Catalytic reduction of benzoate esters and lactones in the presence of $PhMeSiH_2$ and a titanocene-based catalyst

Ronghua Shu, John F. Harrod, and Anne-Marie Lebuis

Abstract: $PhMeSiH_2$ reduces ethyl benzoate in the presence of a Cp_2TiMe_2 (Cp = η^5-cyclopentadienyl) catalyst to give $PhMeSi(OEt)(OCH_2Ph)$ (**1**). Small to moderate amounts of toluene are also produced, depending on the reaction conditions. Under 40 psi of H_2 the same reaction gives quantitative reduction of the ester to toluene. PhCHO is reduced, under the same conditions as the ester, to a mixture of $PhMeSi(OCH_2Ph)_2$ and toluene in proportions similar to that observed with the ester. A stoichiometric reaction of $PhMeSiH_2$, PhCOOEt, and Cp_2TiMe_2 resulted in the formation of known $[Cp_2Ti(OEt)]_2$ (**2**) in 75% isolated yield. A mechanism is proposed in which the C=O of the ester inserts into a Ti–H bond. A Ti-mediated transfer of the ethoxy group from the resulting (α-ethoxy)benzyloxytitanium intermediate to silicon produces PhMeSi(OEt)H and PhCHO. **1** is generated via hydrosilation of PhCHO by PhMeSi(OEt)H. Both β- and γ-butyrolactones react with $PhMeSiH_2$ in the presence of a catalytic amount of Cp_2TiMe_2 to produce copolymers -[O-PhMeSi-O$(CH_2)_3$CHR]$_n$- (R = H, **3**; R = Me, **4**) ($M_w \approx 1 \times 10^3$; $M_w/M_n \approx 1.3$). A mechanism analogous to that proposed for the ethyl benzoate reduction is proposed. A reaction of $PhMeSiH_2$ and γ-butyrolactone with a stoichiometric amount of Cp_2TiMe_2 in the presence of tetrahydofuran (THF) produces $Cp_2Ti(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ti(OC_4H_8)Cp$ (**5**) (65% isolated yield) whose structure is determined by X-ray crystallography.

Key words: hydrosilation, esters, lactones, titanocene, catalysis.

Résumé : En présence d'un catalyseur de Cp_2TiMe_2 (Cp = η^5-cyclopentadiényle), le $PhMeSiH_2$ réduit le benzoate d'éthyle en conduisant à la formation de $PhMeSi(OEt)(OCH_2Ph)$, **1**. Suivant les conditions expérimentales utilisées, il y a aussi formation de faibles quantités de toluène. À une pression de H_2 de 40 << psi >>, la même réaction conduit à une réduction quantitative de l'ester en toluène. Dans les mêmes conditions de réduction, le PhCHO fournit un mélange de $PhMeSi(OCH_2Ph)_2$ et de toluène dont les proportions sont semblables à celles observées avec l'ester. Une réaction stoechiométrique de $PhMeSiH_2$, PhCOOEt et de Cp_2TiMe_2 conduit à la formation du $[Cp_2Ti(OEt)]_2$, **2**, déjà connu, avec un rendement isolé de 75%. On propose un mécanisme dans lequel le C=O de l'ester s'insère dans une liaison Ti-H. Un transfert du groupe éthoxy, sous l'influence du Ti, de l'intermédiaire (α-éthoxy)benzoyloxytitane vers le silicium conduit à la formation de PhMeSi(OEt)H et de PhCHO. Le produit **1** est généré par le biais d'une hydrosilation du PhCHO par le PhMeSi(OEt)H. Les β- et γ-butyrolactones réagissent toutes les deux avec le $PhMeSiH_2$, en présence d'une quantité catalytique de Cp_2TiMe_2 pour conduire à la formation de copolymères -[O-PhMeSi-O$(CH_2)_3$CHT]$_n$- (R = H, **3**; R Me, **4**) ($M_w \approx 10^3$; $M_w/M_n \approx 1{,}3$). On propose un mécanisme semblable à celui suggéré pour la réduction du benzoate d'éthyle. Une réaction du $PhMeSiH_2$ avec la γ-butyrolactone et une quantité stoechiométrique de Cp_2TiMe_2 dans du tétrahydrofurane (THF) conduit à la formation de $Cp_2Ti(\mu\text{-}H)(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)Ti(OC_4H_8)Cp$, **5** (rendement de 65% en produit isolé) dont on a déterminé la structure par diffraction des rayons X.

Mots clés : hydrosilation, esters, lactones, titanocène, catalyse.

