Novel Alkylidenating Agents via the α Lithiation of Monoalkyl Group 4 Metal Derivatives: Methylidene-Metal Complexes and Their Active Lithiated Precursors[‡]

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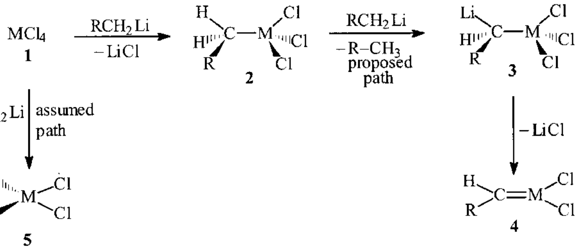
The interaction of the Group 4 metal chlorides, MCl_4, where M = Ti, Zr, Hf, with two equiv. of methyllithium at –78 °C in toluene has led to the corresponding methylidene-metal complex, $H_2C{=}MCl_2$, possibly complexed with LiCl. That this complex was stable to at least –40 °C was demonstrated by adding chemical trapping agents at this temperature: 1) benzophenone was quantitatively converted into 1,1-diphenylethylene when M = Ti or Zr; with the Hf analogue, a 1:3 mixture of 1,1-diphenylethylene and 1,1-diphenylethanol was produced; 2) propiophenone reacted with the methylidene complex to yield 2-phenyl-1-butene, 38 % (M = Ti) or 25 % (M = Zr), with the majority of the propiophenone being recovered (the unreacted ketone is attributed to enolate salt formation competing with the methylidenation); 3) diphenylacetylene reacted with $H_2C{=}TiCl_2$ by cycloaddition in 50 % yield, ultimately to give a 1:1 mixture of α-methyl-*cis*-stilbene and α-methyl-*trans*-stilbene; and finally 4) norbornene was polymerized in a ROMP process by either the methylidene-titanium or methylidene-zirconium complex, but the titanium catalyst exhibited higher activity. The stability of such methylidene complexes proved to be highly temperature- and solvent-dependent: 1) the methylidene complex in toluene was no longer detectable by chemical trapping when the reaction mixture was warmed to 0 °C or above; 2) the generation of the methylidene complex in THF was uniformly unsuccessful even at –78 °C or above. From these observations this study concludes that in toluene the free methylidene complex, $H_2C{=}MCl_2$, is not present but rather the agent is still bonded to LiCl. At higher temperatures in toluene or even at –78 °C in THF, the LiCl dissociates from such complexation and the free methylidene dimerizes to $[Cl_2M{-}CH_2]_2$, as is known in the case of $Cp_2Ti{=}CH_2$.

Introduction

As a novel, general approach to transition metal-alkylidenes we have initiated the study of base-mediated α,μ dehydrohalogenations[2] in monoalkyl Group 4 metal trihalides **2** as depicted in Scheme 1. A straightforward and known route to such monomethyl derivatives as **2** is the interaction of Group 4 metal tetrachlorides MCl_4 (**1a**–**1c**, M = Ti, Zr, Hf) with a methylating agent (MeMgX, MeLi, Me_nAlCl_{3-n}, Me_2Zn, or Cp_2TiMe_2) in a 1:1 ratio.[3] With excess MeMgX, for example, further methylation of **2** can yield successively Me_2MCl_2, Me_3MCl and Me_4Ti.[4] The impetus for the present investigation was the question of whether an excess of methyllithium might act on **2**, not as a methylating agent, but a lithiating agent to produce **3** and ultimately methylidene **4** by an α,μ elimination of LiCl (Scheme 1, R = H). In several previous reports the action of two equiv. of methyllithium was assumed to yield Me_2TiCl_2 (**5**) directly but without corroborating evidence.[5]



Scheme 1.

