**, the overall transformation has been termed an *alkylative reduction*. This process, also applied individually to $ZrCl_4$, $HfCl_4$, $CrCl_3$, and VCl_3, in general accord with the procedure outlined in Equation (9), has

$$Ni(acac)_2 \xrightarrow[COD]{Et_2Al} [Et_2Ni] \longrightarrow Ni^0 \xrightarrow{COD} (COD)_2Ni \qquad (7)$$

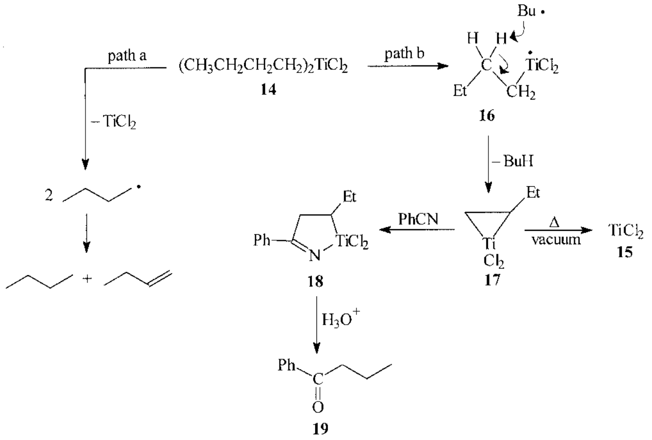




$$\underset{\mathbf{13}}{TiCl_4} \xrightarrow[THF]{2\ nBuLi} \underset{\mathbf{14}}{[\,nBu_2TiCl_2\,]} \xrightarrow{THF} \underset{\mathbf{15}}{TiCl_2{\cdot}2\,THF} \qquad (9)$$

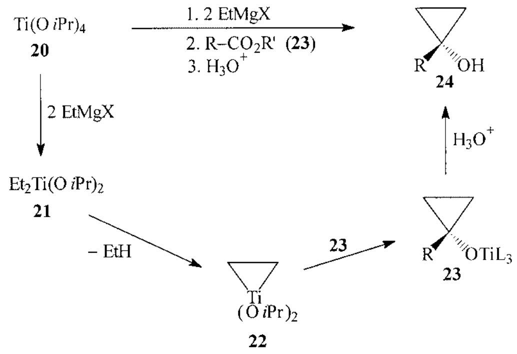
proved to be satisfactory for providing THF solutions of $ZrCl_2$,[20–21] $HfCl_2$,[20–21] CrCl,[22] and VCl[23] or slurries of the same subvalent reagents with by-product LiCl from reactions conducted in toluene.

In the reductive elimination of nBu$_2$TiCl$_2$ (**14**) in THF leading to $TiCl_2$·2THF, one might have expected the evolution of a 1:1 mixture of butane and 1-butene. Actually butane was the principal gas evolved and the 1-butene was largely bound to the $TiCl_2$ as a 2-ethyl-1-titanacyclopropane complex (**17**). This finding raises the possibility that such decomposition never leads to two separate 1-butyl radicals (path a) but that the first butyl radical abstracts a β-hydrogen en passant from the second butyl group still bonded to the titanium (**16**, path b) (Scheme 2). Complex **17** was chemically trapped with benzonitrile to form **18**, whose hydrolysis then yielded valerophenone (**19**). Although reasonably stable even in warm THF, **17** loses 1-butene at higher temperatures under reduced pressure to yield **15**.[24]



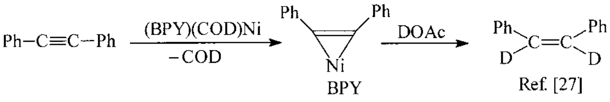
Scheme 2.

A most noteworthy illustration of such bis-reductive elimination which leaves the alkene bonded to the transition metal is the Kulinkovich cyclopropanol synthesis (**20** → **24**; Scheme 3).[25] The treatment of either stoichiometric or catalytic amounts of titanium(IV) isopropoxide Ti(OiPr)$_4$ (**20**) with *at least* 2 equiv. of an ethyl Grignard reagent generates intermediate Et$_2$Ti(OiPr)$_2$ (**21**), whose decomposition according to path b in Scheme 2 would yield the Kulinkovich reagent **22**. Insertion of the ester **23** into **22** and rearrangement would thereby provide the cyclopropanolate derivative **23**.[26]

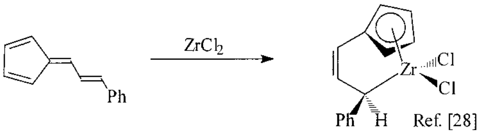


Scheme 3.

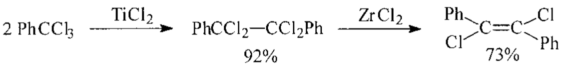
The THF-soluble forms of the foregoing subvalent transition metal salts are eminently suitable for various oxidative addition reactions, such as simple *epimetallations* [Equations (10)[27] and (11)[28]], cyclization [Equations (11) and (13)], reductive cleavages [Equations (12) and (14)] and reductive dimerizations [Equations (12) and (14)] presented in Equations (10)–(14).



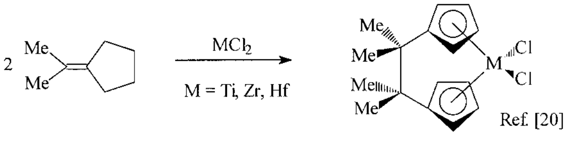
(10)



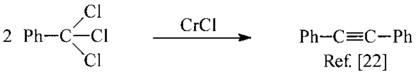
(11)



(12)



(13)



(14)

2. *β-Metal Hydride Elimination*

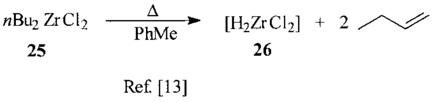
Transition metal alkyls more stable to homolysis and having a β-hydrogen are prone to metal hydride elimination, especially in nondonor solvents. Consider the thermal behavior of the nBu$_2$MCl$_2$ derivatives where M = Ti or Zr. The labile titanium derivative **24** undergoes reductive elimination in toluene or in THF above 0 °C [Equation (15)],[20] while the zirconium analog **25** undergoes reductive elimination in THF [Equation (16)][20] but metal hydride elimination in warm toluene [Equation (17)].[13] The H_2ZrCl_2 (**26**) can be captured by hydrozirconation of a suitable substrate as displayed in Scheme 4.

$$\underset{\mathbf{24}}{n\mathrm{Bu_2TiCl_2}} \xrightarrow[\text{PhH or THF}]{\Delta} \mathrm{TiCl_2}\ \text{(cf. Scheme 2)} \tag{15}$$

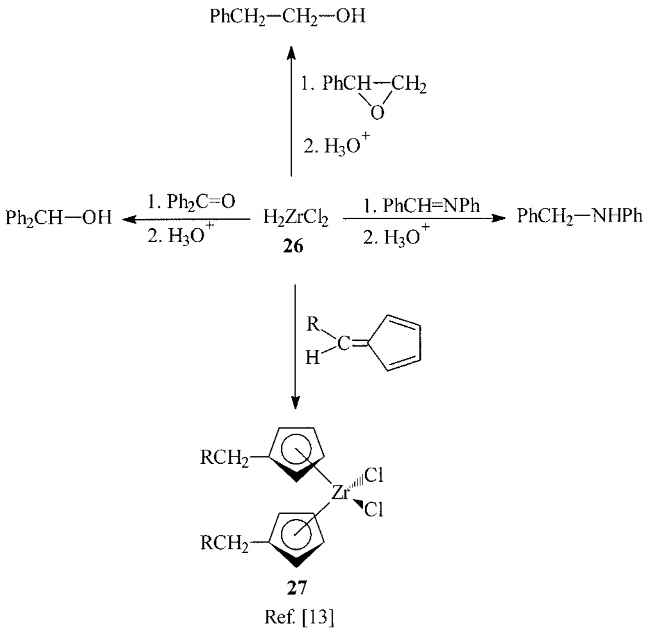
Ref. [20–21]

$$\underset{\mathbf{25}}{n\mathrm{Bu_2ZrCl_2}} \xrightarrow[\text{THF}]{\Delta} \mathrm{ZrCl_2} \tag{16}$$

Ref. [20]

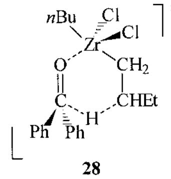


(17)

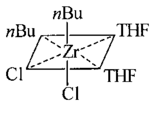


Scheme 4.

