

$(\eta^5\text{-C}_5\text{Me}_5)_2(\text{Me})\text{Ti-OC}(\text{Me})=\text{CH}_2$: titanium enolate or titanium alkoxide?

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Abstract

While proton and carbon NMR spectroscopy suggest that $(\text{Cp}^*)_2(\text{Me})\text{Ti-OC}(\text{Me})=\text{CH}_2$ (**1**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) is a typical O-bound titanium enolate, this material does not exhibit typical enolate reactivity. Specifically, **1** does not react with either methyl iodide or with benzaldehyde. However, some reagents that are typically used in electrophilic attack of metal-alkyl or metal-alkoxide bonds do react with **1**. In some cases the electrophile displaces the enolate moiety, while in other cases selectivity for substitution of the titanium-bound methyl group is displayed. Thus the reactivity of **1** is more typical of that expected from a titanium alkoxide or an alkyl titanium rather than a titanium enolate. The possible use of the $(\text{Cp}^*)_2(\text{Me})\text{Ti}$ moiety as a protecting group for ketones is discussed.

Introduction

Because of their extensive use in C–C bond forming reactions, enolates are among the most important organometallic reagents. A relatively new direction in the study of enolate chemistry involves the syntheses and evaluation of the reactivity of enolates of Ti [1–5] and other transition metals [6–9]. Preliminary results suggest that some of these materials may be much more useful than the usual lithium enolates when stereochemical control is required in C–C bond formation [5,6]. Recently, we discovered that titanium enolates could be synthesized in virtually quantitative yield via the reaction of most ketones with the hindered alkylidene $\text{Cp}^*_2\text{Ti}=\text{CH}_2$ (**2**), which was generated *in situ* from $\text{Cp}^*_2\text{Ti}(\text{Me})_2$ (**3**) [10]. This particular reaction is particularly noteworthy because enolate formation takes place with very high regioselectivity, and extraordinarily high stereospecificity. In this paper, we discuss some aspects of the chemical reactivity of $\text{Cp}^*_2(\text{Me})\text{Ti-OC}(\text{Me})=\text{CH}_2$ (**1**), the enolate of acetone.

Results and discussion

As we have previously reported, reaction of **3** with most thermally stable ketones results in virtually quantitative yield to the titanium enolate [10]. In cases where *E*- and *Z*-stereoisomeric enolates are possible, the *E* form is always highly favored

(*E/Z* ratios are typically greater than 97/1). The high stereospecificity of enolate formation suggested that this reaction might be quite useful in processes such as the diastereoselective aldol reaction, where stereochemical control in enolate formation can lead to stereochemical control in the formation of the final product [11]. Consequently, we set out to investigate the chemical reactivity of these new enolates.

The simplest of these materials is $\text{Cp}^*\text{}_2(\text{Me})\text{Ti}-\text{OC}(\text{Me})=\text{CH}_2$ (**1**), the enolate of acetone. While this is obviously not an appropriate substrate for investigations concerning stereochemical aspects of C–C bond formation, we nonetheless decided to use **1** in our initial investigations because of the simplicity of its proton NMR spectrum, and because there is no possibility of *E* to *Z* isomerization (which may occur under certain conditions with more complicated enolates [12]). Since the proton and carbon NMR spectra of **1** are typical of those expected for a reactive O-bound transition metal enolate [9], we initially expected that **1** would exhibit typical enolate reactivity.

Conventional enolates are useful because carbon electrophiles attack at the carbon atom and lead to the formation of a new C–C bond [13]. Compounds that are considered to be highly reactive carbon electrophiles include methyl iodide (and many other primary alkyl halides), as well as benzaldehyde (and many other aldehydes) [13]. In a reaction with a typical lithium or titanium enolate, addition of the electrophile at low temperature is followed by a short period of aging (usually at low temperature) and finally work-up of the products. Unexpectedly, our studies have shown that **1** does not exhibit typical enolate reactivity. Specifically, **1** did not react significantly with either benzaldehyde, or with methyl iodide at ambient temperatures (ca. 25 °C) in ether.