In order to determine which course of reaction might take place, either preferentially or randomly, we have studied the behavior of the individual halides, $TiCl_4$, $ZrCl_4$, and $HfCl_4$, with two equiv. of methyllithium in an ether/toluene medium at low temperatures. We had hoped to decide whether the methyl analogs of **3** and **4**, namely **5** and **6**, would thereby be formed by means of chemical trapping with benzophenone (**7**). From the extensive work of Reetz and coworkers on titanium alkyls,[6] **5**, if formed, should insert the C=O group of **7** into the C–M bond and give alcoholate **8**, and upon hydrolysis, alcohol **9** (Scheme 2). On the other hand, were **6** (or its lithiated precursor; cf. infra) present, then a smooth methylidenation leading to 1,1-diphenyl-

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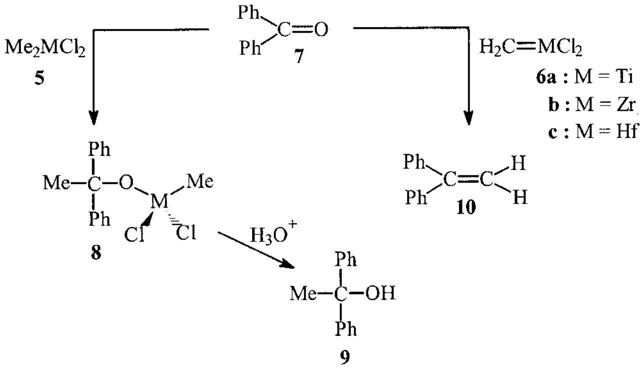
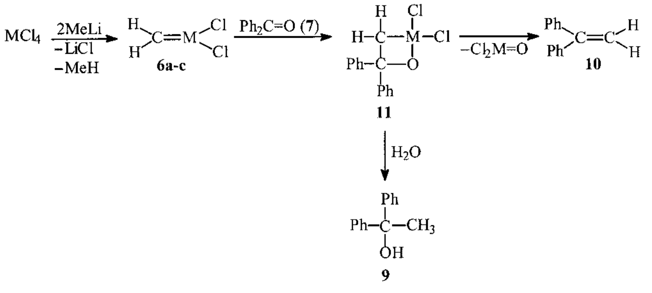
ethylene (**10**) should ensue. Such expectations have their firm substantiation in the extensive studies of the Tebbe reagent and its many analogs.[7]



Scheme 2.

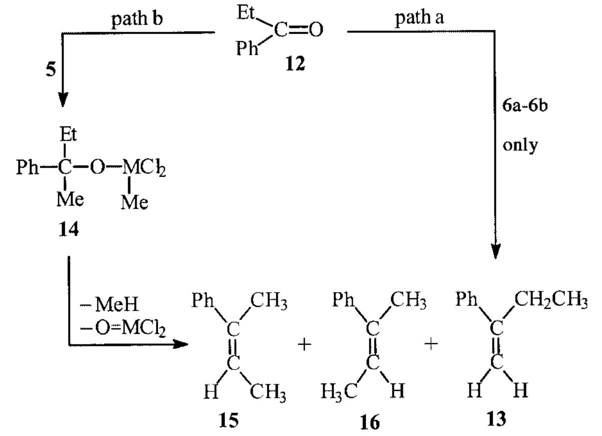
Results

Addition of two equiv. of methyllithium in ether to a solution or suspension of one equiv. of MCl_4 (**1a**–**1c**, M = Ti, Zr, or Hf) in toluene and cooled to –78 °C resulted in a red-brown (Ti) or milky-white suspension (Zr, Hf). The mixture was allowed to warm to –40 °C and then treated with 0.90 equiv. of benzophenone (**7**). Hydrolytic workup gave a quantitative yield of 1,1-diphenylethylene (**10**) with $TiCl_4$ and with $ZrCl_4$. In the case of $HfCl_4$ the yield of **10** was only 27% and the balance of the product was 1,1-diphenyl-1-ethanol (**9**) [73%]. With Scheme 3 as the reference, the methylidene complex **6a**,**6b**, or **6c** (or its lithiated precursor) was clearly formed, in whole or in part, in each case and was trapped via intermediate **11** by the benzophenone.[8] As will be mentioned below, there is reason to attribute the high yield of the alcohol **9** in the Hf case to the greater thermal stability of the C–Hf bond in **11** and hence its partial persistence to the hydrolysis step.[9]



Scheme 3.