[Traduit par la Rédaction]

Introduction

Titanocene derivatives have been widely applied as catalysts for the hydrogenation and hydrosilation of carbonyl compounds (1). Hydrosilation of ketones (2) has received the most attention, but Buchwald and co-workers have also developed procedures for the reduction of both lactones (3) and esters (4). A variety of esters, including those containing bromo-, phenoxy-, amino-, alkenyl- or cyclopropyl-groups, as well as α,β-unsaturated esters, can be reduced with triethoxysilane and catalytic amounts of titanocene dichloride, preactivated with butyllithium (4*a*). This procedure can also be used for the selective reduction of methyl esters in the presence of *tert*-butyl esters. For substrates containing a terminal olefin, or an epoxide, a more hindered titanocene dichloride species, such as ethylene-1,2-bis(tetrahydroindenyl)titanium dichloride ([EBTHI]$TiCl_2$), is required. Other procedures involving safer and cheaper reagents, such as poly(methylhydrosiloxane) instead of $(EtO)_3SiH$ and EtMgBr instead of *n*-BuLi, were also reported (4*c*).

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Most of the reported work on the hydrosilation of esters and lactones, catalyzed by titanocene derivatives, has been focused on its use for synthesis of alcohols, while little is known of the mechanism or the nature of the intermediates in the reactions. On the other hand, our interest in hydrosilation chemistry has been focused on the organosilicon products and the titanocene intermediates (5). In the present paper, we describe a detailed analysis of the intermediates and products for some titanocene catalyzed hydrosilations of esters and lactones. The results of these studies provide the first direct evidence for the participation of Cp_2Ti in a catalytic hydrosilation reaction catalyzed by Cp_2TiMe_2. Our interest in these reactions evolved from an earlier study of hydrosilation–hydrogenation of pyridine carboxylic esters (6).

Results and discussion

Reduction of ethyl benzoate under hydrosilation conditions

To remove the complications arising from the presence of the ring nitrogen in isonicotinate esters, we re-investigated the reduction of ethyl benzoate under hydrosilation conditions (eq. [1] — this equation is not balanced but shows the observed reactants and products). Under most conditions studied, benzyloxysilane (**1**) was the major product. Toluene was generally a minor product, but was the only product when the reaction was carried out under a hydrogen atmosphere.

$$[1]\quad \text{PhCOOEt} + \text{PhMeSiH}_2 \xrightarrow{\text{Cp}_2\text{TiMe}_2} \underset{\mathbf{1}}{\text{MePhSi(OCH}_2\text{Ph)(OEt)]}} + \text{PhMe}$$

The results of a number of reactions carried out under a range of conditions are summarized in Table 1. It is difficult to derive any conclusion from the results under Ar due to the scatter in the data. Nevertheless, it is reasonable to conclude that the C–O bond reduction is favored by higher temperatures and by the presence of H_2.

An isolated sample of **1** did not react with $PhMeSiH_2$ in the presence of Cp_2TiMe_2. Reactions of benzaldehyde and anisole were also briefly studied as substrates for the reaction with $PhMeSiH_2$ in the presence of Cp_2TiMe_2. A reaction of benzaldehyde at room temperature for 1 h, with a ratio of $PhCHO–PhMeSiH_2–Cp_2TiMe_2$ of 1:2:0.15, gave roughly equal amounts of $PhMeSi(OCH_2Ph)_2$ and $PhCH_3$. Under the same conditions, anisole gave only a trace of product ($PhCH_3$, ca. 0.5%). After an additional 4 h at 60°C, the yield of $PhCH_3$ increased to ca. 10%.

A reaction of $PhMeSiH_2$, PhCOOEt, and Cp_2TiMe_2 in a molar ratio of 2:1:1 gave a 75% isolated yield of the known ethoxy titanocene(III) dimer, $[Cp_2Ti(OEt)]_2$ (**2**, ref. 7). This pale green complex reacts slowly with $PhMeSiH_2$ at room temperature to give a blue product that exhibits a catalytic activity similar to that of Cp_2TiMe_2 for reduction of PhCOOEt to **1**, but with no detectable production of toluene.

Reactions of lactones with $PhMeSiH_2$ and Cp_2TiMe_2

Both γ- and β-butyrolactone reacted with $PhMeSiH_2$ in the presence of a Cp_2TiMe_2 catalyst to yield the ring-opened copolymers **3** (eq. [2]) and **4** (eq. [3]), respectively.

Table 1. Yields of toluene from reactions of ethyl benzoate with $PhMeSiH_2$ and Cp_2TiMe_2 under various conditions.

Cp_2TiMe_2/PhCOOEt (%)	*T* (°C)	Yield of toluene (%)^a
5	20	5
10	20	10
20	20	19
30	20	11
40	20	13
10	0	2
20^b	20	4
20^c	20	3
20	40	40
20^d	40	100

Note: Except where indicated, reactions were run under Ar with 10 mol% catalyst, based on $PhMeSiH_2$. All reactants were added to the reactor at the same time. Conversions were quantitative and the balance of the product was **1**.

