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Novel reactions of low valent titanium and zirconium reagents generated by reduction of Cp_2TiCl_2 and Cp_2ZrCl_2 with magnesium and 1,2-dibromoethane

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Abstract

The reduction of Cp_2MCl_2 (M = Ti or Zr) with Grignard grade magnesium and 1,2-dibromoethane in THF at 0 °C gives the corresponding metallocene-ethylene complexes along with hydride species, as indicated by the reaction with diphenylacetylene to give 1,2-diphenyl-(*E*)-1-butene. The reactions of the Cp_2ZrCl_2/1,2-dibromobenzene/Mg system in THF with diphenylacetylene and norbornene are also described.

Introduction

We recently observed that the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system isomerizes some 1-alkenes into *trans*-2-alkenes [1]. 1,2-Dibromoethane is frequently used for activating magnesium for Grignard reactions [2] and we have utilized it for activating the magnesium towards reduction of Cp_2TiCl_2. If the role of 1,2-dibromoethane is just to activate the magnesium, then the resulting species would be the titanocene, 'Cp_2Ti' or its equivalent, and it has been reported that the reduction of Cp_2TiCl_2 with Mg/Hg gives titanocene or its equivalent [3]. We report here that in our studies on the reactions of the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system, we have observed that the titanocene equivalent prepared by use of this system shows the reactions of both a titanocene-ethylene complex and a titanium hydride species.

Results and discussion

Titanocene, generated by the reduction of Cp_2TiCl_2 and Mg/Hg [3], has been reported to give the corresponding metallacycle **1** on treatment with diphenylacetylene, 1,2,3,4-tetraphenyl-(*E*,*E*)-1,3-butadiene being formed after hydrolysis (**2**) (eq. 1).

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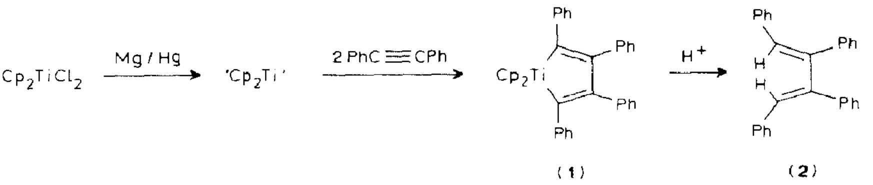
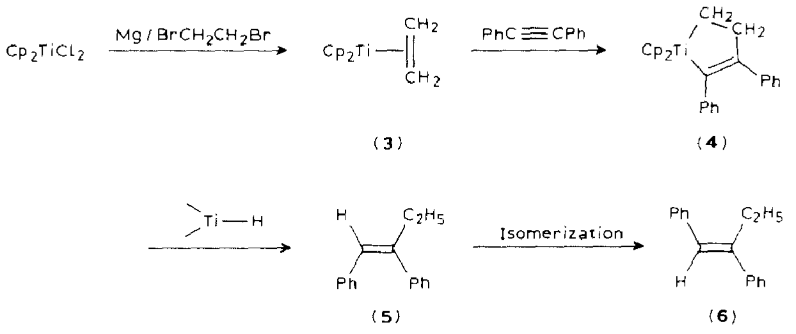


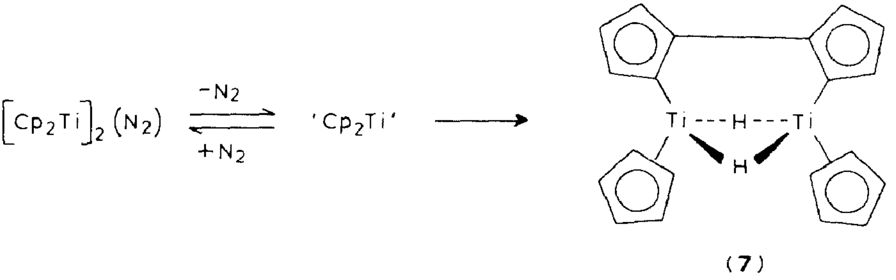
(1)

