Oxidative alkylation of ($\eta^5$-C$_5$Me$_5$)$_2$TiR (R = Cl, Me, Et, CH=CH$_2$, Ph, OMe, N=C(H)$_t$Bu) to ($\eta^5$-C$_5$Me$_5$)$_2$Ti(Me)R by group 12 organometallic compounds MMe$_2$

Gerrit A. Luinstra and Jan H. Teuben

Groningen Center for Catalysis and Synthesis, Department of Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen (Netherlands)
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Abstract

Oxidative alkylation of Cp*$_2$TiX (Cp*: $\eta^5$-C$_5$Me$_5$; X = OMe, Cl, N=C(H)$_t$Bu) and Cp*$_2$TiMe by CdMe$_2$ or ZnMe$_2$ gives diamagnetic Cp*$_2$Ti(Me)X and Cp*$_2$TiMe$_2$ respectively, and cadmium or zinc. The reactions of Cp*$_2$TiR (R = Et, CH=CH$_2$, Ph) with MMe$_2$ (M = Cd, Zn) give statistical mixtures of Cp*$_2$Ti(Me)R, Cp*$_2$TiMe$_2$ and Cp*$_2$TiR$_2$. Dimethylmercury does not react with Cp*$_2$TiX.

Introduction

We previously described the preparation of Cp*$_2$Ti(R)Cl (Cp*: $\eta^5$-C$_5$Me$_5$; R = alkyl, aryl, H) by oxidative chlorination of Cp*$_2$TiR complexes with PbCl$_2$ [1]. Subsequent treatment of Cp*$_2$Ti(R)Cl with lithium, sodium or potassium reagents MR' gave (mixed) bis alkyl/aryl complexes Cp*$_2$Ti(R)R' [2]. However, in most cases the products were unstable at temperatures at which they were formed ($\approx$ -10 °C). This considerably handicapped our attempts to study C-H activation in these tetravalent titanium hydrocarbyls. For this reason we tried to develop a new, low temperature, route to mixed Cp*$_2$Ti(R)R' derivatives. In view of the clean oxidation of Cp*$_2$TiR with PbCl$_2$, we decided to explore oxidative alkylation of Cp*$_2$TiR with group 12 dialkyl complexes MR'$_2$ (eq. 1).

Cp*$_2$TiR + $\frac{1}{2}$MR'$_2$ → Cp*$_2$Ti(R)R' + $\frac{1}{2}$M

M = Zn, Cd, Hg; R' = Me, Et

The results are described below. Preliminary data on the oxidative alkylation of Cp*$_2$TiX (X = OMe, Cl) with ZnMe$_2$ have been published [3]. Recently, comparable oxidation reactions between Cp*$_2$SmNa and AlH$_3$·THF were reported to yield Cp*$_2$SmAlH$_4$·THF (Cp*: $\eta^5$-C$_5$H$_4$Bu), and that between Cp*$_2$Sm and Al$_2$Et$_6$ to give Cp*$_2$SmAlEt$_4$ [4].
Experimental section

All operations were performed under an inert atmosphere by Schlenk, vacuum-line or glove box techniques. Solvents were distilled from Na/K alloy prior to use. Cp*₂TiCl was synthesized by a published procedure [5a]. The compounds Cp*₂TiR (R = Me, Et, C₂H₅, Ph) were prepared from Cp*₂TiCl and Grignard reagents in diethyl ether [5b], Cp*₂TiOMe from Cp*₂TiMe and methanol, Cp*₂TiN=C(H)Bu from Cp*₂TiEt and BuC≡N [6]. Organocadmium compounds were prepared as described previously [7] from CdCl₂, and dimethylzinc was prepared as previously described [8]. HgMe₂ (Merck-Schuchardt) was used as received. IR spectra were recorded on a Pye Unicam SP3-300 or Bruker IFS-88 as Nujol mulls between KBr disks. NMR spectra were recorded in benzene-d₆ on Bruker WH-90 or Varian VXR-300 spectrometers. Chemical shifts are reported in ppm and referenced to residual protons in deuterated benzene (δ = 7.15 ppm for ¹H NMR, δ = 127.96 ppm for ¹³C NMR). Elemental analyses were carried out at the Microanalytical Department of this University under the supervision of A.F. Hamminga. All data given are the average of at least two independent determinations.

\[\text{Cp}^*\text{₂Ti(Me)OMe (1)}\]

