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Invited Paper

Insertion of Carbon-Heteroatom Multiple Bonds into Bis(η^5-cyclopentadienyl)titanacyclobutenes

James Douglas MEINHART and Robert Howard GRUBBS*
Contribution No. 7667 from the Arnold and Mabel Beckman Laboratory of Chemical Synthesis, California Institute of Technology, Pasadena, California, 91125, U.S.A.
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Titanacyclobutenes that are readily produced by the reaction of Tebbe reagent with disubstituted acetylenes react with a variety of heteroatom multiple bonds. The reaction with aldehydes and ketones is particularly clean and has been studied mechanistically. The aldehyde or ketone carbonyl oxygen coordinates to the titanium center in a preequilibrium step before ring expansion to the product metallaoxacyclohexenes.

Introduction

Insertion of unsaturated organic molecules into transition-metal carbon bonds has received much attention during the past thirty years. Insertion of carbon–carbon multiple bonds into transition-metal alkyl .complexes has been the focus of many laboratories due to the economic importance of polyolefins.[1] Carbon–heteroatom multiple bonds (i.e. ketone, ester, nitrile, and imine) also insert into transition-metal alkyl complexes.[2] Application of transition-metal alkyl complexes rather than main group complexes for nucleophilic addition to carbon–heteroatom bonds has the potential to alter the reactivity and selectivity by the appropriate combination of ancillary ligands.

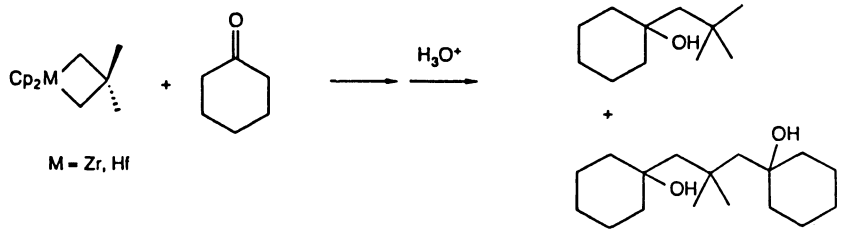
Organic chemistry contains many examples of metal alkyl addition to carbon–heteroatom multiple bonds. The Grignard reaction is a classic example of this type of reaction. Alkyl and aryl compounds derived from Li, Na, Al, and Cd are commonly used in organic synthesis.[3] The reactivity of these complexes is generally 1,2 addition to carbonyl groups, with varying selectivity.

Few transition-metal organometallic reagents have been developed for addition to carbon–heteroatom functionality. Dialkylcuprate complexes (R_2CuLi) add to α,β-unsaturated ketones in a 1,4 sense to yield a γ-alkylated ketone.[4] In contrast, an alkyllithium reagent adds in a 1,2 sense to the same ketone to yield an alcohol. This modified selectivity of a main group complex via a transition metal may provide new methods for regio- and stereo-controlled reactions.

Likewise, $(Pr^iO)_3TiCl$, when treated with a Grignard reagent, forms an alkyl titanium derivative, which is selective for aldehydes in the presence of ketones and nitriles.[5] Thus, the need for protection-deprotection of sensitive functionality may be reduced. This same titanium reagent also reacts in a highly diastereoselective manner with ketones and aldehydes. Transition-metal alkyl complexes from the left half of the transition block are highly reactive toward carbonyl compounds due to the oxophilicity of the metal.

Several reactions are known where a transition metal complex serves as a catalyst, transferring or coupling alkyl groups from a donor complex to the unsaturated substrate.[6]

Recently, 1,2-addition of carbonyl compounds to metallacyclobutane complexes has been postulated by product analysis.[7]

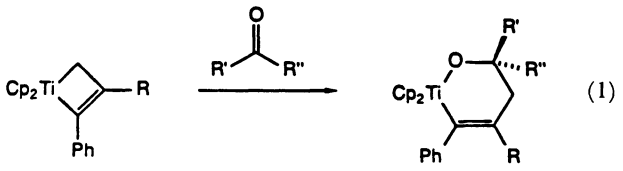


Due to the lack of methylene transfer chemistry of titanacyclobutenes, the reactivity of titanacyclobutenes with carbon–heteroatom bonds was investigated. Titanacyclobutenes[8] offer a unique template for the study of insertion into titanium–carbon bonds.

