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Oxidative alkylation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}$ ($\text{R} = \text{Cl, Me, Et, CH=CH}_2, \text{Ph, OMe, N=C(H)tBu}$) to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti(Me)R}$ by group 12 organometallic compounds MMe_2

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Oxidative alkylation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiR}$ ($\text{R} = \text{Cl}, \text{Me}, \text{Et}, \text{CH}=\text{CH}_2, \text{Ph}, \text{OMe}, \text{N}=\text{C}(\text{H})^t\text{Bu}$) to $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{Me})\text{R}$ by group 12 organometallic compounds MMe_2

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Abstract

Oxidative alkylation of Cp^*TiX ($\text{Cp}^*: \eta^5\text{-C}_5\text{Me}_5$; $\text{X} = \text{OMe}, \text{Cl}, \text{N}=\text{C}(\text{H})^t\text{Bu}$) and Cp^*TiMe by CdMe_2 or ZnMe_2 gives diamagnetic $\text{Cp}^*\text{Ti}(\text{Me})\text{X}$ and Cp^*TiMe_2 respectively, and cadmium or zinc. The reactions of Cp^*TiR ($\text{R} = \text{Et}, \text{CH}=\text{CH}_2, \text{Ph}$) with MMe_2 ($\text{M} = \text{Cd}, \text{Zn}$) give statistical mixtures of $\text{Cp}^*\text{Ti}(\text{Me})\text{R}$, Cp^*TiMe_2 and Cp^*TiR_2 . Dimethylmercury does not react with Cp^*TiX .

Introduction

We previously described the preparation of $\text{Cp}^*\text{Ti}(\text{R})\text{Cl}$ ($\text{Cp}^*: \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{alkyl}, \text{aryl}, \text{H}$) by oxidative chlorination of Cp^*TiR complexes with PbCl_2 [1]. Subsequent treatment of $\text{Cp}^*\text{Ti}(\text{R})\text{Cl}$ with lithium, sodium or potassium reagents MR' gave (mixed) bis alkyl/aryl complexes $\text{Cp}^*\text{Ti}(\text{R})\text{R}'$ [2]. However, in most cases the products were unstable at temperatures at which they were formed ($\approx -10^\circ\text{C}$). 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 $\text{Cp}^*\text{Ti}(\text{R})\text{R}'$ 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).

$\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$; $\text{R}' = \text{Me}, \text{Et}$

The results are described below. Preliminary data on the oxidative alkylation of Cp^*TiX ($\text{X} = \text{OMe}, \text{Cl}$) with ZnMe_2 have been published [3]. Recently, comparable oxidation reactions between $\text{Cp}'_3\text{SmNa}$ and $\text{AlH}_3 \cdot \text{THF}$ were reported to yield $\text{Cp}'_2\text{SmAlH}_4 \cdot \text{THF}$ ($\text{Cp}': \eta^5\text{-C}_5\text{H}_4^t\text{Bu}$), and that between Cp^*Sm and Al_2Et_6 to give $\text{Cp}^*\text{SmAlEt}_4$ [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. $\text{Cp}^{\star}_2\text{TiCl}$ was synthesized by a published procedure [5a]. The compounds $\text{Cp}^{\star}_2\text{TiR}$ ($\text{R} = \text{Me}, \text{Et}, \text{C}_2\text{H}_5, \text{Ph}$) were prepared from $\text{Cp}^{\star}_2\text{TiCl}$ and Grignard reagents in diethyl ether [5b], $\text{Cp}^{\star}_2\text{TiOMe}$ from $\text{Cp}^{\star}_2\text{TiMe}$ and methanol, $\text{Cp}^{\star}_2\text{TiN}=\text{C}(\text{H})^t\text{Bu}$ from $\text{Cp}^{\star}_2\text{TiEt}$ and $^t\text{BuC}\equiv\text{N}$ [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.

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

A solution of $\text{Cp}^{\star}_2\text{TiOMe}$ (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%). ^1H NMR δ 1.79 (s, 30H, $\text{Cp}^{\star}$), 3.82 (s, 3H, OCH_3), 0.09 (s, 3H, CH_3). ^{13}C NMR δ 11.77 (q, C_5Me_5 ; $J(\text{CH})$ 126 Hz), 119.3 (s, C_5Me_5), 42.17 (q, TiMe ; $J(\text{CH})$ 124 Hz), 62.6 (q, OMe ; $J(\text{CH})$ 139 Hz). IR: 2795 (m), 2720 (w), 1130 (vs), 1020 (m), 502 (s). Anal. Found: C, 72.05; H, 9.99; Ti, 13.13. $\text{C}_{22}\text{H}_{36}\text{TiO}$ calc.: C, 72.51; H, 9.96; Ti, 13.14%. A similar procedure was used for the reaction of $\text{Cp}^{\star}_2\text{TiOMe}$ with dimethylzinc (scale 0.34 mmol, room temperature, reaction time 48 h, yield 82% of **1**).