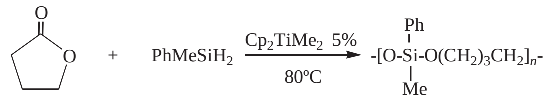
[a] Based on ^1H NMR integration.

[b] Ethyl benzoate was added dropwise after the reaction of $PhMeSiH_2$ and Cp_2TiMe_2 was complete.

[c] $PhMeSiH_2$ (0.10 mL, 0.7 mmol) was added to the mixture of Cp_2TiMe_2 (0.088 g, 0.43 mmol) and ethyl benzoate (0.30 mL, 2.13 mmol). After the solution color changed from orange to dark violet blue an additional 0.50 mL of $PhMeSiH_2$ was added dropwise to the mixture.

[d] The reaction was run under 40 psi H_2.

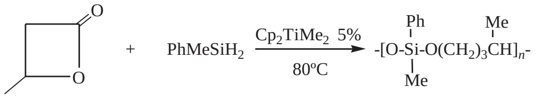
[2]



$$-[\text{O-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{Si}}}\text{-O(CH}_2)_3\text{CH}_2]_n\text{-}$$

3

[3]



$$-[\text{O-}\underset{\text{Me}}{\overset{\text{Ph}}{\text{Si}}}\text{-O(CH}_2)_3\overset{\text{Me}}{\text{CH}}]_n\text{-}$$

4

The polymers were recovered in ca. 30% yields, as amorphous white solids, by precipitation of the reaction mixtures with excess methanol. Molecular weights, determined by GPC, were in the range of 2–4 × 10^3 D, with polydispersities in the range of 1.2–1.3. The balance of the reaction products was not fully characterized, but from their IR and NMR spectra appeared to be a mixture of lower molecular-weight oligomers of the same structure as the isolated solid.

Stoichiometric reactions of Cp_2TiMe_2, $PhMeSiH_2$, and either γ- or β-butyrolactone, in a molar ratio of 1:2:1 in hexane–THF (15:2 v/v), yielded dark grayish-brown crystals. Given the reaction of ethyl benzoate, described above, and the known oxophilicity of Ti, a product containing Ti–O bonds was expected. To our surprise, a structure determination by X-ray crystallographic analysis showed the product to be **5** (Fig. 1).

Molecule **5** contains two inequivalent Ti atoms. One, Ti1, is coordinated to a η^5-C_5H_5 ligand, a bridging η^5-C_5H_4 ligand, and a THF molecule. The other, Ti2, is η^1-bonded to the bridging C_5H_4 ligand and to two η^5-C_5H_5 ligands. More importantly, a hydrogen-atom bridge, located in the difference map, connects the two Ti atoms. The mean distance

Fig. 1. The structure of **5**, showing thermal ellipsoids at the 30% probability level.

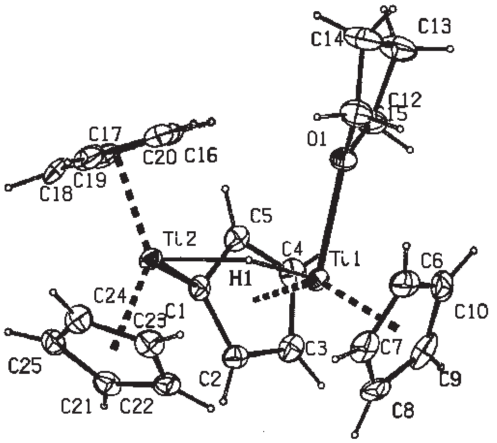


Table 2. A comparison of some selected molecular parameters for compounds **5** and **5′**.

5		**5′**	
Bond lengths (Å)			
Ti1—O1	2.239(3)	Ti1—O1	2.26(1)
Ti1—Ti2	3.329(2)	Ti1—Ti2	3.363(2)
Ti2—C1	2.207(5)	Ti1—C5	2.19(2)
Ti1—C1	2.325(5)	Ti1—C1	2.34(2)
Ti1—C2	2.307(5)	Ti1—C5	2.32(2)
Ti1—C3	2.363(5)	Ti1—C4	2.32(2)
Ti1—C4	2.365(5)	Ti1—C3	2.37(2)
Ti1—C5	2.333(5)	Ti1—C2	2.37(2)
Ti1—(C6–10)	2.3796[a]	Ti1—(C10–14)	2.38
Bond angles (deg)			
Ti2-Ti1-O1	95.65(10)	Ti2-Ti1-O1	96.1(30)
Ti2-C1-C5	125.3(4)	Ti2-C5-C1	125.6(12)
Ti2-C1-C2	123.3(3)	Ti2-C5-C4	124.2(13)

Note: The numbering schemes for the two structures are slightly different. Those for **5′** are those used in ref. 8.