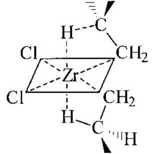
The interesting preparation of the substituted zirconocene dichloride **27** by this route is most noteworthy. Whether the hydride **26** is first generated from **25** and then reacts with the substrate, as implied in Equation (17), or whether the substrate reacts with **25** to assist in the H_2ZrCl_2 transfer, as in transition state **28** is not yet known. However, a likely basis for the dramatic solvent effect lies in the structures of **25** in THF (**25a**) and in toluene (**25b**), respectively.



28



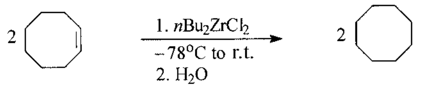
25a



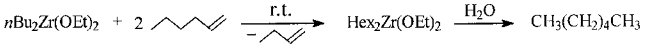
25b

The structural instability of $n\mathrm{Bu_2ZrCl_2}$ in THF and its relative stability in hydrocarbons at 25 °C likely has its origin in the coordination sphere existing about the Zr center: in THF **25** has presumably an octahedral coordination involving solvent ligands (**25a**); and in hydrocarbons, without strong coordinating ligands, β-agostic C–H···Zr interactions may help stabilize Zr–C bonds to homolysis while also favoring heterolytic β-hydride eliminations (**25b**).[13]

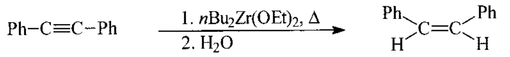
The stability of transition metal alkyls to reductive elimination is also strongly dependent upon the ligands. Although $n\mathrm{Bu_2ZrCl_2}$ is unstable in THF above 0 °C, it is stable at 25 °C in hydrocarbons. A solution of $n\mathrm{Bu_2Zr(OEt)_2}$ is stable at reflux in either THF and hydrocarbons. Thus $n\mathrm{Bu_2ZrCl_2}$ in hydrocarbons at 25 °C or $n\mathrm{Bu_2Zr(OEt)_2}$ in THF or in hydrocarbons can serve as hydrozirconating agents for olefins and acetylenes [Equations (18), (19), and (20)].[14] Because of their ease and economy of preparation such hydrozirconating agents have distinct advantages over the zirconocene hydrides, such as the Schwartz reagent, Cp_2ZrHCl, and its variants.[29]



(18)



(19)



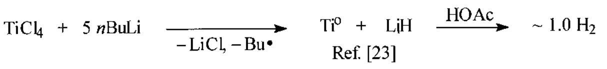
(20)

3. *Combined Reductive and β-Metal Hydride Eliminations*

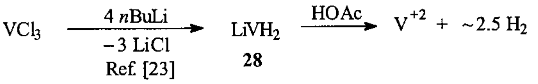
In attempts to generate anionic *ate* complexes of transition metal alkylates, $\mathrm{LiM}n\mathrm{Bu}_{m+1}$ (**27**), a higher valent chloride MCl_m (**26**), such as $TiCl_4$, $CrCl_3$ or VCl_3, was treated with m+1 equiv. of n-butyllithium at –78 °C in THF [Equation (21)].

$$\underset{\mathbf{26}}{\mathrm{MCl}_m} + m{+}1\ n\mathrm{BuLi} \longrightarrow \underset{\mathbf{27}}{\mathrm{LiM}n\mathrm{Bu}_{m+1}} + m\ \mathrm{LiCl} \tag{21}$$

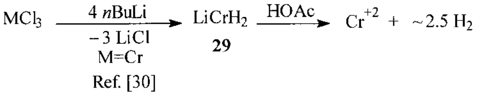
Upon bringing the individual reaction mixtures to room temperature and removing the volatiles in vacuo, gasometric analyses of the residues with glacial acetic acid gave essentially only hydrogen gas with traces of butane, thus ruling out significant amounts of **27**. From the amounts of evolved H_2, the actual course of such reactions were concluded to be those shown in Equations (22), (23), and (24).[30]



$$\mathrm{TiCl_4} + 5\,n\mathrm{BuLi} \xrightarrow[-\mathrm{LiCl},\,-\mathrm{Bu}\bullet]{} \underset{\text{Ref. [23]}}{\mathrm{Ti^0} + \mathrm{LiH}} \xrightarrow{\mathrm{HOAc}} \sim 1.0\,\mathrm{H_2} \qquad (22)$$

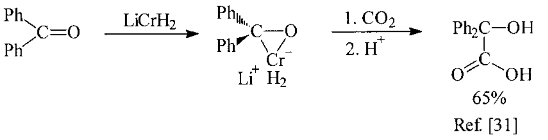


$$\mathrm{VCl_3} \xrightarrow[\substack{-3\,\mathrm{LiCl}\\ \text{Ref. [23]}}]{4\,n\mathrm{BuLi}} \underset{\mathbf{28}}{\mathrm{LiVH_2}} \xrightarrow{\mathrm{HOAc}} \mathrm{V^{+2}} + \sim 2.5\,\mathrm{H_2} \qquad (23)$$

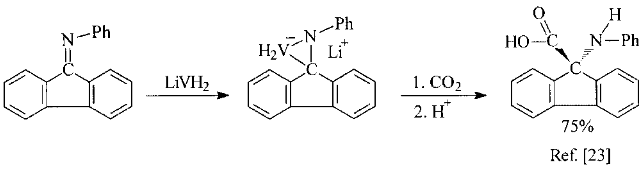


$$\mathrm{MCl_3} \xrightarrow[\substack{-3\,\mathrm{LiCl}\\ \mathrm{M{=}Cr}\\ \text{Ref. [30]}}]{4\,n\mathrm{BuLi}} \underset{\mathbf{29}}{\mathrm{LiCrH_2}} \xrightarrow{\mathrm{HOAc}} \mathrm{Cr^{+2}} + \sim 2.5\,\mathrm{H_2} \qquad (24)$$

In the absence of aggregation estimates the formulations given as **28** and **29** must be considered as empirical, rather than molecular or ionic, with the further understanding that the Li center is likely solvated by THF units. But it is evident that the formation of **28** and **29** and even $\mathrm{Ti^0}$ must have involved the decomposition of an *ate* complex $\mathrm{LiM}n\mathrm{Bu}_{m-1}$ by concurrent reductive elimination of *n*-butyl radicals and β-metal hydride loss. Such $\mathrm{LiVH_2}$ (**28**) and $\mathrm{LiCrH_2}$ (**29**) reagents have proved to be sufficiently stable to be used for achieving various organic chemical transformations. Although such complexes are most likely at least dimers of their empirical formula, their chemical reactions with polar organic substrates can be formulated as involving an addition of the carbene-like monomer to the unsaturated linkage [Equations (25)[31] and (26)[23]]. In both instances the C–M bond of the three-membered metallocyclic intermediate proved capable of reacting with $\mathrm{CO_2}$. The resulting carboxylic acids could be isolated in good yields. Note that the appended hydrogens in $\mathrm{LiMH_2}$ are *not* primarily involved.



(25)



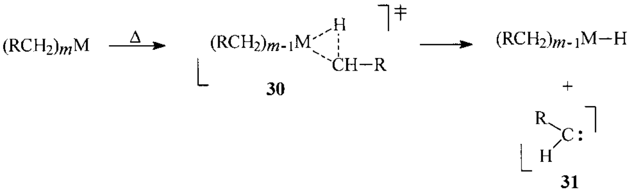
(26)

Such an oxidative addition of a subvalent transition metal to an unsaturated linkage with formation of a three-membered metallocycle has been termed *epimetallation*.[24] [Cf. Equations (10) and (11) for epimetallations achieved by neutral carbene-like reagents.] The exact spin states of reagents **28** and **29** are under current study but their solutions in THF exhibit strong ESR signals.[32]

Further important applications of both neutral and anionic epimetallating agents will be considered under the topic of transfer epimetallation (cf. infra).

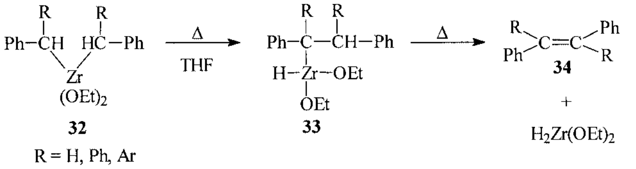
4. α-Metal Hydride Elimination

To the best of our knowledge, an unambiguous α-elimination of a transition metal–hydride bond, as depicted in Equation (27), has not been reported. However, the kind of agostic interaction likely in the transition state **30** of such a process has several documented precedents in the literature.[33] Since a free, high-energy carbene **31** would result from such a postulated reaction, it is understandable why such a process has not been observed at moderate temperatures.