While the failure of **1** to display typical enolate reactivity was unanticipated, it is not without precedent. In fact, Grubbs et al. have shown that enolates with the general composition $\text{Cp}_2(\text{Me})\text{Ti}-\text{OC}(\text{R})=\text{CH}_2$ (**4**, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) are likewise unreactive [1,2]. Since these enolates differ structurally from **1** principally in that they contain Cp rather than Cp^* ligands, it is not too surprising that **1** should exhibit a similar lack of reactivity. Significantly, Grubbs et al. synthesized similar enolates which *do* exhibit enolate reactivity [2,3]. These compounds, which have the general formula $\text{Cp}_2(\text{Cl})\text{Ti}-\text{OC}(\text{R})=\text{CH}_2$ (**5**) differ from **4** in that the Ti-bound methyl group of **4** is replaced in **5** by a Ti-bound Cl. Grubbs attributed the difference in reactivity between **4** and **5** to the presence of an electronegative chloride ligand on **5**, which was said to cause the Ti atom to become a better Lewis acid with respect to the enolate moiety [1]. An alternative explanation is that the enolate moiety in **4** acts as an effective π -donor to the electron deficient Ti atom, and is thereby less susceptible to attack by electrophiles than conventional enolates [14]. In compound **5**, the Ti-bound chloride ligand acts as a π -donor, and thereby limits the degree of π -donation from the enolate moiety. This leads to an enolate which is much more susceptible to attack by electrophiles.

Because of the precedented reactivity differences between compounds **4** and **5**, we attempted to replace the Ti-bound methyl group in **1** with a π -donating ligand. In principle, substitution of a metal-bound alkyl ligand may be accomplished by reaction with a suitable electrophile [15]. However, such reactions with **1** are potentially complicated due to the possibility that electrophiles may react at the Ti-methyl bond, the Ti-oxygen bond, or at the enolate carbon atom. As a consequence, mixtures of products may be expected. However, our results suggest that

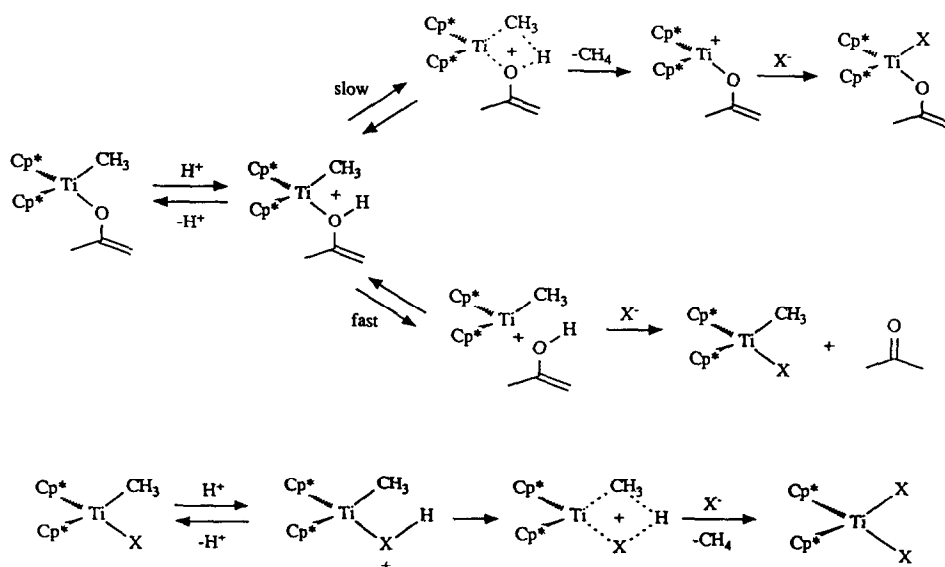


Fig. 1. The reaction of **1** with acidic substrates results in the preferential substitution of the enolate, even though the substitution of the methyl group is thermodynamically favored. Protonation of the enolate oxygen is probably a relatively facile process which preferentially leads to elimination of acetone.