A solution of Cp*₂TiOMe (402 mg, 1.15 mmol) in 10 mL of ether was cooled to -30 °C and CdMe₂ (42 µL, 0.57 mmol) was added. A Cd mirror was immediately formed on the wall of the vessel. After 2 h the volatiles were removed under vacuum, and the yellow residue was extracted with ether. Crystallization at -80 °C yielded 231 mg of yellow-orange 1 (0.63 mmol, 55%). ¹H NMR δ 1.79 (s, 30H, Cp*), 3.82 (s, 3H, OCH₃), 0.09 (s, 3H, CH₃). ¹³C NMR δ 11.77 (q, C₅Me₅; J(CH) 126 Hz), 119.3 (s, C₅Me₅), 42.17 (q, TiMe; J(CH) 124 Hz), 62.6 (q, OMe; J(CH) 139 Hz). IR: 2795 (m), 2720 (w), 1130 (vs), 1020 (m), 502 (s). Anal. Found: C, 72.05; H, 9.99; Ti, 13.13%. C₂₂H₃₆TiO calc.: C, 72.51; H, 9.96; Ti, 13.14%. A similar procedure was used for the reaction of Cp*₂TiOMe with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of 1).

\[\text{Cp}^*\text{₂Ti(Me)Cl (2) and Cp}^*\text{₂Ti(Et)Cl (3)}\]

Cp*₂TiCl (712 mg, 2.01 mmol) was suspended in 25 mL of pentane at -30 °C and CdMe₂ (75 µL, 1.05 mmol) was added from a syringe. A red precipitate separated. Subsequently the mixture was allowed to warm to room temperature and after 2 h the volatiles were removed in vacuum and the yellow residue was extracted with ether. Crystallization at -80 °C yielded 231 mg of yellow-orange 1 (0.63 mmol, 55%). ¹H NMR δ 1.79 (s, 30H, Cp*), 3.82 (s, 3H, OCH₃), 0.09 (s, 3H, CH₃). ¹³C NMR δ 11.77 (q, C₅Me₅; J(CH) 126 Hz), 119.3 (s, C₅Me₅), 42.17 (q, TiMe; J(CH) 124 Hz), 62.6 (q, OMe; J(CH) 139 Hz). IR: 2795 (m), 2720 (w), 1130 (vs), 1020 (m), 502 (s). Anal. Found: C, 72.05; H, 9.99; Ti, 13.13%. C₂₂H₃₆TiO calc.: C, 72.51; H, 9.96; Ti, 13.14%. A similar procedure was used for the reaction of Cp*₂TiOMe with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of 1).

\[\text{Cp}^*\text{₂Ti(Me)N=C(H)}\text{Bu (4)}\]

Cp*₂TiN=C(H)Bu (763 mg, 1.90 mmol) was treated at -30°C with CdMe₂ (68 µL, 0.93 mmol) in 20 mL of ether. The mixture slowly turned yellow-orange. After 4 h stirring volatiles were removed under vacuum, and the residue extracted with
Cp₂TiX + ½CdMe₂ → Cp₂Ti(Me)X + ½Cd
(X = OMe, 1; Cl, 2) (2)

Cp₂TiCl + CdMe₂ → Cp₂TiMe + CdMeCl
(3)

Similarly Cp₂TiCl was treated with CdMe₂ to give Cp₂Ti(.Me)Cl (2) as the only organometallic product. The oxidative alkylation of Cp₂TiCl is a clean reaction.
There was no indication of reaction between Cp\textsubscript{2}^*TiCl and CdMe\textsubscript{2} to give Cp\textsubscript{2}^*TiMe and CdClMe (eq. 3). Also not observed were possible products such as Cp\textsubscript{2}^*TiMe\textsubscript{2} (\textit{vide infra}) or Cp\textsubscript{2}^*TiCl\textsubscript{2}, resulting from oxidation of the last two organotitanium compounds. From an analogous reaction between CdEt\textsubscript{2} and Cp\textsubscript{2}^*TiCl the mono-ethyl derivative Cp\textsubscript{2}^*Ti(Et)Cl (3) was isolated. The sterically more demanding azomethine complex Cp\textsubscript{2}^*TiN=C(H)\textsubscript{t}Bu was smoothly oxidized by CdMe\textsubscript{2} to give the monomethylated product Cp\textsubscript{2}^*Ti(Me)N=C(H)\textsubscript{t}Bu (4) (eq. 4). Compound 4 was isolated as a mixture of two isomers in a 6 to 1 ratio. * The asymmetry in 4 presumably originates from two inequivalent positions of the metal bonded methyl group relative to the azomethine proton.

\[
\text{Cp\textsubscript{2}^*TiN==C(H)'Bu + } \frac{1}{2} \text{CdMe}_2 \rightarrow \text{Cp\textsubscript{2}^*TiMe}_2 \ (5)
\]

Thus, oxidative alkylation of the 15-electron compounds Cp\textsubscript{2}^*TiX (X = OMe, Cl, N=C(H)Bu) with CdR\textsubscript{2} (R = Me, Et) to corresponding diamagnetic alkyl derivatives Cp\textsubscript{2}^*Ti(R)X proceeds smoothly at low temperature. There is no evidence for side (substitution) or subsequent (disproportionation) reactions.