In order to compare the reactivity of the titanocene or its equivalent generated using the present $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system with that of the $Cp_2TiCl_2/Mg/Hg$ reagent system, we carried out the following experiment. Diphenylacetylene was added to the titanocene-equivalent prepared from $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ reagent at room temperature and the mixture was stirred for 12 h under nitrogen. After hydrolysis and work-up, in addition to the expected tetraphenylbutadiene (60%), 1,2-diphenyl-(*E*)-1-butene (**6**) (30%) was also isolated. When the preparation of titanocene was carried out at 0 °C, 1,2-diphenyl-(*E*)-1-butene was isolated in 80% yield. The formation of 1,2-diphenyl-(*E*)-1-butene (**6**) can be rationalized as outlined in eq. 2.



(2)

Initially, it was thought that the product might be **5**, since the conversion of the metallacycle **4** into **5** is well-known reaction for such metallacycles. However, it has been reported that compound **5** is a solid (m.p. 57 °C) [4], whereas compound **6** was obtained as oil, which, although a single compound, could not be crystallised. Accordingly, the compound is assigned structure **6**. The isomerization of **5** to **6** could take place by hydrometallation-β-elimination by the titanocene hydride species formed by the decomposition of titanocene. Decomposition of "titanocene" to titanium hydride **7** species has been reported previously (eq. 3) [5].



(3)

The incorporation of ethyl group into diphenylacetylene under our reaction conditions indicates the intermediacy of the ethylene complex of titanocene 3 and of the metallacycle 4. The $Cp_2ZrCl_2/Mg/BrCH_2CH_2Br$ reagent system also gives 1,2-diphenyl-(*E*)-1-butene (80%) on reaction with diphenylacetylene under similar conditions, indicating the formation of zirconocene-ethylene complex and the corresponding metallacycle as intermediates.

The simple ethylene complexes of Cp_2Ti and Cp_2Zr have not been reported, although the $(C_5Me_5)_2Ti(CH_2{=}CH_2)$ complex has been prepared and characterized [6]. However, metallacycles similar to **4** have been prepared and utilized [7]. In order to examine the stability and reactions of the metallacycle **4**, generated under the present reaction conditions, we treated the reaction mixture with D_2O and stirred for 2 h at room temperature before work-up in runs with both Cp_2TiCl_2 and Cp_2ZrCl_2. In both cases, the 1,2-diphenyl-(*E*)-1-butene (**6**) isolated contained no deuterium. The titanocene metallacycle similar to metallacycle **4** is known to give the corresponding cyclopentanone derivatives on carbonylation with carbon monoxide [5,7]. However, attempted carbonylation of the reaction mixture obtained from reactions involving both Cp_2TiCl_2 and Cp_2ZrCl_2 furnished no product other than 1,2-diphenyl-(*E*)-1-butene (**6**). Clearly, this product was formed before the carbonylation was carried out. It is likely that the metallacycle **4** is cleaved to **5** by the titanium hydride species **7** formed by the decomposition of titanocene (eq. 3).

