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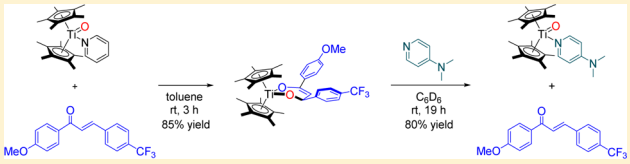
Synthesis, Cycloaddition, and Cycloreversion Reactions of Mononuclear Titanocene−oxo Complexes

Trang T. Nguyen, Gregory D. Kortman, and Kami L. Hull*

Department of Chemistry, University of Illinois at Urbana−Champaign, 600 S. Mathews Avenue, Urbana, Illinois 61801, United States

Supporting Information

ABSTRACT: Titanocene−oxo complexes of the type $Cp^x_2Ti{=}O(L)$ (Cp^x = pentamethylcyclopentadienyl; tetramethylcyclopentadienyl; L = pyridine or derivatives) are synthesized from the corresponding titanocene−ethylene complexes via oxidation with pyridine *N*-oxides or styrene oxide. These oxo complexes react with alkynes, nitriles, and α,β-unsaturated carbonyls to form titanacycles, which undergo exchange reactions with organic substrates or react with 4-dimethylaminopyridine to regenerate the titanocene−oxo. Mechanistic experiments support a dissociative mechanism in which the first step is rate-determining retrocycloaddition followed by trapping of the reactive $[Cp^x_2Ti{=}O]$ species. In the case of the retro-[4+2]-cycloaddition from dioxatitanacyclohexene complexes, a Hammett study gives ρ values of −1.18 and −1.04 for substituents on two different phenyl rings on the metallacycles, suggesting positive charge buildup and a slightly asynchronous cycloreversion in the rate-determining step.



INTRODUCTION

α,β-Unsaturated aldehydes and ketones are both prominent functionalities in and synthetic precursors for pharmaceuticals, natural products, and organic materials.[1−3] Olefination reactions are powerful methodologies for the synthesis of enones; unfortunately, these reactions often require several synthetic steps to access the requisite starting materials and generate stoichiometric waste.[4] The goal of the research presented herein was to develop a new transition-metal-catalyzed cross-coupling reaction for the synthesis of α,β-unsaturated carbonyls from readily available building blocks without the generation of any stoichiometric byproducts in a redox-neutral, atom-economical process.[5] This should be possible by employing a cycle that uses a Ti/Zr=O catalyst to couple a carbonyl with an alkyne, through (i) [2+2]-cycloaddition between the M=O and an alkyne, (ii) insertion of carbonyl into the M−C bond, and, finally, (iii) [4+2]-retrocycloaddition, releasing the α,β-unsaturated carbonyl product and regenerating the M=O catalyst (Figure 1). As the starting materials are already at the requisite oxidation states, the reaction will not require either a stoichiometric oxidant or reductant.

Titanium− and zirconium−imido complexes have shown great utility in both stoichiometric and catalytic reactions. However, similar reactivity with related Ti=O or Zr=O complexes has been relatively underdeveloped. There are many reports for the synthesis of both Ti− and Zr−oxo complexes, which are unstable to isolation, as they are prone to undergo oligomerization to generate μ-oxo products. Therefore, they are generally trapped by the addition of a Lewis basic ligand, such a pyridine, or a substrate that can undergo reaction with the M=O, such as an alkyne or carbonyls, to generate stable

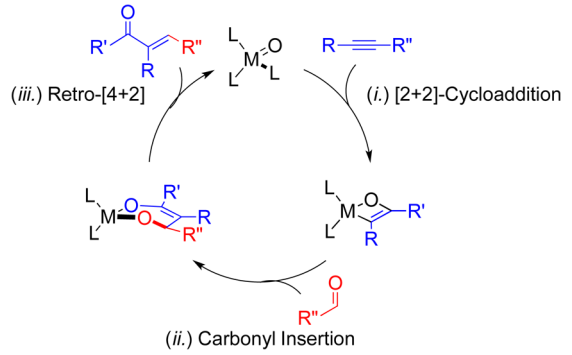


Figure 1. Proposed metal−oxo-catalyzed alkyne−aldehyde coupling reaction.

metallacyclic intermediates. When the Cp* ligand is replaced with the relatively small Cp ligand, dimeric products of the oxometallacyclobutene are observed. Alternatively, it has been shown that sterically encumbering ligands inhibit Ti=O oligomerization and crystal structures of the free [Ti]=O have been obtained.

Recently, we demonstrated each of the steps of our proposed catalytic cycle with a $Cp^*_2Zr{=}O$ complex.[6] Unfortunately, catalytic turnover was not achieved, as the final step, retro-[4+2]-cycloaddition was reversible and thermodynamically disfavored. Further, the aldehyde coupling partner was not stable to the high reaction temperatures required for the retro-[4+2] (150 °C). As such, we were interested in investigating each of the proposed steps with Ti−oxo complexes, as the

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shorter Cp*−Ti bond length may promote the desired retrocycloaddition, as it would be releasing steric strain.

The few known monometallic titanium−oxo complexes have been synthesized with bulky, stabilizing ligands including tetraaza[14]annulene[7,8] and pentasubstituted cyclopentadienyl.[9,10] In addition to their propensity to react with water, it has been reported that these complexes undergo [2+2]-cycloadditions with alkynes and allenes.[11−13] In contrast, the isoelectronic titanium−imido complexes have been used in a number of catalytic reactions.[14−17] Key steps in these catalytic cycles are cycloaddition and cycloreversion involving the Ti═N multiple bond. Cycloreversion has been proposed in reactions of oxatitanacyclohexenes[18] and oxatitanacyclobutenes,[12] but these processes have not been studied in detail. In order to develop the proposed titanocene−oxo-mediated alkyne−aldehyde coupling reaction, it is important to understand the cycloaddition and cycloreversion reactivity of these complexes.

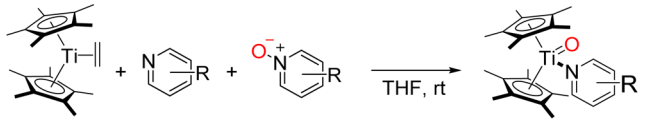
Herein, we report our stoichiometric investigation toward the development of a Ti═O-catalyzed alkyne−aldehyde coupling reaction. Concurrently, we also investigated the overall reactivity of Ti═O complexes and demonstrate an improved synthesis of titanocene−oxo complexes, metallacycle formation reactions of these oxo complexes with unsaturated organic compounds, and mechanistic studies on the retrocycloaddition reactions.

RESULTS AND DISCUSSION

Synthesis of Titanocene−oxo Complexes. Our initial investigations of the proposed alkyne−aldehyde coupling reaction studied the reactivity of $Cp^*_2Ti{=}O$ and $Cp'_2Ti{=}O$ complexes (Cp^*_2 = pentamethylcyclopentadienyl; Cp'_2 = tetramethylcyclopentadienyl). $Cp^*_2Ti{=}O(py)$ (py = pyridine) is a known complex that has been demonstrated to participate in the proposed [2+2]-cycloaddition with both alkynes and allenes; however the reactivity of the resulting oxatitanacyclobutenes is unknown. Additionally, the related $Cp'_2Ti{=}O$ complex was sought, as the Ti═O is slightly less hindered and may be more reactive.

The pyridine-stabilized titanocene−oxo complex $Cp^*_2Ti{=}O(py)$ was first prepared via oxidation of the corresponding titanocene−ethylene complex with nitrous oxide in 59% yield.[7] In our previous report on the reactivity of oxatitanacyclobutenes prepared from titanocene−oxo,[19] attempts to reproduce this result were complicated by impurities in the nitrous oxide gas, which led to low yields (30−40%) in our hands. Given these results we sought to employ more conventional reagents to affect the oxidation of the titanocene−ethylene complex. Pyridine *N*-oxide is a readily available oxidant that is used in a number of catalytic oxidation reactions involving metal−oxo complexes.[20] Further, purification and quantification of this crystalline solid is facile relative to gaseous nitrous oxide. Previously, it was reported that pyridine *N*-oxide oxidizes a titanium−dinitrogen complex, supported by benzamidinate ligands, to the corresponding titanium−oxo. The product was isolated in moderate yield (37%) and contains a coordinated *N*-oxide ligand, even in the presence of pyridine.[21] The oxidation of $Cp^*_2Ti(CH_2CH_2)$ (**1**) (1.0 equiv) with pyridine *N*-oxide (1.0 equiv) in the presence of pyridine (2.0 equiv) produced oxo complex **2a** in 80% isolated yield. Similarly, 3,5-lutidine *N*-oxide was an effective oxidizing reagent for this transformation, generating oxo complex **2b** in 84% isolated yield (Scheme 1).

Scheme 1. Synthesis of Titanium−oxo Complexes 2a and 2b via Oxidation with Pyridine N-Oxides



1

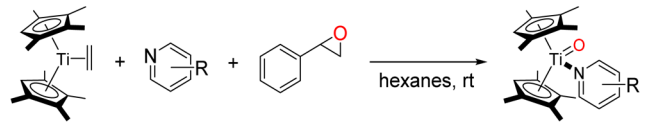
2a 80% **2b** 84%

2a: R = H
2b: R = 3,5-$(CH_3)_2$

We found that the stoichiometry of reagents was critical. Excess oxidant gave rise to byproducts, including titanium μ-oxo clusters,[9,22] which were difficult to separate from **2a** or **2b**. The use of *N*-oxide without added pyridine generated a number of byproducts and very low yield of the terminal oxo. This suggests that a high concentration of pyridine is required to increase the rate of the formation of **2a** relative to the oligomerization. Finally, replacing pyridine with 2-picoline and 2,6-lutidine did not afford the desired products, presumably due to steric hindrance caused by the methyl group(s).

After the initial study by Andersen, titanocene−oxo complexes bearing bulkier ligands than Cp* have been reported,[18] but terminal oxo complexes with less sterically hindered ligands, such as the Cp′, are not known. Oxidation of ethylene complex **3** with nitrous oxide gave product **4a** in the 20−30% range, while the use of pyridine *N*-oxide produced a reduced yield (<10%) of the desired product. The main products in both cases were likely Cp′ titanium μ-oxo clusters resulting from decomposition of the $[Cp'_2Ti{=}O]$ species. This result can be attributed to the smaller size of the Cp′ compared to the Cp* ligand, making it less effective in stabilizing the reactive monomeric titanium−oxo. We hypothesized that the use of nonpolar solvents would cause the desired oxo product to precipitate and thereby prevent oligomerization. However, both nitrous oxide and pyridine *N*-oxide have low solubility in hexane and octane. Styrene oxide, previously used by Chirik in the synthesis of base-free titanocene−oxo complexes,[12] offers a solution to this problem. Reaction of **3** with styrene oxide in the presence of pyridine or 3,5-lutidine in hexane generated **4a** and **4b** in 60% and 62% isolated yield, respectively (Scheme 2).

Scheme 2. Synthesis of Titanocene−oxo Complexes 4a and 4b via Oxidation with Styrene Oxide



3

4a 60% **4b** 62%

4a: R = H
4b: R = 3,5-$(CH_3)_2$

In both cases, the products contained a small amount of an unidentified byproduct that persisted after repeated recrystallization, but it appeared to not interfere with other reactions of **4a** and **4b**. The ratio of product to byproduct was greater than 12:1 based on NMR integration.[23]

Single crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a toluene solution of **4b**. An ORTEP representation of **4b** is shown in Figure 2, and selected bond lengths and angles are given in Table 1. The Ti═O bond length in **4b** is 1.686 Å, within the Ti═O bond length range of known terminal titanium−oxo complexes. Compared to the Cp*−Ti−Cp* angle of 135° in complex **2a**,[9] the Cp′−Ti−Cp′

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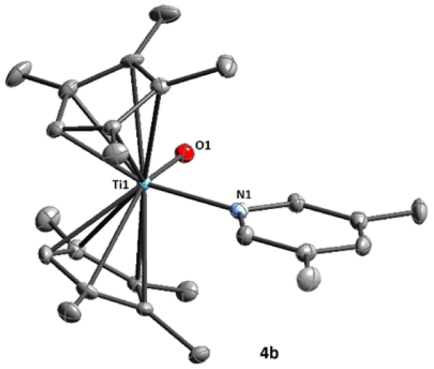


Figure 2. ORTEP diagram of $Cp'_2Ti{=}O(3,5\text{-lutidine})$ (**4b**). Hydrogen atoms and a second molecule are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths and Angles for Oxo Complex 4b

bond	length (Å)	bond	angle (deg)
Ti1–O1	1.6868(18)	O1–Ti1–N1	91.05(9)
Ti1–N1	2.208(2)	CNT1–Ti1–CNT2	131.03(2)

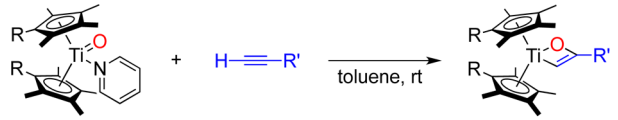
angle in **4b** is smaller (131°), as expected with a less sterically hindered metal center.

