INTERCONVERSIONS OF TITANOCENE-METHYLENE COMPLEXES

B.J.J. van de Heisteeg, G. Schat, O.S. Akkerman and F. Bickelhaupt*
Scheikundig Laboratorium, Vrije Universiteit,
De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract: The Tebbe-type reagent $Cp_2Ti(X)CH_2MgX$ (X = Br, Cl) (2) in diethyl ether/benzene gave, on evaporation of the solvent and solution in toluene, $Cp_2(Br)TiCH_2MgCH_2Ti(Br)Cp_2$ (3). Both compounds differ dramatically in their spectral properties and reactivities. Compound **3** reacts with ethers to give $Cp_2TiCH_2Ti(Cp_2)CH_2$. (4), with PMe₃ to give $Cp_2(MeP_3)Ti=CH_2$ (5) and with benzophenone to give 1,1-diphenylethene. Analogous derivatives were obtained from Cp'_2TiCl_2 ($Cp'=MeC_5H_4$).

The Tebbe reagent (A)¹ has triggered interesting developments in organometallic chemistry. It has been of value for the investigation of intermediates in catalytic processes,^{2,3} for the synthesis of metallacyclobutanes,⁴⁻⁸ and as a synthon in organic chemistry.⁹ New Tebbe-type reagents of the general formula **B** have been developed by the groups of Schwartz,¹⁰ Eisch,⁷ Bickelhaupt,⁸ and Grubbs.^{11,12}



Our group has reported⁸ that the reaction of the methylene di-Grignard reagent 1 with one molar equivalent of Cp₂TiCl₂ gave 2 which in many regards, e.g. the formation of titanacyclobutanes on reaction with alkenes, behaved like a Tebbe reagent. However, the rather normal chemical shift of its CH₂ protons ($\delta = 2.93$ ppm) distinguished it from other Tebbe reagents, the signals of which fall typically into the range of $\delta = 7.9$ ppm. These remarkably low field shifts have been associated with the four-membered ring structure **B**,¹³ and for this reason we suggest that the actual structure of 2 is not that of the four-membered 2a, but a six-membered ring (2b) or open structure (2c), in which magnesium halide (MgX₂: X = Br or Cl) from the coupling reaction is complexed to the organometallic magnesium.



This interpretation has now gained support by the conversion of 2 to the interesting new titanocene-methylene reagent 3. In a typical experiment, a mixture of 1 (0.71 mmol) and Cp_2TiCl_2 (0.18 g; 0.71 mmol) in Et₂O/benzene 1:1 (23 ml) was, after stirring for 1 h at -20 °C, allowed to warm to 5 °C. After removal of the solvents by evaporation, a brownish residue was obtained. Dissolving this residue in toluene (10 ml) gave a red-brown solution and a white precipitate. After removal of the precipitate (MgCl₂?) by filtration, the red-brown solution was used for the identification of 3 by NMR spectroscopy, elemental analysis and chemical reactions. On hydrolysis of 3, no free base was liberated, while determination of the magnesium ions by EDTA titration revealed that the magnesium content was only half of what would be expected for 2; elemental analysis ¹⁴ of a sample (containing some residual toluene) showed the ratio of Ti : Br : Mg to be 2 : 2 : 1, chlorine being absent.



As 2 and 3 have the structural relation of a Grignard reagent and a dialkylmagnesium, we assume that the formation of 3 is caused by a shift of the Schlenk equilibrium due to the insolubility of magnesium chloride (etherate) in toluene. In ether/benzene, this equilibrium is apparently completely shifted to the left, which is in line with the general behaviour of Grignard reagents.¹⁵

Compound 3 is not stable in toluene solution at room temperature; it decomposes within 7 h under formation of the purple-red $4^{16,17}$ (yield : 27%). In contrast, 4 is formed instantaneously and quantitatively on addition of THF or dioxane to 3 in toluene at 5 °C. This reaction may be explained by coordination of the basic ether to the magnesium; this would initiate elimination of MgBr₂ (already present as a structural subunit in 3 !) and leave two titanaalkene moieties $Cp_2Ti=CH_2$ which combine to give 4,¹⁶ possibly within the solvent cage. This mode of reaction is apparently much faster than the retro-reaction $3 \rightarrow 2$; for this reason, it was not possible to achieve this latter process by addition of MgBr₂ in diethyl ether, 4 being the only product observed. It is remarkable and not well understood that 2 gave 4 neither on thermal decomposition nor on addition of basic ethers.