Results

Treatment of a solution of 2,3-diphenyltitanocenacyclobutene, **1a**, with acetone at room temperature for 2 days yields titanocenaoxacyclohexene, **2a**, in quantitative yield (Eq. 1). The reaction is greatly accelerated by warming the sample to 80 °C for

approximately 10—15 minutes. The 3-methyl-2-phenyltitanacyclobutene, **1b**, works equally well.[9] The titanaoxacyclohexenes, **2**, are isolated as yellow solids.



(1)

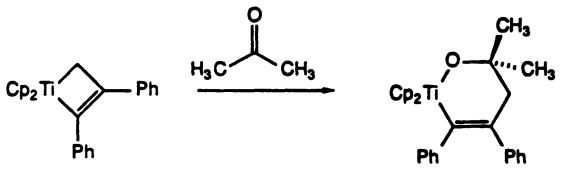
1a : R = Ph
1b : R = CH_3

2

The reaction is general for a variety of organic ketones (Table 1). Methylene transfer reaction to the ketone is not observed. Enolization of the ketone by the titanacyclobutene is not a significant side reaction.

However, titanacyclobutenes with β-hydrogens do not insert ketones to an appreciable extent. The metallacycle begins to react, and the insertion product decomposes rapidly at room temperature.

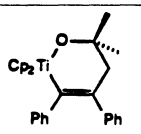
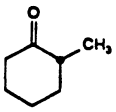
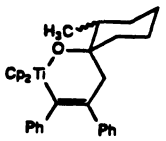
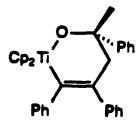
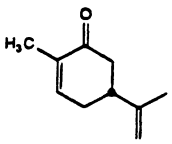
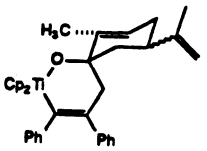
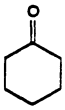
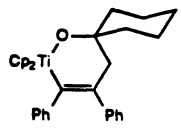
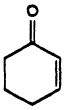
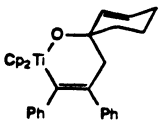
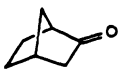
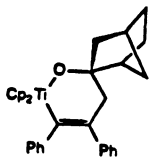
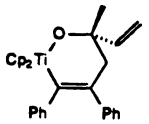
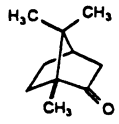
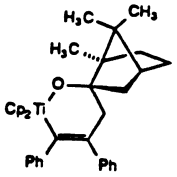
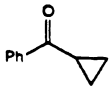
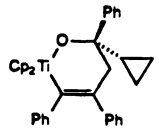
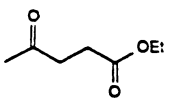
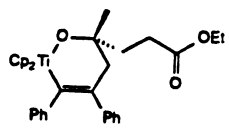
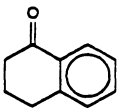
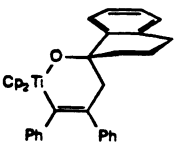
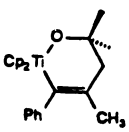
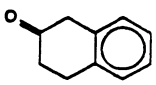
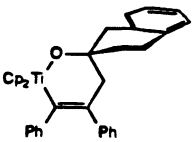
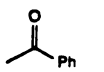
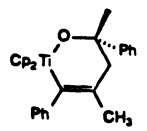
The kinetics of the insertion reaction of acetone into **1a** was monitored by NMR (Eq. 2). The rate expression was first order in metallacycle and ketone, second order overall. At 50 °C a second-order rate constant was calculated, $k_{323}=5.94(3)\times10^{-4}\ M^{-1}\ s^{-1}$.