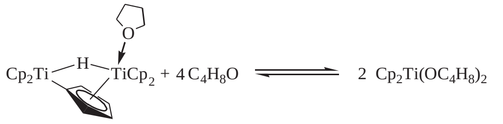
[a] These values are the average values for the five Ti–C distances of the η^5-C_5H_5 ring attached to Ti2.

between the titaniums and the carbon atoms of the η-C_5H_5 rings (2.388 Å) and the distance between C1 and Ti1 (2.207(5) Å) agree with the assignment that three of the C_5 rings are coordinating to Ti1 and Ti2 in η^5-mode, while the fourth bridging ring is coordinating η^5 to Ti1 and η^1 to Ti2. The formula of **5** ($C_{24}H_{28}OTi_2$) corresponds to a dimer of Cp_2Ti coordinated to a molecule of THF. The crystal structure also reveals that in the lattice there is half a molecule of THF per formula unit of **5**.

The values of the molecular parameters for **5** (a number of which are compared in Table 2) are essentially the same as those reported by Pez (8) for compound **5′**, which differed only in the absence of the hydride bridge. We believe these compounds to be the same. Small differences in the parameter values are attributed to the fact that our data were collected at –60°C, while those of Pez were collected at 23°C. In addition, our measurements were carried out with Cu Kα radiation in order to favour detection of the hydride, while Pez used Mo Kα radiation. In a preliminary study, we also failed to detect the bridging hydride using Mo Kα radiation. Finally, there is a slight difference due to the fact that the Pez structure is reported in the monoclinic space group *I*2/*a*, which is a non-conventional orientation of the *C*2/*c* group used by us.

Solutions of **5** in THF are strongly paramagnetic. NMR spectra of such solutions are very broad and strongly shifted, and give essentially no clue to the structure. Their EPR spectra also consist of a very broad single peak, which gives no structural information. Pez also concluded that his compound was paramagnetic on the basis of the temperature dependence of the ^{1}H NMR chemical shift. The originally proposed structure, without a bridging hydrogen atom, is an odd- electron count system and therefore would be expected to have one unpaired electron. Addition of the bridging hydrogen atom results in an even-electron count and the molecule is expected to be diamagnetic. A simple rationalization of these observations is that **5** dissociates in the weakly coordinating THF solvent to give a titanocene(II) complex (**6**), as in eq. [4]. Although Cp_2TiL_2 complexes are well known for strong-field ligands such as PR_3 (9) and CO (10), the ground states of such complexes are normally spin singlets. The bipyridyl complex is unusual, in that it has a spin-triplet ground state, interpreted to be the result of a Ti(III) coordinated to a bipyridyl radical anion ligand (11). It is not unreasonable however to assume that a Ti(II)-centered triplet ground state could be preferred with a σ-bonding weak-field ligand such as THF that coordinates through O. Indeed, both theoretical (12) and experimental (13) results support the conclusion that the ground state of *uncomplexed* Cp_2Ti is a triplet. We are continuing to study the magnetochemistry and EPR properties of solutions of **5** in order to resolve this question.

[4]



5 **6**

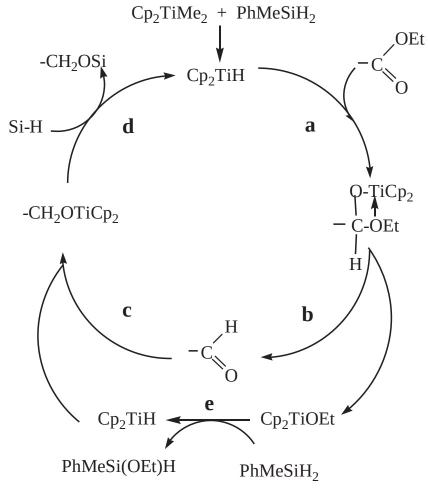
The two titanium atoms in **5** can be formally assigned either as Ti(II) and Ti(IV), or both as Ti(III). This oxidation-state ambiguity, and the structural motif of a hydride bridge accompanying another more-complex bridging group, is now a common feature of titanocene chemistry (6, 14–16).