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

$\text{Cp}^{\star}_2\text{TiCl}$ (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 $\text{Cp}^{\star}_2\text{Ti}(\text{Et})\text{Cl}$ (**3**), starting from 559 mg (1.61 mmol) of $\text{Cp}^{\star}_2\text{TiCl}$ 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 $\text{Cp}^{\star}_2\text{TiCl}$ were carried out at room temperature in toluene.

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

$\text{Cp}^{\star}_2\text{TiN}=\text{C}(\text{H})^t\text{Bu}$ (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 Cp[∗]₂TiR

R	Solvent	T (°C)	Time (h)	Scale (mmol)	Yield (%)
Me	Et ₂ O	0	30	1.46	78
Ph	Et ₂ O	20	50	0.56	- ^a
C ₂ H 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 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, CCMe₃), 27.3 (q, C(CH₃)₃; 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)₃; J(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 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 HgMe₂ and ZnMe₂.

Results

Reaction of Cp[∗]₂TiX (X = Cl, OMe, N=C(H)^tBu) with dimethylcadmium

It is known that Cp₂V (C₅H₅) reacts with organocadmium compounds CdR₂ 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 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 CdMe₂ at -30 °C is immediate, and gives an orange solution of Cp[∗]₂Ti(Me)OMe (**1**) with deposition of Cd metal (eq. 2).

Similarly Cp[∗]₂TiCl was treated with CdMe₂ 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 $\text{Cp}^*_2\text{TiMe}_2$ (*vide infra*) or $\text{Cp}^*_2\text{TiCl}_2$, resulting from oxidation of the last two organotitanium compounds. From an analogous reaction between CdEt_2 and Cp^*_2TiCl the mono-ethyl derivative $\text{Cp}^*_2\text{Ti}(\text{Et})\text{Cl}$ (**3**) was isolated. The sterically more demanding azomethine complex $\text{Cp}^*_2\text{TiN}=\text{C}(\text{H})^t\text{Bu}$ was smoothly oxidized by CdMe_2 to give the monomethylated product $\text{Cp}^*_2\text{Ti}(\text{Me})\text{N}=\text{C}(\text{H})^t\text{Bu}$ (**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.

Thus, oxidative alkylation of the 15-electron compounds Cp^*_2TiX ($\text{X} = \text{OMe}$, Cl , $\text{N}=\text{C}(\text{H})^t\text{Bu}$) with CdR_2 ($\text{R} = \text{Me}$, Et) to corresponding diamagnetic alkyl derivatives $\text{Cp}^*_2\text{Ti}(\text{R})\text{X}$ proceeds smoothly at low temperature. There is no evidence for side (substitution) or subsequent (disproportionation) reactions.

Reaction of Cp^*_2TiR ($\text{R} = \text{Me}$, 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 $\text{Cp}^*_2\text{TiMe}_2$ in high yields, demonstrating that Cp^*_2TiR ($\text{R} = \text{alkyl}$) compounds are also readily oxidized (eq. 5).

However, reactions of other titanium alkyl derivatives Cp^*_2TiR with CdMe_2 were less straightforward. The vinyl derivative $\text{Cp}^*_2\text{TiC}_2\text{H}_3$ reacted with CdMe_2 to $\text{Cp}^*_2\text{Ti}(\text{Me})\text{C}_2\text{H}_3$ (**6**), but the compound contained about 5% $\text{Cp}^*_2\text{TiMe}_2$ *. 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, $\text{Cp}^*_2\text{TiMe}_2$ and $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ [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 ^1H NMR spectrum (Me : -0.27 vs -0.87 ppm and $\text{N}=\text{C}(\text{H})$: 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 azomethine proton at $\nu(\text{CH}) = 2745\text{ cm}^{-1}$ 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 $\text{Cp}^*_2\text{TiMe}_2$, $\text{Cp}^*_2\text{Ti}(\text{Et})\text{Me}$ and $\text{Cp}^*_2\text{TiEt}_2$ (eq. 6). From other studies it is known that the last two compounds decompose to $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ and methane or ethane, respectively [2]. Apparently, the alkyl ligands are readily exchanged at low temperature between trivalent 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.