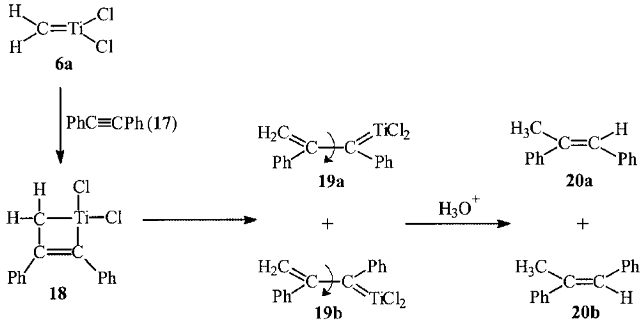
In order to substantiate that the methylidenating agent active in converting benzophenone (**7**) into 1,1-diphenylethylene (**10**) was **6** or its lithium precursor, rather than **5**, propiophenone (**12**) was allowed to react with the titanium or zirconium methylidenating reagent in a 1:1 molar ratio at –40 °C. As shown in Scheme 4, were $H_2C{=}MCl_2$ (**6a**–**6b**, M = Ti, Zr) the sole active agent, then only olefin **13** would be formed (path a). If on the other hand Me_2MCl_2 (**5**) were the active agent, then alcoholate **14** would result. Its decomposition with elimination would afford some amounts of three isomeric olefins **13**, **15**, and **16** (path b). In the actual trial only olefin **13** was observed with either the Ti or Zr reagent. This finding reinforces the conclusion that the structure of the active agent is $H_2C{=}MCl_2$ in both cases. However, it is important to note that yields of olefin **13** were modest (Ti, 38%; Zr, 25%) and much of ketone **9** was recovered (62–75%). The most straightforward explanation for much remaining ketone in this reaction is that some base has generated the enolate salt of **12**. Corroboration for the presence of the enolate of **12** comes from a reaction mixture of **9** with **6a**, which was worked up with D_2O: the methylene group of **9** was >90% monodeuterated (cf. infra).



Scheme 4.

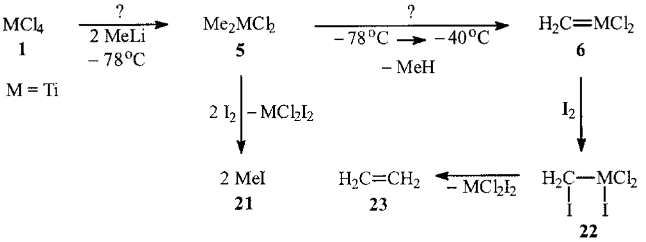
Further corroboration for the presence of a methylidene-like complex in the titanium case was sought by the addition of one equiv. of diphenylacetylene (**17**) to the putative $H_2C{=}TiCl_2$ reagent at –40 °C. Hydrolytic workup revealed that 50% of **17** had been converted into a 1:1 mixture of α-methyl-*cis*-stilbene (**20a**) and α-methyl-*trans*-stilbene (**20b**). In chemical behavior well-precedented by the reactions of Tebbe-like reagents with acetylenes,[7e,10] such an outcome supports the cycloaddition reaction proposed in Scheme 5 to form **18** with subsequent ring opening to produce conformationally isomeric vinylcarbene complexes **19a** and **19b**. Random protolytic workup of such equilibrating conformers would nicely provide a 1:1 *cis*,*trans*-mixture of olefins **20a** and **20b**.

In a preliminary study it has also been shown that either $H_2C{=}TiCl_2$ (**6a**) or $H_2C{=}ZrCl_2$ (**6b**) in toluene is capable of reacting as a ROMP catalyst towards norbornene at –40 °C. The white solid obtained upon hydrolytic workup was shown in both cases to exhibit ^1H and ^{13}C NMR spectra identical with those of *cis*-polynorbornene, as produced by known ROMP polymerizations.[11] Apparently, **6a** and **6b** initiate ROMP processes by [2+2] cycloaddition to norbornene, quite analogous to the manner in which **6a** adds to diphenylacetylene (**17**) to form **18** in Scheme 5 below. However, it is noteworthy that the titanium analog **6a** was much more reactive than the zirconium catalyst **6b**.