initial electrophilic attack may be selective. For example, reaction of **1** with the weak acid $\text{NMe}_2\text{Oct} \cdot \text{HCl}$ ($\text{Oct} = n\text{C}_8\text{H}_{18}$) gave a mixture which contained $\text{Cp}^*_2\text{TiCl}_2$ (**6**) as the major product, along with some $\text{Cp}^*_2(\text{Me})\text{TiCl}$ (**7**). Significantly, no trace of the desired $\text{Cp}^*_2(\text{Cl})\text{Ti-OC}(\text{Me})=\text{CH}_2$ (**8**) was observed. These results are consistent with an initial reaction in which the electrophile attacks the Ti-oxygen bond to convert **1** to **7**, some of which then reacts with additional $\text{NMe}_2\text{Oct} \cdot \text{HCl}$ to give **6** (Fig. 1). The initial electrophilic substitution of the enolate in **1** is undoubtedly a kinetic effect since conversion of **1** to **8** should be more exothermic by several hundred kilojoules per mole [16]. Protonation of the enolate at an oxygen-bound lone pair to give an enol-like intermediate may be the first step in this reaction [17]. Similarly, reaction of **1** with the weak acid phenol exhibited some preference for initial substitution of the enolate, although the reaction was rather sluggish.

The addition of bromine to **1** resulted in a rapid, very clean reaction. The products consisted of the monosubstituted Cp^*_2TiBr (**9**) as the major constituent, along with smaller quantities of the disubstituted $\text{Cp}^*_2\text{TiBr}_2$ (**10**). None of the desired bromo-substituted enolate, $\text{Cp}^*_2(\text{Br})\text{Ti-OC}(\text{Me})=\text{CH}_2$ (**11**) was detected. Significantly, no 2-butanone was detected in a reaction that was monitored via proton NMR spectroscopy. This result is important because it rules out the production of the disubstituted product **10** via a reaction which first gives the enolate **11** and methyl bromide, followed by reaction of enolate **11** with methyl bromide.

While reaction of **1** with $\text{NMe}_2\text{Oct} \cdot \text{HCl}$, phenol, or bromine led to preferential substitution of the titanium-oxygen bond, the reaction of **1** with iodine or with HgCl_2 led to preferential displacement of the titanium-bound methyl group. Addition of a stoichiometric amount of iodine to **1** in C_6D_6 resulted in a rapid reaction to give predominately the desired monosubstituted enolate $\text{Cp}^*_2(\text{I})\text{Ti-OC}(\text{Me})=\text{CH}_2$

(**12**), a smaller amount of the disubstituted $\text{Cp}^*_2\text{TiI}_2$ (**13**), and methyl iodide. Since no butanone was observed, the production of **13** via reaction of **12** with methyl iodide can be ruled out. Similar reactivity was noted in both ether and hexane, although the reaction was significantly slower in hexane.

The reaction of HgCl_2 with **1** was rapid, quantitative, and highly selective for the formation of the desired enolate $\text{Cp}^*_2(\text{Cl})\text{Ti}-\text{OC}(\text{Me})=\text{CH}_2$ (**8**). However, we were not able to cleanly separate this product from the accompanying MeHgCl by extractions, or by fractional recrystallizations. This created a serious problem because MeHgCl slowly but cleanly converts **8** to **6**. (This process may involve the reaction of **8** with HgCl_2 , which can be produced from MeHgCl via the Schlenk equilibrium [8]). In order to circumvent this problem, we followed the addition of HgCl_2 to **1** by the addition of a stoichiometric amount of methyllithium. This procedure converted the MeHgCl to HgMe_2 , which was then removed along with the rest of the volatile components *in vacuo*. By this procedure, **8** was isolated in yields of ca. 80%. We note that the proton NMR spectrum of **8** shows that, like the precursor **1**, this compound contains an oxygen-bound enolate moiety.

Preliminary investigation of the reactivity of **8** indicated that this compound, like the precursor **1**, does not exhibit typical enolate reactivity. Specifically, addition of methyl iodide to solutions containing **8** resulted in no discernible reaction. Benzaldehyde does react with **8**, but the product is not the expected aldolate. Although we have not yet determined the identity of the product of this reaction, we have been able to show that it is not the expected aldolate since the identical material is the major product of the reaction of $\text{Cp}^*_2\text{TiMe}_2$ (**3**) with benzoyl chloride [19].