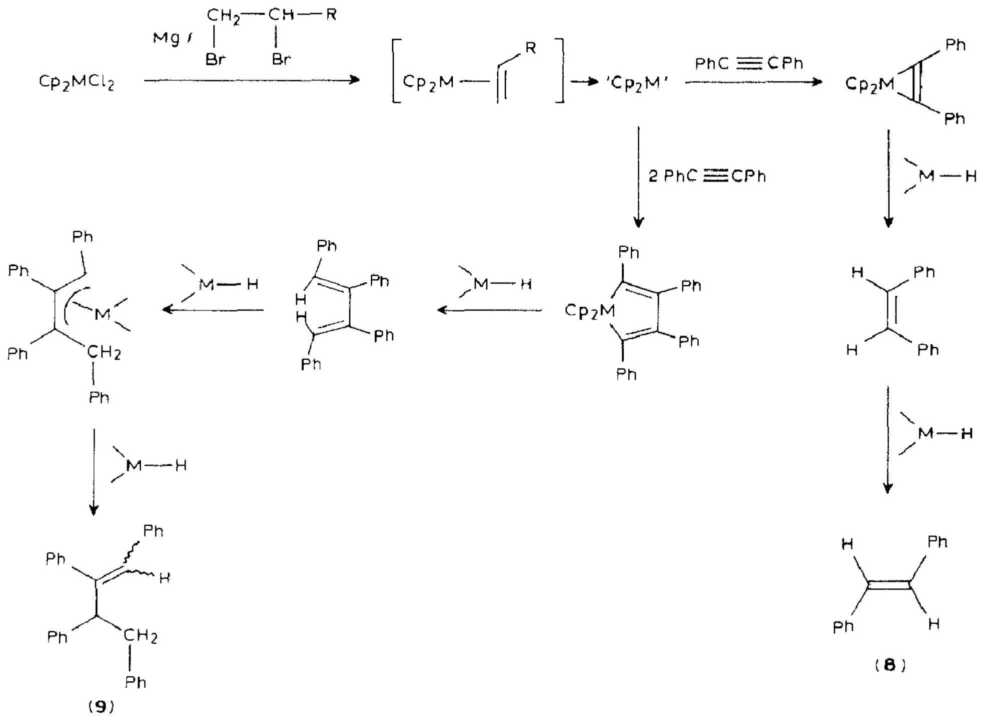
Whereas 1-decyne underwent polymerization on reaction with the $Cp_2TiCl_2/Mg/BrCH_2CH_2Br$ system, it was unaffected by the zirconium system under the present conditions. It is noteworthy that 'Cp_2Ti' prepared by the reaction of Cp_2TiCl_2 with Na/Hg in toluene under argon has been reported to catalyze polymerization of alkynes [9].

In order to examine whether higher alkene complexes can be prepared by use of the $Cp_2MCl_2/Mg/BrCH_2CHBrR$ ($M = Ti$ or Zr) systems, we carried out experiments replacing 1,2-dibromoethane with 1,2-dibromodecane or 1,2-dibromostyrene under similar conditions. Surprisingly, the corresponding alkylated stilbenes were not formed on reaction with diphenylacetylene, and the products were *trans*-stilbene (**8**) (35%) and 1,2,3,4-tetraphenyl-1-butenes (**9**) (50%) along with 1-decene/2-decene or styrene. The formation of these products can be tentatively rationalized as indicated in Scheme 1.

Surprisingly, these products are not obtained in runs involving 1,2-dibromoethane. Presumably, 'Cp_2M' species generated when 1,2-dibromodecane or 1,2-dibromostyrene is used are more reactive, and give metal hydride species capable of reducing tetraphenylbutadiene and diphenylacetylene to *trans*-stilbene (Scheme 1).

Recently, zirconocene-benzyne complexes have received much attention [10]. The titanocene- and zirconocene-benzyne complexes are generally prepared by the thermal decomposition of diphenylmetallocene [11,12]. The titanocene-benzyne complex has been prepared in 15% yield by the reaction of Cp_2TiCl_2 with 1-bromo-2-fluorobenzene in the presence of magnesium in THF [13]. It was of interest to examine whether the titanocene- and zirconocene-benzyne complexes could be prepared in situ by using for utilization in reactions with organic substrates Cp_2MCl_2 ($M = Ti$ or Zr) and 1,2-dibromobenzene in the presence of magnesium.

