Oxidative alkylation of \((\eta^5\text{-C}_5\text{Me}_5)\text{TiR}\) (R = Cl, Me, Et, CH=CH_2, Ph, OMe, N=C(H)tBu) to \((\eta^5\text{-C}_5\text{Me}_5)\text{Ti(Me)R}\) by group 12 organometallic compounds MMe_2

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Oxidative alkylation of \( (\eta^5\text{-C_5Me_5})_2\text{TiR} \) (R = Cl, Me, Et, CH=CH\(_2\), Ph, OMe, N=C(H)\(_t\)Bu) to \( (\eta^5\text{-C_5Me_5})_2\text{Ti(Me)}\text{R} \) by group 12 organometallic compounds MMe\(_2\)

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Abstract

Oxidative alkylation of Cp\(^*\)

\( \text{TiCl} \) (Cp\(^*\): \( \eta^5\text{-C_5Me_5} \); X = OMe, Cl, N=C(H)\(_t\)Bu) and Cp\(^*\)TiMe by CdMe\(_2\) or ZnMe\(_2\) gives diamagnetic Cp\(^*\)Ti(Me)X and Cp\(^*\)TiMe\(_2\) respectively, and cadmium or zinc. The reactions of Cp\(^*\)TiR (R = Et, CH=CH\(_2\), Ph) with MMe\(_2\) (M = Cd, Zn) give statistical mixtures of Cp\(^*\)Ti(Me)R, Cp\(^*\)TiMe\(_2\) and Cp\(^*\)TiR\(_2\). Dimethylmercury does not react with Cp\(^*\)TiX.

Introduction

We previously described the preparation of Cp\(^*\)Ti(R)Cl (Cp\(^*\): \( \eta^5\text{-C_5Me_5} \); R = alkyl, aryl, H) by oxidative chlorination of Cp\(^*\)TiR complexes with PbCl\(_2\) [1]. Subsequent treatment of Cp\(^*\)Ti(R)Cl with lithium, sodium or potassium reagents MR gave (mixed) bis alkyl/aryl complexes Cp\(^*\)Ti(R)R' [2]. However, in most cases the products were unstable at temperatures at which they were formed (\( \approx -10 \degree C \)). 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\(^*\)Ti(R)R' derivatives. In view of the clean oxidation of Cp\(^*\)TiR with PbCl\(_2\), we decided to explore oxidative alkylation of Cp\(^*\)TiR with group 12 dialkyl complexes MR\(_2\) (eq. 1).

\[
\text{Cp}^*\text{TiR} + \frac{1}{2}\text{MR}'_2 \rightarrow \text{Cp}^*\text{Ti(R)}\text{R'} + \frac{1}{2}\text{M}
\]

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

The results are described below. Preliminary data on the oxidative alkylation of Cp\(^*\)TiX (X = OMe, Cl) with ZnMe\(_2\) have been published [3]. Recently, comparable oxidation reactions between Cp\(^*\)SmNa and AlH\(_3\) · THF were reported to yield Cp\(^*\)SmAlH\(_4\) · THF (Cp\(^*\): \( \eta^5\text{-C_5H_4Bu} \)), and that between Cp\(^*\)Sm and Al\(_2\)Et\(_6\) to give Cp\(^*\)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$_2$TiCl was synthesized by a published procedure [5a]. The compounds Cp$_2$TiR (R = Me, Et, C$_2$H$_5$, Ph) were prepared from Cp$_2$TiCl and Grignard reagents in diethyl ether [5b], Cp$_2$TiOMe from Cp$_2$TiCl and methanol, Cp$_2$TiN=C(H)tBu from Cp$_2$TiEt and tBuC=N [6]. Organocadmium compounds were prepared as described previously [7] from CdCl$_2$, and dimethylzinc was prepared as previously described [8]. HgMe$_2$ (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-$d_6$ on Bruker WH-90 or Varian VXR-300 spectrometers. Chemical shifts are reported in ppm and referenced to residual protons in deuterated benzene ($d_6 = 7.15$ ppm for $^1$H NMR, $d_6 = 127.96$ ppm for $^{13}$C 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.