\textit{Reaction of Cp\textsubscript{2}^*TiR (R = Me, Et, Ph, C}_2H\textsubscript{3} with dimethylcadmium}

The clean formation of 1-4 from the corresponding Cp\textsubscript{2}^*TiX compounds looked very promising, so we decided to extend our investigations to alkyl and aryl derivatives Cp\textsubscript{2}^*TiR. Reaction of Cp\textsubscript{2}^*TiMe with CdMe\textsubscript{2} at 0 °C gave Cp\textsubscript{2}^*TiMe\textsubscript{2} in high yields, demonstrating that Cp\textsubscript{2}^*TiR (R = alkyl) compounds are also readily oxidized (eq. 5).

\[
\text{Cp\textsubscript{2}^*TiMe} + \frac{1}{2} \text{CdMe}_2 \rightarrow \text{Cp\textsubscript{2}^*TiMe}_2 + \frac{1}{2} \text{Cd} \ (5)
\]

However, reactions of other titanium alkyl derivatives Cp\textsubscript{2}^*TiR with CdMe\textsubscript{2} were less straightforward. The vinyl derivative Cp\textsubscript{2}^*TiC\textsubscript{2}H\textsubscript{3} reacted with CdMe\textsubscript{2} to Cp\textsubscript{2}^*Ti(Me)C\textsubscript{2}H\textsubscript{3} (6), but the compound contained about 5% Cp\textsubscript{2}^*TiMe\textsubscript{2} *. The outcome was even worse for Cp\textsubscript{2}^*TiEt. Cp\textsubscript{2}^*TiEt was treated with CdMe\textsubscript{2} at -60 °C for 100 h during which a cadmium mirror was slowly formed. For analysis, the reaction mixture was filtered at low temperature (-30 °C) and subsequently thermolyzed at room temperature. The originally yellow-orange solution turned green during this process (± 5 min). The \textit{^1}H NMR spectrum of the thermolysis mixture revealed the presence of two new compounds, Cp\textsubscript{2}^*TiMe\textsubscript{2} and Cp\textsubscript{2}^*Ti(η\textsuperscript{2}-C\textsubscript{2}H\textsubscript{4}) [10], in a 1 to 3 ratio. The product ratio was independent of solvent (THF)

\* This is indicated by the large shift difference between the both groups in the \textit{^1}H NMR spectrum (Me: -0.27 vs -0.87 ppm and N=C(H): 7.78 vs 7.05 ppm for the major and minor isomer, respectively, cf. \textit{^13}C NMR). In addition, in the IR spectrum of 4 there are two absorptions for the azomethide proton at ν(CH) = 2745 cm\textsuperscript{-1} and 2630 cm\textsuperscript{-1}, for the major and minor isomer, respectively. Cf. J.E. Bercaw, D.L. Davies and P.T. Wolczanski, \textit{Organometallics}, 5 (1986) 443.)

\* Recrystallization from concentrated pentane extracts of the reaction mixture at 0 °C allowed isolation of pure 6 in poor yield (39%).

\[
Cp\textsubscript{2}^*TiN==C(H)'Bu + \frac{1}{2} \text{CdMe}_2 \rightarrow \text{Cp\textsubscript{2}^*TiMe}_2 \ (5)
\]
or toluene). In a separate experiment, gas formed during thermolysis was collected with a Toepler pump, and shown to consist of a mixture of ethane and methane (1 to 2 ratio) to a total of 0.73 equiv. per titanium. This indicates the in situ formation of a statistical mixture of $\text{Cp}^*\text{TiMe}_2$, $\text{Cp}^*\text{Ti(Et)Me}$ and $\text{Cp}^*\text{TiEt}_2$ (eq. 6). From other studies it is known that the last two compounds decompose to $\text{Cp}^*\text{Ti(\eta}^2\text{-C}_2\text{H}_4)$ and methane or ethane, respectively [2]. Apparently, the alkyl ligands are readily exchanged at low temperature between tervalent titanium and cadmium (vide infra). The same mixture was formed by reaction of $\text{Cp}^*\text{TiMe}$ and CdEt$_2$. This reaction is slower, and does not proceed at -60 °C but at -35 °C; slow formation of cadmium was again observed.