Our investigations have shown that both enolates **1** and **8** are unusual owing to their lack of typical enolate reactivity. Indeed, enolate **1** seems to react more like a typical metal alkyl or metal alkoxide rather than an enolate. This notable lack of enolate reactivity may be due, in part, to the fact that the enolate moiety is deactivated due to π -donation of the titanium (*vide supra*). However, at least part of this lack of reactivity is undoubtedly due to steric effects. Structural studies of compounds which contain the Cp^*_2Ti moiety [20] show that the Cp^* ligands are extremely bulky and suggest that attack of the incoming ligand is effectively blocked from all directions except from the open cleft of the molecule. In addition, the bulk of the Cp^* ligands constrains the enolate moiety to be in the plane perpendicular to the plane containing the two Cp^* ring centroids, and the Ti atom. Attack of the enolate from above or below the plane containing that ligand is therefore prohibited for steric reasons.

The lack of typical enolate reactivity of **1**, coupled with the fact that enolates like **1** may be synthesized in high yield via reaction of ketones with **3** suggests an important practical application: the $\text{Cp}^*_2(\text{Me})\text{Ti}$ may be an attractive protecting group for ketones. For example, reaction of an unsymmetrical diketone with **3** would result in selective conversion [10] of the more accessible ketone functionality to an *unreactive* Ti-enolate. Subsequent reaction with LDA could be convert the unprotected ketone functionality to a conventional enolate. After reaction of the conventional enolate moiety, the products could then be treated with HCl (or an ammonium chloride) to convert the Ti-enolate back to the ketone, and in the process generate $\text{Cp}^*_2\text{TiCl}_2$. The $\text{Cp}^*_2\text{TiCl}_2$ could then be recovered and converted back to **3** [21].

Experimental

General considerations

Due to the expense of the enolate **1**, most of the experiments were conducted on a very small scale in a nitrogen-filled glovebox (Braun MB-150 M). The solvents were dried and freshly distilled prior to use [22,23]. Phenol and mercuric chloride were sublimed prior to use. Dimethyloctyl ammonium chloride was prepared by reaction of the amine with aqueous HCl, followed by precipitation of the product, and purification by vacuum sublimation. Bromine, benzaldehyde, and methyl iodide were purified according to published procedures [23]. Iodine was used as received. Methyllithium, obtained as a solution in ether, was assayed immediately prior to use [24]. $\text{Cp}^*_2\text{Ti}(\text{Me})_2$ was prepared from $\text{Cp}^*_2\text{TiCl}_2$ according to the published procedure [21].

In order to aid in the identification of the various products of the reactions reported herein, authentic samples of some of the products were synthesized via independent routes. An authentic sample of **7** was synthesized via reaction of **3** with one equivalent of $\text{NMe}_2\text{Oct} \cdot \text{HCl}$. An authentic sample of $\text{Cp}^*_2(\text{Me})\text{Ti}(\text{OC}_6\text{H}_5)$ was synthesized from **3** and one equivalent of phenol. Reaction of **3** with an excess of phenol gave an authentic sample of $\text{Cp}^*_2\text{Ti}(\text{OC}_6\text{H}_5)_2$.

^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded using a JEOL GX-270 FT-NMR. Samples for NMR analysis were dissolved in C_6D_6 . NMR spectra were referenced to the δ 7.15 resonance of $\text{C}_6\text{D}_5\text{H}$. A summary of the ^1H NMR spectra of the products is presented in Table 1. For reactions between **1** and the various electrophiles, the amounts of the products were determined by comparison of the integrated intensities of their appropriate ^1H NMR resonances to the integrated intensity of a peak due to a measured amount of cyclohexane.