[2+2]-Cycloaddition and -Cycloreversion of Titanocene–oxo with Alkynes. With the Ti=O complexes in hand, our next step was to synthesize a variety of sterically and electronically differentiated oxatitanacyclobutenes via [2+2]-cycloaddition with alkynes, with the eventual goal of investigating their aptitude to undergo carbonyl insertion.

Previously, Bergman demonstrated that oxo complex **2a** undergoes cycloaddition reactions with terminal alkynes (RCCH; R = Ph, *p*-tolyl, *t*-Bu, and Me) and diphenylacetylene; terminal alkynes react preferentially over internal alkynes, and the [2+2]-cycloaddition is reversible. Experimental data provided in the report is limited;[12] as such, for known compounds full experimental details are provided. We found that **2a** and **4a** reacted with aryl acetylenes to give quantitative NMR yields of the oxatitanacyclobutene products in less than an hour at room temperature. Both electron-donating (*p*-MeO–) and -withdrawing (3,5-di-CF_3– and *p*-F–) substituents were tolerated. Isolated yields were lower for some of the Cp* products due to the high solubility of the resulting metallacycles (Table 2). Product formation was not observed with *p*-nitrophenylacetylene (Table 2, entry 6); rather, an intractable mixture was observed. This result could be attributed to the strongly electron withdrawing nitro group, which makes the terminal alkyne sufficiently acidic to undergo deprotonation by the titanocene–oxo.

This facile [2+2]-cycloaddition reaction of terminal alkynes was in sharp contrast with the reaction of internal alkynes, which required higher equivalents of alkynes and more forcing conditions. At room temperature, reactions of **2a** and **4a** with 1-phenyl-1-propyne and diphenylacetylene (4 equiv) proceeded very slowly, generating the titanacycle products in less than 5% NMR yield after 7 days. At elevated temperature (60 °C), **2a** reacted with these internal alkynes to generate products **7a** and **7b** in 50% and 43% isolated yield, respectively (Scheme 3). Attempts to increase conversion at higher temperature and longer reaction time were not successful, as decomposition of **2a** was observed.

Table 2. Scope of Terminal Alkynes in [2+2]-Cycloaddition Reaction with Titanocene–oxo Complexes[a]



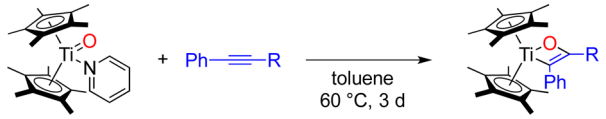
2a: R = CH_3
4a: R = H

5: R = CH_3
6: R = H

entry	Cp^x	R′ (product)	yield[b]
1	Cp*	Ph– (**5a**)	95%
2	Cp*	*p*-MeO-C_6H_4– (**5b**)	92%
3	Cp*	3,5-$(CF_3)_2$-C_6H_3– (**5c**)	88%
4	Cp*	*p*-F-C_6H_4– (**5d**)	70%
5	Cp*	*p*-NO_2-C_6H_4– (**5e**)	0%[c]
6	Cp′	3,5-$(CF_3)_2$-C_6H_3– (**6a**)	94%

[a]Reaction conditions: 1.0 equiv of titanocene–oxo, 1.2 equiv of alkyne. [b]Isolated yields. [c]Starting materials were consumed, resulting in an intractable mixture.

Scheme 3. [2+2]-Cycloaddition Reaction of 2a with Internal Alkynes

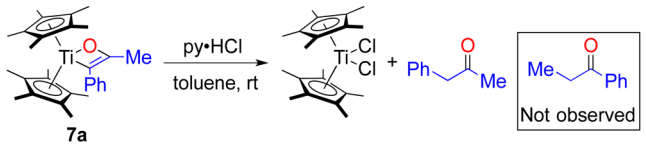


2a

7a: R = Me
7b: R = Ph

Interestingly, reaction of **2a** with the asymmetric alkyne 1-phenyl-1-propyne produced titanacycle **7a**, in which the phenyl group was α to the titanium and methyl group β. This structure of **7a** was supported by NMR as well as experimental data: treatment of **7a** with pyridine hydrochloride resulted in formation of benzyl methyl ketone; the other regioisomer of **7a** should generate ethyl phenyl ketone instead (Scheme 4).

Scheme 4. Protonation of Oxatitanacyclobutene 7a



7a

This result suggests the dominance of a steric effect, where the relatively flat sp^2 carbon of the phenyl ring is preferred between the two Cp* rings over the tetrahedral methyl group. Higher temperatures (>60 °C) did not facilitate the reactions of **4a** with internal alkynes; rather decomposition of starting material was observed.

Oxatitanacyclobutene complex **6a** has been shown to undergo alkyne exchange with *para*-tolylacetylene at 75 °C to generate oxatitanacyclobutene **6** where R = tolyl and phenyl acetylene.[12] We found that the alkyne exchange reaction occurred at room temperature without formation of any byproducts (Table 3). Investigation of the exchange between oxatitanacyclobutenes and free terminal alkynes can provide information about the relative stability of the various titanacycles. With strongly electron deficient metallacycle **5c** (Ar^1 = 3,5-$(CF_3)_2$-C_6H_3–), no exchange was observed even at elevated temperature, suggesting that **5c** is significantly more stable than **5a**,**b** due to the electron-withdrawing CF_3 groups (Table 3,

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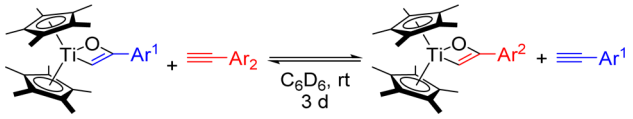
Table 3. Alkyne Exchange Reaction of Oxatitanacyclobutenes[a]



entry	Ar^1	Ar^2	conversion[b]
1	Ph (**5a**)	4-OMe-C_6H_4	24%
2	Ph (**5a**)	4-F-C_6H_4	24%
3	4-OMe-C_6H_4 (**5b**)	4-F-C_6H_4	52%
4	3,5-$(CF_3)_2$-C_6H_3 (**5c**)	4-F-C_6H_4	0%

[a]Reaction conditions: 1.0 equiv of oxatitanacyclobutene, 1.0 equiv of alkyne. [b]Determined by NMR integration.

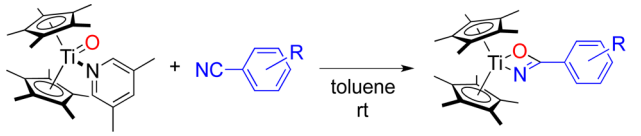
entry 4). This metallacycle is also more thermally stable, as no reactions occurred upon heating at 80 °C for 3 days, while **5a** was previously reported to rearrange to a hydroxyacetylide complex at elevated temperatures (45−75 °C).[12]

The reaction rate is dependent on the substituent on the metallacycle. When **5a** and **5b** were treated with *para*-fluorophenylacetylene, the more electron rich **5b** reacted faster, achieving 52% conversion after 3 days (Table 3, entry 3), while **5a** gave 24% conversion (entry 2). When **5a** was treated with two different phenylacetylene derivatives, both reactions had the same conversion of 24% after 3 days (Table 3, entries 1 and 2). This is consistent with electron-donating groups on Ar^1 accelerating the rate of the exchange by promoting the retro-[2+2]- and supports a unimolecular [2+2]-cycloreversion rate-determining step, followed by trapping of the free titanocene−oxo with alkyne.

[2+2]-Cycloaddition Reaction of Titanocene−oxo Complexes with Nitriles. With the Ti=O complexes in hand, we next chose to investigate other [2+2]-cycloadditions, so that their reactivity could be directly compared to related complexes.

The titanocene−sulfido complex $Cp^*_2Ti{=}S(py)$ has been reported to react with benzonitrile in 2 h to form a product assigned as an azathiatitanacyclobutene in 65% isolated yield.[24] On the other hand, treatment of titanocene−oxo complex **2b** with benzonitrile resulted in less than 10% conversion after 24 h. To explore potential effects of aryl substitution on this reaction, a solution of **2b** in C_6D_6 was treated with different benzonitrile derivatives, and the reactions were monitored by ^1H NMR. Complete conversion to a single product was observed with 3-bromobenzonitrile and 3,5-bis-(trifluoromethyl)benzonitrile, generating products **8a** and **8b** in 82% and 85% isolated yield, respectively (Scheme 5). Integration of ^1H NMR spectra indicated a monoinsertion product with one benzonitrile molecule incorporated. Using two or more equivalents of nitriles did not lead to formation of other products. This monoinsertion mode is consistent with

Scheme 5. [2+2]-Cycloaddition Reaction of 2b with Benzonitriles



2b

8a: R = 3-Br (82%)
8b: R = 3,5-$(CF_3)_2$ (85%)

similar reactions of titanocene−sulfido but different from that of zirconocene−oxo, which reacts with benzonitrile to form a six-membered metallacycle.[25]

X-ray quality crystals were grown by slow diffusion of hexane into a toluene solution of **8b**. An ORTEP representation is shown in Figure 3, with selected bond lengths and angles in

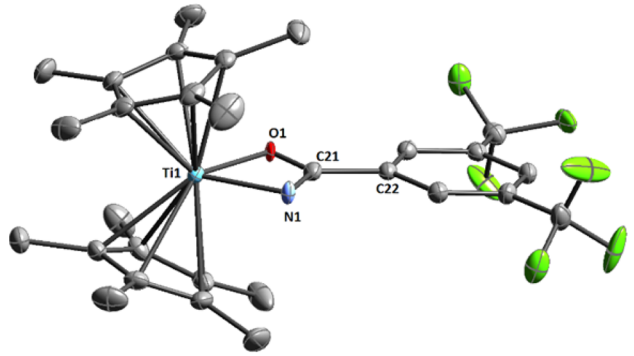


Figure 3. ORTEP diagram of $Cp^*_2Ti[OC(3,5\text{-}(CF_3)_2C_6H_3)N]$ (**8b**). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

Table 4. Selected Bond Lengths and Angles for 8b

bond	length (Å)	bond	angle (deg)
Ti1−O1	2.070(11)	Ti1−O1−C21	83.7(5)
O1−C21	1.278(7)	O1−C21−N1	120.4(3)
C21−N1	1.383(8)	C21−N1−Ti1	85.9(5)
N1−Ti1	1.950(13)	N1−Ti1−O1	70.0(3)

Table 4. The titanium center is in a pseudotetrahedral environment with a flat metallacycle. The Ti1−O1 and Ti1−N1 bond lengths are within the range of known titanium−oxygen and titanium−nitrogen single bonds.