We observed that the reaction of Grignard-grade magnesium with Cp_2MCl_2 ($M = Ti$ or Zr) and 1,2-dibromobenzene at room temperature in the presence of diphenylacetylene or norbornene gave only biphenyl. It seemed thus that if both the

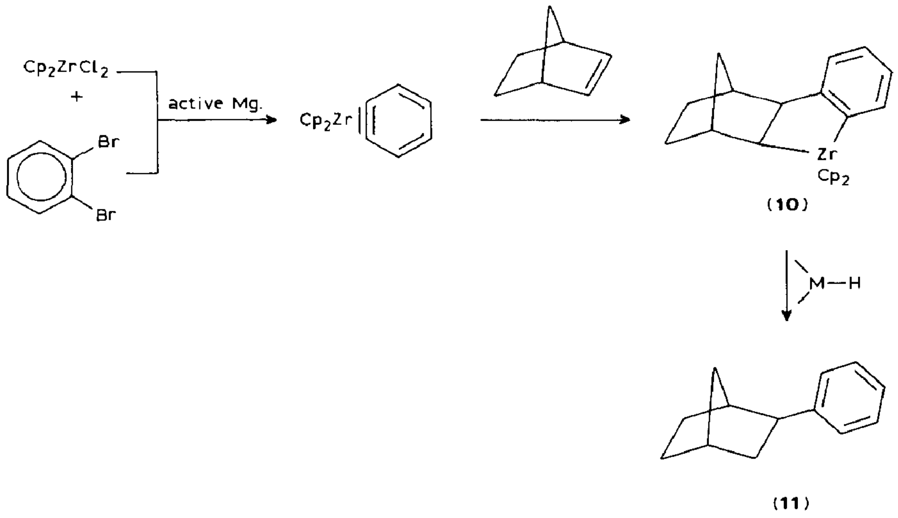


Scheme 1

reduction of Cp_2MCl_2 and the reaction with 1,2-dibromobenzene could be carried out at lower temperature, then it might be possible to prepare the corresponding benzyne complexes of Cp_2M. Grignard-grade magnesium did not react with 1,2-dibromobenzene at −24 °C, but active magnesium prepared in situ from $MgBr_2$ and potassium metal [14], did react with 1,2-dibromobenzene (5 mmol) at −24 °C in the presence of Cp_2ZrCl_2 (2.5 mmol). Norbornene (5 mmol) was added to this reagent system and the mixture were stirred for 3 h at −24 °C and then at room temperature for 12 h. After work-up *exo*-2-phenylnorbornane (**11**) was isolated in 60% yield. The result can be rationalized in terms of eq. 4.

However, the metallacycle product **10**, prepared by the exchange of olefin from 3-n-butylzirconaindan in the presence of excess norbornene (1.1–20 molar equivalent) in the absence of solvent has been found to be stable even at 100 °C [15], but in solutions these metallacyclopentanes decompose and give only phenylalkanes. Presumably, in the present case, since zirconium hydride species formed from the decomposition of "Cp_2Zr" is present, reductive cleavage of this metallacycle to *exo*-2-phenylorbornane takes place (eq. 4).

In runs with Cp_2TiCl_2 in the place of Cp_2ZrCl_2, only biphenyl formation was observed. When diphenylacetylene was used in place of norborene only *trans*-stilbene was isolated (70%) in addition to biphenyl (70%). This behaviour is similar to that of the Cp_2M and $>$M–H species generated from Cp_2MCl_2/Mg/$BrCH_2$-CH(Br)R system, which convert diphenylacetylene into *trans*-stilbene (Scheme 1). We have also observed that Cp_2ZrCl_2/Mg/$BrCH_2CH_2Br$ system isomerizes *cis*-stilbene to *trans*-stilbene. This observation further confirms the presence of metal hydride species along with metallocenes and/or their equivalents.



(4)

Simple ethylene complexes of Cp_2Ti and Cp_2Zr have not been reported, although $(C_5Me_5)_2Ti(CH_2{=}CH_2)$ complex has been prepared and characterized [6]. The 1,2-dibromoethane/Mg/Cp_2MCl_2 (M = Ti or Zr) and 1,2-dibromobenzene/Mg/ Cp_2ZrCl_2 systems are promising as simple reagent system for the in situ preparation of the corresponding ehtylene and benzyne complexes.