Scheme 5.

The foregoing findings leave little doubt that some form of the methylidene complex, **6a**–**6b**, resulted from the 2:1 interaction of methyllithium and MCl_4 and was present at –40 °C when various substrates were added. Nevertheless, one must still consider whether the dimethylmetal dichloride **5** might have been the primary reaction product formed at –78 °C but then decomposed upon warming to –40 °C to yield **6** (Scheme 6). To address this, $TiCl_4$ in toluene at –78 °C was treated with two equiv. of MeLi and after 30 min at that temperature, two equiv. of I_2 were then added. Were **5** present, it would have undergone iodinolysis to generate methyl iodide (**21**). On the other hand, had **5** already decomposed to **6**, iodinolysis should have led to **22** and then to ethylene (**23**), as other methylenedimetallics, such as **25** or **26** have been shown to react.[12] In the present experiment no trace of methyl iodide has been detected and therefore no Me_2TiCl_2 was generated even at –78 °C.

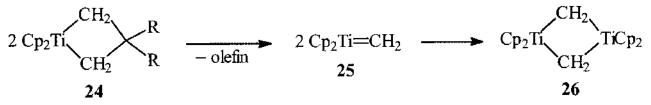


Scheme 6.

As a fitting subject for continuing studies, a pronounced solvent effect must be noted: when the MCl_4 was dissolved or dispersed at –78 °C in THF, rather than toluene, and the methyllithium added, the reaction was then brought either to –40 °C or to –20 °C and the benzophenone added. In neither case did any of the benzophenone react. Yet the hydrolysis of such reaction runs gave copious evolutions of methane gas, which showed that methyl–metal bonds were still present. Even for reactions in toluene, when the benzophenone was added at room temperature, rather than –20 °C, again no reaction of the ketone was observed. Clearly, the active reagent **6** decomposes above –20 °C.

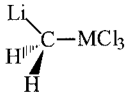
Discussion

The foregoing results are consistent with the reaction pathway in toluene as depicted in Scheme 1, where the suggested neutral methylidenating agent is **4** (R = H). However, the presence of uncomplexed **4** seems unlikely in view of the known behavior of titanocene methylene (**25**), as exhibited when generated from the Tebbe reagent[13] or the Grubbs titanacyclobutane (**24**) adducts.[14] Rapid dimerization to the less reactive 1,3-dititanacyclobutane (**26**) occurs (Scheme 7).



Scheme 7.

Accordingly, we propose that the active methylidenating agent generated from MCl_4 and methyllithium in toluene is not free **6** (or, **4**, R = H) but a complex of **6** with LiCl, either as σ complex **27** or π complex **28**.



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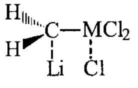

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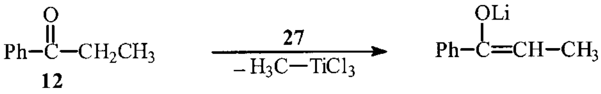
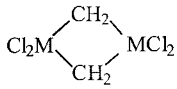
The organolithium form of **6**, such as **27**, could be responsible for the extensive enolate salt formation observed as a side reaction in the methylidenation of propiophenone (**12**) [Equation (1)].



$$\underset{\mathbf{12}}{\mathrm{Ph{-}C({=}O){-}CH_2CH_3}} \xrightarrow[-\,\mathrm{H_3C{-}TiCl_3}]{\mathbf{27}} \mathrm{Ph{-}C(OLi){=}CH{-}CH_3} \qquad (1)$$

Furthermore, the failure to observe any methylidenation of ketones in THF or in toluene at 20 °C can be ascribed to the promoted dissociation of LiCl from **27** or **28** and the subsequent formation of the unreactive dimer of **6**, namely **29**.



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In line with this interpretation, the reaction given in Scheme 1 is under continuing study. Our hope is to obtain both NMR spectroscopic evidence and deuterium-labeling upon hydrolysis with D_2O as support for the presence of intermediate **29**. Furthermore, by conducting the reaction of MCl_4 with methyllithium in the presence of phosphanes, we hope that such phosphanes will displace LiCl from **27** or **28** to produce a stable monomeric form of **6** useful in diverse methylidenations.