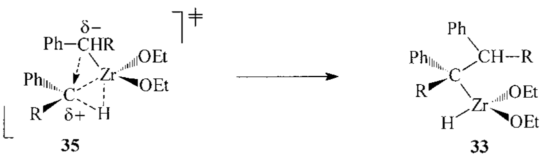
(27)

For this reason, we were both mystified and delighted recently to observe the rearrangement illustrated in Equation (28), transforming **32** into **33** and ultimately upon further heating into **34** [Equation (28)].[34]

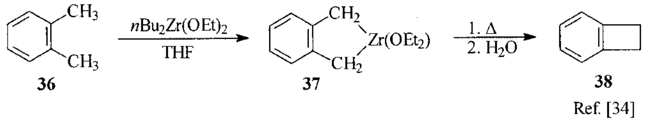


(28)

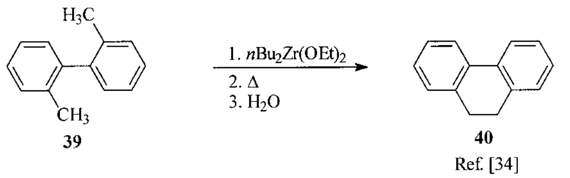
Forming the Zr–H bond in **33** in exchange for the Zr–CHRPh bond in **32** can readily be conceived as passing through a transition state **35**, in which an agostic C···H···Zr interaction has developed a carbene-like complex of PhRC: bonded to Zr. Such atom and charge separation could provide the low-energy pathway for the 1,2-nucleophilic shift of the CHRPh group to generate rearranged product **33** (Scheme 5). A similar C–C bond-forming rearrangement appears to be the route to ring closures of *o*-xylene (**36**) to benzocyclobutene (**38**), assumed to occur via **37** [Equation (29)] and of 2,2′-dimethylbiphenyl (**39**) to 9,10-dihydrophenanthrene (**40**) via an analogous zirconacycle [Equation (30)].[34] The ramifications and applicability of this unexpected and unusual C–C bond-making process with alkyls of zirconium and other transition metals entice us to further studies.



Scheme 5.



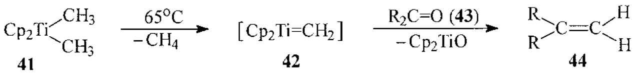
(29)



(30)

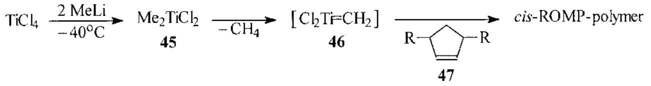
5. *α,μ-Elimination of Alkane*

The formation of alkylidenes by the thermal elimination of alkane from transition metal centers bearing at least two alkyl groups has previously been proposed.[35] Since higher alkyls of transition metals are rarely stable, such so-termed α,μ-eliminations[1] have been usually invoked for dimethyl derivatives, such as in the thermolysis of dimethyltitanocene (**41**). Postulating the intermediacy of titanocene–methylidene **42** is supported by the formation of the olefination product **44** when carbonyl substrate **43** is present (Scheme 6).[35] For purely alkyl derivatives such decomposition via metal alkylidenes is less readily justified. Weakly coordinated Me_4Ti decomposes around –78 °C into methane and Ti–C fragments, whose formation is consistent with Ti^{II} and Ti^{III} intermediates.



Scheme 6.

But recently it has been proposed that Me_2TiCl_2 (**45**), generated at –40 °C in toluene according to Scheme 7, would undergo instant decomposition to **46**. Detection of **46** was judged to be successful by the subsequent ROMP activity shown by the reaction mixture in the polymerization of dicyclopentadiene (**47**).[36] However, discordant with this conclusion is the known stability of **45** at +35 °C and higher, when prepared by alternative methods. Recently it has been established that **45** does not result from the reaction of 2 equiv. of MeLi with $TiCl_4$.[1] Thus we may conclude this section by observing that an intramolecular α,*μ*-elimination of methane from Me_2ML_n is not a facile decomposition pathway. However, when such α,*μ*-eliminations involve the elements of HE (E = X, OR, SR, etc.), then such reactions appear to occur at room temperature or lower. (Cf. infra for bimolecular processes.)



Scheme 7.

Metatheses or Double Decompositions

In these reactions two reactants, A–B and A′–B′, whose fragments are coupled by a covalent or ionic bond, exchange partners to form two new compounds [Equation (31)]. Any equilibrium involved is now recognized as driven in a given direction by LeChatelier's principle and by that set of products having a negative Gibbs free energy. In the early 19th century, however, it is amusing to note that the equilibrium state was thought to be determined by the relative chemical *affinity* of the fragments for each other. With this romantic interpretation, the renowned German writer, J. W. von Goethe, employed such a figurative metathesis for the plot of his famous novel, *Selective Affinities.* The story line concerns the wavering and fickle attractions of two loving couples brought accidentally into close proximity.[37]

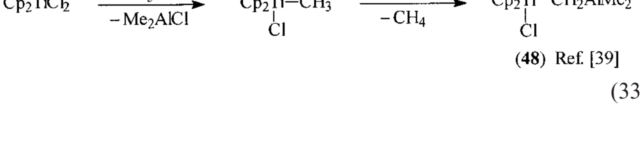
$$A{-}B + A'{-}B' \rightleftharpoons A{-}B' + A'{-}B \qquad (31)$$

1. *Metal–Hydrogen Metathesis*

Such metatheses or metallations have been observed between alkyl metallocenes of early transition metals like scandium [Equation (32)][38] and titanium [Equation (33)],[39] in which latter case the Tebbe reagent (**48**) is produced.

$$Cp^*_2Sc{-}CH_3 + R{-}H \longrightarrow Cp^*_2Sc{-}R + CH_4 \qquad (32)$$

($R{-}H = {}^{13}CH_4$, arenes, styrenes, alkynes) Ref. [38]

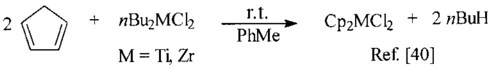


$$Cp_2TiCl_2 \xrightarrow[-Me_2AlCl]{Me_3Al} Cp_2\underset{\displaystyle Cl}{\underset{|}{Ti}}{-}CH_3 \xrightarrow[-CH_4]{Me_3Al} Cp_2\underset{\displaystyle Cl}{\underset{|}{Ti}}{-}CH_2AlMe_2$$

(**48**) Ref. [39]

(33)

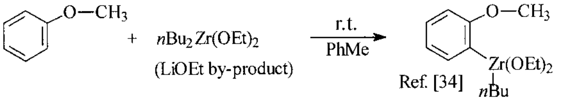
In more recent examples the metallating ability of purely alkyl metal derivatives has been put to effective use in preparing other π- and σ-bonded organometallics [Equations (34),[40] (35),[40] (36),[34] and (37)[34]].



(34)

$$2\ \text{R–C}{\equiv}\text{C–H} + n\text{Bu}_2\text{ME}_2 \xrightarrow[\text{PhMe}]{\text{r.t.}} (\text{R–C}{\equiv}\text{C})_2\text{ME}_2 + 2\ n\text{BuH} \quad \text{M = Ti, Zr} \quad \text{Ref. [40]} \tag{35}$$

$$2\ \text{Ph–CH}_3 + n\text{Bu}_2\text{Zr(OEt)}_2 \xrightarrow[\text{PhMe}]{\text{r.t.}} (\text{Ph–CH}_2)_2\text{Zr(OEt)}_2 + 2\ n\text{BuH} \quad \text{(LiOEt by-product)} \quad \text{Ref. [34]} \tag{36}$$

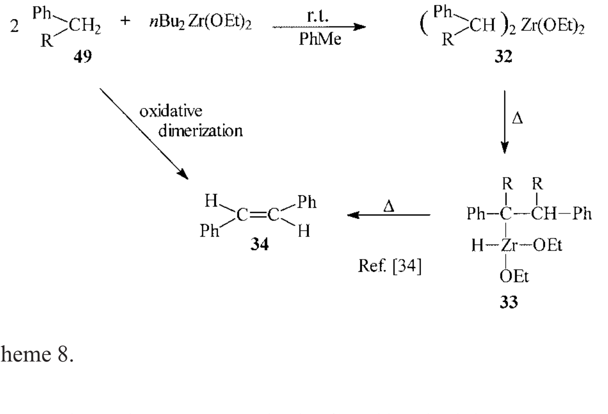


(37)

