Oxidative alkylation of (η^5-C$_5$Me$_5$)$_2$TiR (R = Cl, Me, Et, CH=CH$_2$, Ph, OMe, N=C(H)^{t}Bu) to (η^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*: η^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*: η^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 ($\approx -10\,^\circ$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).

$$\text{Cp*}_2\text{TiR} + \tfrac{1}{2}\text{MR'}_2 \rightarrow \text{Cp*}_2\text{Ti(R)R'} + \tfrac{1}{2}\text{M} \tag{1}$$

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'$_3$SmNa and AlH$_3$ · THF were reported to yield Cp'$_2$SmAlH$_4$ · THF (Cp': η^5-C$_5$H$_4{}^t$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, C_2H_3, Ph) were prepared from Cp^*_2TiCl and Grignard reagents in diethyl ether [5b], Cp^*_2TiOMe from Cp^*_2TiMe and methanol, $Cp^*_2TiN=C(H)^tBu$ from Cp^*_2TiEt and $^tBuC\equiv N$ [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 ($\delta = 7.15$ ppm for ^1H NMR, $\delta = 127.96$ 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.

$Cp^*_2Ti(Me)OMe$ (1)

A solution of Cp^*_2TiOMe (402 mg, 1.15 mmol) in 10 mL of ether was cooled to $-30\,°C$ and $CdMe_2$ (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%). ^1H NMR δ 1.79 (s, 30H, Cp^*), 3.82 (s, 3H, OCH_3), 0.09 (s, 3H, CH_3). ^{13}C NMR δ 11.77 (q, C_5Me_5; $J(CH)$ 126 Hz), 119.3 (s, C_5Me_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 Cp^*_2TiOMe with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of 1).

$Cp^*_2Ti(Me)Cl$ (2) and $Cp^*_2Ti(Et)Cl$ (3)

Cp^*_2TiCl (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 $Cp^*_2Ti(Et)Cl$ (3), starting from 559 mg (1.61 mmol) of Cp^*_2TiCl 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 Cp^*_2TiCl were carried out at room temperature in toluene.

$Cp^*_2Ti(Me)N=C(H)^tBu$ (4)

$Cp^*_2TiN=C(H)^tBu$ (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 $CdMe_2$ with Cp^*_2TiR

R	Solvent	T (°C)	Time (h)	Scale (mmol)	Yield (%)
Me	Et_2O	0	30	1.46	78
Ph	Et_2O	20	50	0.56	– [a]
C_2H_3	Pentane	– 60	100	2.34	39
Et	Toluene	– 60	100	1.06	– [a]
	THF	– 60	100	1.11	– [a]

[a] The reaction products were not separately isolated; the composition was determined by ^{1}H 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). ^{1}H NMR (ppm) major isomer: δ 1.70 (s, 30H, Cp*), 0.96 (s, 9H, ^{t}Bu), -0.27 (s, 3H, CH_3), 7.78 (s, 1H, CHN); minor isomer: δ 1.70 (s, 30H, Cp*), 0.97 (s, 9H, ^{t}Bu), -0.87 (s, 3H, CH_3), 7.05 (s, 1H, CHN). ^{13}C NMR (ppm) major isomer: δ 11.81 (q, C_5Me_5; J(CH) 126 Hz), 114.6 (s, C_5Me_5), 41.6 (s, CCMe$_3$), 27.3 (q, C(CH_3)$_3$; J(CH) 127 Hz), 163.9 (dm, C(H)N; J(CH) 163 Hz), 30.3 (q, TiCH_3; J(CH) 123 Hz); minor isomer: δ 11.92 (q, C_5Me_5; J(CH) 125 Hz), 116.1 (s, C_5Me_5), 38.7 (s, CMe$_3$), 26.9 (q, C(CH_3)$_3$; J(CH) 127 Hz), 161.9 (dm, C(H)N; J(CH) 157 Hz), 39.7 (q, TiCH_3; 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. $C_{26}H_{43}TiN$ calc.: C, 74.79; H, 10.38; Ti, 11.47%.
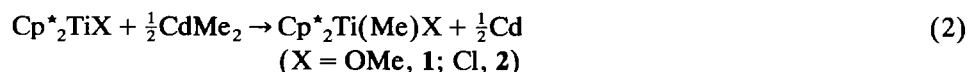
Reactions of $CdMe_2$ with Cp^*_2TiR (R = alkyl, aryl) were performed similarly; for details see Table 1. Similar experimental procedures were used for the reactions of Cp^*_2TiR with $HgMe_2$ and $ZnMe_2$.