$$\text{Cp}^*\text{TiEt} \xrightarrow{\text{CdMe}_2 / \text{Cd}} \frac{1}{4}\text{Cp}^*\text{TiMe}_2 + \frac{1}{2}\text{Cp}^*\text{Ti(Me)Et} + \frac{1}{4}\text{Cp}^*\text{TiEt}_2$$

The phenyl derivative $\text{Cp}^*\text{TiPh}$ did not react with CdMe$_2$ at low temperature (-35°C). At room temperature a slow reaction was observed: after 4 days’ stirring some starting material was still present, together with a mixture of $\text{Cp}^*\text{TiMe}_2$ [11], $\text{Cp}^*\text{Ti(Me)Ph}$ [2] and $\text{Cp}^*\text{TiPh}_2$ [11] (ratio $\approx 1:2:1$). Once again no clean oxidative alkylation was observed. Thus, alkyl and aryl derivatives of $\text{Cp}^*\text{TiR}$ are oxidized to bis-alkyl (aryl/alkyl) complexes $\text{Cp}^*\text{Ti(R)R}'$, but in contrast to anionic derivatives $\text{Cp}^*\text{TiX}$, their reactions are accompanied by extensive disproportitions. Since isolation of pure compounds from the reaction mixture is practically impossible, the oxidative alkylation of $\text{Cp}^*\text{TiR}$ with CdR$_2$ is not a useful alternative to the treatment of $\text{Cp}^*\text{Ti(R)Cl}$ with MR' reagents for preparation of mixed alkyl compounds $\text{Cp}^*\text{Ti(R)R}'$. The usefulness of this reaction for the synthesis of $\text{Cp}^*\text{Ti(R)R}'$ (R ≠ R') type compounds is therefore limited, but it certainly has potential for the synthesis of thermally labile $\text{Cp}^*\text{TiR}_2$ complexes.

Since oxidative alkylation of $\text{Cp}^*\text{TiR}$ did take place with CdMe$_2$, although without the selectivity needed for synthetic application, we turned our attention to other group 12 MMe$_2$ compounds.

**Reaction of $\text{Cp}^*\text{TiCl}$ and $\text{Cp}^*\text{TiR}$ (R = Me, Et) with HgMe$_2$**

No reaction was observed between $\text{Cp}^*\text{TiCl}$ and HgMe$_2$, not even during 48 h at room temperature. Similarly when a mixture of $\text{Cp}^*\text{TiMe}$ and HgMe$_2$ was stirred for 100 h at room temperature the $\text{Cp}^*\text{TiMe}$ was almost completely recovered. In contrast, a rapid reaction was observed when HgMe$_2$ was mixed with $\text{Cp}^*\text{TiEt}$ at 0 °C. The solution turned yellow within 15 minutes, and mercury separated. Analysis of the reaction mixture by $^1$H NMR spectroscopy showed that, as when CdMe$_2$ was used, a mixture of $\text{Cp}^*\text{TiMe}_2$ and $\text{Cp}^*\text{Ti(\eta}^2\text{-C}_2\text{H}_4)$ (ratio 1/3) had been formed. The reason for the differences in reactivity between $\text{Cp}^*\text{TiMe}$ and $\text{Cp}^*\text{TiEt}$ towards HgMe$_2$ is not clear.

**Reaction of $\text{Cp}^*\text{TiX}$ (X = OMe, Cl) and $\text{Cp}^*\text{TiR}$ (R = Me, Et) with ZnMe$_2$**

Treatment of toluene solutions of $\text{Cp}^*\text{TiOMe}$ and $\text{Cp}^*\text{TiCl}$ with ZnMe$_2$ at room temperature slowly (ca. 24 h) gives quantitative yields of 1 and 2, respectively. This is remarkable since dialkylzinc compounds are normally considered
substitution or reducing agents, rather than oxidants [12]. Reduction of 2 by zinc metal formed in situ was not observed; probably there is a kinetic reason for this, since zinc metal is known to reduce tetravalent titanium halides [13]. ZnMe₂ reacts more slowly than CdMe₂ with Cp*₂TiOMe or Cp*₂TiCl. At 0 °C no zinc precipitation was observed during 4 h in each case. As in the reactions with CdMe₂ no substitution or disproportionation reactions were observed with titanium species Cp*₂TiX containing anionic substituents.