(2)

1a **2a**

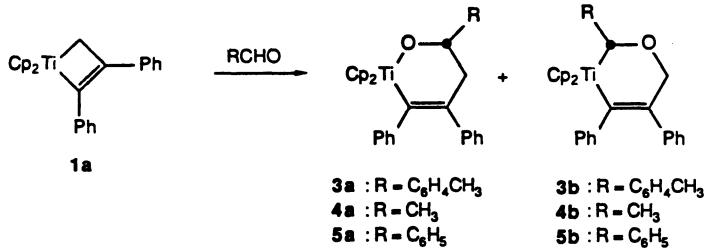
Table 1. Ketone Insertion into Titanacyclobutenes

Ketone	Titanacycle	Product		Ketone	Titanacycle	Product	
	**1a**		**2a**		**1a**		**2i**
	**1a**		**2b**		**1a**		**2j**
	**1a**		**2c**				
	**1a**		**2d**		**1a**		**2k**
	**1a**		**2e**		**1a**		**2l**
	**1a**		**2f**		**1a**		**2m**
	**1a**		**2g**		**1b**		**2n**
	**1a**		**2h**		**1b**		**2o**

The activation parameters were determined by Eyring analysis of the rate constants over a 40 °C temperature range (Table 2).

The NMR of the reaction solution at room temperature shows sharp signals for the metallacycle but a broad signal for the acetone. Upon cooling, the acetone signal broadens and disappears at ca. −40 °C at 90 MHz. Upon further cooling to −80 °C, the acetone signal begins to sharpen but does not split into a resolved doublet.

Aldehydes also insert cleanly into titanacyclobutenes (Eq. 3). Treatment of a solution of **1a** with *p*-tolualdehyde at room temperature cleanly results in disappearance of the starting material. Examination of the reaction mixture by NMR reveals the formation of two products in a 2:1 ratio. The major product is the expected isomer **3a** containing a titanium-oxygen bond. However, the second product appears to be a regioisomer, **3b**, in which the aldehyde has inserted in the opposite sense, forming a titanium–carbon bond. The dialkyl-substituted oxatitanacyclohexene, **3b**, is much less stable than **3a**. The titanaoxacyclohexenes are moderately air-stable and may be chromatographed on silica. The dialkyl isomers, **3b**, are air-sensitive and decompose upon warming to 80 °C. Insertion of acetaldehyde also yields two isomeric insertion products **4a** and **4b** in a nearly 1:1 ratio.



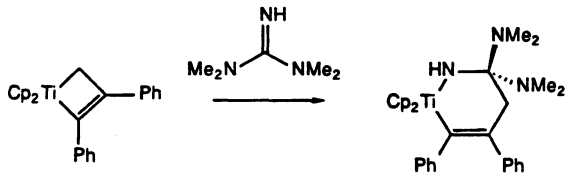
1a

3a : R = $C_6H_4CH_3$ **3b** : R = $C_6H_4CH_3$
4a : R = CH_3 **4b** : R = CH_3
5a : R = C_6H_5 **5b** : R = C_6H_5

(3)

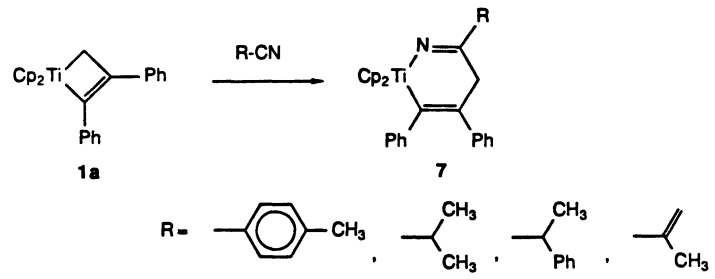
The insertion of benzaldehyde into **1a** has also been studied by Brown-Wensley.[9] Again, two products **5a** and **5b** were observed in a 2:1 ratio. The isomers were physically separated and hydrolyzed with HCl. The organic products were identified and are consistent with proposed regiochemistry.

Several other carbon–heteroatom multiple bonds add to titanacycles **1a**. Tetramethylguanidine inserts to yield an azatitanacyclohexene **6** (Eq. 4). The 90 MHz ^{1}H NMR exhibits a broad singlet for the $N(CH_3)_2$ groups at room temperature. The signal passes through coalescence at +15 °C, and becomes two singlets ($\Delta\nu$=47.8 Hz) at −80 °C. The η^5-cyclopentadienyl resonance also is a singlet until −47 °C when it passes through coalescence and becomes two singlets ($\Delta\nu$=73.5 Hz) at −80 °C.