Results

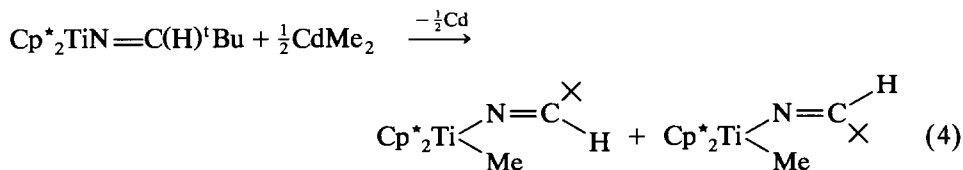### Reaction of Cp^*_2TiX (X = Cl, OMe, N=C(H)^{t}Bu) with dimethylcadmium

It is known that Cp_2V (C;: η^5-C_5H_5) reacts with organocadmium compounds CdR_2 to form bis-alkyl complexes Cp_2VR_2 (R = Me, Et, CH_2Ph) [9]. Since oxidative alkylation is exactly the type of reaction we are interested in, an exploratory study was carried out with $CdMe_2$ as the oxidant. The anionic σ-bonded derivatives Cp^*_2TiOMe, Cp^*_2TiCl and $Cp^*_2TiN=C(H)^tBu$ were selected as substrate molecules, because the expected products $Cp^*_2Ti(Me)X$ are stable and can be isolated and fully characterized at room temperature [2].

Reaction of Cp^*_2TiOMe and $CdMe_2$ at -30°C is immediate, and gives an orange solution of $Cp^*_2Ti(Me)OMe$ (**1**) with deposition of Cd metal (eq. 2).

$$Cp^*_2TiX + \tfrac{1}{2}CdMe_2 \rightarrow Cp^*_2Ti(Me)X + \tfrac{1}{2}Cd \qquad (2)$$
$$(X = OMe, \mathbf{1}; Cl, \mathbf{2})$$

$$Cp^*_2TiCl + CdMe_2 \xrightarrow{\quad} Cp^*_2TiMe + CdMeCl \qquad (3)$$

Similarly Cp^*_2TiCl was treated with $CdMe_2$ to give $Cp^*_2Ti(Me)Cl$ (**2**) as the only organometallic product. The oxidative alkylation of Cp^*_2TiCl is a clean reaction.

There was no indication of reaction between Cp^*_2TiCl and $CdMe_2$ to give Cp^*_2TiMe and $CdClMe$ (eq. 3). Also not observed were possible products such as $Cp^*_2TiMe_2$ (*vide infra*) or $Cp^*_2TiCl_2$, resulting from oxidation of the last two organotitanium compounds. From an analogous reaction between $CdEt_2$ and Cp^*_2TiCl the mono-ethyl derivative $Cp^*_2Ti(Et)Cl$ (3) was isolated. The sterically more demanding azomethine complex $Cp^*_2TiN=C(H)^tBu$ was smoothly oxidized by $CdMe_2$ to give the monomethylated product $Cp^*_2Ti(Me)N=C(H)^tBu$ (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.

$$Cp^*_2TiN=C(H)^tBu + \tfrac{1}{2}CdMe_2 \xrightarrow{-\tfrac{1}{2}Cd}$$

$$Cp^*_2Ti\Big\langle{}^{N=C\diagdown^X_H}_{Me} + Cp^*_2Ti\Big\langle{}^{N=C\diagup^H_X}_{Me} \quad (4)$$

Thus, oxidative alkylation of the 15-electron compounds Cp^*_2TiX (X = OMe, Cl, N=C(H)^{t}Bu) with CdR_2 (R = Me, Et) to corresponding diamagnetic alkyl derivatives $Cp^*_2Ti(R)X$ proceeds smoothly at low temperature. There is no evidence for side (substitution) or subsequent (disproportionation) reactions.