Another indication for the high tendency of **3** to cleave under formation of a titanaalkene is the easy generation of the phosphine adduct **5** when trimethylphosphine was added to **3** in toluene solution at 5° C; **5** was formed instantaneously and in quantitative yield.^{4,18,19} This contrasts with its slow formation from **4** and trimethylphosphine (1-2 h at room temperature).¹⁹ which leads to some decomposition of **5** before its formation is completed. The synthesis of **5** from **3** is therefore clearly to be preferred. Similarly, **3** reacts with benzophenone dissolved in THF at 5 °C within 0.5 h to give 1,1-diphenylethene in 80% yield. When the benzophenone was added as a solution in benzene, both the reaction rate and the yield (20%) were much lower. As in the formation of **4** from **3**, this points to an active role of the base THF in complexing the MgBr₂.

Most revealing for the structure assignment of **3** are the spectroscopic data.¹⁴ The ¹H and ¹³C NMR spectra show extreme low field shifts for the CH₂ group; the values (δ (¹H) = 9.87 ppm, δ (¹³C) = 223,3 ppm) begin to approach those of metallaalkenes.² Both this low field shift and the ready dissociation of **3** to titanaalkenes can be explained in terms of the metallaalkene-Lewis acid interaction in Tebbe-type reagents.^{10,13,20,21} A weak Lewis acid such as MgBr₂ leads to a weak methylene-metal bond and enhances the double bond character in the methylene-titanium bond; this causes a lowering of the LUMO and thus an increase of the paramagnetic contribution to the chemical shift.^{17,22}

Finally, we should mention that the analogues **3'** and **5'** were obtained from **1** and $Cp'_{2}TiCl_{2}$ ($Cp' = MeC_{5}H_{4}$) as starting materials in analogy to the preparation of **3** and **5**, respectively.²³

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- 14. 3, ¹H NMR ([D₈]toluene; 90 MHz, C₆D₅CHD₂ at 2.03 ppm as internal standard) δ 9.87 (s, 4H, CH₂), 5.65 ppm (s, 20H,Cp). ¹³C NMR ([D₈]toluene; 250 MHz, C₆D₅CHD₂ at 20.53 ppm as internal standard). δ 223.3 (t, ¹J(CH) = 122 Hz, CH₂), 109.4 ppm (d, ¹J(CH) = 172 Hz, Cp). Elemental analysis: found C, 52.87; H, 5.00; Br, 22.84; Čl, 0.7; Mg, 3.60; Ti, 14.87. C₂₂H₂₄Br₂MgTi₂, C, 46.49; H, 4.27; Br, 28.12; Mg, 4.26; Ti, 16.86. The sample was not pure but consisted of 3 (84.5%), Cp2TiMe2 (2.7%) and toluene (12.8%).
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- (1986). $5^{4,19}$, ¹H NMR ([D₈]toluene; 90 MHz, C₆D₅CHD₂ at 2.03 ppm as internal standard) δ 11.96 (d, ³J(PH) = 7.3 Hz, 2H, CH₂), 5.2 ppm (d, ³J(PH) = 2.6 Hz, 10H, Cp); Me₃P not determined. (1986). (198 18.
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- **3'**, ¹H NMR ([D₈]toluene, 90 MHz, C_6D_5 CHD₂ at 2.03 ppm as internal standard) δ 9.64 (s, 4H, CH₂), 23. 5.47 - 5.67 (bm, 16H, C₅H₄), 1.96 ppm (s, 12H, CH₃).

5', ¹H NMR ([D₈]toluene; 90 MHz, C₆D₅CHD₂ at 2.03 ppm as internal standard) δ 11.91 (d, ³J(PH) = 7.9 Hz, 2H, CH₂), 5.38 - 5.28 and 5.26 - 4.83 (bm, 8H, C₅H₄), 2.04 ppm (CH₃-C₅H₄).

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