This reaction appeared to be sensitive to both the electronic property and position of the substituents, as electron-deficient, *meta*-substituted benzonitriles formed the [2+2] products in good yields while *ortho*- and *para*-substituted ones gave no reactions. In the proton NMR spectra of the metallacycles **8a** and **8b** the Cp* methyl peak is shifted approximately 0.25 ppm upfield, compared to the oxo. On the other hand, when **2b** was treated with *ortho*- and *para*-bromobenzonitriles, proton NMR spectra showed only one Cp* peak, which shifted very slightly (0.01−0.03 ppm) from that of **2b**, and broadening of the nitrile and amine peaks.[23] These observations suggest fast pyridine−nitrile exchange on the NMR time scale and no [2+2]-cycloaddition. It appears that the stereoelectronic properties of the substituents have a strong influence on the nitrile group. Electron-withdrawing groups at the *meta* position make the group more electrophilic and reactive in [2+2]-cycloaddition, while electron-donating substituents increase the electron density on the nitrogen atom of the nitrile group, making it a good ligand for the titanium complex. Interestingly, Bergman reported the cycloaddition reaction of the titanocene−sulfido complex with *meta*-tolunitrile, while reactions with the *ortho* and *para* isomers were not discussed.[24]

The azaoxatitanacyles **8a** and **8b** underwent nitrile exchange reactions at room temperature (Scheme 6). This reaction was approached from both directions, and an approximately 6:1

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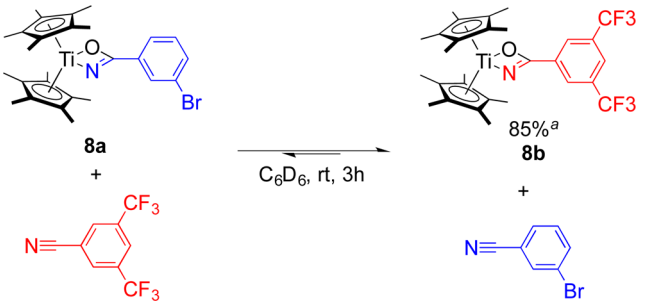
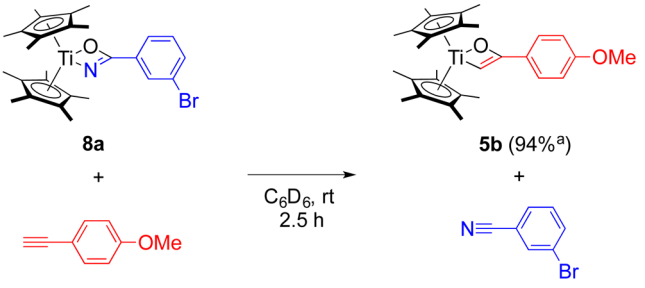
Scheme 6. Nitrile Exchange Reaction of 8a and 8b[b]



[a]Determined by NMR integration. [b]Reaction conditions: 1.0 equiv of oxaazatitanacyclobutene, 1.0 equiv of nitrile.

ratio of **8b** to **8a** was observed in both cases after 3 h, as determined by integration of ^{1}H NMR spectra. In addition, titanacycle **8a** reacted with *para*-methoxyphenylacetylene to generate **5b** and free nitrile in almost quantitative yield after 2.5 h (Scheme 7). In comparison, the alkyne exchange reaction of

Scheme 7. Reaction of 9a with Terminal Alkyne[b]



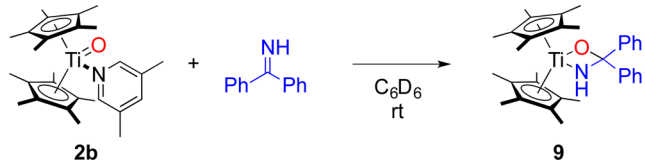
[a]Determined by ^{1}H NMR integration. [b]Reaction conditions: 1.0 equiv of oxaazatitanacyclobutene, 1.0 equiv of alkyne.

8b was significantly slower, reaching 50% conversion (by ^{1}H NMR) after 24 h. The equilibrium favors the oxatitanacyclobutene, as no reaction was observed when **5b** was treated with benzonitriles.

[2+2]-Cycloaddition Reaction of Titanocene−oxo Complexes with Imines. Alkynes, nitriles, and carbonyl compounds have been shown to undergo cycloaddition reactions with a number of terminal chalcogenido complexes of zirconium and titanium. One class of unsaturated organic substrates yet to be studied in this reaction is imine. To explore the reactivity of titanocene−oxo toward this functional group, **2b** was treated with *N*-phenyl benzophenone imine, *N*-phenyl *para*-methoxybenzaldehyde imine, and benzophenone imine in benzene-d_6. While the first two compounds did not show any change by ^{1}H NMR spectra, reaction with benzophenone imine immediately resulted in an orange-red solution, and ^{1}H NMR showed formation of a new product with a Cp* peak significantly more upfield (1.761 ppm) than that of **2b** (1.912 ppm). This product is assigned to be the cyclic ketal **9** (Scheme 8) based on NMR evidence that the two phenyl rings are equivalent and no imine signal is found in the ^{13}C NMR spectrum. This observation that **2b** reacts with benzophenone imine and not with *N*-phenyl-*para*-methoxybenzaldehyde imine can be attributed to the increase in steric bulk on the imine nitrogen, hindering its approach to the Cp*Ti=O.

Reactions of Oxatitanacyclobutenes with Carbonyl Compounds. With oxatitanacyclobutenes in hand, the next

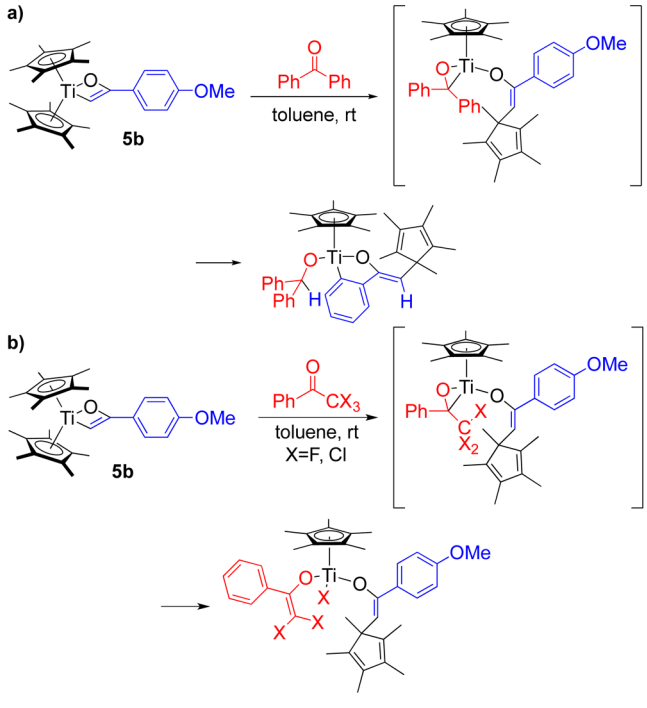
Scheme 8. [2+2]-Cycloaddition Reaction of 2b with Benzophenone Imine



step in developing our proposed catalytic cycle was to develop conditions that promote carbonyl insertion into the Ti−C bond. These studies would allow direct comparison to the related oxazirconoacyclobutenes, which are known to insert into carbonyls to generate dioxazirconacyclohexenes.

We recently reported facile reductive elimination from **5a** and **5b** upon treatment with phenyl ketone derivatives to generate an oxatitanacyclopropane intermediate (Scheme 9).[19] This intermediate has been successfully intercepted in a number of transformations, including carbonyl insertion and C−H, C−C, and C−X (X = F, Cl) activation.

Scheme 9. Reaction of 6a with (a) Benzophenone and (b) Trifluoroacetophenone



To further study the impact of substituents on the metallacycle on this transformation, disubstituted metallacycle **8a** was treated with 2,2,2-trifluoroacetophenone and 4-methoxybenzaldehyde. In contrast to the facile reaction of **5b** with trifluoroacetophenone, which resulted in C−Cp* bond-forming reductive elimination and subsequent C−F bond activation, no reaction was observed between **7a** with this 2,2,2-trifluoroacetophenone (Scheme 10a). One explanation is that the second substituent on the metallacycle hinders the approach of the ketone, preventing the Lewis base promoted ring slip/reductive elimination.

Reaction of **7a** with 4-methoxybenzaldehyde resulted in a mixture of products from which the free alkyne could be observed by ^{1}H NMR by comparison with an authentic sample

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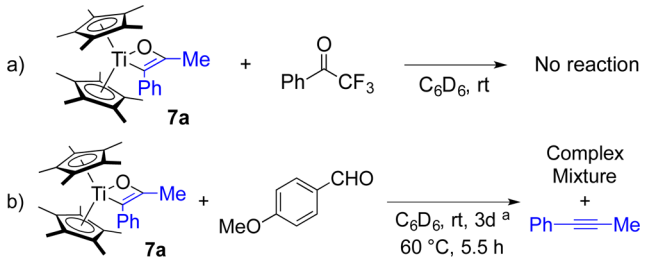
Organometallics XXXX, XXX, XXX−XXX

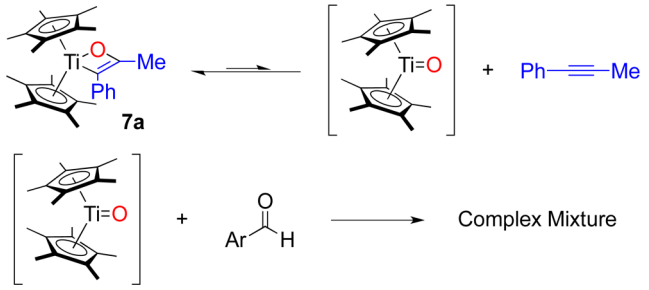
Scheme 10. Reactions of 7a with Carbonyl Compounds



[a]No reaction was observed at room temperature.

(Scheme 10b). Since **7a** did not undergo reductive elimination, a different pathway must be invoked to explain its reaction with aldehyde. As previously proposed in the alkyne exchange reaction of complexes **5**, oxatitanacyclobutene **7a** could undergo a retro-[2+2]-cycloaddition, followed by trapping of the free titanocene–oxo by an aldehyde (Scheme 11). This

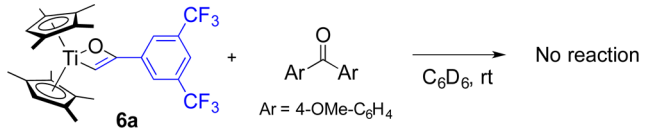
Scheme 11. Proposed Mechanism for the Reaction of 7a with Aldehydes



hypothesis was supported by observation that reaction of DMAP-trapped oxo complex **2c** with 4-methoxybenzaldehyde generated a mixture whose NMR spectrum superimposed with the spectrum of the reaction shown in Scheme 10.[23] In the reactions of **5** with aldehydes, the reductive elimination pathway was faster and might account for most of the products.

In our recent study on the reactivity of oxatitanacyclobutenes, we suggested that the crowded metal center was crucial to the reductive elimination step. To test this hypothesis, complex **7a** was treated with 4,4′-bismethoxybenzophenone (Scheme 12). No reductive elimination was observed; rather

Scheme 12. Treatment of Oxatitanacyclobutene 6a with Benzophenone Resulted in No Reaction[23]

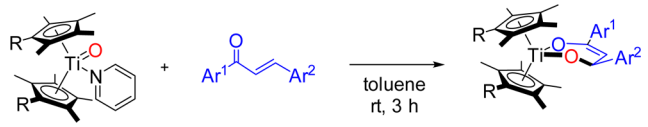


only slight shifts were seen in the ^{1}H and ^{13}C NMR spectra, suggesting coordination but no reductive elimination or carbonyl insertion. One possible explanation is that the smaller size of the Cp′ ligand allows for ketone coordination without invoking ring slip, which is required for reductive elimination.[26]

Further, unlike analogous azatitanacyclobutene[16,17] and aza- and oxazirconacyclobutenes,[6,27,28] no carbonyl insertion products were observed when **5a–e** and **6a** were combined with various aldehydes (RCOH; R = Ph, Bu, H) under a wide array of reaction conditions (−78 to 25 °C; polar and nonpolar solvents, etc.). The lack of carbonyl insertion into the Ti–C bond of oxatitanacyclobutenes under a wide variety of conditions is a critical setback in our overall goal of developing the alkyne–aldehyde coupling reaction.

Reaction of Titanocene–oxo with α,β-Unsaturated Carbonyls. Although we were unable to synthesize the desired dioxatitanacyclohexene via carbonyl insertion, we were interested in investigating the reactivity of these complexes relative to the analogous dioxazirconacyclohexenes.[6] On the basis of our recent investigations into Zr=O complexes, we proposed that these titanacycles could be prepared by [4+2]-cycloaddition reaction of titanocene–oxo complexes with α,β-unsaturated carbonyls, as similar reactivity has been reported with titanocene–sulfido complex $Cp^*_2Ti{=}S(py)$.[24] Complexes **2a** and **4a** reacted with chalcone **10a** and its derivatives to generate dioxatitanacyclohexenes **11** and **12**, respectively, in quantitative NMR yield and good to excellent isolated yields (Table 5). Both electron-donating and -withdrawing groups on the enones were well tolerated.