Since the zirconations described in Equations (36) and (37) are not observed with $n\text{Bu}_2\text{ZrCl}_2$, it is proposed that the metallating action of $n\text{Bu}_2\text{Zr(OEt)}_2$ is catalyzed by the LiOEt by-product, generated from the reagent-forming reaction in Equation (38).

$$\text{Zr(OEt)}_4 + 2\ n\text{BuLi} \xrightarrow[-78^{\circ}\text{C}]{\text{THF}} n\text{Bu}_2\text{Zr(OEt)}_2 + 2\ \text{LiOEt} \tag{38}$$

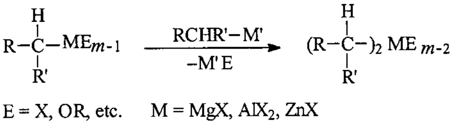
Also, the zirconation of Ph–CH$_3$ in Equation (36) should be compared with the analogous zirconated derivatives **32**, which is thus obtainable from Ph$_2$CH$_2$. Accordingly, such a zirconation of Ph(R)CH$_2$ (**49**), followed by a C–C bond coupling shown in Equation (28) to give **33** and then **34,** represents a novel and valuable synthetic transformation that may be termed oxidative dimerization (Scheme 8). Further intramolecular examples of such a process, already given in Section 5 above, are those of Equations (29) and (30).



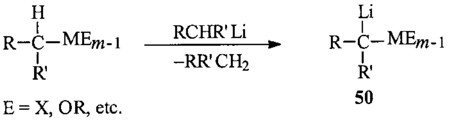
Scheme 8.

2. Metal–Hydrogen Metathesis Combined with α,μ-Elimination

Although the reaction of less active main-group alkyls like RMgX, R$_n$AlX$_{3-n}$, and R$_2$Zn with transition metal salts, ME$_m$, generally involves metal–metal metathesis [(Section 3 infra and Equation (39)], the potent alkyllithiums can also metallate C–CHR′–ML$_{m-1}$ intermediates [Equation (40, **50**; cf. formation of **48** in Equation (33)].

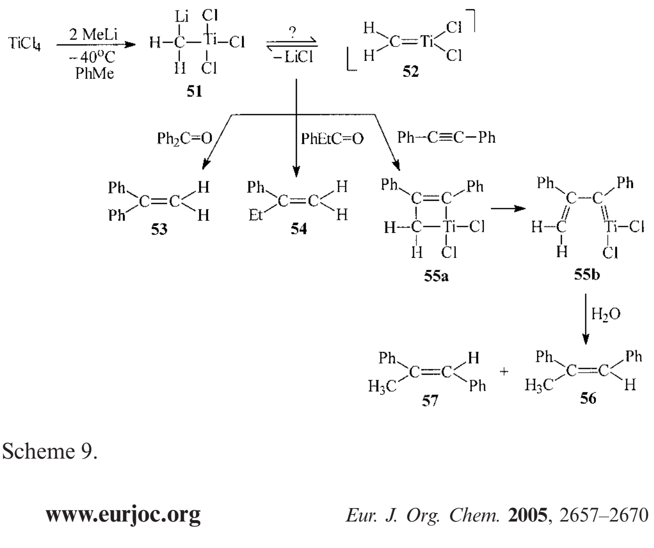


$$\text{R–C(H)(R')–ME}_{m-1} \xrightarrow[\text{–M'E}]{\text{RCHR'–M'}} (\text{R–C(H)(R')–})_2\text{ME}_{m-2} \quad \text{E = X, OR, etc.} \quad \text{M = MgX, AlX}_2\text{, ZnX} \tag{39}$$



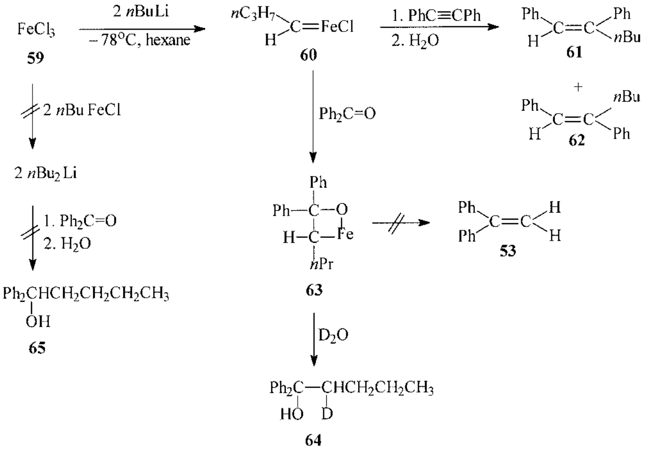
$$\text{R–C(H)(R')–ME}_{m-1} \xrightarrow[\text{–RR'CH}_2]{\text{RCHR'Li}} \underset{\mathbf{50}}{\text{R–C(Li)(R')–ME}_{m-1}} \quad \text{E = X, OR, etc.} \tag{40}$$

Such an unusual metallation was uncovered recently in the reaction of TiCl$_4$ with 2 equiv. of methyllithium in toluene at –40 °C. Instead of leading to Me$_2$TiCl$_2$ (**45**) as proposed by previous workers (Scheme 7),[36] it has been shown that **51** is generated and serves as a source of methylidene **52**. The availability of **52**, with or without the prior α,μ-elimination of LiCl, has been shown by three types of chemical trapping: 1) with benzophenone to give 1,1-diphenylethylene (**53**); 2) with propiophenone to yield only olefin **54**, thereby distinguishing **52** from **45**;[41a] and 3) with diphenylacetylene to produce a 1:1 mixture of **56** and **57** upon hydrolysis via cycloadduct **55a** and its electrocyclic ring opening to **55b** (Scheme 9).[1] A similar pathway to the zirconium alkylidene, nPrCH=ZrCl$_2$ (**58**), appears to be followed in allowing ZrCl$_4$ to react with 2 equiv. of nBuLi in THF. Here again, it is not yet known whether **58** or its LiCl adduct is the actual alkylidenating agent.[41b] Even a late transition metal salt like FeCl$_3$ (**59**) can form such a reagent (**60**) that can be trapped with diphenylacetylene to give a mixture of olefins (**61** and **62**) and possibly with benzophenone to give ultimately deuteriated **64**. In the case of **60** the reaction with ketones would not give directly the olefin **53**, but ferracycle **63**. Workup with D$_2$O, which would lead to **64**, would be required to establish the intermediacy of **63**,



Scheme 9.

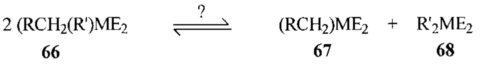
rather than **65**, which could have resulted from simple addition of an *n*Bu–Zr bond to the ketone (Scheme 10).[42]



Scheme 10.

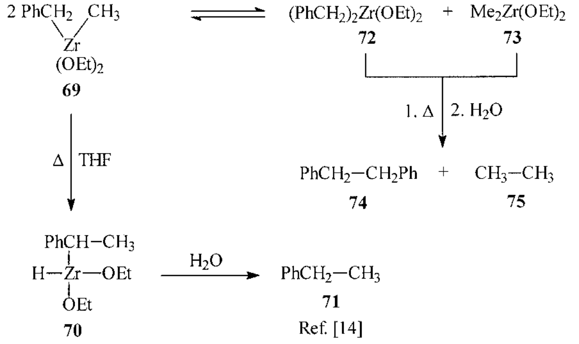
3. Metal–Metal Metathesis

This type of metathesis has long been the principal route to transition metal alkyls from transition metal salts and the main group alkyls of lithium, magnesium and aluminum, as generalized in Equation (4).[43] However, even though undeniably important, such metal–metal metathesis is certainly not novel and thus not particularly relevant to this review. But in the form of a redistribution reaction of mixed transition metal alkyls, this metathesis takes on novelty and significance in carbon–carbon bond-forming reactions of $RCH_2(R')ME_2$ (**66**) intermediate [cf. Equation (28)]. Regardless of the mechanisms of forming **66** and its consumption, the two alkyl groups bonded to M in **66** become C–C-bonded to each other. Thus whether or not **66** can undergo a redistribution reaction [Equation (41)] will decide which new C–C bond-coupling products can be formed. If only **66** is present, then solely $R–CH_2–R'$ could be produced upon hydrolytic workup.