Reaction of Cp^*_2TiR (R = Me, Et, Ph, C_2H_3) with dimethylcadmium

The clean formation of 1–4 from the corresponding Cp^*_2TiX compounds looked very promising, so we decided to extend our investigations to alkyl and aryl derivatives Cp^*_2TiR. Reaction of Cp^*_2TiMe with $CdMe_2$ at 0°C gave $Cp^*_2TiMe_2$ in high yields, demonstrating that Cp^*_2TiR (R = alkyl) compounds are also readily oxidized (eq. 5).

$$Cp^*_2TiMe + \tfrac{1}{2}CdMe_2 \rightarrow Cp^*_2TiMe_2 + \tfrac{1}{2}Cd \qquad (5)$$
$$(5)$$
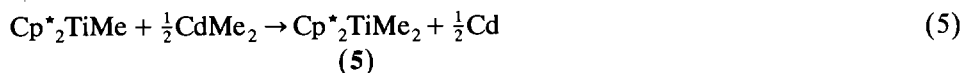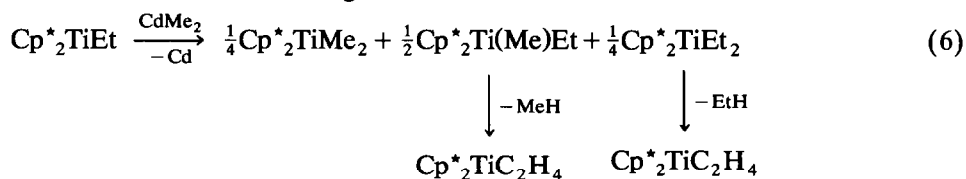
However, reactions of other titanium alkyl derivatives Cp^*_2TiR with $CdMe_2$ were less straightforward. The vinyl derivative $Cp^*_2TiC_2H_3$ reacted with $CdMe_2$ to $Cp^*_2Ti(Me)C_2H_3$ (6), but the compound contained about 5% $Cp^*_2TiMe_2$ *. The outcome was even worse for Cp^*_2TiEt. Cp^*_2TiEt 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 ^1H NMR spectrum of the thermolysis mixture revealed the presence of two new compounds, $Cp^*_2TiMe_2$ and $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ [10], in a 1 to 3 ratio. The product ratio was independent of solvent (THF

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* This is indicated by the large shift difference between the both groups in the ^1H 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 $\nu(CH) = 2745$ cm^{-1} and 2630 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 $Cp^*_2TiMe_2$, $Cp^*_2Ti(Et)Me$ and $Cp^*_2TiEt_2$ (eq. 6). From other studies it is known that the last two compounds decompose to $Cp^*_2Ti(\eta^2-C_2H_4)$ 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 Cp^*_2TiMe 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.

$$Cp^*_2TiEt \xrightarrow[-Cd]{CdMe_2} \tfrac{1}{4}Cp^*_2TiMe_2 + \tfrac{1}{2}Cp^*_2Ti(Me)Et + \tfrac{1}{4}Cp^*_2TiEt_2 \qquad (6)$$