The mechanism of ester hydrosilation–reduction

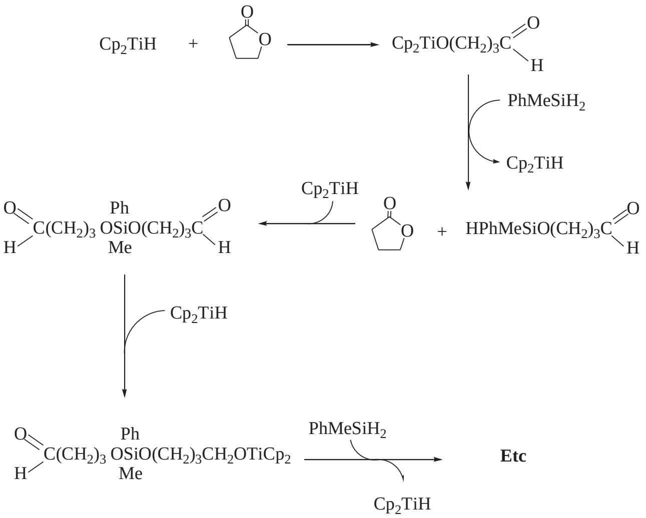
Earlier studies of hydrosilation–reduction of esters (17) and lactones (18) in the presence of titanocene-based catalysts were carried out from the perspective of their usefulness in organic synthesis. In no case was the intermediate organosilicon compound identified or isolated. Nevertheless, a reasonable mechanism involving addition of a Ti–H bond across the carbonyl group, followed by release of the alkoxy silicon product was proposed. A similar mechanism is shown in Scheme 1.

The cycle shown in Scheme 1 rationalizes all of the features of the hydrosilation reaction. There is ample evidence from earlier studies for the generation of Cp_2TiH by reaction of Cp_2TiMe_2 with a hydrosilane (5*a* and refs. therein). Step **a** is a plausible insertion of C=O into a Ti–H bond. The

Scheme 1. A catalytic cycle for the hydrosilation of benzoate esters.



Scheme 2. A cycle for the titanocene-hydride catalyzed co-polymerization of γ-butyrolactone–$PhMeSiH_2$.



observation that a stoichiometric reaction of Cp_2TiMe_2, $PhMeSiH_2$, and PhCOOEt gives **2** in high yield is explained by the assumption that the initially formed (1-phenyl-1-ethoxy)methoxy titanocene is unstable with respect to transfer of the ethoxy group to the Ti, perhaps by an initial intramolecular coordination of the EtO oxygen to the metal. The intermediate benzaldehyde was not detected under catalytic conditions, perhaps because of an additional rapid reaction. It was however shown that benzaldehyde is reduced under these conditions to give $PhMeSi(OCH_2Ph)_2$ (presumably by step **c**) and toluene in proportions similar to those observed in the reaction with PhCOOEt. For the benzaldehyde reaction, there is no possibility of EtO transfer to the Si and hence it raises the question as to why the observed product in the ester reaction (step **d**, Scheme 1) is $PhMeSi(OEt)(OCH_2Ph)$ rather than $PhMeHSi(OCH_2Ph)$, or $PhMeSi(OCH_2Ph)_2$. A problem is also presented by the fact that $PhMeSiH_2$ does react with $[Cp_2Ti(OEt)]_2$ (step **e** Scheme 1), and the latter is also a precatalyst for the hydrosilation of PhCOOEt. Neither of these reactions, however, are fast enough to account for the rate of the Cp_2TiMe_2 catalyzed hydrosilation of PhCOOEt.

Both of these problems would be resolved if the slowness of the reaction of **2** with $PhMeSiH_2$ was due to a slow dissociation of the dimer, which masks the intrinsic reactivity of monomeric $Cp_2Ti(OR)$. The assumption of the production of a highly reactive monomeric $Cp_2Ti(OEt)$ in step **c** permits the rapid recycling of this intermediate through loop **d**, to allow for the transfer of the EtO group to silicon and regeneration of the catalyst, Cp_2TiH. Finally, once the reaction is underway, the Si–H in the σ-bond metathesis in step **d** would have to be mainly PhMe(EtO)SiH, rather than $PhMeSiH_2$.

Although the steps in the catalytic loop of Scheme 1 can explain the features of the hydrosilation reaction of PhCOOEt, they fail to explain the complete reduction (deoxygenation) to toluene. The fact that toluene is the only product when the reaction is carried out under moderate pressure of H_2 suggests that high concentrations of Ti–H favour complete deoxygenation. Reactions of hydrosilanes with Cp_2TiMe_2 produce a mixture of $CpTiSiR_3$ and Cp_2TiH, which have been isolated and characterized as bridged dimers (5*b*, 15). The balance between the amounts of silyl and hydride complexes is a function of the silane concentration, with the silyl species being favored by high silane concentration. It is also likely that H_2 is in equilibrium with these species as shown in eq. [5] (although this has never been unequivocally demonstrated). The fact that $PhMeSi(OEt)(OCH_2Ph)$ does not react under the catalytic reduction conditions excludes it as an intermediate in the production of toluene. On the other hand, the similarity of the products from the PhCOOEt and PhCHO reductions suggests that $Cp_2Ti(OCH_2Ph)$ is a plausible intermediate in the production of toluene.