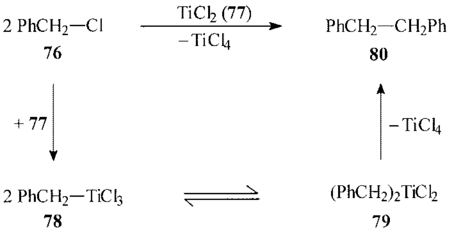
$$\underset{\mathbf{66}}{2\,(RCH_2(R')ME_2)} \overset{?}{\rightleftharpoons} \underset{\mathbf{67}}{(RCH_2)ME_2} + \underset{\mathbf{68}}{R'_2ME_2} \qquad (41)$$

But if redistribution according to Equation (41) were to have occurred, leading to **67** and **68**, then C–C coupling would yield products like $R–CH_2–CH_2–R$ and $R'–R'$ as well. This is illustrated by the thermal behavior of $PhCH_2(Me)Zr(OEt)_2$ [**69**; cf. Equation (47) for its method of preparation]. As with other dialkyl-substituted zirconium dialkoxides (**32**), heating **69** leads to **70**, whose hydrolysis results in the formation of ethylbenzene (**71**) (Scheme 11). But that the heating of **69** also produced a redistribution of **69** into **72** and **73** was revealed by hydrolytic workup: both hydrocarbons **74** and **75** were now also found.[14] Clearly, intermediates **72** and **73** had individually undergone C–C bond formation in a manner parallel to the process, **69** → **70** and thereby revealed their presence in the reaction.



Scheme 11.

Another reaction requiring a redistribution reaction to produce crucial intermediates like **66** is the essentially quantitative coupling of benzylic halides by titanium(II) chloride (Scheme 12). The most likely pathway would involve oxidative addition of the C–Cl bond of **76** to **77**, forming **78**, a redistribution reaction to bond two benzyl groups to the same Ti center (**79**) and finally reductive elimination of **77** to form the coupling product **80**.

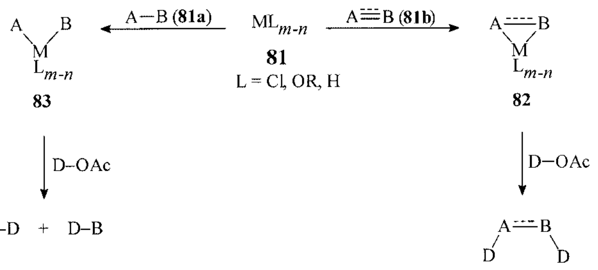


Scheme 12.

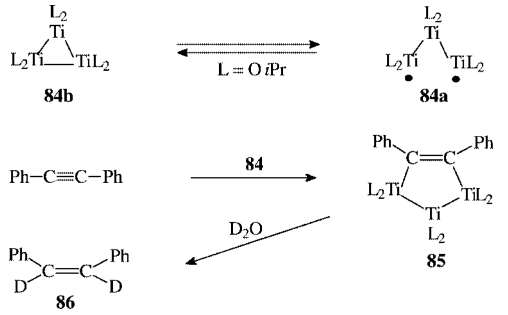
4. Transfer Epimetallation

This type of bimolecular double decomposition has been reserved for last in this review, because in many respects it is perhaps the most novel reaction of transition metal alkyls, having great generality and applicability in organic synthesis and bearing mechanistic insights important to the functionalization and polymerization of π-bonded organic molecules. Before we attempt to document and justify this formidable claim, it is essential to distinguish transfer epimetallation from the simple epimetallations already exemplified [cf. supra: Equations (10), (11), (25), and (26)].

Simple epimetallation is the oxidative addition of a relatively stable (often carbene-like) subvalent transition complex **81** to a π- or σ-bond of substrate AB (**81a**,**b**) leading to a three-membered metallocycle **82** or bond-cleavage product **83** (Scheme 13). Such epimetallating agents are generally available by the partial alkylation of the stable MCl_m [or $M(OR)_m$] to produce R_nMCl_{m-n} [Equation (4)] and the reductive elimination for the R groups [Equations (7)–(10)]. The presence of A–M and B–M bonds in the reaction products can be corroborated by conducting the hydrolytic workup with *O*-deuterioacetic acid (DOAc) and ascertaining the site(s) of any deuterium incorporation. By adhering to the foregoing preparative method for **81**, both neutral and anionic epimetallating agents have been generated as solutions in THF, such as $TiCl_2$, $ZrCl_2$, $HfCl_2$, VCl, and CrCl;[13,19,22] $Ti(O\textit{i}Pr)_2$[24,44] and $Zr(OEt)_2$;[14] and finally $LiCrH_2$[30] and $LiVH_2$.[23] Because such reagents can be solvated and are undoubtedly oligomeric, their epimetallating action on π-bonded substrates can be slow and incomplete. For example, a solution of titanium isopropoxide (**84**) in toluene and free of THF and Li*Oi*Pr by-product displays an ESR triplet signal most consistent with a biradical of the open-chain trimer type, **84a**, likely in equilibrium with the diamagnetic ring trimer **84b** (Scheme 14).[45] The presence of such an equilibrium would explain why the 2:1 ratio of **84** and diphenylacetylene in THF would react after 12 h at 25 °C to give upon hydrolysis with D_2O only 31% of deuteriated *cis*-stilbene (**86**), together with 4% of bibenzyl. Although 2 equiv. of monomeric **84** are potentially available, actually only 0.67 equiv. of **84a** and **84b** are available to slowly form the five-membered metallocycle **85**. Even when the same ratio of reagents was allowed to react in refluxing THF for 12 h, the amount of **86** rose only to 74%.[44]

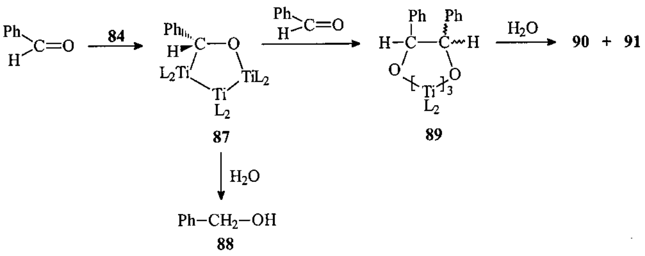


Scheme 13.



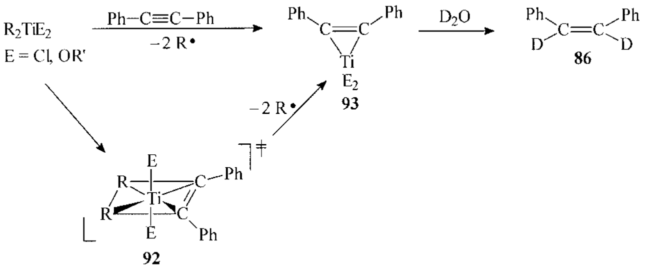
Scheme 14.

Similarly, a 1:2 mixture of benzaldehyde and **84** in THF at 25 °C gave upon hydrolysis 62% of benzyl alcohol (**88**), 28% of a 1:1 mixture of *rac*- and *meso*-1,2-diphenyl-1,2-ethanediols (**90**) and 10% *trans*-stilbene (**91**). The large proportion of reductive dimers **90** and **91** is consistent with the formation of **87** and its fairly rapid insertion of a second aldehyde monomer into its C–Ti bond to yield **89** (Scheme 15). Analogous difficulties also accompany the use of $TiCl_2$ in epimetallations. Therefore, such problems as incomplete simple epimetallation and competitive reductive dimerization are great drawbacks on the generalized use of ML_{m-n} for the epimetallations depicted in Scheme 13.



Scheme 15.

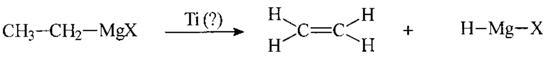
Accordingly, the first observation of transfer epimetallation has represented a significant advance both in synthesis and in mechanism. When R_2TiCl_2 or $R_2Ti(O\textit{i}Pr)_2$ (R = *n*Bu, *t*Bu, *i*Pr) was prepared in THF at –78 °C according to Equation (9), mixed for example with 0.5–1.0 equiv. of diphenylacetylene and warmed to 20 °C, workup with D_2O led to >90% of **86**, with little or no bibenzyl or oligomer (Scheme 16). By contrast, $TiCl_2$ in THF at 25 °C does not react at all with diphenylacetylene and even after 60 h at reflux hydrolysis gave no *cis*-stilbene but only 14% of (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene.