Table 5. Scope of Enones in [4+2]-Cycloaddition Reaction with Titanocene–oxo[a]



entry	Cp^x, Ar_1, Ar_2	product	yield[b]
1	Cp*, Ar_1 = Ar_2 = Ph (a)	**11a**	65%
2	Cp*, *p*-CF_3-C_6H_4 ; *p*-MeO-C_6H_4 (b)	**11b**	82%
3	Cp*, *p*-CF_3-C_6H_4 ; *p*-Me-C_6H_4 (c)	**11c**	78%
4	Cp*, *p*-CF_3-C_6H_4 ; Ph (d)	**11d**	74%
5	Cp*, *p*-CF_3-C_6H_4 ; *p*-Cl-C_6H_4 (e)	**11e**	81%
6	Cp*, Ar_1 = Ar_2 = *p*-CF_3-C_6H_4 (f)	**11f**	88%
7	Cp*, *p*-NMe_2-C_6H_4; *p*-CF_3-C_6H_4 (g)	**11g**	81%
8	Cp*, *p*-MeO-C_6H_4; *p*-CF_3-C_6H_4 (h)	**11h**	85%
9	Cp*, Ph; *p*-CF_3-C_6H_4 (i)	**11i**	60%
10	Cp*, *p*-Br-C_6H_4; *p*-CF_3-C_6H_4 (j)	**11j**	58%
11	Cp′, Ar_1 = Ar_2 = Ph (a)	**12a**	61%
12	Cp′, *p*-NMe_2-C_6H_4; *p*-CF_3-C_6H_4 (g)	**12g**	75%
13	Cp′, *p*-MeO-C_6H_4; *p*-CF_3-C_6H_4 (h)	**12h**	80%

[a]Reaction conditions: oxo complex 0.26 mmol, 1.0 equiv, enone 0.26 mmol, 1.0 equiv, toluene 4 mL, reactions were stirred at rt for 3 h. [b]Isolated yield.

Single crystals suitable for X-ray diffraction crystallography were grown by cooling a concentrated hexane solution of **11a**. Selected bond lengths and angles are included in Table 6. As illustrated in the ORTEP representation (Figure 4), the metal is

Table 6. Selected Bond Lengths and Angles for 11a

bond	length (Å)	bond	angle (deg)
Ti–O1	1.871(7)	O1–Ti–O2	89.82(9)
Ti–O2	1.964(6)	Ti–O1–C11	127.0(6)
O1–C11	1.410(6)	Ti–O2–C13	118.7(7)
O2–C13	1.500(13)	O2–C13–C12	105.8(4)
C11–C12	1.341(9)	C13–C12–C11	123.7(2)
C12–C13	1.511(8)	C12–C11–O1	125.3(5)

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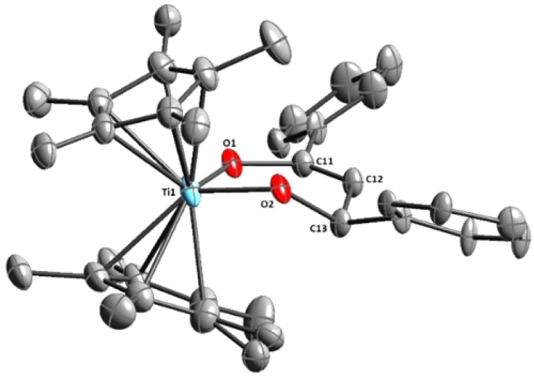


Figure 4. ORTEP diagram of $Cp^*_2Ti[OC(Ph)CHCH(Ph)O]$ (**11a**). Hydrogen atoms are omitted for clarity. Ellipsoids are drawn at the 50% probability level.

in a pseudotetrahedral environment. This complex contains a boat-like titanacycle with the C13 phenyl ring at the equatorial position. The Ti−O bonds are within the range reported for Ti−O single bonds with the Ti−alkoxide (Ti−O2) bond length longer than the Ti−enolate (Ti−O1) bond length (1.964(6) Å compared to 1.871(7) Å).

Retro-[4+2]-Cycloaddition of Dioxatitanacyclohexene Complexes 11 and 12. In the preparation of complexes **11**, we observed that with electron-donating groups on both of the phenyl rings the product was not stable and decomposed to the enone and metal−oxo cluster. This cluster was the oligomerization product of free $[Cp^*_2Ti{=}O]$, which was potentially generated from retro-[4+2]-cycloaddition. This reaction has been proposed in the reactions of titanacycles but has not been studied in detail. To probe the mechanism, dioxatitanacyclohexenes **11** and **12** were treated with α,β-unsaturated ketones, and enone exchange reactions were observed. The rate of this reaction was strongly dependent on the electronic nature of the substituents on the phenyl rings; slower reactions were observed with more electron deficient metallacycles. Between the two phenyl rings on the metallacyles, electron-donating substituents on the enol phenyl ring had a more profound impact in promoting this enone exchange reaction (Scheme 13). Starting with an equimolar solution of **11b** and **10f**, 50% conversion to **11f** to **10b** was reached in 4.2 h, while reaction between **11h** and **10f** had a $t_{1/2}$ of only 1.5 h. These observations suggest that in the retro-[2+2]-cycloaddition step an electron-donating group can better stabilize the transition state when it is located on the phenol ring. This substituent effect was further studied with Hammett experiments in the later part of our study.

The formation of dioxatitanacyclohexene product can be considered the result of the oxo species $[Cp^*_2Ti{=}O]$ being trapped by an enone. We hypothesized that other reagents that react more favorably with titanium−oxo should also promote the generation of α,β-unsaturated ketones from dioxatitanacyclohexenes. One class of such reagents is strong Lewis bases such as 4-dimethylaminopyridine (DMAP), which can stabilize the monomeric titanocene−oxo species. Reactions of DMAP with dioxatitanacyclohexenes **11** and **12** generated the corresponding enones and the DMAP-trapped titanium−oxo complexes **2c** and **4c**, respectively (Table 7). These oxo complexes were independently synthesized via ligand exchange reaction of the corresponding pyridine-trapped oxo complexes **2a** and **4a** with DMAP (Scheme 14).

Scheme 13. Enone Exchange Reaction of 11b and 11h

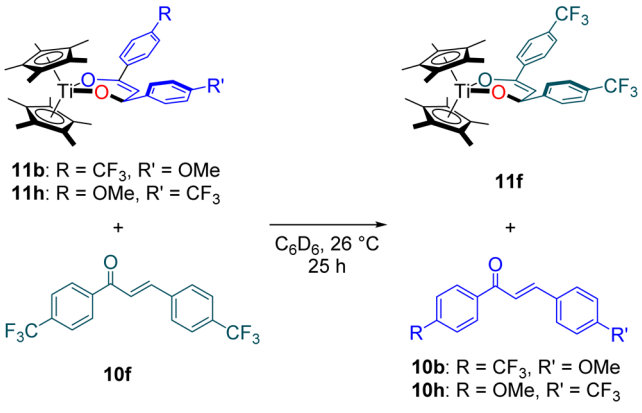
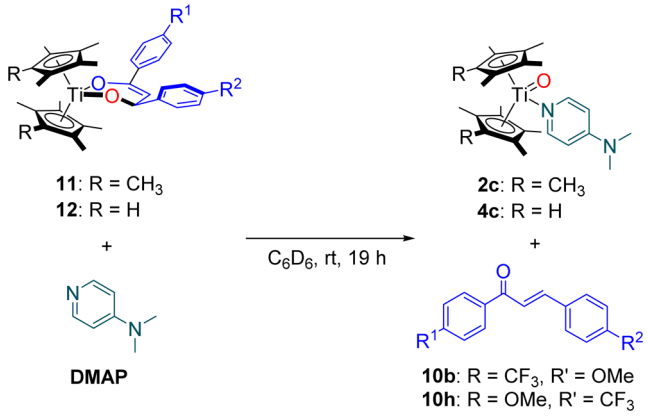


Table 7. Scope of Dioxatitanacyclohexenes in the Retro-[4+2]-Cycloaddition and Subsequent Trapping with DMAP[a]

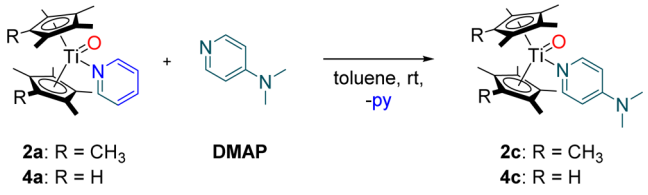


entry	Cp^x, R^1, R^2	yield **10**[b]	yield **2c** (**4c**)[b]
1	Cp*, H, H (**11a**)	40%	38%
2	Cp*, MeO; CF_3 (**11h**)	80%	37%[c]
3	Cp′, H, H (**12a**)	0%[d]	0%
4	Cp′, MeO; CF_3 (**12h**)	34%[e]	35%[c]
5	Cp′, NMe_2; CF_3 (**12g**)	81%[f]	69%

[a]Reaction conditions: 1 equiv of metallacycle (0.02 M in C_6D_6), 20 equiv of DMAP. [b]NMR yield determined by comparison of the product to an internal standard in ^{1}H NMR spectra after 19 h. [c]Lower yield of oxo compared to enone was attributed to low solubility of oxo product, as it precipitated out of solution. [d]No reactions at 80 °C and longer reaction time. [e]Reaction was run at 60 °C. [f]Yield determined after 5 h.

Similar to the enone exchange reaction, the rate of reactions between dioxatitanacyclohexenes **11** and **12** with DMAP is strongly influenced by electronic effects: slower reactions were

Scheme 14. Synthesis of DMAP-Trapped Titanocene−oxo Complexes 2c and 4c via Ligand Exchange



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Organometallics XXXX, XXX, XXX−XXX

observed with more electron deficient metallacycles. Substitutions on the phenyl rings and ligands on the metal were both important. Electron-donating substituents led to significant increases in yield (Table 7, entries 1 and 2, entries 4 and 5). Reactions of metallacycles bearing the Cp′ ligand were much slower, as evident from reactions of **11h** and **12h**: reaction of **11h** with DMAP afforded an 80% yield of **10h** in 19 h at room temperature (Table 7, entry 2), while **12h** only gives 34% of product **10h** at 60 °C in the same reaction time (Table 7, entry 4). This facile cycloreversion and its dependence on electronic effects are different from reactions of dioxazirconacyclohexenes, which require heating over 100 °C.[19] A similar retro-[4+2]-cycloaddition from diazatitanacyclohexenes has been reported to be part of a titanium−imido-catalyzed imine−alkyne coupling reaction; in this case also, high temperature is required to promote the cycloreversion.[3] In comparison to these systems, the facile cycloreversion of oxatitanacycles bearing a Cp* ligand is quite remarkable. One possible explanation is the release of strain. Observation that dioxatitanacyclohexenes bearing the less bulky Cp′ ligand undergo significantly slower reactions supports this hypothesis.

Next, mechanistic experiments were undertaken to gain insight into the cycloreversion reaction. All kinetic investigations were preformed using initial rate kinetics, as clean kinetic profiles were not observed to three half-lives, as decomposition was observed after extended reaction times.[27] The reaction of **11b** with DMAP is first order in **11b** (Figure 5)

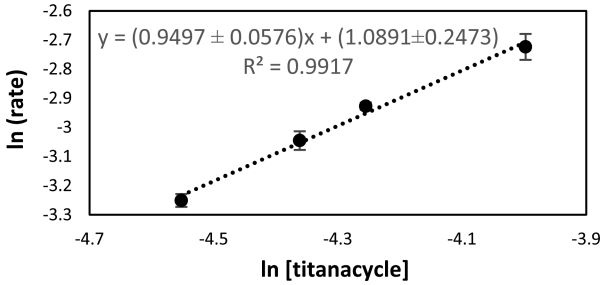
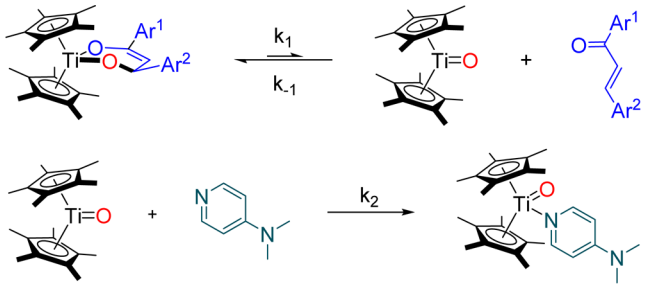


Figure 5. Natural log plot of the retro-[4+2]-cycloaddition reaction showing the reaction is first order in titanacycle **11b**.

and zero order in DMAP, supporting a dissociative mechanism in which the retro-[4+2]-cycloaddition is the rate-determining step (Scheme 15). Product inhibition was observed when the enone product was added to the reaction (Figure 6), suggesting a reversible cycloreversion step. These empirical data are consistent with the rate law (eq 1) derived from the proposed mechanism.