Finally, it should be borne in mind that in keeping with their alkylidenating activity both $H_2C{=}TiCl_2$ (**6a**) and $H_2C{=}ZrCl_2$ (**6b**) have exhibited ROMP catalytic activity toward norbornene, and that accordingly, more stable phosphane derivatives of **6** would be worthy of evaluation as catalysts in future ROMP processes.

Experimental Section

Instrumentation, Analysis, and Starting Reagents: All reactions were carried out under a positive pressure of anhydrous, oxygen-free argon. All solvents employed with organometallic compounds were dried and distilled from a sodium metal-benzophenone ketyl mixture prior to use.[15] The IR spectra were recorded with a Perkin–Elmer instrument (model 457), and samples were measured either as mineral oil mulls or as KBr films. The NMR spectra (^{1}H and ^{13}C) were recorded with a Bruker spectrometer (model EM-360) and tetramethylsilane (Me_4Si) was used as the internal standard. The chemical shifts reported are expressed on the δ scale in parts per million (ppm) from the Me_4Si reference signal. The GC/MS measurements and analyses were performed with a Hewlett–Packard GC 5890/Hewlett–Packard 5970 mass-selective-detector instrument. The gas chromatographic analyses were carried out with a Hewlett–Packard instrument (model 5880) provided with a 2-m OV-101 packed column or with a Hewlett–Packard instrument (model 4890) having a 30-m SE-30 capillary column. Melting points were determined on a Thomas–Hoover Unimelt capillary melting point apparatus and are uncorrected. In all reaction workups a satisfactory material balance of at least 95% of the expected mass was obtained. In most cases such reaction mixtures were analyzed directly by integration of appropriate signals in their ^{1}H NMR spectra.

Reaction of Methyllithium with Titanium(IV) Chloride in Toluene: To anhydrous titanium(IV) chloride (1.1 mL, 10 mmol) dissolved in toluene (60 mL) at –78 °C was added slowly methyllithium (14.3 mL of 1.4 M solution, 20.0 mmol) in diethyl ether solution at –78 °C under argon. The resulting reddish-brown mixture was allowed to stir at –78 °C for a few minutes before being allowed to warm to –40 °C.

A toluene solution of benzophenone (**7**) [1.82 g, 10 mmol] was added to the foregoing solution of assumed complex **6a** (M = Ti) [11.1 mmol] in toluene at –40 °C and the resulting reddish-brown mixture was allowed to warm to room temperature overnight. Upon hydrolytic workup, 1,1-diphenylethylene (**10**) was obtained in quantitative yield as shown by ^{1}H and ^{13}C NMR spectroscopy. 1,1-Diphenylethylene (**10**):^{1}H NMR ($CDCl_3$): δ = 7.31 (Ar, 10 H), 5.4 (s, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 150.09 (C), 141.49, 128.23, 128.13, 127.65 (Ar), 114.17 (CH_2) ppm.

An identical reaction at –78 °C between $TiCl_4$ (10 mmol) in toluene (60 mL) and methyllithium (20 mmol) in diethyl ether was conducted for 30 min with stirring. Thereupon, at the same temperature, diiodine (2.2 equiv.) was introduced and the mixture allowed to come to 25 °C overnight. Hydrolysis and excess iodide removal with aqueous $NaHSO_3$ and drying of the toluene layer with anhydrous $NaSO_4$ yielded a separated toluene layer. *Without any evaporation* the ^{1}H and ^{13}C NMR spectra of this layer was recorded and revealed no detectable signals for methyl iodide.

Reaction of Methyllithium with Zirconium(IV) Chloride in Toluene: To anhydrous zirconium(IV) chloride (1.73 g, 7.4 mmol) suspended in toluene (60 mL) at –78 °C was added slowly methyllithium (10.6 mL of 1.4 M solution, 14.8 mmol) in diethyl ether solution at –78 °C under argon. The resulting milky-white mixture of **6b** (M = Zr) and LiCl was allowed to stir at –78 °C for 2h before allowing it to warm up to –40 °C.