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 $\text{Cp}^*_2\text{TiMe}_2$ [11], $\text{Cp}^*_2\text{Ti}(\text{Me})\text{Ph}$ [2] and $\text{Cp}^*_2\text{TiPh}_2$ [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 $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$, 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 $\text{Cp}^*_2\text{Ti}(\text{R})\text{Cl}$ with MR' reagents for preparation of mixed alkyl compounds $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$. The usefulness of this reaction for the synthesis of $\text{Cp}^*_2\text{Ti}(\text{R})\text{R}'$ ($\text{R} \neq \text{R}'$) type compounds is therefore limited, but it certainly has potential for the synthesis of thermally labile $\text{Cp}^*_2\text{TiR}_2$ 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 ($\text{R} = \text{Me}, \text{Et}$) 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 $\text{Cp}^*_2\text{TiMe}_2$ and $\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ (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 ($\text{X} = \text{OMe}, \text{Cl}$) and Cp^*_2TiR ($\text{R} = \text{Me}, \text{Et}$) with ZnMe_2

Treatment of toluene solutions of $\text{Cp}^*_2\text{TiOMe}$ 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 $\text{Cp}^{\star}_2\text{TiOMe}$ or $\text{Cp}^{\star}_2\text{TiCl}$. 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 $\text{Cp}^{\star}_2\text{TiX}$ containing anionic substituents.

The reactions of ZnMe_2 with $\text{Cp}^{\star}_2\text{TiR}$ ($\text{R} = \text{Me}, \text{Et}$) closely resemble those of CdMe_2 . $\text{Cp}^{\star}_2\text{TiMe}$ reacts quickly at room temperature with ZnMe_2 in toluene to give **5** in almost quantitative yield. In contrast to the slow reaction of $\text{Cp}^{\star}_2\text{TiX}$ with ZnMe_2 , oxidation is complete within 0.5 hour at room temperature. Reaction of $\text{Cp}^{\star}_2\text{TiEt}$ with ZnMe_2 once again resembles that with other group 12 compounds MMe_2 . Treatment of brown $\text{Cp}^{\star}_2\text{TiEt}$ with ZnMe_2 at -80°C gives a green solution, showing the characteristic color of $\text{Cp}^{\star}_2\text{TiMe}$, 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 $\text{Cp}^{\star}_2\text{TiR}$ 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 $\text{Cp}^{\star}_2\text{TiMe}_2$ and $\text{Cp}^{\star}_2\text{Ti}(\eta^2\text{-C}_2\text{H}_4)$ (ratio 1 : 3).

Apparently ligand exchange between MR'_2 ($\text{M} = \text{group 12 metal}$) and $\text{Cp}^{\star}_2\text{TiR}$ is faster than oxidative transfer of an alkyl group, making them unsuitable for the synthesis of mixed bisalkyl $\text{Cp}^{\star}_2\text{Ti}(\text{R})\text{R}'$ compounds. Synthesis of $\text{Cp}^{\star}_2\text{Ti}(\text{Me})\text{X}$ (X : anionic σ -bonded group) by oxidative alkylation certainly has useful synthetic potential [3].

Discussion and conclusions

Oxidative alkylation

Compounds $\text{Cp}^{\star}_2\text{TiX}$ ($\text{X} = \text{OMe}, \text{Cl}, \text{N}=\text{C}(\text{H})^t\text{Bu}$) and $\text{Cp}^{\star}_2\text{TiR}$ ($\text{R} = \text{alkyl}, \text{aryl}$) are oxidized by zinc and cadmium MR'_2 compounds to $\text{Cp}^{\star}_2\text{Ti}(\text{R}')\text{X}$ and $\text{Cp}^{\star}_2\text{Ti}(\text{R}')\text{R}$. The cadmium compounds react more rapidly than the zinc complexes, and in general $\text{Cp}^{\star}_2\text{TiR}$ ($\text{R} = \text{alkyl}$) are more readily oxidized than $\text{Cp}^{\star}_2\text{TiX}$. 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 trivalent $\text{Cp}^{\star}_2\text{TiX}$ and $\text{Cp}^{\star}_2\text{TiR}$ compounds by oxidative alkyl transfer.

Mechanism of oxidative alkylation

The oxidative alkylations of Cp_2V [9] and $\text{Cp}^{\star}_2\text{V}$ [14] with CdMe_2 to give dialkyl derivatives Cp_2VR_2 and $\text{Cp}^{\star}_2\text{VR}_2$ 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 $\text{Cp}^{\star}_2\text{TiX}$

* This was confirmed by oxidizing the cold reaction mixture with PbCl_2 , to give some $\text{Cp}^{\star}_2\text{Ti}(\text{Me})\text{Cl}$ (^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 ($D(\text{Ti-Me}) = 67.2$ 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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