The reactions of ZnMe₂ with Cp*₂TiR (R = Me, Et) closely resemble those of CdMe₂. Cp*₂TiMe reacts quickly at room temperature with ZnMe₂ in toluene to give 5 in almost quantitative yield. In contrast to the slow reaction of Cp*₂TiX with ZnMe₂, oxidation is complete within 0.5 hour at room temperature. Reaction of Cp*₂TiEt with ZnMe₂ once again resembles that with other group 12 compounds MMMe₂. Treatment of brown Cp*₂TiEt with ZnMe₂ at -80°C gives a green solution, showing the characteristic color of Cp*₂TiMe, suggesting that ligand exchange takes place rather than oxidation (eq. 7). * Kept at -80 °C no zinc precipitation was observed during 5 days. After 5 days at -35 °C only a small amount of zinc had been formed. Apparently, ZnR₂ reagents do not oxidize compounds Cp*₂TiR at low temperature. At room temperature rapid precipitation of zinc was observed. Analysis of the reaction mixture with ¹H NMR showed that it again consisted of a mixture of Cp*₂TiMe₂ and Cp*₂Ti(η⁷-C₂H₄) (ratio 1 : 3).

Cp*₂TiEt + ZnMe₂ → Cp*₂TiMe + ZnMeEt

(7)

Apparently ligand exchange between MR₂ (M = group 12 metal) and Cp*₂TiR is faster than oxidative transfer of an alkyl group, making them unsuitable for the synthesis of mixed bisalkyl Cp*₂Ti(R)R' compounds. Synthesis of Cp*₂Ti(Me)X (X: anionic σ-bonded group) by oxidative alkylation certainly has useful synthetic potential [3].

Discussion and conclusions

Oxidative alkylation

Compounds Cp*₂TiX (X = OMe, Cl, N≡C(H)²Bu) and Cp*₂TiR (R = alkyl, aryl) are oxidized by zinc and cadmium MR₂ compounds to Cp*₂Ti(R')X and Cp*₂Ti(R')R. The cadmium compounds react more rapidly than the zinc complexes, and in general Cp*₂TiR (R = alkyl) are more readily oxidized than Cp*₂TiX. Oxidative addition reactions of ZnR₂ were not previously known, but have now been shown to proceed like those of the corresponding cadmium compounds [12]. Mercury derivatives do not react with tervalent Cp*₂TiX and Cp*₂TiR compounds by oxidative alkyl transfer.

Mechanism of oxidative alkylation

The oxidative alkylation of Cp₂V [9] and Cp*₂V [14] with CdMe₂ to give dialkyl derivatives Cp₂VR₂ and Cp*₂VR₂ respectively, were reported previously. The reaction was judged to proceed by a complex route, starting with insertion of carbenoid vanadocene into a Cd-C bond. Oxidative alkylation of Cp*₂TiX

* This was confirmed by oxidizing the cold reaction mixture with PbCl₂, to give some Cp*₂Ti(Me)Cl (¹H NMR [1]).
(Cp^*₂TiR), which has one unpaired electron, cannot proceed in this way and a low energy concerted process is more likely. Fast radical (and non-radical) self-exchange of alkyl groups between group 12 dialkyls, e.g. CdMe₂, has been reported [15,16], indicating that despite fairly high dissociation energies for the first homolysis \(D_1 (> 45 \text{ kcal/mol})\) [17], low activation energy processes are feasible through multicenter transition states. The rapid, non-oxidative ligand exchange indicates that ZnMe₂ (and also Cd) interact with Cp^*₂TiR compounds. Although no mechanistic studies were carried out, it is reasonable to assume that in this interaction a radical pathway becomes kinetically accessible. It can also be predicted that oxidative alkylation is likely to be accompanied by disproportionation.

**Thermodynamic consequences**

The observed oxidative alkylation of Cp^*₂TiX and Cp^*₂TiR by ZnMe₂ also has some thermodynamic implications. The mean M-C bond dissociation energy of 44 kcal/mol in ZnMe₂ sets a lower limit for the Ti-C bond dissociation energy of 44 kcal/mol. This is consistent with data for reaction solution calorimetric studies by Dias \((D(Ti-Me) = 67.2 \text{ kcal/mol in } \text{Cp}^*₂\text{TiMe}₂)\) [18]. Since the determination of carbon-metal bond dissociation energies is not always experimentally simple, this type of oxidation reaction could (at least) be helpful for estimating lower limits for dissociation energies.

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**References**

   2 (1964) 49.