$\text{Cp}_2\text{Ti}(\text{Me})\text{OMe (1)}$

A solution of $\text{Cp}_2\text{TiOMe}$ (402 mg, 1.15 mmol) in 10 mL of ether was cooled to $-30$ °C and CdMe$_2$ (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%). $^1$H NMR $\delta$ 1.79 (s, 30H, Cp$_2$), 3.82 (s, 3H, OCH$_3$), 0.09 (s, 3H, CH$_3$). $^{13}$C NMR $\delta$ 11.77 (q, C$_5$Me$_5$; $J$(CH) 126 Hz), 119.3 (s, C$_5$Me$_5$), 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. C$_{22}$H$_{36}$TiO calc.: C, 72.51; H, 9.96; Ti, 13.14%. A similar procedure was used for the reaction of $\text{Cp}_2\text{TiOMe}$ with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of 1).

$\text{Cp}_2\text{Ti}(\text{Me})\text{Cl (2)}$ and $\text{Cp}_2\text{Ti}(\text{Et})\text{Cl (3)}$

$\text{Cp}_2\text{TiCl}$ (712 mg, 2.01 mmol) was suspended in 25 mL of pentane at $-30$ °C and CdMe$_2$ (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 orange-red residue was extracted with THF. The extract was kept at $-80$ °C to give 458 mg (1.24 mmol, 62%) of red crystalline 2. A similar procedure was followed for $\text{Cp}_2\text{Ti}(\text{Et})\text{Cl (3)}$, starting from 559 mg (1.61 mmol) of $\text{Cp}_2\text{TiCl}$ and 83 µL (0.80 mmol) of CdEt$_2$. Yield: 312 mg 3 (0.82 mmol, 51%). Both 2 and 3 were identified by comparison of their IR and NMR spectra with authentic samples [2]. Similar reactions of ZnMe$_2$ (scale 2.77 mmol) and HgMe$_2$ (scale 1.26 mmol) with $\text{Cp}_2\text{TiCl}$ were carried out at room temperature in toluene.

$\text{Cp}_2\text{Ti}(\text{Me})\text{N=C(H)Bu (4)}$

$\text{Cp}_2\text{TiN=C(H)Bu}$ (763 mg, 1.90 mmol) was treated at $-30$°C with CdMe$_2$ (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


Table 1  
Experimental conditions and yields in reaction of CdMe₂ with Cp₂TiR

<table>
<thead>
<tr>
<th>R</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Scale (mmol)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>Et₂O</td>
<td>0</td>
<td>30</td>
<td>1.46</td>
<td>78</td>
</tr>
<tr>
<td>Ph</td>
<td>Et₂O</td>
<td>20</td>
<td>50</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>C₅H₅</td>
<td>Pentane</td>
<td>-60</td>
<td>100</td>
<td>2.34</td>
<td>39</td>
</tr>
<tr>
<td>Et</td>
<td>Toluene</td>
<td>-60</td>
<td>100</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>THF</td>
<td>-60</td>
<td>100</td>
<td></td>
<td>1.11</td>
<td>-</td>
</tr>
</tbody>
</table>

* The reaction products were not separately isolated; the composition was determined by ¹H NMR spectroscopy.

ether. The extract was kept at -80 °C to give 575 mg (1.37 mmol, 73%) of crystalline 4 as a mixture of two isomers (ratio 6 : 1). ¹H NMR (ppm) major isomer: δ 1.70 (s, 30H, Cp*), 0.96 (s, 9H, tBu), -0.27 (s, 3H, CH₃), 7.78 (s, 1H, CHN); minor isomer: δ 1.70 (s, 30H, Cp*), 0.97 (s, 9H, tBu), -0.87 (s, 3H, CH₃), 7.05 (s, 1H, CHN). ¹³C NMR (ppm) major isomer: δ 11.81 (q, C₅Me₅; J(CH) 126 Hz), 114.6 (s, C₅Me₅), 41.6 (s, CMe₃), 27.3 (q, C(CH₃)); J(CH) 127 Hz), 163.9 (dm, C(H)N; J(CH) 163 Hz), 30.3 (q, TiCH₃; J(CH) 123 Hz); minor isomer: δ 11.92 (q, C₅Me₅; J(CH) 125 Hz), 116.1 (s, C₅Me₅), 38.7 (s, CMe₃), 26.9 (q, C(CH₃)); δ(CH) 127 Hz), 161.9 (dm, C(H)N; J(CH) 157 Hz), 39.7 (q, TiCH₃; J(CH) 123 Hz). IR (cm⁻¹): 2745 (s), 2630 (m), 1765 (w), 1680 (vs), 1630 (w), 1360 (m), 1330 (w), 1250 (w), 1200 (s), 1170 (w), 1110 (w), 1065 (w), 1020 (m), 890 (w), 880 (w), 675 (s), 480 (m). Anal. Found: C, 74.27; H, 10.39; Ti, 11.52. C₂₆H₄₃TiN calc.: C, 74.79; H, 10.38; Ti, 11.47%.