Synthesis of $\text{Cp}^*_2(\text{Me})\text{Ti}-\text{OC}(\text{Me})=\text{CH}_2$ (**1**)

Small-scale syntheses of Ti-enolates (0.1 mmol) from ketones and **3** have previously been described [10]. We have found that scale-up is relatively straightforward, as is illustrated by the large-scale (10 mmol) synthesis of **1**. In a nitrogen-filled glove box, a 250 mL flask was charged with 3.52 g $\text{Cp}^*_2\text{Ti}(\text{Me})_2$ (**3**, 10.1 mmol), 100 mL toluene, and 10 mL acetone (136 mmol). A magnetic stir bar was placed in the flask, which was then fitted with a condenser and an inert-gas adaptor. The flask was taken out of the glove box, and connected to a nitrogen line. The flask was immersed in a 115°C oil bath. After allowing the stirred solution to reflux for 24 hours, the solvent was removed *in vacuo*. The red orange residue was extracted with pentane. The pentane was removed to give **1** as dry, orange crystalline material which is ca. 97% pure (the major impurity being unreacted **3**) [10]. 3.67 g of the product (9.1 mmol of 97% pure product; 90% yield) were isolated. $^{13}\text{C}\{\text{H}\}$ NMR spectrum in C_6D_6 : δ 11.8 ($\text{C}_5(\text{CH}_3)_5$); 23.0 ($-\text{OC}(\text{CH}_3)=\text{CH}_2$); 44.1 ($\text{Ti}-\text{CH}_3$); 83.9 ($-\text{OC}(\text{CH}_3)=\text{CH}_2$); 120.7 (C_5Me_5); 165.9 ($-\text{OC}(\text{CH}_3)=\text{CH}_2$).

Note that the acetone used in this preparation must be of high purity, free from water and alcohols. Improper "purification" of acetone may actually increase the alcohol content [23,25]. If there is any suspicion that the ketone contains small amounts of water or alcohol it is best to run the reaction with a stoichiometric amount of the ketone. (Similarly, reactions with expensive ketones may be run

Table 1

Proton NMR data for some of the compounds cited in this paper; all spectra were collected in C_6D_6 and referenced indirectly to TMS via the δ 7.15 resonance of residual C_6D_5H ; a precise position for the *m*-hydrogens of $Cp^*_2(CH_3)Ti(OC_6H_5)$ could not be assigned due to overlap with the solvent peak

Compound	Assignment	δ
$Cp^*_2(Me)Ti-O(CH_3)C=CH_2$ (1)	$Ti-CH_3$	0.33 (s, 3H)
	$OC(CH_3)C=CH_2$	1.70 (s, 3H)
	$C_5(CH_3)_5$	1.79 (s, 30H)
	$OC(CH_3)C=CHH$	3.74 (s, 1H)
	$OC(CH_3)C=CHH$	3.84 (s, 1H)
$Cp^*_2(Cl)Ti-O(CH_3)C=CH_2$ (8)	$C_5(CH_3)_5$	1.86 (s, 30H)
	$OC(CH_3)C=CH_2$	1.91 (s, 3H)
	$OC(CH_3)C=CHH$	3.96 (s, 1H)
	$OC(CH_3)C=CHH$	4.05 (s, 1H)
$Cp^*_2(I)Ti-O(CH_3)C=CH_2$ (12)	$C_5(CH_3)_5$	1.94 (s, 30H)
	$OC(CH_3)C=CH_2$	1.99 (s, 3H)
	$OC(CH_3)C=CHH$	3.95 (s, 1H)
	$OC(CH_3)C=CHH$	4.01 (s, 1H)
$Cp^*_2(CH_3)TiCl$ (7)	$Ti-CH_3$	0.23 (s, 3H)
$Cp^*_2(CH_3)TiBr$ (9)	$C_5(CH_3)_5$	1.77 (s, 30H)
	$Ti-CH_3$	0.02 (s, 3H)
$Cp^*_2(CH_3)TiI$	$C_5(CH_3)_5$	1.90 (s, 30H)
	$Ti-CH_3$	0.29 (s, 3H)
$C^*_2TiCl_2$ (6)	$C_5(CH_3)_5$	1.88 (s, 30H)
$Cp^*_2TiBr_2$ (10)	$C_5(CH_3)_5$	1.83 (s, 30H)
$Cp^*_2TiI_2$ (13)	$C_5(CH_3)_5$	1.80 (s, 30H)
$Cp^*_2Ti(CH_3)_2$ (3)	$C_5(CH_3)_5$	2.06 (s, 30H)
	$Ti-CH_3$	-0.58 (s, 6H)
	$C_5(CH_3)_5$	1.73 (s, 30H)
$Cp^*_2(CH_3)Ti(OC_6H_5)$	$Ti-CH_3$	1.73 (s, 30H)
	$C_5(CH_3)_5$	0.51 (s, 3H)
	$C_5(CH_3)_5$	1.73 (s, 30H)
$Cp^*_2Ti(OC_6H_5)_2$	<i>o</i> -protons of $-OC_6H_5$	6.44 (d, 2H, $J = 7.7$ Hz)
	<i>p</i> -protons of $-OC_6H_5$	6.68 (t, 1H, $J = 7.5$ Hz)
	<i>m</i> = protons of $-OC_6H_5$	~ 7.15 (pseudo t, 1H, $J \sim 6$ Hz)
	$C_5(CH_3)_5$	1.81 (s, 30H)
	<i>o</i> -protons of $-OC_6H_5$	6.93 (d, 4H, $J = 7.7$ Hz)
	<i>p</i> = protons of $-OC_6H_5$	6.80 (t, 2H, $J = 7.2$ Hz)
	<i>m</i> = protons of $-OC_6H_5$	7.25 (pseudo t, 4H, $J \sim 7$ Hz)