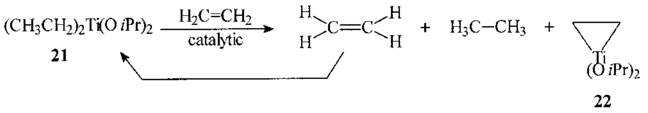
Scheme 16.

The facility and greater extent of epimetallation suggest that the conversion to **93** passes through an octahedral transition state **92**, in which the coordinated alkyne injects electron density into the antibonding σ-orbitals of the *trans*-R–Ti bonds, thereby promoting their homolysis and the formation of **93**. Such transfer epimetallations have proved to be facile and generally applicable to π-linkages such as C=C, C≡C, C=O, C=N, C≡N, N=N, and NO_2.[46]

The facility of transfer epimetallation also permits such coordinate $TiCl_2$ transfer to play a role in the Kulinkovich cyclopropanol synthesis (Scheme 3).[47] The ethylene set free by the titanium-catalyzed elimination of MgHX from the Grignard reagent [Equation (42), cf. Finkbeiner–Cooper reaction)[48]] can even at –78 °C induce transfer epimetallation catalytically to accelerate the production of the Kulinkovich intermediate **22** [Equation (43)] and hence the course of the cyclopropanol synthesis.[47]



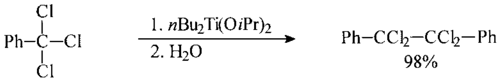
$$CH_3{-}CH_2{-}MgX \xrightarrow{Ti\,(?)} H_2C{=}CH_2 + H{-}Mg{-}X \quad (42)$$



(43)

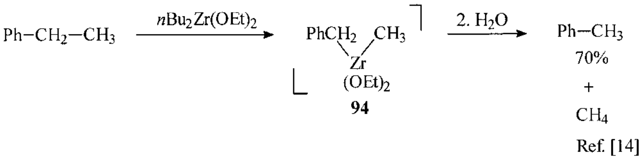
Not only π-bonds can undergo transfer epimetallation but a variety of σ-bonds as well [cf. **83**, Scheme 13 and Equations (44), (45), and (46)]. The cleavage of the relatively stable, homopolar C–C bonds in Equation (46) and Equation (47) are especially noteworthy.[14] Epimetallated intermediates like **94** seem to be involved.

$$2\ Ph{-}CH_2{-}Cl \xrightarrow[2.\ H_2O]{1.\ nBu_2Ti(O\,iPr)_2} \underset{88\%}{Ph{-}CH_2{-}CH_2{-}Ph} + \underset{12\%}{Ph{-}CH_3} \qquad (44)$$



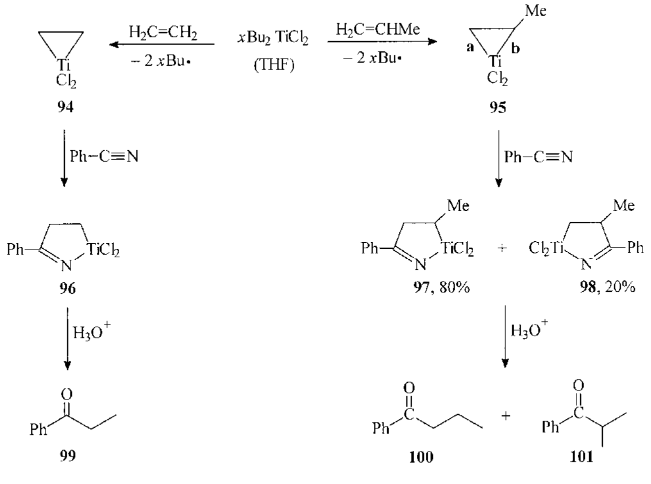
$$Ph{-}CCl_3 \xrightarrow[2.\ H_2O]{1.\ nBu_2Ti(OiPr)_2} \underset{98\%}{Ph{-}CCl_2{-}CCl_2{-}Ph} \qquad (45)$$

$$Ph{-}CH_2{-}CH_2{-}Ph \xrightarrow[2.\ H_2O]{1.\ nBu_2Zr(OEt)_2} \underset{50\%\ \text{Ref. [14]}}{Ph{-}CH_3} \qquad (46)$$



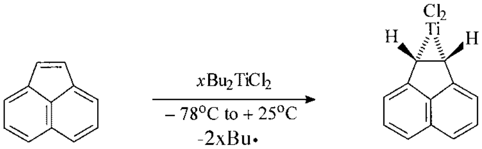
(47)

The final important aspect to consider is the possible role of transfer epimetallation in the stereoselective polymerization of olefins. In the course of these studies all types of olefins and acetylenes were found to undergo efficient transfer epimetallation by means of xBu$_2$TiCl$_2$ ($x = n$ or t) in THF at room temperature (cf. Scheme 16). Such transfer epimetallation of ethylene and of propylene was achieved and verified by passing the individual olefin gases into a solution of xBu$_2$TiCl$_2$ in THF at 0 °C. The formation of titanacycles **94** and **95** was demonstrated by their capture with benzonitrile to yield the five-membered titanacycles, **96** from ethylene and **97** and **98** in a 4:1 ratio from propylene (preferential nitrile insertion at bond **a** of **95** by steric control). The structures of **96**, **97**, and **98** were established by their acidic hydrolysis to ketones **99**, **100**, and **101**, respectively (Scheme 17).[49–51]



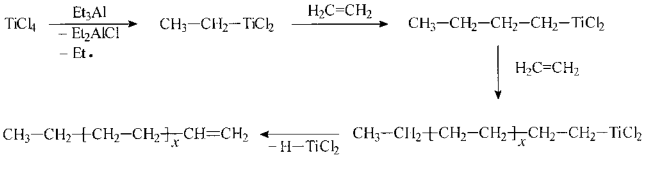
Scheme 17.

When similar transfer epimetallations were then attempted in hexane starting at –78 °C and warming to 25 °C, again sterically substituted alkynes and olefins, like diphenylacetylene (Scheme 16) and acenaphthylene [Equation (48)] underwent complete epimetallation. But in sharp contrast, when xBu$_2$TiCl$_2$ in hexane was treated with ethylene or propylene at –78 °C, immediate polymerization was initiated at that temperature. Hydrolytic workup of the reaction with ethylene gas gave linear, high-density polyethylene (mp >125 °C, IR), while the polypropylene obtained from propylene gas consisted of about 90% isotactic and 10% atactic polymer. Similar treatments of such monomers as 1-hexene and styrene likewise led principally to the corresponding isotactic polymer.



(48)

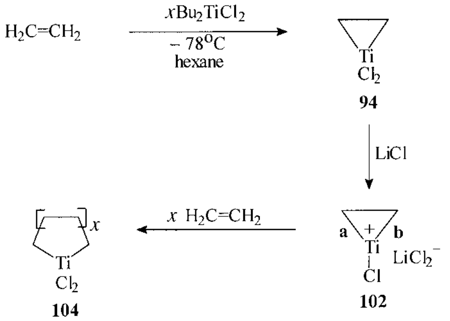
These surprising polymerizations initiated by xBu$_2$TiCl$_2$ in hexane or toluene suspension raise the possibility for a novel site and initiating step for Ziegler–Natta olefin polymerization. Such polymerizations, conventionally carried out in hydrocarbon slurry with combinations of Ti, Zr, or V salts and a main group alkyl (R_nAlCl_{3-n}, RLi, or R_2Mg), have long been considered to occur by stepwise, multiple insertions of the olefin monomer units into an initial carbon–transition metal bond thought to exist on the catalyst surface (e.g., Scheme 18 for the $TiCl_4$–Et_3Al system). But the behavior of xBu$_2$TiCl$_2$ toward diphenylacetylene either in THF or in hexane *does not involve insertion of the alkyne unit* into the x-butyl-C–Ti bond. Rather a transfer epimetallation takes place to generate the titanacyclopropene depicted in Scheme 16. Even ethylene or propene react with xBu$_2$TiCl$_2$ in THF to undergo transfer epimetallation in THF solution (formation of **94** and **95**), rather than olefin insertion into a Bu–Ti bond. Since **94** and **95** are organotitanium(IV) dichlorides, in THF they would exist as solvates, $R_2TiCl_2{\cdot}2THF$, and thus rendered inactive in olefin polymerizations.



Scheme 18.