A toluene solution of benzophenone (**7**) [1.08 g, 5.9 mmol] was added to the foregoing solution of assumed of complex **6b** (M = Zr) [7.4 mmol] in toluene at –40 °C. The resulting white mixture was then allowed to warm to room temperature overnight, and upon hydrolytic workup, the clear liquid of 1,1-diphenylethylene (**10**) was obtained in quantitative yield as shown by ^{1}H and ^{13}C spectroscopy.

Reaction of Methyllithium with Hafnium(IV) Chloride in Toluene: To anhydrous hafnium(IV) chloride (580 mg, 1.8 mmol) suspended in toluene (60 mL) at –78 °C was added slowly methyllithium (2.60 mL of 1.4 M solution, 3.6 mmol) in diethyl ether solution at –78 °C under argon. The resulting white mixture was allowed to stir at –78 °C for 2h before allowing it to warm up to –40 °C.

A toluene solution of benzophenone (**7**) [0.33g, 1.81 mmol] was added to the foregoing solution of assumed complex **6c** (M = Hf) [2.0 mmol] in toluene at –40 °C, and the resulting white mixture was allowed to warm to room temperature overnight. Upon hydrolytic workup, a liquid mixture of 1,1-diphenylethylene (**10**) [27%] and 1,1-diphenylethanol (**9**) [73%] was obtained as shown by ^{1}H and ^{13}C NMR spectroscopy. 1,1-Diphenylethanol (**9**): ^{1}H NMR ($CDCl_3$): δ = 7.00–7.50 (Ar), 2.60 (s, 1 H), 1.80 (s, Me) ppm. ^{13}C NMR ($CDCl_3$): δ = 148.00, 128.10, 126.87, 125.84 (Ar), 76.16 (COH), and 30.75 (CH_3) ppm.

Chemical Trapping of Group 4 Methylidenes with Propiophenone

Titanium-methylidene 6a (M = Ti): A toluene solution of propiophenone (**12**) [1.31 mL, 10 mmol] was added to complex **6a** (M = Ti) [10 mmol] in toluene at –40 °C, and the resulting mixture was allowed to warm to room temperature overnight. Upon hydrolytic workup, a liquid mixture of 2-phenyl-1-butene (**13**) and recovered propiophenone (**12**) was obtained in 38% and 62% yields, respectively, as shown by ^{1}H and ^{13}C NMR spectroscopy. 2-Phenyl-1-butene (**13**): ^{1}H NMR ($CDCl_3$): δ = 1.10 (t, 3 H), 2.50 (q, 2 H), 5.05 (s, 1 H), 5.27 (s, 1 H), 7.1–7.5 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.92, 28.04, 110.90, 125.98, 127.22, 128.19, 141.51, 150.01 ppm.

In a reaction run identical with the foregoing, the reaction mixture was worked up with D_2O. In the ^{1}H NMR spectrum of the propiophenone the integration of the CH_2 signal versus the CH_3 resonance gave a ratio of 1.05:3.00. This ratio indicates that the methylene group was >90% monodeuterated.

Zirconium-methylidene 6b (M = Zr): A toluene solution of propiophenone (**12**) [0.77 mL, 5.9 mmol] was added to a solution of complex **6b** (M = Zr) [5.9 mmol] in toluene at –40 °C, and the resulting mixture was allowed to warm to room temperature overnight. Upon hydrolytic workup, a liquid mixture of 2-phenyl-1-butene (**13**) and recovered propiophenone (**12**) was obtained in 25% and 75% yields, respectively, as shown by ^{1}H and ^{13}C NMR spectroscopy.

Reaction of Titanium-methylidene 6a (M = Ti) with Diphenylacetylene (17): A solution of diphenylacetylene (**17**) [1.78 g, 10 mmol] in toluene (60 mL) was added to a solution of complex **6a** (M = Ti) [10 mmol] in toluene at –40 °C, and the resulting reddish-brown mixture was allowed to warm to room temperature overnight. Upon hydrolytic workup, a colorless solid residue consisting of diphenylacetylene (**17**), α-methyl-*cis*-stilbene (**20a**), and α-methyl-*trans*-stilbene (**20b**) was obtained in amounts of 50%, 25% and 25% yields, respectively, as shown by ^{1}H and ^{13}C NMR spectroscopy. Diphenylacetylene (**17**): ^{1}H NMR ($CDCl_3$): δ = 7.51, 7.41–7.22 (Ar, 10 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 131.59, 128.33, 128.26, 123.31, 89.43 (C=C) ppm.