Scheme 15. Proposed Mechanism of Retro-[4+2]-Cycloaddition Reaction of Dioxatitanacyclohexenes



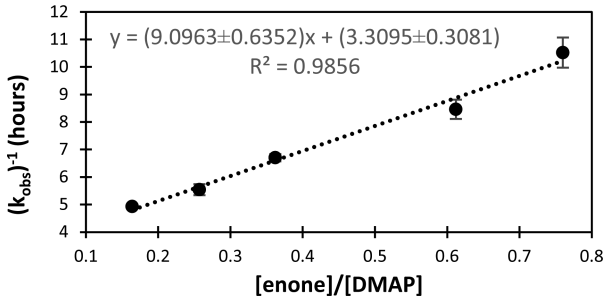


Figure 6. Inversed observed rate constants increase with the enone/DMAP ratio. The linear relationship is consistent with the rate law in eq 1.

$$\text{rate} = \frac{k_1 k_2[\text{metallacycle}][\text{DMAP}]}{k_{-1}[\text{enone}] + k_2[\text{DMAP}]} \quad (1)$$

Hammett plots were constructed for substituents on each of the two phenyl rings while keeping the other ring as *p*-$CF_3C_6H_4$. Negative ρ values of −1.18 and −1.09 were obtained when σ^+ parameters were used (Figures 7 and 8), similar to that

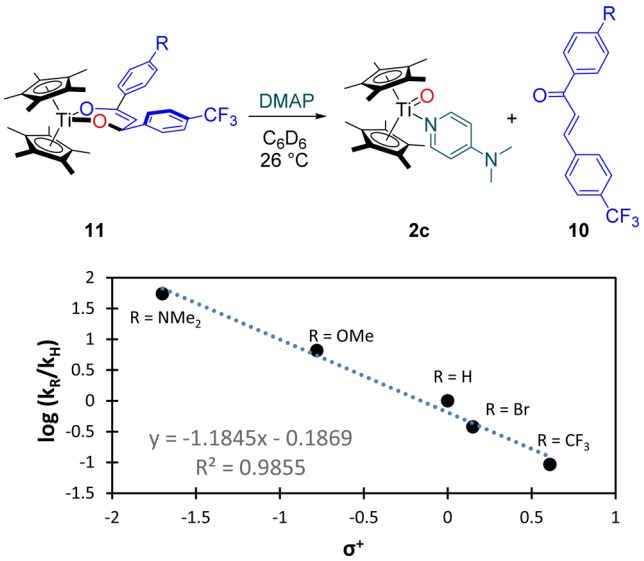


Figure 7. Hammett plot for substituents on the enolic phenol ring with σ^+ (top) and σ_p (bottom).

previously obtained in the retro-[4+2]-cycloaddition reactions of azaoxazirconacyclohexenes.[17] A plot of σ_p rather than σ^+ does not give a linear correlation for substituents on the allylic phenol ring but produces ρ values of −2.07 with substituents on the enolic phenol ring.[23] The negative values indicate that positive charge is developed in the transition state, and the small absolute values imply slight deviation from a synchronous retro-[4+2]-cycloaddition. The more negative ρ value associated with the enolic phenyl ring is consistent with experimental observation that placing electron-donating substituents on this ring increases the reaction rate more than when it is placed on the other ring.

CONCLUSION

The synthesis and reactivity of Ti−oxo complexes have been explored. We have demonstrated that pyridine *N*-oxide and styrene oxide are excellent alternatives to nitrous oxide as oxidants in the synthesis of monomeric titanocene−oxo

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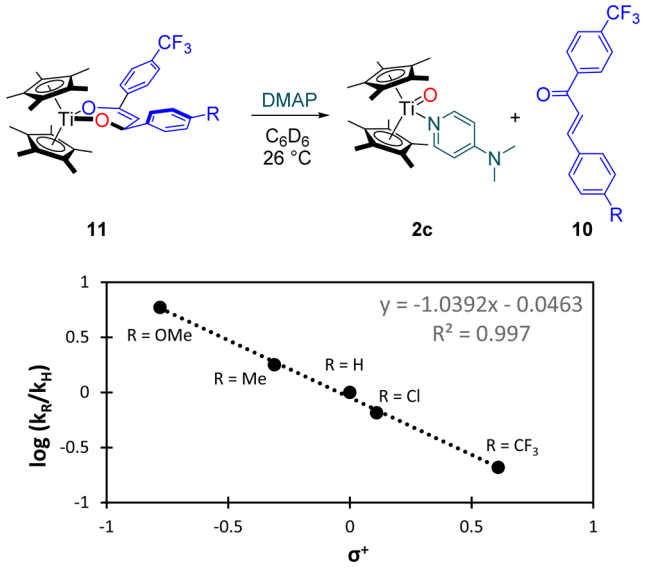

Figure 8. Hammett plot for substituents on the allylic phenyl ring.

complexes with high yield and simple operation. Titanocene–oxo complexes bearing less bulky ligands than Cp* have been successfully synthesized through judicious oxidant and solvent selection. These methods should facilitate future research on these reactive oxo complexes. Further, our studies demonstrate that titantium–oxo complexes undergo reversible cycloaddition reactions with alkynes, nitriles, and α,β-unsaturated ketones to form isolable metallacycle products. Finally, these complexes undergo cycloreversion at room temperature in the presence of reagents that can react with and trap the [Cp^x_2Ti=O] species.

The reactivity of these titanocene complexes differs significantly from those of analogous zirconocene complexes. Titanocene–oxo complexes react preferably with terminal alkynes and nitriles to form four-membered metallacycles. The resulting titanacyclobutenes undergo retro-[2+2]-cycloaddition reaction at room temperature, as evident by alkyne and nitrile exchange reactions. Zirconocene–oxo complexes, on the other hand, react preferentially with internal alkynes and form double-addition products with benzonitrile, to afford the six-membered metallacycle.[25] The [2+2]-cycloaddition products oxazirconacyclobutenes undergo facile aldehyde insertion to form dioxazirconacyclohexenes, while oxatitanacyclobutenes react with aldehydes in a nonconstructive fashion due to a combination of favorable retro-[2+2]-cycloaddition and reductive elimination of the Cp* ligand. The facile reductive elimination of a Cp* ligand and a Ti–C bond from the titanacycle is a unique and fascinating reactivity of oxatitanacyclobutenes.[8] In comparison, the Cp* ligand in oxazirconacyclobutenes reacts only at 160 °C and through C–H activation at one of the methyl groups. Finally, dioxametallacyclohexene complexes of these two metals offer direct comparison in retro-[4+2]-cycloaddition. Titanocene metallacycles **11** and **12** undergo reaction at room temperature with high yields and recapture of the oxo complex, while their zirconium counterparts require temperatures above 120 °C to affect this transformation. In addition, stabilizing the reactive zirconocene oxo with dative ligands is difficult, and chalcone has been used instead as a trapping reagent, forming another dioxazirconacyclohexene.[6]

These studies were undertaken with the eventual goal of developing a Ti-catalyzed aldehyde–alkyne coupling reaction for the synthesis of enones. Over the course of these experiments, we demonstrated that carbonyl insertion into titanacyclobutenes does not occur; rather an array of other reactions, including reductive elimination and retro-[2+2]-cycloaddition, take place preferentially. This is especially unfortunate, as the [4+2]-retrocycloaddition from the dioxatitanacyclohexene is relatively facile, especially in comparison to the analogous zirconium complex.

In general, titanocene complexes are more reactive in both cycloaddition and retro-cycloaddition reactions and less reactive in insertion reactions compared to zirconocene complexes. This difference in reactivity can be attributed to the more crowded metal center in titanocene complexes. These facile cycloaddition and cycloreversion reactions offer useful insights into the development of titanium–oxo-mediated reactions.

EXPERIMENTAL SECTION

General Experimental Procedures. All reactions were carried out in oven-dried (at 140 °C, for at least 4 h) glassware under an atmosphere of nitrogen unless otherwise indicated. Air- or moisture-sensitive materials were synthesized and stored in a nitrogen-filled glovebox. Column chromatography was performed with silica gel from Grace Davison Discovery Sciences (35–75 μm), packed as a slurry, and run under positive pressure. Analytical thin-layer chromatography (TLC) was performed on precoated glass silica gel plates with F-254 indicator purchased from EMD Chemicals Inc. Visualization was done by short-wave (254 nm) ultraviolet light. Distillations were performed using a 3 cm short-path column either under reduced pressure or under positive pressure of nitrogen.

Instrumentation. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Unity 500 MHz (125 MHz for ^{13}C, 470 MHz for ^{19}F) spectrometer. Spectra were collected in $CDCl_3$ or C_6D_6 and were referenced using residual protic solvent (^{1}H NMR: 7.26, ^{13}C NMR: 77.16 ppm for $CDCl_3$, ^{1}H NMR: 7.15, ^{13}C NMR: 128.06 ppm for C_6D_6). ^{19}F NMR were referenced internally using C_6F_6 (^{19}F NMR: −163.04 ppm). Chemical shifts were reported in parts per million (ppm), and multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet). Coupling constants (J) are reported in hertz, and integrations are provided. High-resolution mass spectrometry was performed at the School of Chemical Sciences Mass Spectrometry Laboratory located at the University of Illinois at Urbana–Champaign. X-ray crystallography was done at the George L. Clark X-ray Facility and 3M Materials Laboratory at the University of Illinois at Urbana–Champaign. Microanalysis was performed at the School of Chemical Sciences Microanalysis Laboratory located at the University of Illinois at Urbana–Champaign. Bulk purity of samples is represented in Supporting Information by ^{1}H, ^{13}C, and ^{19}F NMR spectra.

Materials. Solvents used for extraction, column chromatography, and recrystallizations of air-stable materials were reagent grade and used as received. Solvents for reactions, extractions, and recrystallizations of air- and water-sensitive materials were dried on a Pure Process Technology Glass S3 Contour Solvent Purification system equipped with activated stainless steel columns following manufacture's recommendations for solvent preparation and dispensing. Solvents were then further dried by storing over 4 Å molecular sieves that had been activated by heating to 200 °C under dynamic vacuum for at least 24 h. Pyridine, 3,5-lutidine, phenylacetylene, hexafluorobenzene, and styrene oxide were distilled under an atmosphere of nitrogen, transferred to a nitrogen-filled glovebox, and stored over activated molecular sieves for at least 24 h prior to use. C_6D_6 was degassed by freeze–pump–thaw cycles, stored in a nitrogen-filled glovebox, and dried over activated molecular sieves for at least 24 h prior to use. $(TiCl_3)_3AlCl_3$, diphenylacetylene (Alfa Aesar), C_2H_4 (Specialty Gases of America), n-BuLi, 1-phenyl-1-propyne, 3-phenyl-1-propyne, chalcone, benzonitrile and derivatives (Aldrich), DMAP (ACROS Organic), 4′-methoxyphenylacetylene, and 4′-fluorophenylacetylene

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(Oakwook Chemical) were used as received. Pentamethylcyclopentadiene was obtained from Boulder Scientific and distilled prior to use. Lithium cyclopentadienides were prepared by dissolving the corresponding cyclopentadiene in hexane followed by slow addition of 1.11 equiv of 1.6 M *n*-BuLi in hexane (Aldrich) at 0 °C. The mixture was allowed to warm to room temperature overnight with stirring. The product was collected by filtration, washed with hexane, and dried under vacuum. The following compounds were synthesized by literature procedures: $TiCl_3(THF)_3$,[29] 3,5-lutidine *N*-oxide,[30] 3,5-bis(trifluoromethyl)phenylacetylene,[31] chalcone derivatives **9b** to **9j**.[32]

Bis(pentamethylcyclopentadienyl)titanium(IV) Dichloride. This procedure was adopted from a previously reported synthesis of titanocene dichloride with $TiCl_3(THF)_3$.[33] For an earlier synthesis of $Cp^*_2TiCl_2$ reported by Bercaw see ref 34. In a glovebox, $TiCl_3(THF)_3$ (5.03 g, 13.58 mmol, 1.0 equiv), Cp*Li (4.82 g, 33.94 mmol, 2.5 equiv), and THF (60 mL) were combined in a 250 mL round-bottomed, thick-wall vessel. The vessel was sealed with a screw cap, and the reaction was heated at reflux overnight in a fume hood. The reaction was allowed to cool to room temperature, then further cooled in an ice bath. Concentrated HCl (55 mL) was added with stirring, and the reaction mixture went from purple-blue to reddish-brown. The mixture was extracted with chloroform (3 × 60 mL), dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness. The dark brown solid residue was dissolved in chloroform (30−40 mL) in a 500 mL beaker; then methanol (300 mL) was carefully layered on top of this solution. After a day or two at room temperature, large needles of $Cp^*_2TiCl_2$ formed and were collected by filtration, washed with methanol, and dried under vacuum. Dark reddish-purple, long needles, 3.59 g, 68% yield. ^{1}H NMR (500 MHz, chloroform-*d*): δ 2.00 (s, 30H). ^{13}C NMR (126 MHz, chloroform-*d*): δ 128.64, 13.06.