$$\downarrow -MeH \qquad\qquad \downarrow -EtH$$

$$Cp^*_2TiC_2H_4 \qquad Cp^*_2TiC_2H_4$$

The phenyl derivative Cp^*_2TiPh 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 $Cp^*_2TiMe_2$ [11], $Cp^*_2Ti(Me)Ph$ [2] and $Cp^*_2TiPh_2$ [11] (ratio $\approx 1:2:1$). Once again no clean oxidative alkylation was observed. Thus, alkyl and aryl derivatives of Cp^*_2TiR are oxidized to bis-alkyl (aryl/alkyl) complexes $Cp^*_2Ti(R)R'$, but in contrast to anionic derivatives Cp^*_2TiX, their reactions are accompanied by extensive disproportionations. Since isolation of pure compounds from the reaction mixture is practically impossible, the oxidative alkylation of Cp^*_2TiR with CdR'_2 is not a useful alternative to the treatment of $Cp^*_2Ti(R)Cl$ with MR' reagents for preparation of mixed alkyl compounds $Cp^*_2Ti(R)R'$. The usefulness of this reaction for the synthesis of $Cp^*_2Ti(R)R'$ ($R \neq R'$) type compounds is therefore limited, but it certainly has potential for the synthesis of thermally labile $Cp^*_2TiR_2$ complexes.

Since oxidative alkylation of Cp^*_2TiR 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 Cp^*_2TiCl and Cp^*_2TiR (R = Me, Et) with $HgMe_2$

No reaction was observed between Cp^*_2TiCl and $HgMe_2$, not even during 48 h at room temperature. Similarly when a mixture of Cp^*_2TiMe and $HgMe_2$ was stirred for 100 h at room temperature the Cp^*_2TiMe was almost completely recovered. In contrast, a rapid reaction was observed when $HgMe_2$ was mixed with Cp^*_2TiEt at $0°C$. The solution turned yellow within 15 minutes, and mercury separated. Analysis of the reaction mixture by ^1H NMR spectroscopy showed that, as when $CdMe_2$ was used, a mixture of $Cp^*_2TiMe_2$ and $Cp^*_2Ti(\eta^2-C_2H_4)$ (ratio 1/3) had been formed. The reason for the differences in reactivity between Cp^*_2TiMe and Cp^*_2TiEt towards $HgMe_2$ is not clear.

Reaction of Cp^*_2TiX (X = OMe, Cl) and Cp^*_2TiR (R = Me, Et) with $ZnMe_2$

Treatment of toluene solutions of Cp^*_2TiOMe and Cp^*_2TiCl 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]. $ZnMe_2$ reacts more slowly than $CdMe_2$ 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 $CdMe_2$ no substitution or disproportionation reactions were observed with titanium species Cp^*_2TiX containing anionic substituents.

The reactions of $ZnMe_2$ with Cp^*_2TiR (R = Me, Et) closely resemble those of $CdMe_2$. Cp^*_2TiMe reacts quickly at room temperature with $ZnMe_2$ in toluene to give **5** in almost quantitative yield. In contrast to the slow reaction of Cp^*_2TiX with $ZnMe_2$, oxidation is complete within 0.5 hour at room temperature. Reaction of Cp^*_2TiEt with $ZnMe_2$ once again resembles that with other group 12 compounds MMe_2. Treatment of brown Cp^*_2TiEt with $ZnMe_2$ 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 $Cp^*_2TiMe_2$ and $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ (ratio 1:3).

$$Cp^*_2TiEt + ZnMe_2 \rightarrow Cp^*_2TiMe + ZnMeEt \qquad (7)$$

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)^{t}Bu) 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 ZnR_2 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 Cp_2V [9] and Cp^*_2V [14] with $CdMe_2$ to give dialkyl derivatives Cp_2VR_2 and $Cp^*_2VR_2$ 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

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* This was confirmed by oxidizing the cold reaction mixture with $PbCl_2$, 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. $CdMe_2$, has been reported [15,16], indicating that despite fairly high dissociation energies for the first homolysis D_1 (> 45 kcal/mol [17]), low activation energy processes are feasible through multicenter transition states. The rapid, non-oxidative ligand exchange indicates that $ZnMe_2$ (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 $ZnMe_2$ also has some thermodynamic implications. The mean M–C bond dissociation energy of 44 kcal/mol in $ZnMe_2$ 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 ($D(Ti-Me) = 67.2$ kcal/mol in $Cp^*_2TiMe_2$) [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.

Acknowledgements

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