stoichiometrically.) The product yields may be slightly lower than the 90% reported herein, but a purer product will be obtained.

Synthesis of $Cp^*_2(Cl)Ti-OC(Me)=CH_2$ (8)

A small flask was charged with 400 mg $Cp^*_2(Me)Ti-OC(Me)=CH_2$ (1, 1.00 mmol, 97% pure) and 266 mg $HgCl_2$ (0.98 mmol). 15 mL ether was then added and the solution was stirred. Within 2 minutes, the solution changed color from orange to red. After stirring a total of 10 minutes, 0.65 mL of a 1.50 M methyllithium solution was added. After stirring the solution for 5 minutes, the volatile components were removed *in vacuo*. The resulting dark residue was extracted with five 1 mL portions of hexane. The hexane extracts were combined and then filtered through Celite. The hexane was removed *in vacuo* to give 331 mg (0.81 mmol, 81%

Table 2

Distribution of products in the reactions of **1** with various electrophiles; the yields reported were determined by NMR spectroscopy, and are based on the amount of **1** originally present

Electrophile	Conditions ^a	Cp [*] ₂ (CH ₃)Ti (OCMe=CH ₂)	Cp [*] ₂ (X) Ti(CH ₃)	Cp [*] ₂ Ti(X) ₂	Cp [*] ₂ (X)Ti (OCMe=CH ₂)
NMe ₂ Oct·HCl	Ether, 1 h ^b	nd ^e	8%	51%	nd
	Ether, 24 h ^b	nd	20%	21%	nd
	Hexane, 1 h ^b	nd	16%	43%	nd
	Hexane, 24 h ^b	nd	20%	19%	nd
C ₆ H ₅ OH	Ether, 1 h	62%	12%	12%	nd
	Ether, 24 h	50%	11%	5%	nd
	Hexane, 1 h	75%	12%	5%	nd
	Hexane, 24 h	69%	20%	nd	nd
Br ₂	Ether, 1 h	nd	76%	nd	nd
	Hexane, 1 h	nd	68%	37%	nd
	Benzene- <i>d</i> ₆ , 1 h ^c	nd	60%	40%	nd
I ₂	Ether, 1 h	nd	nd	34%	66%
	Hexane, 1 h	71%	5%	5%	22%
	Benzene- <i>d</i> ₆ , 1 h ^d	nd	nd	33%	67%
CH ₃ I	Ether, 1 h	100%	—	—	—
C ₆ H ₅ CHO	Ether, 1 h	100%	—	—	—

^a Except where otherwise is indicated, all reactions were initially 0.010–0.012 *M* in **1**. ^b These solutions were 0.006 *M* in **1**. ^c This solution was 0.12 *M* in **1**. ^d This solution was 0.06 *M* in **1**. ^e None detected (less than 5%).

yield) of **8** as a red microcrystalline material. The proton NMR spectrum of **8** is included in Table 1.