1a **6**

(4)



1a **7**

(5)

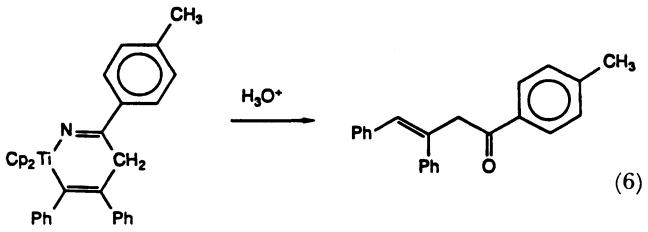
Table 2. Rate Constants and Activation Parameters for Acetone Insertion into **1a**

Temperature/K	k/M^{-1} s^{-1} × 10^4
293	3.51(7)
301	5.9(1)
313	16.8(2)
323	29.5(4)

$\Delta G^{\ddagger}_{301}$ = 22.0(5) kcal mol^{-1}. $\Delta H^{\ddagger}$ = 13.1(4) kcal mol^{-1}. $\Delta S^{\ddagger}_{301}$ = −29(1) eu.

Nitriles also react with titanacyclobutenes (Eq. 5); however, the reactions are not as clean as ketone insertions, and the products are not as stable. Treatment of a solution of **1a** in 400 μL of C_6D_6 with one equivalent of benzonitrile yielded, over 24 hours, a 1-aza-2-titanacyclohexa-3,6-diene complex, **7**. The product was stable for days in solution but eventually decomposed. The insertion reaction works for a variety of nitriles: *p*-tolyl, 1-methylpropyl, 1-phenylpropyl, and methacrylonitrile. Acetonitrile yielded

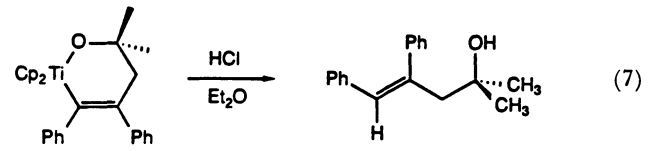
several products that decomposed rapidly at room temperature. Insertion of nitriles into titanacycle **1b** was also facile. Hydrolysis of the insertion products yields the corresponding ketones (Eq. 6).



(6)

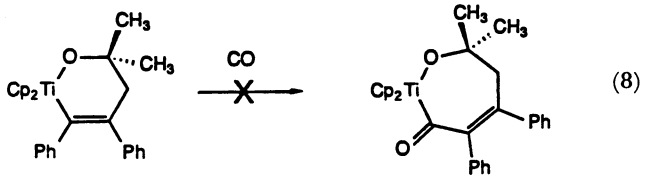
A variety of substrates do not react with the titanacyclobutenes: esters, carbonates, CO_2, CS_2, and imines.

The titanaoxacyclohexenes **2a** can be removed from the metal fragment by hydrolysis with HCl to yield a homoallylic alcohol in high yield (Eq. 7).



(7)

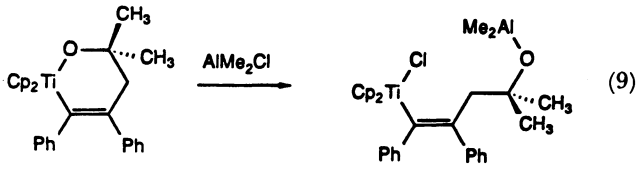
We had hoped to insert CO into the remaining titanium–carbon bond of **2a** to eventually yield a lactone (Eq. 8). However, all attempts to react **2a** with CO either thermally or photochemically failed.



(8)

2a

Lewis acids are known to accelerate migratory insertions of CO into metal–carbon bonds.[10,11] Treatment of **2a** with one equivalent of dimethylaluminum chloride results in immediate formation of a new complex. The new complex was dark-red and the NMR spectrum was very complex. Treatment of this complex with CO yield starting material **2a**. The deep-red color of the reaction mixture and analysis of the NMR spectrum suggest that the Ti–O bond transmetallates to the dimethylaluminum chloride, forming a titanocene alkenyl chloride and aluminum alkoxide (Eq. 9). Trimethyltin chloride did not react with **2a**.