Bis(tetramethylcyclopentadienyl)titanium(IV) Dichloride, Cp'_2TiCl_2. This complex was prepared following the procedure described above for $Cp^*_2TiCl_2$ using $TiCl_3(THF)_3$ and Cp′Li. Dark red flakes, 65% yield. ^{1}H NMR (500 MHz, chloroform-*d*): δ 6.00 (s, 2H), 2.05 (s, 12H), 1.90 (s, 12H). ^{13}C NMR (126 MHz, chloroform-*d*): δ 135.89, 125.22, 113.19, 14.98, 13.20.

Bis(pentamethylcyclopentadienyl)titanium−Ethylene, $Cp^*_2Ti(C_2H_4)$ (1). This complex was prepared using a modified procedure from a previously reported method.[35] In a 250 mL Schlenk flask containing a magnetic stirbar and nitrogen inlet were combined $Cp^*_2TiCl_2$ (1.97g, 5.06 mmol, 1.0 equiv) and toluene (60 mL). To the reaction mixture was added a 1.5 M solution of *n*-BuLi in hexane (7.4 mL, 2.2 equiv) over 30 min at −78 °C, and the solution was stirred for 1 h. The headspace was quickly evacuated and put under static vacuum; then an ethylene balloon was attached. After removal of the balloon, the cooling bath was removed and the reaction was allowed to warm to room temperature. The reaction was accompanied by the generation of gas and a color change from red to brownish-green. After 48 h, all volatiles were removed under vacuum and the resulting brownish-green residue was taken up in hexane and filtered. The filtrate was evaporated to dryness, and the resulting green solid was washed with cold pentane. Green crystalline solid, 1.4 g, 80% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 2.04 (s, 4H), 1.68 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 119.75, 104.96, 11.84.

Bis(pentamethylcyclopentadienyl)titanium(IV)−oxo, $Cp^*_2Ti{=}O$(py) (2a). In a glovebox, titanocene−ethylene complex **1** (0.5 g, 1.45 mmol, 1.0 equiv) was dissolved in THF (10 mL) in a 100 mL round-bottom flask containing a magnetic stirbar. To this solution was added pyridine (0.23 mL, 2.89 mmol, 2.0 equiv), and the mixture was stirred for 30 min before a solution of pyridine *N*-oxide (1.45 mmol, 1.0 equiv) in THF (2.0 mL) was added dropwise. The reaction mixture was stirred at room temperature for 5 h; then all volatiles were removed under vacuum, resulting in a yellow solid. This solid was scrapped onto a fritted funnel and washed with hexane, giving the product as a yellow solid, 0.48 g, 80% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.91 (s, br, 1H), 7.50 (s, br, 1H), 6.75 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.46 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 6.6 Hz, 2H), 1.86 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 156.48, 150.01, 136.46, 124.66, 122.57, 117.13, 12.06.

Bis(pentamethylcyclopentadienyl)titanium(IV)−oxo, $Cp^*_2Ti{=}O$(3,5-lutidine) (2b). **2b** was prepared following the procedure described above for **2a**, using **1a** (1.0 equiv), 3,5-lutidine (2.3 equiv), and 3,5-lutidine *N*-oxide (1.0 equiv). Light orange solid, 84% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.70 (s, 1H), 7.29 (s, 1H), 6.50 (s, 1H), 1.91 (s, 30H), 1.81 (s, 3H), 1.64 (s, 3H). ^{13}C NMR (126 MHz, benzene-d_6): δ 153.54, 147.90, 138.00, 134.40, 131.49, 117.06, 17.89, 17.61, 12.10. Anal. Calcd for $C_{27}H_{39}NOTi$: C, 73.46; H, 8.90; N, 3.17. Found: C, 73.05; H, 8.78; N, 3.46.

Bis(pentamethylcyclopentadienyl)titanium(IV)−oxo, $Cp^*_2Ti{=}O$(DMAP) (2c). Titanocene−oxo complex **2a** (0.1 g, 0.242 mmol, 1.0 equiv) was dissolved in toluene (4 mL) in a 20 mL scintillation vial containing a magnetic stirbar. DMAP (29 mg, 0.242 mmol, 1.0 equiv) was added with stirring. The reaction was stirred at room temperature for 2 h, and the product was collected by filtration as a light yellow solid, 99 mg, 90% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.70 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 7.34 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.82 (m, 2H), 2.03 (s, 30H), 2.02 (s, 6H). Low solubility did not allow for a ^{13}C NMR. Anal. Calcd for $C_{27}H_{40}N_2OTi$: C, 71.04; H, 8.83; N, 6.14. Found: C,70.96; H, 8.69; N, 6.22.

Bis(tetramethylcyclopentadienyl)titanium−Ethylene, $Cp'_2Ti(C_2H_4)$ (3). **3** was prepared following the procedure described for **1** starting with Cp'_2TiCl_2. Green crystalline solid, 69% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 4.10 (s, 2H), 2.44 (s, 12H), 2.03 (s, 4H), 1.07 (s, 12H). ^{13}C NMR (126 MHz, benzene-d_6): δ 123.91, 119.05, 111.91, 102.69, 13.48, 12.65. Anal. Calcd for $C_{20}H_{30}Ti$: C, 75.46;H, 9.50. Found: C, 75.21; H, 9.50.

Bis(tetramethylcyclopentadienyl)titanium(IV)−oxo, $Cp'_2Ti{=}O$(py) (4a). Titanocene−ethylene complex **3** (0.92 g, 2.89 mmol, 1.0 equiv) was dissolved in *n*-hexane (28 mL) in a 100 mL round-bottom flask containing a magnetic stirbar, followed by addition of pyridine (0.56 mL, 6.94 mmol, 2.4 equiv), and the mixture was stirred for 30 min. A solution of styrene oxide (0.33 mL, 2.89 mmol, 1.0 equiv) in hexane (2 mL) was added dropwise. The reaction mixture gradually turned dark yellow with formation of solid particles. The reaction mixture was stirred overnight, and a yellow powder product was collected by filtration and washed with cold pentane. Yellow solid, 0.67 g, 60% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.96 (d, $^3J_{HH}$ = 5.9 Hz, 1H), 7.53 (d, $^3J_{HH}$ = 5.8 Hz, 1H), 6.72 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 6.41 (m, 2H), 5.45 (s, 2H), 2.31 (s, 6H), 2.20 (s, 6H), 1.64 (s, 6H), 1.41 (s, 6H). ^{13}C NMR (126 MHz, benzene-d_6): δ 156.93, 149.95, 136.80, 124.86, 122.92, 121.64, 120.06, 116.91, 112.05, 110.02, 14.86, 13.19, 12.11, 11.18. Anal. Calcd for $C_{23}H_{31}NOTi$: C, 71.68; H, 8.11; N, 3.63. Found: C, 71.43; H, 7.99; N, 3.34.

Bis(tetramethylcyclopentadienyl)titanium(IV)−oxo, $Cp'_2Ti{=}O$(3,5-lutidine) (4b). **4b** was prepared following the procedure described for **4a**, starting with **3**, 3,5-lutidine, and styrene oxide. Yellow solid, 62% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.77 (s, 1H), 7.37 (s, 1H), 6.48 (s, 1H), 5.52 (s, 2H), 2.36 (s, 6H), 2.24 (s, 6H), 1.76 (s, 3H), 1.72 (s, 6H), 1.60 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (126 MHz, benzene-d_6): δ 154.04, 147.67, 138.37, 134.62, 131.99, 121.40, 120.09, 116.65, 112.03, 109.96, 17.84, 17.64, 14.92, 13.27, 12.14, 11.20. Anal. Calcd for $C_{25}H_{35}NOTi$: C, 72.63; H, 8.53; N, 3.39. Found: C, 72.68; H, 8.52; N, 3.61.

Bis(tetramethylcyclopentadienyl)titanium(IV)−oxo, $Cp'_2Ti{=}O$(DMAP) (4c). **4c** was prepared following the procedure described for **2c**, starting with **4a** and DMAP. Light yellow solid, 79% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.72 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 7.37 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 5.79 (m, 2H), 5.58 (s, 2H), 2.41 (s, 6H), 2.33 (s, 6H), 2.02 (s, 6H), 1.86 (s, 6H), 1.67 (s, 6H). Low solubility did not allow for ^{13}C NMR. Anal. Calcd for $C_{25}H_{36}N_2OTi$: C, 70.09; H, 8.47; N, 6.54. Found: C, 70.18; H, 8.24; N, 6.63.

Bis(pentamethylcyclopentadienyl)phenyloxatitanacyclobutene, $Cp^*_2Ti[OC(Ph)CH]$ (5a). To a 20 mL scintillation vial was added titanocene−oxo **2a** (330 mg, 0.80 mmol, 1.0 equiv), toluene (5 mL), and a magnetic stirbar. Phenylacetylene (105 μL, 0.96 mmol, 1.2 equiv) was added dropwise with stirring; an immediate color change from orange to green was observed. The reaction mixture was stirred at room temperature for 2 h before all volatiles were removed under vacuum. The dark green residue was taken up in

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hexane and filtered to remove any solid. The filtrate was concentrated and cooled to −30 °C overnight, affording dark green crystals. The product was collected by filtration, washed with cold hexane, and dried under vacuum overnight, 331 mg, 95% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.01 (dd, $^3J_{HH}$ = 8.2 Hz, $^5J_{HH}$ = 1.5 Hz, 2H), 7.67 (s, 1H), 7.30 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz, 2H), 7.12 (tt, $^3J_{HH}$ = 7.3 Hz, $^5J_{HH}$ = 1.3 Hz, 1H), 1.71 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 167.24, 135.68, 128.30, 126.53, 125.23, 121.45, 11.63. One signal is underneath solvent peaks. NMR data were in agreement with a previous report.[12]

Bis(pentamethylcyclopentadienyl)(4-methoxyphenyl)-oxatitanacyclobutene, Cp*$_2$Ti[OC(4-OMe-C$_6$H$_4$)CH] (5b). **5b** was prepared following the procedure described for **6a**, starting with **2a** and 4-methoxyphenylacetylene. Dark green solid, 92% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.94 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 7.60 (s, 1H), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.34 (s, 3H), 1.75 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6) δ 166.19, 159.32, 126.40, 121.37, 113.98, 54.82, 11.65, two signals are underneath solvent peaks. HRMS (ESI): calcd for $C_{29}H_{38}O_2Ti$ 467.2430 $[MH]^+$, found 467.2433. Anal. Calcd for $C_{29}H_{38}O_2Ti{\cdot}1/9(H_2O)$: C, 74.35; 8.22. Found: C, 74.09; H, 7.82.

Bis(pentamethylcyclopentadienyl)[3,5-bis(trifluoromethyl)-phenyl]oxatitanacyclobutene, Cp*$_2$Ti[OC(3,5-(CF$_3$)$_2$-C$_6$H$_3$)CH] (5c). **5c** was prepared following the procedure described for **5a**, starting with **2a** and 3,5-bis(trifluoromethyl)phenylacetylene. Dark green solid, 88% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.44 (s, 2H), 7.69 (s, 1H), 7.58 (s, 1H), 1.57 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 168.64, 138.48, 131.72 (q, $^2J_{CF}$ = 32.6 Hz), 126.97, 124.57 (q, $^1J_{CF}$ = 273.4 Hz), 124.33 (q, $^3J_{CF}$ = 3.9 Hz), 122.17, 119.36 (hept, $^3J_{CF}$ = 3.9 Hz), 11.47. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.92. HRMS (ESI): calcd for $C_{30}H_{34}F_6OTi$ 573.2071 $[MH]^+$, found 573.2072. Anal. Calcd for $C_{30}H_{34}F_6OTi$: C, 62.94; H, 5.99. Found: C, 62.79; H, 6.00.