$$[5]\quad Cp_2TiH + R_3SiH \rightleftharpoons Cp_2TiSiR_3 + H_2$$

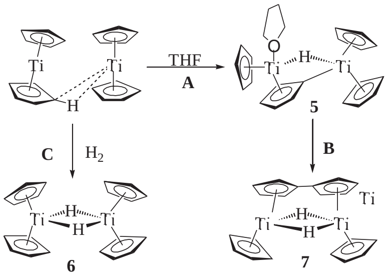
The mechanism of lactone–silane co-polymerization

A plausible mechanism for the titanocene-hydride mediated co-polymerization of γ-butyrolactone and $PhMeSiH_2$ is shown in Scheme 2. This scheme couples two of the steps proposed in Scheme 1 for the reduction of ethylbenzoate; namely, the addition of Cp_2TiH to an aldehyde and a σ-bond metathesis between Ti–O and Si–H to give Si–O and Ti–H. In this case the ring-opening step is an intramolecular version of steps **a** and **b** in Scheme 1. In the lactone reactions no cleavage of C–O bonds was observed.

The mechanism of formation of 5

Compound **5** is expected to be formed from the dimerization of bis(η^5-cyclopentadienyl)Ti. The manner in which the latter species may be generated by reaction of Cp_2TiMe_2 with a hydrosilane has been discussed at length elsewhere (5*b* and refs. therein). It is our belief that titanocene(II), or its dimer (**5**) is normally present in reactions involving Si–H and Cp_2TiMe_2, but its detection in solution is precluded by its electronic structure. (Its paramagnetism interferes with NMR measurements and a triplet ground state can be very difficult to observe by EPR.)

Scheme 3. In **A**, one molecule of Cp_2Ti inserts into a C–H bond of a second molecule. In **B**, a second intramolecular insertion of Ti into a C–H bond of the Cp_2Ti unit of **5** occurs, followed by coupling of the two C_5H_4 fragments. In **C**, a molecule of H_2 reacts with two Cp_2Ti molecules, perhaps by initial formation of the Cp_2TiH_2, followed by reaction with the second Cp_2Ti molecule.



It has also been postulated that titanocene, as a result of its carbene-like character, will insert into X–H bonds and, in the absence of other choices, it will insert into one of its own C–H bonds (19). Pez (8) recognized this possibility when he first isolated and characterized **5**. A second similar-intramolecular insertion takes **5** to the hydride-bridged fulvalenyl dititanium complex (**7**), originally reported by Bercaw and co-workers (20) and structurally characterized by Troyanov et al. (21). The relationship between the various titanocene hydrides is shown in Scheme 3.

Conclusions

The titanocene-catalyzed hydrosilation of esters to the alkoxide level can be rationalized by a conventional Ti–H mediated reduction of the ester, followed by alkoxide transfer to Si. Further reduction to the hydrocarbon level occurs under unusually mild conditions, particularly in the presence of a hydrogen atmosphere. Although the mechanism is not known, it is likely that this reaction occurs via X–H (X = H or Ti) induced C–O cleavage of a benzyloxy-Ti complex.

Experimental

General manipulations and materials

All manipulations were performed under an atmosphere of nitrogen or argon using Schlenk techniques. Dry oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. γ-Butyrolactone and (±)-β-butyrolactone were purchased from Aldrich and distilled prior to use. Ethyl benzoate, benzaldehyde, and benzyl alcohol were purchased from Aldrich and purified by distillation over calcium hydride before use. Dimethyltitanocene (22) and phenylmethylsilane (23) were prepared by the procedures described in the literature.

Benzylmethyl ether was prepared by a Williamson synthesis using the following procedure: sodium (2.3 g, 0.1 mol) was added in small pieces to benzyl alcohol (11 g, 0.1 mol) in ether (50 mL). After the sodium had dissolved, CH_3I (16 g, 0.11 mol) was added dropwise from a syringe. A white solid precipitated during the addition of CH_3I. The suspension was stirred for 1 h and then dilute HCl (5 mL concentrated HCl in 30 mL H_2O) was added dropwise. The organic phase was washed with distilled water three times and then dried with $MgSO_4$. Pure benzylmethyl ether was obtained in 80% isolated yield by distillation.

^1H NMR spectra were recorded on a Varian XL-200, Varian XL-300, Gemini-200, or Unity-500 spectrometer using an internal solvent as a reference. ^{13}C NMR spectra were recorded on a Unity-500 spectrometer using C_6D_6 (128.0 ppm) as a reference. GPC analyses were run with THF as solvent and calibrated relative to polystyrene standards.