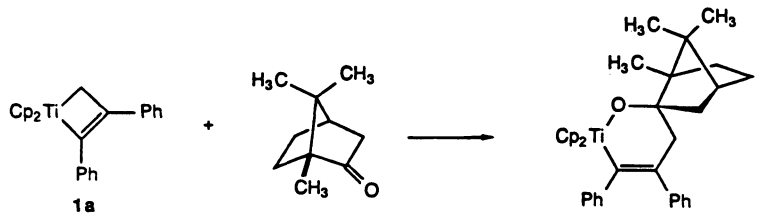
(9)

Discussion

Titanocenacyclobutenes readily insert ketones to yield titanocenaoxacyclohexenes. The reaction is quite general for many ketones, and a few examples deserve mention.

The insertion shows very little facial selection for cyclohexenone derivatives. Insertion of 2-methylcyclohexanone yields two diastereomeric products in nearly equal ratios. Insertion of *l*-carvone gives two diastereomeric products in a 62:38 ratio. The lack of diastereoselection reflects both a lack of adverse steric interactions at the transition state and the relatively high reaction temperature. Attempting to increase the diastereoselection by reducing the temperature is impractical because of the slow reaction rate at room temperature.

Titanacyclobutenes will add very sterically crowded ketones, such as *d*-camphor, although the reaction is much slower. The NMR data and difference NOE experiments suggest that the metallacycle adds to the *endo*-face of the camphor molecule (Eq. 10).[12]



(10)

Phenyl cyclopropyl ketone inserts without any rearrangement to produce a single product in high yield. If the insertion mechanism involved a one-electron reduction or oxidation of the ketone, the cyclopropyl carbinyl radical could open.[13] Although rearrangement is not observed, this experiment does not conclusively rule out a radical mechanism.

Ethyl levulinate reacts exclusively at the methyl ketone to yield the expected oxacyclohexene, **2m**. Simple esters such as methyl benzoate do not react with the titanacyclobutenes. This selectivity for ketones over esters may arise from two factors. Esters are slightly weaker bases than ketone (1–2 pK_a units).[14] The carbonyl carbon of an ester is less electrophilic compared to a ketone, due to resonance from the other oxygen atom.[15] Both factors, the less

basic carbonly oxygen and the less electrophilic carbon, contribute to the selectivity. Steric factors are not significant. Unlike ketones, which display an exchanged broadened NMR signal for the ketone during reaction, the NMR signals of the ester remain sharp.

The NMR spectra during the reaction suggest that the ketone is associated with the metallacycle prior to reaction. Titanacyclobutenes are formally 16-electron complexes and have a vacant orbital into which the carbonyl may coordinate. Variable temperature NMR experiments confirm a dynamic process with a very low activation barrier, possibly ketone coordination, occurs. Kinetic data and activation parameters (Table 2) are consistent with a second-order reaction. A rapid pre-equilibrium does not change the observed rate analysis.[16]

The regiochemistry of aldehyde insertion also provides information about the mechanism. Formation of a titanium–carbon bond compared to a more thermodynamically stable titanium-oxygen bond is very unusual. The estimated energy difference of a Ti–C and Ti–O bond is ca. 50 kcal mol^{-1}.[17] The formation of a Ti–C bond has been observed in the head-to-tail coupling of diphenylketene units in a titanium diphenylketene complex.[18]

A possible explanation for the product distribution is kinetic control of the insertion proceeding via a π-bound aldehyde complex. An organic carbonyl group can coordinate either in a π-sense or σ-sense to the metallacycle. A $Cp_2V(acetone)^+$ complex in which the acetone molecule is η^1-coordinated through the sp^2 lone pair of the oxygen atom has been structurally characterized.[19] The variable temperature NMR results may be explained, by a reversible coordination of the carbonyl group in either geometry. However, a π-complex is the necessary transition state for the insertion due to orbital overlap constraints.[20] If η^1-coordination of the oxygen atom lead directly to product, then only **3** should be formed because the carbon would never interact with the titanium. A π-complex could give two isomeric complexes, one with the oxygen atom toward the metallacycle and one with the oxygen away from the metallacycle. Due to steric interactions, ketones react only with the alkyl substituents directed away from the η^5-cyclopentadienyl rings, resulting in the observed regiospecificity. Since aldehydes have only one alkyl group, they can twist slightly to accommodate reaction in either direction (Fig. 1). Larger substituents on the aldehyde