Reaction of **1** with I₂ in C₆D₆

A 10 dram vial was charged with 35.2 mg of **1** (0.086 mmol, 95% pure) and 750 μ L C₆D₆. A second vial was charged with 22.9 mg I₂ (0.090 mmol) and 750 μ L C₆D₆. The I₂ solution was added to the solution containing **1**. 6.0 mg cyclohexane was added to the mixture and the solution was stirred, and then transferred to an NMR tube which was then sealed. A ¹H NMR spectrum was collected after one hour. The results of this reaction are summarized in Table 2.

Reaction of **1** with Br₂ in C₆D₆

A 10 dram vial was charged with 125.4 mg of **1** (0.305 mmol, 95% pure) and 1.50 mL of C₆D₆. A second vial was charged with 49.5 mg Br₂ (0.310 mmol) and 1.0 mL C₆D₆. The bromine solution was added to the solution of **1**, and the resulting mixture was stirred for 3 hours. 64.1 mg cyclohexane was added and the solution was filtered through a small plug of glass wool. The results of this reaction are summarized in Table 2.

General procedure used for the reactions of electrophiles with **1** and with **8** in ether and in hexane

Except where otherwise noted, the exactly the same procedure was used for each of these reactions. In each case, an analytical balance was used to determine the

exact amounts of **1** (or **8**), electrophile, and cyclohexane that were used. Except where noted, the ratio of electrophile to **1** fell within the range 0.88–1.02. A batch of **1** which was 95% pure was used in these experiments.

A 10 dram vial was charged with 0.061 ± 0.001 mmol (24.6–25.7 mg) of **1**. A small stir bar and 2.0 mL of solvent, either hexane or ether, were added. The solution was stirred to dissolve the organometallic. A separate vial was charged with 0.058 ± 0.005 mmol of the electrophile and 3.0 mL of the same solvent. The solution containing the electrophile was then added to the solution which contained **1**. After the indicated time, either 1 hour or 24 hours, the volatiles were quickly removed *in vacuo*. The dried residue was dissolved in 3 mL of C_6D_6 , and 12.0 ± 1.0 mg of cyclohexane was added. The solution was then filtered through a plug of glass wool and placed in an NMR tube. The 1H NMR spectrum was then collected. The amount of each product was determined by careful integration of the spectrum and comparison of the integrated intensities of the peaks due to the Cp^* protons of each product to integrated intensity of the cyclohexane peak. Unless otherwise noted, the results of these reactions are summarized in Table 2.

Reaction of 1 with Br_2 , I_2 , and C_6H_6OH in hexane and in ether. The general procedure was used without modification.

Reactions of 1 with $NMe_2Oct \cdot HCl$ in hexane and in ether. The electrophile was suspended in 8.0 mL of solvent. Otherwise, the general procedure was followed.

Attempted reaction of 1 with benzaldehyde in ether. 20.0 mg **1** (0.048 mmol) and 6.0 mg benzaldehyde (0.055 mmol) were used. In this case, the ratio of electrophile to **1** was 1.15. Otherwise, the general procedure was followed. NMR analysis indicated that 100% unreacted **1** remained after 1 hour.

Attempted reaction of 1 with CH_3I in ether. 21.4 mg of **1** (0.052 mmol) and 8.7 mg CH_3I (0.061 mmol) were used. In this case, the ratio of electrophile to **1** was 1.17. Otherwise, the general procedure was followed. NMR analysis indicated that 100% unreacted **1** remained after 1 hour.

Attempted reaction of 8 with CH_3I in ether. The general procedure was used without modification. NMR analysis indicated that 96% unreacted **8** remained after one hour.

Reaction of 8 with benzaldehyde in ether. The general procedure was used. NMR analysis revealed that 44% of the initial amount of **8** was still present after one hour, but 46% was converted to a new Cp^*_2Ti -containing product. Although we have not yet identified this product, we can rule out the possibility of this being the expected aldolate based on its proton NMR spectrum. 1H NMR of the product: δ 1.84 (s, $C_5(CH_3)_5$), no evidence of aromatic protons.

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