Reaction of ethyl benzoate with $PhMeSiH_2$ catalyzed by Cp_2TiMe_2

$PhMeSiH_2$ (0.20 mL, 1.4 mmol) and ethyl benzoate (0.10 mL, 0.70 mmol) were added to Cp_2TiMe_2 (14 mg, 0.07 mmol). After a while, the solution color changed to dark blue then brown with vigorous gas evolution. After stirring at room temperature for 1 h, quantitative conversion of ethyl benzoate to a mixture of toluene and **1** was observed by ^1H NMR (molar ratio 1:9). ^1H NMR (300 MHz, C_6D_6) for **1**: 0.34 (s, 3H, Si-CH_3), 1.15 (t, 3H, OCH_2CH_3), 3.70 (q, 2H, OCH_2CH_3), 4.78 (m, 2H, $PhCH_2O$-), 6.9–8.0 (m, Ph-*H*).

All of the experiments to obtain the data in Table 1 were carried out following the above general procedure, with the exception of the last entry, which was carried out in a stirred mini-autoclave rather than a Schlenk tube and with all of the reactants scaled up by a 10-fold.

Preparation of $[Cp_2Ti(\mu\text{-OEt})]_2$

$PhMeSiH_2$ (0.70 mL, 4.9 mmol) and ethyl benzoate (0.40 mL, 2.5 mmol) were added to a solution of Cp_2TiMe_2 (0.50 g, 2.4 mmol in 40 mL toluene and 10 mL benzene). The solution turned dark green with precipitation of green crystals of $[Cp_2Ti(\mu\text{-OEt})]_2$, which were filtered, washed with hexane, and dried in vacuo (0.40 g, 75% isolated yield). The identity of the product was confirmed by comparison of its IR spectrum and X-ray diffraction pattern to those of an authentic sample (7).

Reaction of ethyl benzoate and $PhMeSiH_2$ in the presence of $[Cp_2Ti(\mu\text{-OEt})]_2$

$PhMeSiH_2$ (0.34 mL, 2.60 mmol) was added to $[Cp_2Ti(\mu\text{-OEt})]_2$ (50 mg, 0.11 mmol). The mixture was stirred at room temperature for 24 h (during this time the formation of some 1,2-dimethyl-1,2-diphenyldisilane was observed by ^1H NMR). Ethyl benzoate (0.17 mL, 1.06 mmol) was then added. Gas evolution was observed in 5 min, while the solution changed from green to yellow-green. Conversion (86%) of the ester to **1** was obtained in 12 h. No toluene was detected by ^1H NMR.

Reaction of benzaldehyde and $PhMeSiH_2$ in the presence of Cp_2TiMe_2

$PhMeSiH_2$ (0.40 mL, 3.06 mmol) and benzaldehyde (0.20 mL, 1.97 mmol) were added to Cp_2TiMe_2 (55 mg, 0.28 mmol) at room temperature. After a while, the solution color changed to purple then dark blue accompanied by gas evolution. After 1 h toluene was observed in a 50% yield (based on ester, by ^1H NMR). The reaction mixture was diluted with C_6D_6 (1.0 mL) and saturated with gaseous HCl to destroy the presumed $Cp_2Ti(OCH_2Ph)$. Volatiles were removed under vacuum and collected in an NMR tube. The resulting mixture contained toluene and $PhCH_2OH$ in roughly equal amounts, as shown by spiking the mixture with authentic samples.

Reaction of $PhCH_2OMe$ and $PhMeSiH_2$ in the presence of Cp_2TiMe_2

$PhMeSiH_2$ (0.60 mL, 4.20 mmol) and $PhCH_2OMe$ (0.30 mL, 2.46 mmol) were added to Cp_2TiMe_2 (0.10 g, 0.48 mmol). The solution color changed from orange to dark blue, accompanied by gas evolution. After stirring at 60°C for 4 h, toluene was detected in the solution by ^1H NMR in an amount equivalent to 10% of the reactant ether.

In the absence of Cp_2TiMe_2, reactions of $PhCH_2OMe$ with $PhMeSiH_2$ or $(EtO)Me_2SiH$ at 60°C for 12 h yield no toluene.