Reactions of CdMe₂ with Cp₂TiR (R = alkyl, aryl) were performed similarly; for details see Table 1. Similar experimental procedures were used for the reactions of Cp₂TiR with HgMe₂ and ZnMe₂.

Results

Reaction of Cp₂TiX (X = Cl, OMe, N=C(H)ᵗBu) with dimethylcadmium

It is known that Cp₂V (C:: C₅H₅) reacts with organocadmium compounds Cd₂ to form bis-alkyl complexes Cp₂VR₂ (R = Me, Et, CH₂Ph) [9]. Since oxidative alkylation is exactly the type of reaction we are interested in, an exploratory study was carried out with CdMe₂ as the oxidant. The anionic σ-bonded derivatives Cp₂TiOMe, Cp₂TiCl and Cp₂TiN=C(H)ᵗBu were selected as substrate molecules, because the expected products Cp₂Ti(Me)X are stable and can be isolated and fully characterized at room temperature [2].

Reaction of Cp₂TiOMe and CdMe₂ at -30 °C is immediate, and gives an orange solution of Cp₂Ti(Me)OMe (I) with deposition of Cd metal (eq. 2).

\[
\text{Cp}_2\text{TiX} + \frac{1}{2}\text{CdMe}_2 \rightarrow \text{Cp}_2\text{Ti(Me)X} + \frac{1}{2}\text{Cd} \\
(X = \text{OMe, I; Cl, 2})
\]

\[
\text{Cp}_2\text{TiCl} + \text{CdMe}_2 \rightarrow \text{Cp}_2\text{TiMe} + \text{CdMeCl} \\
(3)
\]

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\(^*\)\(_2\)TiCl and CdMe\(_2\) to give Cp\(^*\)\(_2\)TiMe and CdClMe (eq. 3). Also not observed were possible products such as Cp\(^*\)\(_2\)TiMe\(_2\) (vide infra) or Cp\(^*\)\(_2\)TiCl\(_2\), resulting from oxidation of the last two organotitanium compounds. From an analogous reaction between CdEt\(_2\) and Cp\(^*\)\(_2\)TiCl the mono-ethyl derivative Cp\(^*\)\(_2\)Ti(Et)Cl (3) was isolated. The sterically more demanding azomethine complex Cp\(^*\)\(_2\)TiN=C(H)\(_t\)Bu was smoothly oxidized by CdMe\(_2\) to give the monomethylated product Cp\(^*\)\(_2\)Ti(Me)N=C(H)\(_t\)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.

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

Thus, oxidative alkylation of the 15-electron compounds Cp\(^*\)\(_2\)TiX (X = OMe, Cl, N=C(H)\(_t\)Bu) with CdR\(_2\) (R = Me, Et) to corresponding diamagnetic alkyl derivatives Cp\(^*\)\(_2\)Ti(R)X proceeds smoothly at low temperature. There is no evidence for side (substitution) or subsequent (disproportionation) reactions.