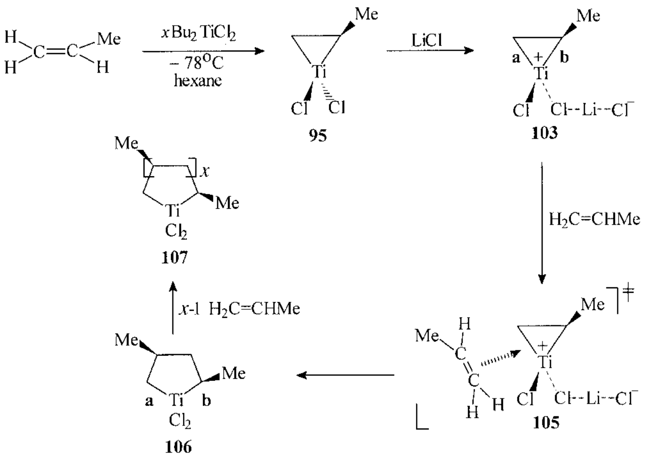
In light of the foregoing observations, we feel justified in proposing a novel active site for the initiation and chain growth in Ziegler–Natta polymerization, which is an experimentally supported alternative to the completely hypothetical process outlined in Scheme 18. This novel proposal can also explain the stereoselectivity of the chain growth observed with α-olefins in terms of straightforward steric effects. Thus the need to make unsubstantiated assumptions about the oxidation state of the titanium (assumed as Ti^{3+}) or concerning the nature and dimensions of the catalyst surface (assumed as a fragment of a $TiCl_3$ lattice) is thereby obviated.

We propose that either ethylene or propylene gas reacts with a suspension of $x\mathrm{Bu_2TiCl_2}$ and LiCl in hexane to undergo prompt epimetallation to form **94** (Scheme 19) or **95** (Scheme 20), respectively. The Lewis-acidic LiCl could then induce titanium(IV) cationic character in these titanacyclopropanes to produce active sites **102** and **103**, respectively. Rapid and multiple ethylene monomer insertions into either bond **a** or **b** of **102** would lead to a titanacyclopolymethylene (**104**) and thus to linear polyethylene upon hydrolysis or upon H_2TiCl_2 elimination.



Scheme 19.

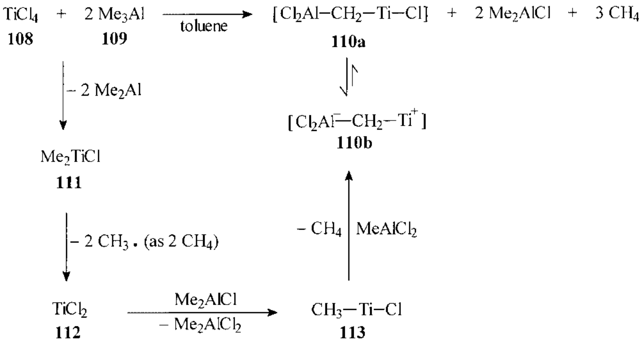
In the polymerization of propylene via titanacyclopropyl cation **103** (Scheme 20), steric factors will favor insertion of the propylene into bond **a**. It will be recalled that there is experimental support for such a steric effect: in the reaction of **95** with benzonitrile insertion into the less hindered bond **a** occurred four times as rapidly as insertion into bond **b**. But additional steric factors are involved in the regioselectivity and the stereoselectivity with which a propylene unit adds into bond **a** of **103**. The sterically favored transition state (**105**) would have the propylene unit approach bond **a** of **103** from the underside, so as to be away from the projecting ring methyl. Furthermore, the propylene methyl



Scheme 20.

would avoid being under the ring or next to the bulky $TiCl_2{\cdot}LiCl$ center. Collapse of transition state **105** would lead to titanacycle **106**, whose formation would set the pattern for further selective insertions into bond **a**, governed by the same steric factors determining the formation of **106** from **103**. The appeal of this novel model for stereoselective olefin polymerization is that it offers a coherent molecular explanation in terms of well-known steric and electronic factors, thus avoiding the inevitable guesswork of any explanation invoking "surface effects".

Finally, we judge it fitting that we close this discussion of the role of transition metal alkyls in olefin polymerization with an analysis of the complex reactions taking place in the Ziegler catalyst system, $TiCl_4$ and Me_3Al in a 1:2 ratio (Scheme 21).[52] The overall reaction between **108** and **109** has been shown to produce the black solid **110a** (as the zwitterionic form, **110b**), based upon analytical, spectroscopic and chemical evidence. As the possible route to **110**, one could propose the following feasible steps: 1) metal–metal metathesis between **108** and **109**, leading to **111**; 2) reductive elimination from **111** to produce **112**; 3) metal–metal metathesis between **112** and Me_2AlCl to form **113**; and 4) metal–hydrogen metathesis between **113** and $MeAlCl_2$ to produce **110**. This specific example serves to demonstrate that much more profound and interesting reactions take place in Ziegler catalyst systems than the generally as-



Scheme 21.

sumed straightforward and prosaic reaction given in Equation (49).

$$R_3Al + TiCl_4 \rightarrow R_2AlCl + R\text{–}TiCl_3 \quad (49)$$

Such zwitterionic catalysts of both titanium **110** and zirconium have proved to be one-component, stereoselective polymerization and oligomerization catalysts for olefins and acetylenes. Their activity can be readily explained in terms of epimetallation and of the three-membered metallocycles portrayed in Schemes 19 and 20.

Summary

The detailed investigation of both the simple and double decomposition modes of transition metal alkyls has indeed brought to light a large number of useful and novel reagents and processes of great appeal in organic synthesis. In the sequence they are considered, the following can be enumerated: 1) *reductive elimination* applied to mixed alkyls of the type R_nME_{m-n} to yield subvalent, carbene- or free-radical-like ME_{m-n}, which can add to or cleave π- or σ-bonds in a process of *epimetallation*; 2) *β-metal hydride elimination*, in which mixed alkyls such as $n\text{Bu}_2\text{TiCl}_2$ or $n\text{Bu}_2\text{Zr(OEt)}_2$ can serve as sources of metal hydrides and thus as *hydrometallating agents*; 3) *combined reductive and β-metal hydride eliminations*, whereby unstable metallate complexes, such as $\text{LiCr}n\text{Bu}_4$ or $\text{LiV}n\text{Bu}_4$ can decompose to *anionic epimetallating agents*, MH_2^-, capable of adding to C=O and C=N functions without involving the M–H bonds; 4) *α-metal hydride elimination*, which seems to be involved in the *thermal C–C bond coupling* of mixed zirconium(IV) alkyls of the type, $(RR'CH)_2Zr(OEt)_2$; 5) *α,μ-eliminations* which are exhibited by lithiated alkyls of the type, $RHC(Li)\text{–}ME_{n-1}$, and which lead to alkylidenes, $RHC{=}ME_{n-2}$, capable of *alkylidenation and ROMP* catalysis; 6) *metal–hydrogen metathesis*, whereby reagents such as $n\text{Bu}_2\text{Zr(OEt)}_2$ can effect the *zirconation* of various allylic, benzylic, acetylenic and aryl C–H bonds; 7) *metal–metal metathesis*, especially as exemplified by the *redistribution reaction* of zirconium alkyls of the type $RR'Zr(OEt)_2$, thereby setting the stage for *C–C bond coupling* (cf. supra: point 4); 8) *transfer epimetallation*, in which *epimetallation* (point 1) is achieved directly by R_nME_{m-n} with displacement of the R groups, rather than by ME_{m-n}, in a smooth, high-yielding process; 9) *transfer epimetallation* of olefins by $n\text{Bu}_2\text{TiCl}_2$ in hydrocarbon media as a superior model for the active site and the stereoselective chain growth observed in Ziegler–Natta olefin polymerization.

Experimentally observed examples of each of the nine foregoing reagents and/or processes are drawn principally from early transition metal alkyls of titanium, zirconium, hafnium, vanadium and chromium. Where available, the experimental conditions predisposing to a certain decomposition route or reaction mechanism are given due consideration.

Acknowledgments

Our extensive studies of transition metal alkyls have now been under way for over a decade. During this time our efforts have enjoyed the financial support of the U.S. National Science Foundation, Akzo Corporate Research America, Solvay Corporation of Brussels, Belgium, DSM Corporation, Geleen, The Netherlands, Alexander von Humboldt Stiftung of Bonn, Germany, and Boulder Scientific Company of Mead, Colorado. As is evident from the literature citations, our efforts reported herein are also based upon the zealous and perceptive research of previous doctoral students in our group, namely Drs. Xian Shi, Joseph Alila, Fredrick Owuor, Peter Otieno and John Gitua. Finally, present group members, Tsz Chan and Charles Ogindo, have performed valuable orienting experiments.