Bis(pentamethylcyclopentadienyl)(4-fluorophenyl)-oxatitanacyclobutene, Cp*$_2$Ti[OC(4-F-C$_6$H$_4$)CH] (5d). **5d** was prepared following the procedure described for **5a**, starting with **2a** and 4-fluorophenylacetylene. Dark green solid, 70% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.80 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HF}$ = 5.6 Hz, 2H), 7.50 (s, 1H), 6.95 (t, J = 8.8 Hz, 2H), 1.70 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 166.20 (d, $^4J_{CF}$ = 2.2 Hz), 163.54, 161.60, 131.91 (d, $^3J_{CF}$ = 2.8 Hz), 126.57 (d, $^2J_{CF}$ = 7.6 Hz), 121.56, 115.03 (d, $^1J_{CF}$ = 21.3 Hz), 11.59. ^{19}F NMR (470 MHz, benzene-d_6): δ −117.66. HRMS (ESI): calcd for $C_{28}H_{35}FOTi$ 455.2230 $[MH]^+$, found 455.2225. Anal. Calcd for $C_{28}H_{35}FOTi{\cdot}2/9(H_2O)$: C: 73.36; H, 7.79. Found: C, 73.37; H, 7.66.

Bis(tetramethylcyclopentadienyl)[3,5-bis(trifluoromethyl)-phenyl]oxatitanacyclobutene, Cp′$_2$Ti[OC(3,5-(CF$_3$)$_2$-C$_6$H$_3$)CH] (6a). **6a** was prepared following the procedure described for **5a**, starting with **4a** and 3,5-bis(trifluoromethyl)phenylacetylene. Dark green solid, 94% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.43 (s, 2H), 7.70 (s, 1H), 7.59 (s, 1H), 5.37 (s, 2H), 1.72 (s, 6H), 1.51 (s, 6H), 1.50 (s, 6H), 1.40 (s, 6H). ^{13}C NMR (126 MHz, benzene-d_6): δ 167.62, 138.11, 131.73 (q, $^2J_{CF}$ = 32.6 Hz), 129.25, 127.98, 127.70, 124.58 (q, $^3J_{CF}$ = 3.8 Hz), 124.51 (q, $^1J_{CF}$ = 273.29 Hz), 120.60, 119.75 (hept, $^3J_{CF}$ = 3.9 Hz), 119.34, 111.02, 13.63, 13.49, 11.96, 10.81. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.94. HRMS (ESI): calcd for $C_{28}H_{30}F_6OTi$ 545.1759 $[MH]^+$, found 545.1750. Anal. Calcd for $C_{28}H_{30}F_6OTi$: C, 61.78; H, 5.55. Found: C, 61.36; H, 5.48.

Cp*$_2$Ti[OC(CH$_3$)C(C$_6$H$_5$)] (7a). In a glovebox, titanium−oxo complex **2b** (213 mg, 0.484 mmol, 1.0 equiv) and 1-phenyl-1-propyne (243 μL, 1.94 mmol, 4.0 equiv) were dissolved in toluene (5 mL) in a 20 mL scintillation vial containing a magnetic stirbar. The vial was sealed with a Teflon-lined screw cap and heated at 60 °C for 3 days. All volatiles were then removed under vacuum, resulting in a dark brown, oily residue. This residue was dissolved in pentane (2.0 mL) and kept at −30 °C for 3 days, affording light brown crystals. The product was collected by filtration, washed with cold pentane, and dried under vacuum. Light brown solid, 109 mg, 50% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.31 (dd, $^3J_{HH}$ = 8.3, 7.3 Hz, 2H), 6.99 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 6.97 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 2.28 (s, 3H), 1.73 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 169.05, 143.70, 128.49, 128.04, 127.22, 122.38, 121.95, 18.73, 11.97. HRMS (ESI): calcd for $C_{29}H_{38}OTi$ 450.2402 $[M]^+$, found 450.2405. Anal. Calcd for $C_{29}H_{38}OTi{\cdot}(1/6)H_2O$: C, 76.81; H, 8.52. Found: C, 76.81; H, 8.45.

Cp*$_2$Ti[OC(C$_6$H$_5$)C(C$_6$H$_5$)] (7b). **7b** was prepared following the procedure described for **7a**, starting with **2b** and diphenylacetylene. Dark brown solid, 43% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.02 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.4 Hz 2H), 7.17 (m, 2H), 7.14 (m, 2H), 7.07 (m, 3H), 6.91 (tt, J = 7.3, 1.3 Hz, 1H), 1.73 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 170.62, 143.44, 136.36, 131.96, 128.98, 128.73, 128.17, 127.06, 126.41, 122.86, 122.74, 11.92. NMR data were in agreement with a previous report.[12]

Cp*$_2$Ti[OC(3-Br-C$_6$H$_4$)N] (8a). To a 20 mL scintillation vial was added titanocene−oxo **2b** (168 mg, 0.38 mmol, 1.0 equiv), toluene (3 mL), and a magnetic stirbar. 3-Bromobenzonitrile (173 mg, 0.95 mmol, 2.5 equiv) was added with stirring; an immediate color change from orange to red was observed. The reaction was stirred at room temperature overnight, then kept at −30 °C for 3 h. The product was collected by filtration, washed with cold hexane, and dried under vacuum. Red powder, 161 mg, 82% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 8.79 (s, 1H), 8.34 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.32 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 6.92 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 1.68 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 143.53, 137.85, 132.00, 130.24, 129.97, 125.76, 123.61, 122.94, 11.38. Anal. Calcd for $C_{27}H_{34}BrNOTi{\cdot}(1/3)H_2O$: C, 62.08; H, 6.69; N, 2.68. Found: C, 62.04; H, 6.51; N, 2.89.

Cp*$_2$Ti[OC(3,5(CF$_3$)$_2$-C$_6$H$_3$)N] (8b). **8b** was prepared following the procedure described for **9a**, starting with **2b** and one equivalent of 3,5-bis(trifluoromethyl)benzonitrile. Red powder, 85% yield. ^{1}H NMR (500 MHz, benzene-d_6) δ 8.99 (s, 2H), 7.83 (d, 1H), 1.62 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 142.53, 138.18, 131.81 (q, $^2J_{CF}$ = 33.1 Hz), 126.89 (q, $^3J_{CF}$ = 4.3 Hz), 124.33 (q, $^1J_{CF}$ = 273.42 Hz), 124.08, 122.25 (hept, $^3J_{CF}$ = 3.9 Hz), 11.29. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.86. Anal. Calcd for $C_{29}H_{33}F_6NOTi{\cdot}(3/11)H_2O$: C, 60.23; H, 5.85; N, 2.42. Found: C, 60.25; H, 6.07; N, 2.56.

Cp*$_2$Ti[OC(3,5(CF$_3$)$_2$-C$_6$H$_3$)N] (9). To a 20 mL scintillation vial were added benzophenone imine (51 mg, 0.28 mmol, 1.0 equiv), titanocene−oxo **2b** (150 mg, 0.34 mmol, 1.2 equiv), toluene (1.4 mL), and a magnetic stirbar. The resulting reddish-orange solution was stirred for 24 h at room temperature before all volatiles were removed under vacuum. The orange-red residue was taken up in hexane and filtered to remove excess **2b**. The filtrate was evaporated to yield **9** as a very dense red oil, 117 mg, 81% yield. A small amount of benzophenone imine proved to be difficult to remove from this oil. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.65 (ddt, J = 13.8, 6.0, 1.4 Hz, 4H), 7.20 (td, J = 7.6, 6.1 Hz, 4H), 7.12 (m, 2H), 3.54 (s, 1H), 1.76 (s, 30H). ^{13}C NMR (126 MHz, benzene-d_6): δ 129.54, 128.64, 127.99, 127.79, 119.54, 11.88.

Cp*$_2$Ti[OC(C$_6$H$_5$)CHCH(C$_6$H$_5$)O] (11a). To a 20 mL scintillation vial were added chalcone **10a** (54 mg, 0.26 mmol, 1.0 equiv), titanocene−oxo **2b** (115 mg, 0.26 mmol, 1.0 equiv), toluene (4 mL), and a magnetic stirbar. The reaction mixture was stirred at room temperature for 3 h before all volatiles were removed under vacuum. Hexane (10 mL) was added to the vial, and the mixture was stirred thoroughly and kept at −30 °C overnight. The product containing trapped hexane (as shown in NMR spectra and crystal structure) was collected by filtration, washed with cold hexane, and dried under vacuum. Dark brown solid, 99 mg, 65% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.86 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.3 Hz, 2H), 7.74 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H), 7.38 (t, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.4 Hz, 2H), 7.30 (t, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.5 Hz, 2H), 7.21 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 7.17 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 6.64 (s, br, 1H), 5.55 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 1.89 (s, 15H), 1.79 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 160.81, 148.97, 142.92, 128.32, 128.16, 127.09, 127.04, 126.53, 125.70, 125.28, 124.53, 100.02, 83.17, 12.40, 11.92. Anal. Calcd for $C_{35}H_{42}O_2Ti{\cdot}1/2(C_6H_{14})$: C, 77.93; H, 8.43. Found: C, 78.03; H, 8.44.

Cp*$_2$Ti[OC(4-CF$_3$-C$_6$H$_4$)CHCH(4-OMe-C$_6$H$_4$)O] (11b). **11b** was prepared following the procedure described for **11a**, starting with **2b** and enone **10b**. Brown solid, 82% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.75 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.62 (d, $^3J_{HH}$ = 8.6 Hz,

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2H), 7.49 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.00 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.59 (s, br, 1H), 5.53 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 3.41 (s, 3H), 1.88 (s, 15H), 1.76 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 159.02, 158.78, 146.17, 140.69, 128.65 (q, $^2J_{CF}$ = 31.9 Hz), 128.38, 125.70, 125.48 (q, $^1J_{CF}$ = 272.16 Hz), 125.36, 125.10 (q, $^3J_{CF}$ = 3.8 Hz), 124.67, 113.83, 102.18, 82.95, 54.87, 12.36, 11.90. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.19. HRMS (ESI): calcd for $C_{37}H_{43}F_3O_3Ti$ 641.2722 $[MH]^+$, found 641.2721. Anal. Calcd for $C_{37}H_{43}F_3O_3Ti\cdot(2/5)H_2O$: C, 68.6; H, 6.82. Found: C, 68.5; H, 6.68.

Cp*$_2$Ti[OC(4-CF$_3$-C$_6$H$_4$)CHCH(4-Me-C$_6$H$_4$)O] (11c). 11c was prepared following the procedure described for **11a**, starting with **2b** and enone **10c**. Brown solid, 78% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.72 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.64 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.48 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.22 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 6.61 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 5.54 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 2.24 (s, 3H), 1.87 (s, 15H), 1.76 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 158.93, 146.19, 145.64, 135.94, 129.08, 128.64 (q, $^2J_{CF}$ = 31.9 Hz), 127.17, 125.70, 125.49 (q, $^1J_{CF}$ = 272.3 Hz), 125.41, 125.11 (q, $^3J_{CF}$ = 3.8 Hz), 124.71, 102.28, 83.10, 21.21, 12.36, 11.89. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.19. HRMS (ESI): calcd for $C_{37}H_{43}F_3O_2Ti$ 625.2773 $[MH]^+$, found 625.2772. Anal. Calcd for $C_{37}H_{43}F_3O_2Ti\cdot3/5(H_2O)$: C, 69.94; H, 7.01. Found: C, 69.59; H, 6.77.

Cp*$_2$Ti[OC(4-CF$_3$-C$_6$H$_4$)CHCH(C$_6$H$_5$)O] (11d). 11d was prepared following the procedure described for **11a**, starting with **2b** and enone **10d**. Brown solid, 74% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.71 (d, $^3J_{HH}$ = 7.8 Hz, 2H) 7.69 (d, $^3J_{HH}$ = 8.0 Hz, 2H) 7.48 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.60 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 5.51 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 1.86 (s, 15H), 1.75 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 159.12, 148.52, 146.17, 128.66 (q, $^2J_{CF}$ = 32.0 Hz), 128.39, 127.02, 126.74, 125.69, 125.48, 125.47 (q, $^1J_{CF}$ = 272.4 Hz), 125.10 (q, $^3J_{CF}$ = 3.8 Hz), 124.77, 102.23, 83.07, 12.35, 11.87. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.20. HRMS (ESI): calcd for $C_{36}H_{41}F_3O_2Ti$ 611.2616 $[MH]^+$, found 611.2619. Anal. Calcd for $C_{36}H_{41}F_3O_2Ti\cdot2/5(H_2O)$: C, 69.99; H, 6.82. Found: C, 70.02; H, 6.62.