α-Methyl-*cis*-stilbene (20a):^{1}H NMR ($CDCl_3$): δ = 7.12–6.9 (Ar, 10 H), 6.84(H), 2.18(3H) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.37–126.4, 17.6 (CH_3) ppm.

α-Methyl-*trans*-stilbene (20b):^{1}H NMR ($CDCl_3$): δ = 7.25–6.75 (11H); 2.22 (3H) ppm. ^{13}C NMR ($CDCl_3$): δ = 144.37–126.40, 27.3 (CH_3) ppm.

Reactions of Methyllithium with Group 4 Chlorides in THF: Individual reactions, similar to the foregoing, of methyllithium (2 molar equiv.) with either $TiCl_4$ or $ZrCl_4$ (1 equiv.), but in a THF media, were conducted at –78 °C. Subsequent treatment of the reaction mixture, either at –40 °C or at room temperature, gave no product upon workup. Nevertheless, hydrolyses of such reaction mixtures gave copious evolution of methane gas; such gas evolution shows that a C_1 carbon–titanium bond was present in the mixture.

ROMP Process with Norbornene

With $H_2C=TiCl_2$ (6a): Anhydrous norbornene (4.71g, 50 mmol) in toluene (25 mL) was added to the toluene solution (60 mL) of complex **6a** (5 mmol) at –40 °C, and the resulting reddish-brown mixture was allowed to warm to room temperature over 10h. After adding the very dark brown reaction mixture to methanol (60 mL) at room temperature with vigorous stirring, a white amorphous solid (1.04 g) precipitated. This was confirmed to be *cis*-polynorbornene by comparison of its ^1H and ^{13}C NMR values with those in the literature.[8] *cis*-Polynorbornene: ^{13}C NMR ($CDCl_3$): δ = 134.006, 132.928 (CH), 43.106, 41.401, 38.474, 32.477 (CH_2) ppm.

With $H_2C=ZrCl_2$ (6b): Anhydrous norbornene (6.71g, 71 mmol) in toluene (20 mL) was added to the toluene solution (20 mL) of complex **6b** (7.1 mmol) at –40 °C, and the resulting colorless solution was allowed to warm up to room temperature over 10 h. Quenching the very dark brown mixture with methanol (60 mL) at room temperature with vigorous stirring precipitated a white amorphous solid (0.15 g). This was confirmed to be *cis*-polynorbornene by comparison of its ^{13}C NMR values with literature values for *cis*-polynorbornene.[8]

Acknowledgments

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[1] J. J. Eisch, P. R. Munson, J. N. Gitua, *Origins Life Evol. Biosphere* **2004**, *34*, 441–454.

[2] By the term, α,μ dehydrohalogenation, we mean to specify the stepwise proton-removal from an α-carbon atom, followed by the loss of halide anion from the adjacent metal (μ) to form a π C=M linkage.

[3] a) K. H. Thiele, K. Jacob, *Z. Anorg. Allg. Chem.* **1968**, *356*, 195–201; b) M. T. Reetz, S. H. Kung, M. Hüllmann, *Tetrahedron* **1986**, *42*, 2931; c) C. Beerman, H. Bestian, *Angew. Chem.* **1959**, *71*, 618–623; d) H. deVries, *Recueil Trav. Chim.* **1961**, *80*, 866–878; e) E. H. LeButts, U. S. Patent 3,021,349, **1959/62**.