Experimental

The THF solvent was distilled before use from benzophenone-sodium. Dichlorobis(cyclopentadiene)titanium(IV), Cp_2TiCl_2, dichlorobis(cyclopentadiene)zirconium(IV), Cp_2ZrCl_2, 1,2-dibromobenzene and norbornene were purchased from Fluka, Switzerland. Commercial Grignard-grade magnesium was used.

Reaction with diphenylacetylene of the reagent system generated from Cp_2TiCl_2/Mg/ $BrCH_2CH_2Br$ in THF

1,2-Dibromoethane (20 mmol, 3.7 g) was added during 10 min to a THF (80 ml) solution of dichlorodicyclopentadienetitanium(IV), Cp_2TiCl_2, (2.5 mmol, 0.625 g) in the presence of Grignard-grade magnesium (25 mmol, 0.625 g) under nitrogen at 0 °C (ice-bath temperature). The mixture became a dark greenish-black within 25 min. Diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was added and the mixture was brought to room temperature during 2 h, stirred for 12 h, then treated with aqueous HCl (50 ml, 5*N*) and saturated with solid sodium chloride. The organic layer was separated and the aqueous layer was extracted with ether (3 × 50 ml). The combined extract was washed successively with water (50 ml) and brine, then dried over anhydrous $MgSO_4$. The solvent was evaporated and the residue was chromatographed on a silica gel column with hexane as eluent to give 1,2-diphenyl-(*E*)-1-butene (80%, 0.35 g) and (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (5%, 20 mg). m.p. 176–178 °C, Lit. [3] m.p. 183 °C.

Spectral data for 1,2-diphenyl-(*E*)-1-butene; ^1H NMR (in ppm, δ 0 TMS) 7.6–6.9 (m, Ph), 6.4 (s, CH), 2.5 (q, CH_2), 1.1 (t, CH_3). ^{13}C NMR: (in ppm, δ 0

TMS): 145.4, 142.0, 139.1, 132.2, 129.6, 129.1, 128.9, 128.4, 127,4, 126.7, 125.8, 34.0, 13.3. Mass spectral data (*m/e*): 208 (M^+, 50%), 193 ($M^+ - CH_3$, 30%), 179 ($M^+ - CH_2CH_3$, 100%), 115 (193 – Ph, 30%).

In order to examine whether the isomerization of 5 to 6, takes place during the work-up involving 5*N* aqueous HCl, we repeated the experiment but using water (100 ml) instead of the 5*N* HCl and obtained identical products.

Reaction with diphenylacetylene of the reagent system generated from the Cp_2ZrCl_2/Mg/$BrCH_2CH_2Br$ in THF

1,2-Dibromoethane (20 mmol, 3.7) was added during 10 min at 0 °C (ice-bath temperature) under nitrogen to a mixture of dichlorodicyclopentadienezirconium(IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g). Grignard-grade magnesium (25 mmol, 0.625 g), and THF (80 ml). Diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was added and the mixture was allowed to warm to room temperature during 2 h stirred for a further 12 h. Work up as before gave 1,2-diphenyl-(*E*)-1-butene (80%, 0.35 g) and (*E*,*E*)-1,2,3,4-tetraphenyl-1,3-butadiene (5%, 20 mg).

Isomerization of cis-stilbene to trans-stilbene catalysed by the Cp_2ZrCl_2/Mg/$BrCH_2CH_2Br$ reagent system in THF

1,2-Dibromoehtane was added during 10 min at 0 ° C (ice-bath) under nitrogen to a solution of dichlorodicyclopentadienezirconium(IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g) and Grignard-grade magnesium (25 mmol, 0.625 g) in THF (80 ml). *cis*-Stilbene (2.1 mmol, 0.37 g) was added and the mixture was allowed to warm to room temperature during 2 h then stirred for a further 12 h. The usual work-up gave only *trans*-stilbene (80%, 0.29 g), m.p. 123–124° Lit. 17 m.p. 124°. ^{13}C NMR data (in ppm, δ 0 TMS): 137.5, 128.5, 127.7, 126.7. Mass spectral data (*m/e*): 180 (M^+).