**Reaction of Cp\(^*\)\(_2\)TiR (R = Me, Et, Ph, C\(_2\)H\(_4\)) with dimethylcadmium**

The clean formation of 1-4 from the corresponding Cp\(^*\)\(_2\)TiX compounds looked very promising, so we decided to extend our investigations to alkyl and aryl derivatives Cp\(^*\)\(_2\)TiR. Reaction of Cp\(^*\)\(_2\)TiMe with CdMe\(_2\) at 0 °C gave Cp\(^*\)\(_2\)TiMe\(_2\), but the compound contained about 5% Cp\(^*\)\(_2\)TiMe\(_2\) *. The outcome was even worse for Cp\(^*\)\(_2\)TiEt. Cp\(^*\)\(_2\)TiEt was treated with CdMe\(_2\) 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 \(^1\)H NMR spectrum of the thermolysis mixture revealed the presence of two new compounds, Cp\(^*\)\(_2\)TiMe\(_2\) and Cp\(^*\)\(_2\)Ti(η\(^2\)-C\(_2\)H\(_4\)) [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 \(^1\)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. \(^{13}\)C NMR). In addition, in the IR spectrum of 4 there are two absorptions for the azomethide proton at \(\nu(\text{CH}) = 2745 \text{ cm}^{-1}\) and 2630 \text{ cm}^{-1}\, for the major and minor isomer, respectively. Cf. J.E. Bercaw, D.L. Davies and P.T. Wolczanski, *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%).
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 \( \text{Cp}^*\text{Ti}(... \text{C}_2\text{H}_4) \) 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 \( \text{CdEt}_2 \). 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 \( \text{CdMe}_2 \) 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 disproportionations. Since isolation of pure compounds from the reaction mixture is practically impossible, the oxidative alkylation of \( \text{Cp}^*\text{TiR} \) with \( \text{CdR}_2 \) is not a useful alternative to the treatment of \( \text{Cp}^*\text{Ti(R)Cl} \) with \( \text{MR'} \) reagents for preparation of mixed alkyl compounds \( \text{Cp}^*\text{Ti(R)R'} \). The usefulness of this reaction for the synthesis of \( \text{Cp}^*\text{Ti(R)R'} \) (\( R \neq R' \)) 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 \( \text{CdMe}_2 \), 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 \( \text{Cp}^*\text{TiR} \) (\( R = \text{Me, Et} \)) with \( \text{HgMe}_2 \)**

No reaction was observed between \( \text{Cp}^*\text{TiCl} \) and \( \text{HgMe}_2 \), not even during 48 h at room temperature. Similarly when a mixture of \( \text{Cp}^*\text{TiMe} \) and \( \text{HgMe}_2 \) 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 \( \text{HgMe}_2 \) 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 \(^1\text{H} \) NMR spectroscopy showed that, as when \( \text{CdMe}_2 \) was used, a mixture of \( \text{Cp}^*\text{TiMe}_2 \) and \( \text{Cp}^*\text{Ti(... \text{C}_2\text{H}_4)} \) (ratio 1/3) had been formed. The reason for the differences in reactivity between \( \text{Cp}^*\text{TiMe} \) and \( \text{Cp}^*\text{TiEt} \) towards \( \text{HgMe}_2 \) is not clear.

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

Treatment of toluene solutions of \( \text{Cp}^*\text{TiOMe} \) and \( \text{Cp}^*\text{TiCl} \) with \( \text{ZnMe}_2 \) 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 MMe₂. 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, ZnR'₂ 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(η²-C₂H₄) (ratio 1 : 3).

\[
\text{Cp}^*\text{₂TiEt} + \text{ZnMe}_2 \rightarrow \text{Cp}^*\text{₂TiMe} + \text{ZnMeEt} \tag{7}
\]

Apparently ligand exchange between MR'₂ (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)₅Bu) and Cp*₂TiR (R = alkyl, aryl) are oxidized by zinc and cadmium MR'₂ 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 alkylations 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\textsuperscript{*2}TiR), 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. CdMe\textsubscript{2}, has been reported \cite{15,16}, indicating that despite fairly high dissociation energies for the first homolysis $D_1 (> 45$ kcal/mol \cite{17}), low activation energy processes are feasible through multicenter transition states. The rapid, non-oxidative ligand exchange indicates that ZnMe\textsubscript{2} (and also Cd) interact with Cp\textsuperscript{*2}TiR 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\textsuperscript{*2}TiX and Cp\textsuperscript{*2}TiR by ZnMe\textsubscript{2} also has some thermodynamic implications. The mean M-C bond dissociation energy of 44 kcal/mol in ZnMe\textsubscript{2} 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 \cite{18} ($D(Ti-Me) = 67.2$ kcal/mol in Cp\textsuperscript{*2}TiMe\textsubscript{2}). 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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