[4] S. Berger, W. Bock, G. Frenking, V. Jonas, F. Müller, *J. Am. Chem. Soc.* **1995**, *117*, 3820–3829. Indeed, because of the ease with which CH_3TiCl_3 reacts with any excess of CH_3MgI to form successively $(CH_3)_2TiCl_2$, $(CH_3)_3TiCl$, and $(CH_3)_4Ti$, the preparation of none of the partially methylated derivatives, $(CH_3)_nTiCl_{4-n}$, was attempted in such a reaction. Instead $(CH_3)_4Ti$ was prepared from four equiv. of CH_3MgI and $TiCl_4$ at –40 °C. Then the various $(CH_3)_nTiCl_{4-n}$ derivatives were obtained at –78 °C by the redistribution reaction between $TiCl_4$ and $(CH_3)_4Ti$ in the proper stoichiometric ratios.

[5] Publications that have assumed that $TiCl_4$ reacts with two equiv. of methyllithium to form Me_2TiCl_2 are the following: a) J. Liu, D. Zhang, H. Huang, Y. Qian, A. S. C. Chan, *J. Polym. Sci. Polym. Chem. Ed*.**2000**, *38*, 1639–1641; and b) D. Duncan, T. Livinghouse, *Organometallics* **1999**, *18*, 4421–4428. In the latter work the supposed "$(CH_3)_2TiCl_2$" was employed as a metallating agent for an amino functionality ($R–NH_2 \rightarrow [R–N=TiCl_2]$). It should be noted that intermediates **6** or **27** would be expected to react in a similar way with $R–NH_2$.

[6] M. T. Reetz, "Organotitanium Chemistry", in *Organometallics in Synthesis* (Eds.: M. Schlosser), Wiley, New York, **2002**, ch. 7, pp. 107.

[7] a) F. N. Tebbe, G. W. Parshall, G. S. Reddy, *J. Am. Chem. Soc.* **1978**, *100*, 3611–3613; b) K. C. Ott, R. H. Grubbs, *J. Am. chem. Soc.* **1981**, *103*, 5922–5923; c) N. A. Petasis, E. I. Bzowej, *J. Am. Chem. Soc.* **1990**, *112*, 6392–6394; d) L. R. Gillion, R. H. Grubbs, *J. Am. Chem. Soc.* **1986**, *108*, 733–735; e) J. J. Eisch, A. Piotrowski, *Tetrahedron Lett.* **1983**, *24*, 2043–2046.

[8] a) A preliminary report on certain aspects of the 2:1 reaction of MeLi and $TiCl_4$ has appeared in published form in a monograph dedicated to the memory of Professor Kazuo Soga: J. J. Eisch, F. A. Owuor, P. O. Otieno, A. A. Adeosun, in *Progress and Development of Catalytic Olefin Polymerization* (Eds.: T. Sano, T. Uozumi, H. Nakatani, M. Terano), Technology and Education Publishers, Tokyo, **2000**, pp. 88–97; b) Interaction of methyllithium in diethyl ether with the complex $TiCl_4{\cdot}2THF$ in toluene at –40 °C in various ratios has been assumed to produce methyltitanium chlorides of the type, Me_nTiCl_{4-n}: J. Liu, D. Zhang, J. Huang, Y. Qian, A. S. C. Chan, *J. Poly. Sci. A Poly. Chem.* **2000**, *38*, 1639–1641. Particularly, a 2:1 molar ratio of MeLi and $TiCl_4$ was found to act as a potent catalyst for ROMP processes with dicyclopentadiene. The authors have proposed that such active catalysts arose from the generation of Me_2TiCl_2, which then decomposed in situ to produce $Cl_2Ti=CH_2$. Our work supports the direct formation of $Cl_2Ti=CH_2$ without the intermediacy of Me_2TiCl_2. Incompatible with the instability ascribed by these authors to Me_2TiCl_2 at –40 °C is the report that Me_2TiCl_2, prepared from $TiCl_4$ and Cp_2TiMe_2, is a violet-black compound volatile without decomposition at 25 °C at 0.2 Torr. Its thermal decomposition at higher temperatures leads to $TiCl_2$ and methane (E. H. deButts, U. S. Patent 3,021,349, **1959/62**). It is sufficiently stable to have its ^1H NMR spectrum recorded at 35 °C (J. F. Hanlan, J. D. McCowan, *Can. J. Chem.* **1972**, *50*, 747–754).

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