---

[1] J. J. Eisch, A. A. Adeosun, *Eur. J. Org. Chem.* **2005**, 993–997.

[2] R. Bunsen, *Justus Liebigs Ann. Chem.* **1842**, *42*, 14.

[3] a) E. Frankland, *Justus Liebigs Ann. Chem.* **1849**, *71*, 171; b) E. Frankland, *Justus Liebigs Ann. Chem.* **1853**, *85*, 347; c) E. Frankland, *Justus Liebigs Ann. Chem.* **1855**, *95*, 28.

[4] a) M. Gomberg, *J. Am. Chem. Soc.* **1900**, *22*, 757; b) M. Gomberg, *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 3150.

[5] F. Paneth, W. Hofeditz, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1335.

[6] a) F. Paneth, W. Lautsch, *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2702; b) F. Paneth, K. F. Herzfeld, *Z. Elektrochem.* **1931**, *37*, 577.

[7] F. O. Rice, K. K. Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, **1935**, p. 58.

[8] F. A. Cotton, *Chem. Rev.* **1955**, *55*, 551–594.

[9] E. Krause, A. von Grosse, *Die Chemie der metall-organischen Verbindungen*, Verlag Gebrüder Borntraeger, Berlin, **1937**.

[10] H. Gilman, R. G. Jones, *J. Org. Chem.* **1945**, *10*, 505–515.

[11] K. Ziegler, H. G. Gellert, H. Lehmkuhl, W. Pfohl, K. Zosel, *Justus Liebigs Ann. Chem.* **1960**, *629*, 1–13.

[12] a) J. J. Eisch, *J. Am. Chem. Soc.* **1962**, *84*, 3605–3610; b) J. J. Eisch, *J. Am. Chem. Soc.* **1962**, *84*, 3830–3836.

[13] J. J. Eisch, F. A. Owuor, X. Shi, *Organometallics* **1999**, *18*, 1583–1585.

[14] J. J. Eisch, S. Dutta, manuscript in preparation.

[15] A leading reference to the publication series, "Organic Chemistry of Subvalent Transition Metal Complexes" is Part 30: J. J. Eisch, S. Dutta, *Organometallics* **2004**, *23*, 4181–4183.

[16] a) B. Bogdanovic, M. Kröner, G. Wilke, *Liebigs Ann. Chem.* **1966**, *699*, 1–23; b) R. A. Shun, *Inorg. Synth.* **1974**, *15*, 5.

[17] J. J. Eisch, L. E. Hallenbeck, K. I. Han, *J. Org. Chem.* **1983**, *48*, 2963–2968.

[18] a) J. J. Eisch, M. P. Boleslawski, *J. Organomet. Chem.* **1987**, *334*, C1–C4; b) J. J. Eisch, S. I. Pombrik, X. Shi, S. C. Wu, *Macromol. Symp.* **1995**, *89*, 221–229.

[19] J. J. Eisch, X. Shi, J. Lasota, *Z. Naturforsch., Teil B* **1995**, *50*, 342–350.

[20] J. J. Eisch, X. Shi, F. A. Owuor, *Organometallics* **1998**, *17*, 5219–5221.

[21] J. J. Eisch, Y. Qian, J. Weber, unpublished studies.

[22] J. J. Eisch, J. R. Alila, *Organometallics* **1999**, *18*, 2930–2932.

[23] J. J. Eisch, P. O. Fregene, unpublished studies.

[24] J. J. Eisch, *J. Organomet. Chem.* **2001**, *617–618*, 148–157.

[25] O. G. Kulinkovich, S. V. Sviridov, D. A. Vasilevski, T. S. Pritytckaja, *Zh. Org. Khim.* **1989**, *25*, 2245.

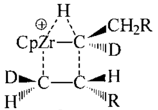
[26] For a more extensive review, cf. O. G. Kulinkovich, A. de Meijere, *Chem. Rev.* **2000**, *100*, 2789.

[27] J. J. Eisch, X. Ma, K. I. Han, J. N. Gitua, C. Krüger, *Eur. J. Inorg. Chem.* **2001**, 77–88.

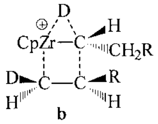
[28] J. J. Eisch, Y. Qian, J. Weber, N. Zandona, F. Siberdt, U. S. Patent 6,087,515, July 11, **2000**.

[29] D. W. Hart, J. Schwartz, *J. Am. Chem. Soc.* **1974**, *96*, 8115–8116.

[30] J. J. Eisch, J. R. Alila, *Organometallics* **2000**, *19*, 1211–1213.
[31] J. J. Eisch, F. A. Owuor, unpublished studies.
[32] Current studies under way with the collaboration of Professor D. C. Doetschman of this Department of Chemistry.
[33] Preferential insertion of (*E*)-1-deuterioalkane, H(D)C=C(H)R, into the Zr–C bond of the more abundant transition state **a**, rather than that of transition state **b** (isotopic preference of H over D in agostic bridging) favors the *erythro*-hydro dimer: H. Krauledat, H. H. Brintzinger, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1412–1413.



a



b

[34] J. J. Eisch, S. Dutta, *Organometallics* **2004**, *23*, 4181–4183.
[35] N. A. Petasis, E. I. Bzowej, *J. Am. Chem. Soc.* **1990**, *112*, 6392–6394.
[36] J. Liu, D. Zhang, J. Huang, Y. Qian, A. S. C. Chan, *J. Poly. Sci. A, Poly. Chem.* **2000**, *38*, 1639–1641.
[37] J. W. von Goethe, *Die Wahlverwandtschaften*, **1809**, translated as *Selective Affinities.* As many an intellectual of his era, Goethe prided himself on also being a natural philosopher and would out of pure curiosity undertake various experiments in geology, chemistry or physics.
[38] M. E. Thompson, S. M. Baxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santasiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203–219.
[39] F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613.
[40] J. J. Eisch, F. A. Owuor, P. O. Otieno, *Organometallics* **2001**, *20*, 4132–4134.
[41] a) Were Me_2TiCl_2 (**45**) present when propiophenone was added, then the tertiary alcoholate, Ph(Et)MeC–O–$TiMeCl_2$ would have resulted. Upon hydrolysis, the corresponding alcohol, Ph(Et)MeCOH, would have been formed. Even if this alcohol were to have undergone dehydration, not only **54** would have been generated but also the *cis*,*trans* mixture of olefins, Ph(Me)C=C(Me)H. Since neither the tertiary alcohol nor any olefin but **54** was detected, the presence of Me_2TiCl_2 can be ruled out. b) A. A. Adeosun, Doctoral Dissertation, State University of New York at Binghamton, **2005**.
[42] a) J. Sohn, Bachelor Honors Thesis, State University of New York at Binghamton, **2003**; b) J. J. Eisch, C. O. Ogindo, unpublished studies.
[43] K. Moedritzer, in: *Organometallic Reactions* (Eds.: E. I. Becker, M. Tsutsui), Wiley-Interscience, New York, **1971**, vol. 2, pp. 1–116.
[44] J. J. Eisch, J. N. Gitua, P. O. Otieno, X. Shi, *J. Organomet. Chem.* **2001**, *624*, 229–238.
[45] J. J. Eisch, J. N. Gitua, D. C. Doetschman, manuscript in preparation.
[46] J. J. Eisch, J. N. Gitua, *Organometallics* **2003**, *22*, 24–26.
[47] J. J. Eisch, A. A. Adeosun, J. N. Gitua, *Eur. J. Org. Chem.* **2003**, 4721–4727.
[48] a) J. J. Eisch, J. E. Galle, *J. Organomet. Chem.* **1978**, *160*, C8–C12; b) G. D. Cooper, H. L. Finkbeiner, *J. Org. Chem.* **1962**, *27*, 1493; c) H. L. Finkbeiner, G. D. Cooper, *J. Org. Chem.* **1962**, *27*, 3395.
[49] J. J. Eisch, J. N. Gitua, *Organometallics* **2003**, *22*, 4172–4174.
[50] J. J. Eisch, J. N. Gitua, P. O. Otieno, A. A. Adeosun, *Macromol. Symp.* **2004**, *213*, 187–198.
[51] J. J. Eisch, J. N. Gitua, U. S. Patent 6,743,872, June 1, **2004**.
[52] J. J. Eisch, P. O. Otieno, *Eur. J. Org. Chem.* **2004**, 3269–3276.

Received February 2, 2005