Cp*$_2$Ti[OC(4-CF$_3$-C$_6$H$_4$)CHCH(4-Cl-C$_6$H$_4$)O] (11e). 11e was prepared following the procedure described for **11a**, starting with **2b** and enone **10e**. Brown solid, 81% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.69 (d, J = 8.1 Hz, 3H), 7.49 (d, J = 8.2 Hz, 2H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.34 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.44 (d, $^3J_{HH}$ = 2.2 Hz, 1H), 5.35 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 1.83 (s, 15H), 1.71 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 159.32, 147.11, 145.99, 132.38, 128.84 (q, $^2J_{CF}$ = 31.8 Hz), 128.50, 128.46, 125.68, 125.63, 125.42 (q, $^1J_{CF}$ = 272.4 Hz), 125.14 (q, $^3J_{CF}$ = 3.8 Hz), 124.91, 101.39, 82.08, 12.32, 11.84. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.23. HRMS (ESI): calcd for $C_{36}H_{40}ClF_3O_2Ti$ 645.2227 $[MH]^+$, found 645.2232. Anal. Calcd for $C_{36}H_{40}ClF_3O_2Ti\cdot2/5(H_2O)$: C, 66.29; H, 6.31. Found: 65.96; H, 6.16.

Cp*$_2$Ti[OC(4-CF$_3$-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (11f). 11f was prepared following the procedure described for **11a**, starting with **2b** and enone **10f**. Brown solid, 88% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.68 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.57 (s, 4H), 7.49 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.46 (s, br, 1H), 5.32 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 1.83 (s, 14H), 1.72 (s, 14H). ^{13}C NMR (126 MHz, benzene-d_6): δ 159.81, 152.62, 145.96, 128.95 (q, $^2J_{CF}$ = 32.0 Hz), 128.76 (q, $^2J_{CF}$ = 32.0 Hz), 126.94, 125.79, 125.65, 125.39 (q, $^1J_{CF}$ = 272.4 Hz), 125.34 (q, $^3J_{CF}$ = 3.7 Hz), 125.19 (q, $^3J_{CF}$ = 3.8 Hz), 125.04, 101.34, 81.89, 12.32, 11.81 (note: only see one of the CF3 quarter). ^{19}F NMR (470 MHz, benzene-d_6): δ −62.16, −62.24. HRMS (ESI): calcd for $C_{37}H_{40}F_6O_2Ti$ 679.2490 $[MH]^+$, found 679.2485. Anal. Calcd for $C_{37}H_{40}F_6O_2Ti$: C, 65.49; H, 5.94. Found: C, 65.26; H, 6.29.

Cp*$_2$Ti[OC(4-NMe$_2$-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (11g). 11g was prepared following the procedure described for **11a**, starting with **2b** and enone **10g**. Dark green solid, 81% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.86 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.65 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.56 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.73 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.57 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 5.35 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 2.57 (s, 6H), 1.91 (s, 15H), 1.83 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 161.94, 153.50, 150.25, 131.37, 128.65 (q, $^2J_{CF}$ = 29.4 Hz), 127.13, 126.57, 125.57 (q, $^1J_{CF}$ = 283.0 Hz), 125.41, 125.22 (q, $^3J_{CF}$ = 3.8 Hz), 124.61, 112.43, 95.89, 82.33, 40.38, 12.43, 11.92. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.07. HRMS (ESI): calcd for $C_{38}H_{46}F_3NO_2Ti$ 654.3038 $[MH]^+$, found 654.3057. Anal. Calcd for $C_{38}H_{46}F_3NO_2Ti\cdot1/3(H_2O)$: C, 69.19; H, 7.13; N, 2.12. Found: C, 68.9; H, 7.06; N, 2.27.

Cp*$_2$Ti[OC(4-OMe-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (11h). 11h was prepared following the procedure described for **11a**, starting with **2b** and enone **10h**. Brown solid, 85% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.62 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.57 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.92 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.53 (s, br, 1H), 5.29 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 3.37 (s, 3H), 1.88 (s, 15H), 1.79 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 161.33, 159.56, 153.26, 135.44, 128.61 (q, $^2J_{CF}$ = 31.7 Hz), 127.07, 126.81, 125.52, 125.48 (q, $^1J_{CF}$ = 272.2 Hz), 125.24 (q, $^3J_{CF}$ = 3.7 Hz), 124.74, 113.65, 97.39, 82.18, 54.83, 12.40, 11.88. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.10. HRMS (ESI): calcd for $C_{37}H_{43}F_3O_3Ti$ 641.2722 $[MH]^+$, found 641.2729. Anal. Calcd for $C_{37}H_{43}F_3O_3Ti\cdot1/3(H_2O)$: C, 68.73; H, 6.81. Found: C, 68.64; H, 6.81.

Cp*$_2$Ti[OC(C$_6$H$_5$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (11i). 11i was prepared following the procedure described for **11a**, starting with **2b** and enone **10i**. Brown solid, 60% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.84 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, 2H), 7.60 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.56 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.31 (dd, $^3J_{HH}$ = 8.0, 7.5 Hz, 2H), 7.18 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), 6.50 (s, br, 1H), 5.37 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 1.86 (s, 15H), 1.76 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 161.54, 153.10, 142.74, 128.53 (q, $^2J_{CF}$ = 32.1 Hz), 127.30, 127.00, 125.65, 125.60, 125.47 (q, $^1J_{CF}$ = 272.5 Hz), 125.25 (q, $^3J_{CF}$ = 3.7 Hz), 124.81, 99.26, 82.02, 12.37, 11.85, one signal is underneath solvent peaks. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.11. HRMS (ESI): calcd for $C_{36}H_{41}F_3O_2Ti$ 611.2616 $[MH]^+$, found 611.2616. Anal. Calcd for $C_{36}H_{41}F_3O_2Ti\cdot1/4(H_2O)$: C, 70.3; H, 6.8. Found: C, 70.31; H, 6.71.

Cp*$_2$Ti[OC(4−Br-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (11j). 11j was prepared following the procedure described for **11a**, starting with **2b** and enone **10j**. Brown solid, 58% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.56 (s, 4H), 7.51 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.41 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 6.44 (s, br, 1H), 5.24 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 1.82 (s, 15H), 1.73 (s, 15H). ^{13}C NMR (126 MHz, benzene-d_6): δ 160.17, 152.81, 141.53, 131.30, 128.66 (q, $^2J_{CF}$ = 31.7 Hz), 127.22, 126.99, 125.70, 125.42 (q, $^1J_{CF}$ = 272.3 Hz), 125.28 (q, $^3J_{CF}$ = 3.7 Hz), 124.94, 121.10, 99.63, 81.98, 12.35, 11.82. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.15. HRMS (ESI): calcd for $C_{36}H_{40}BrF_3O_2Ti$ 691.1701$[MH]^+$, found 691.1706. Anal. Calcd for $C_{36}H_{40}BrF_3O_2Ti$: C, 62.71; H, 5.85. Found: C, 62.86; H, 5.98.

Cp′$_2$Ti[OC(C$_6$H$_5$)CHCH(C$_6$H$_5$)O] (12a). 12a was prepared following the procedure described for **11a**, starting with **4a** and chalcone **10a**. Reddish-brown solid, 61% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.80 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 1.4 Hz, 2H), 7.61 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.5 Hz, 2H), 7.30 (dd, $^3J_{HH}$ = 8.4, 6.9 Hz, 2H), 7.24 (dd, $^3J_{HH}$ = 8.3, 7.1 Hz, 2H), 7.16 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 1H), one multiplet under solvent peak, 6.44 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 5.97 (s, 1H), 5.78 (s, 1H), 5.47 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 1.88 (s, 3H), 1.82 (s, 3H), 1.81 (s, 3H), 1.80 (s, 3H), 1.73 (s, 3H), 1.69 (s, 3H), 1.68 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (126 MHz, benzene-d_6): δ 159.57, 148.75, 142.18, 133.75, 133.20, 128.37, 128.15, 127.74, 127.43, 127.11, 126.91, 125.66, 122.29, 121.64, 120.83, 118.68, 112.65, 112.30, 110.16, 101.29, 84.98, 14.34, 13.86, 13.48, 13.30, 12.55, 12.04, 11.87, 11.82. HRMS (ESI): calcd for $C_{33}H_{38}O_2Ti$ 515.2430 $[MH]^+$, found 515.2420. Anal. Calcd for $C_{33}H_{38}O_2Ti$: C, 77.03; H, 7.44. Found: C, 76.72; H, 7.26.

Cp′$_2$Ti[OC(4-NMe$_2$-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (12g). 12g was prepared following the procedure described for **11a**, starting with **4a** and chalcone **10g**. Dark green solid, 75% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.81 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.55 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.41 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 6.05 (s, 1H), 5.86 (s, 1H), 5.30 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 2.56 (s, 6H), 1.97 (s, 3H), 1.92 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H), 1.81 (s, 3H), 1.72 (m, 9H). ^{13}C NMR (126 MHz, benzene-d_6): δ 160.86, 153.21, 150.28, 133.58, 133.53, 130.59, 128.80, 128.76 (q, $^2J_{CF}$

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= 32.0 Hz), 127.77, 127.70, 126.56, 125.44 (q, $^1J_{CF}$ = 272.7 Hz), 125.28 (q, $^3J_{CF}$ = 3.7 Hz), 122.41, 121.19, 120.91, 118.69, 112.98, 112.59, 112.38, 97.14, 83.90, 40.34, 14.39, 13.97, 13.50, 13.27, 12.56, 11.98, 11.95, 11.87. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.14. HRMS (ESI): calcd for $C_{36}H_{42}F_3NO_2Ti$ 626.2725 $[MH]^+$, found 626.2723. Anal. Calcd for $C_{36}H_{42}F_3NO_2Ti{\cdot}1/6(H_2O)$: C, 68.79; H, 6.79; N, 2.23. Found: C, 68.65; H, 6.68; N, 2.6.

Cp′$_2$Ti[OC(4-OMe-C$_6$H$_4$)CHCH(4-CF$_3$-C$_6$H$_4$)O] (12h). **12h** was prepared following the procedure described for **11a**, starting with **4a** and chalcone **10h**. Brownish-red solid, 80% yield. ^{1}H NMR (500 MHz, benzene-d_6): δ 7.75 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.53 (s, 4H), 6.89 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.37 (s, br, 1H), 6.03 (s, 1H), 5.85 (s, 1H), 5.25 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 3.36 (s, 3H), 1.93 (s, 3H), 1.88 (s, 3H), 1.83 (s, 3H), 1.79 (s, 3H), 1.78 (s, 3H), 1.71 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H). ^{13}C NMR (126 MHz, benzene-d_6): δ 160.21, 159.61, 152.95, 134.69, 133.64, 133.62, 128.97, 128.87 (q, $^2J_{CF}$ = 32.0 Hz), 127.79, 127.71, 126.80, 125.40 (q, $^1J_{CF}$ = 272.4 Hz), 125.31 (q, $^3J_{CF}$ = 3.7 Hz), 122.48, 121.30, 121.14, 118.86, 113.65, 113.11, 112.68, 98.60, 83.76, 54.83, 14.37, 13.93, 13.45, 13.26, 12.52, 11.96, 11.90, 11.83. ^{19}F NMR (470 MHz, benzene-d_6): δ −62.17. HRMS (ESI): calcd for $C_{35}H_{39}F_3O_3Ti$ 613.2409 $[MH]^+$, found 613.2412. Anal. Calcd for $C_{35}H_{39}F_3O_3Ti{\cdot}1/2(H_2O)$: C, 67.63; H, 6.49. Found: C, 67.52; H, 6.22.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00111.

^{1}H NMR spectra of reactions monitored by NMR, kinetic experiments, ^{1}H, ^{13}C, and ^{19}F NMR spectra of titanocene complexes (PDF)

Crystallographic data for **4b**, **8b**, and **11a** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kamihull@illinois.edu.

Notes

The authors declare no competing financial interest.

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