Reaction with diphenylacetylene of the reagent system generated from Cp_2ZrCl_2/Mg/1,2-dibromodecane in THF

1,2-Dibromodecane (10 mmol, 3.0 g) was added dropwise during 10 min to a mixture of THF (80 ml), dichlorodicyclopentadienezirconium(IV), Cp_2ZrCl_2, (2.5 mmol, 0.73 g), and Grignard-grade magnesium (25 mmol, 0.625 g) at 0 °C under nitrogen. When the mixture become light yellow in colour (after ca. 25 min) a solution of diphenylacetylene (2.1 mmol, 0.38 g) in THF (5 ml) was injected and the mixture was allowed to warm to room temperature during 2 h, during which it turned black. Stirring was continued for 12 h, and the usual work-up gave 1-decene (containes 2-decene to the extent of 5%), *trans*-stilbene (15%) m.p. 123–124 °C and 1,2,3,4-tetraphenyl-1-butene (60%, 0.23 g), m.p. 142–143 °C. ^1H NMR (in ppm, δ 0 TMS): 7.2–6.7 (m, Ph). 6.6 (s, CH), 4.0 (t, CH), 3.2 (t or overlap by doublets, CH_2 due to the presence of adjacent chiral centre). ^{13}C NMR (in ppm, δ 0 TMS): 145.3, 141.2, 140.5, 137.4, 130.1, 129.3, 128.8, 128.0, 127.7, 126.6, 124.1, 56.5, 40.0. Mass spectral data (*m/e*): 360 (M^+, 10%), 269 ($M^+ - CH_2Ph$, 80%), 191 (269 – Ph, 100%), 91 ($PhCH_2^+$, 90%). Analysis: calcd.: C, 93.33; H, 6.66%. Found: C, 93.93; H, 6.79%.

Reaction with norbornene of the reagent system generated from Cp_2ZrCl_2/Mg/1,2-dibromobenzene in THF

The active form of magnesium was prepared by treating magnesium bromide, prepared from Grignard-grade magnesium (20 mmol, 0.5 g) and 1,2-dibromoethane

(20 mmol, 3.7 g) at room temperature, with potassium metal (30 mmol, 1.2 g) in refluxing THF (80 ml) for 3 h. 1,2-Dibromobenzene (5 mmol, 1.17 g) and dichlorodicyclopentadienezirconium(IV), Cp_2ZrCl_2, (2.5 mmol), 0.73 g) were then added at $-24°C$ under nitrogen, and after 20 min a THF (5 ml) solution of norbornene (5 mmol, 0.5 g) was injected. The mixture was stirred for 2 h at $-24°C$ then allowed to warm to room temperature and stirred for a further 12 h. Butanol (5 ml) was then added to destroy any excess of potassium metal followed by water (100 ml). The usual ether extraction gave *exo*-2-phenylnorbornane (60%, calculated on the basis of zirconocene dichloride used) and biphenyl (20%, m.p. 72° C). ^1H NMR data (in ppm, δ 0 TMS) of *exo*-2-phenylnorbornane, 7.3 (m, Ph), 2.8 (m, CH), 2.4 (m, CH_2), 1.9–1.2 (m, CH_2, remaining protons). ^{13}C NMR data: (in ppm, δ 0 TMS) 147.7, 128.3, 127.1, 125.4, 47.4, 42.9, 39.17, 36.8, 36.1, 30.6, 28.9. The IR spectrum of the sample identical to that of a sample obtained by reaction of norbornene with benzene in concentrated H_2SO_4 [16].

When the procedure was repeated without using Cp_2ZrCl_2, only biphenyl (80%, 0.3 g) was isolated.

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