Reaction of γ-butyrolactone and $PhMeSiH_2$ catalyzed by Cp_2TiMe_2

γ-Butyrolactone (0.30 mL, 3.9 mmol) and $PhMeSiH_2$ (0.60 mL, 4.2 mmol) were added to a solution of Cp_2TiMe_2 (0.05 g, 0.24 mmol in 1 mL THF). After thorough mixing, the solution was stirred for 10 h at 80°C. The product was added dropwise to 10 mL of well-stirred dry methanol; 0.3 g of a white precipitate were obtained. The compound was assigned as $\text{-[OSiPhMeO(CH}_2)_4]_n$- based on ^1H and ^{13}C NMR spectra. GPC analysis indicated a $M_w = 4.9 \times 10^3$, $M_w/M_n = 1.3$. ^1H NMR (300 MHz, C_6D_6) δ: 0.40 (s, 3H, Si-CH_3), 1.7 (m, 4H, $CH_2(C\mathit{H}_2)_2CH_2$), 3.75 (m, 4H, $C\mathit{H}_2(CH_2)_2C\mathit{H}_2$), 7.0–8.0 (m, 5H, Ph-*H*). ^{13}C NMR (500 MHz, C_6D_6) δ: –5 (1C, Si$\mathit{C}H_3$), 29 (2C, $CH_2(\mathit{C}H)2CH$), 62 (2C, $\mathit{C}H_2(CH_2)_2\mathit{C}H_2$), 130, 134 (6C, C_6H_5).

Reaction of (±)-β-butyrolactone and $PhMeSiH_2$ in the presence of Cp_2TiMe_2

(±)-β-Butyrolactone (0.30 mL, 3.7 mmol) and $PhMeSiH_2$ (0.55 mL, 3.8 mmol) were added to a solution of Cp_2TiMe_2 (0.05 g, 0.24 mmol, in 1 mL THF). After thorough mixing, the solution was stirred for 8 h at 80°C. The product was added dropwise to 10 mL of well-stirred methanol. A white precipitate (0.28 g) was obtained. The compound was identified as $\text{-[OSiPhMeO(CH}_2)_2CH(CH_3)]_n$- based on its ^1H NMR spectrum. GPC analysis indicated a $M_w = 1.8 \times 10^3$ with $M_w/M_n = 1.2$. ^1H NMR (300 MHz, C_6D_6) δ: 0.40 (s, 3H, Si-CH_3), 1.1 (m, 3H, $CH_2CH_2CH(C\mathit{H}_3)$), 1.4 (m, 2H, $CH_2C\mathit{H}_2CH(CH_3)$), 3.6 (m, 2H, $C\mathit{H}_2\ CH_2CH(CH_3)$), 3.9 (m, 1H, $CH_2CH_2C\mathit{H}(CH_3)$), 7.1–7.9 (m, 5H, Ph-*H*).

Sythesis of crystalline $C_{26}H_{32}O_{1.5}Ti_2$ (5)

γ-Butyrolactone (0.02 mL, 0.26 mmol) and $PhMeSiH_2$ (0.07 mL, 0.49 mmol) were added to a Cp_2TiMe_2 in hexane–THF solution (50 mg, 0.24 mmol, in 15 mL hexane and 2 mL THF). After thorough mixing, the flask was left undisturbed for 24 h. Dark gray plates of **5** (33 mg) crystallized from the solution (65% isolated yield). Anal. calcd. for $C_{26}H_{32}O_{1.5}Ti_2$: C 67.86, H 6.96, O 4.35, Ti 20.84; found: C 67.58, H 6.75. The low CH analysis is probably due to loss of lattice THF during sample isolation. The IR spectrum of **5** showed the same features as that of the compound described by Pez (8). Despite several attempts, we were not able to assign an IR band due to the bridging hydride of **5**, or to its deuterated analogue, prepared with $PhMeSiD_2$.

Collection of X-ray data and structure determination of 5

Data were collected on a crystal of **5** of dimensions of 0.52 × 0.29 × 0.01 mm mounted in a glass capillary under argon.[2] *Crystal data*: $C_{24}H_{28}O_1Ti_2\cdot 1/2C_4H_8O_1$; FW = 456.299; monoclinic, $C2/c$; $a = 31.232(13)$, $b = 7.998(3)$, $c = 19.603(9)$ Å, $\beta = 116.78(3)°$; $Z = 8$, $Z' = 1$; $D_c = 1.387$ g cm^{-3}. Data were collected on a CAD4 diffractometer using Cu Kα radiation. In all, 29561 reflections were measured, of which 4145 unique (R_{int} 14.9%) reflections were used for structure solution and refinement. Data were corrected for absorption ($\mu = 63.48\ cm^{-1}$; transmission range: 0.2708–0.9287). Final agreement factors: R_1: (obsd./all) 0.059/0.094; wR_2: 0.143/0.157. The structure was solved by SHELXLS-96 (24) and refined in SHELXL-96 (25). All nonhydrogen atoms are anisotropic. Hydrogen atoms are calculated except the bridging hydride, which was located in the difference map and refined isotropically with the restraint that both Ti–H distances be similar.

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[2] Supplementary material may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. For information on obtaining material electronically go to http://www.nrc.ca/cisti/irm/unpub_e.shtml. Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 169316). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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