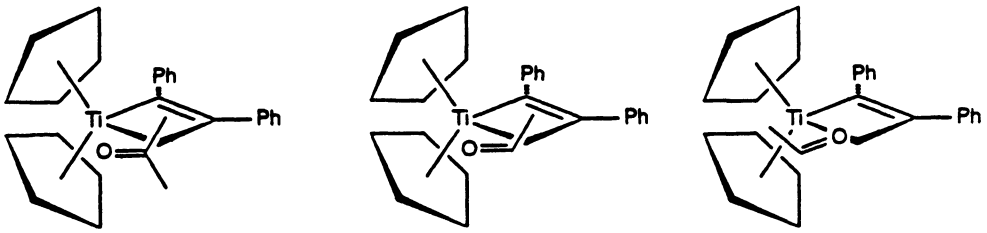


Fig. 1. Proposed carbonyl complexes of **2a**.

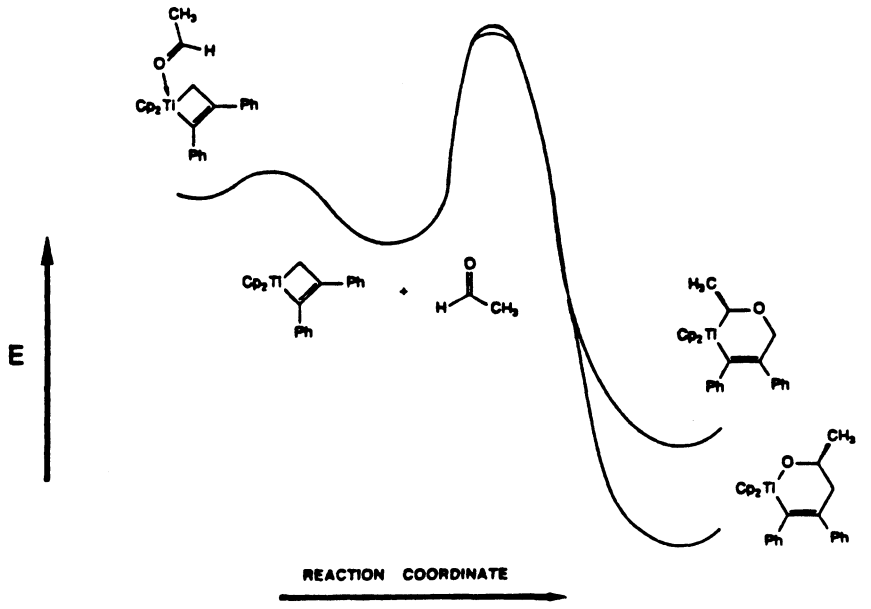


Fig. 2. Proposed energy profile for aldehyde and ketone insertion.

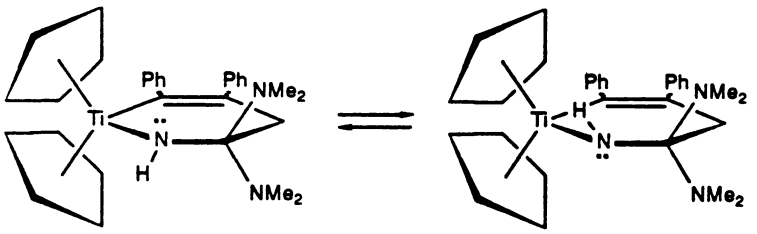
favor the Ti–O product as predicted. The metal center is d^0, and a rotation barrier resulting from back-bonding to the π^* orbital should not exist.

The products are also consistent with an early transition state. Based on the Hammond postulate, an early transition state should be "reactant-like" and not reflect the relative stability of the products.[21] A substituents-effect study of the kinetics may provide information about the polarization of the transition state. A proposed reaction coordinate is shown in Fig. 2.

Insertion of nitriles is analogous to insertion of ketones. However, the products appear to be less stable. The remaining methylene group at the γ-position may be quite acidic due to resonance delocalization (Eq. 11), and deprotonation could lead to decomposition. Nitrile insertions into zirconocene hydride and alkyl complexes yield stable complexes.[22] If the nitrile insertion product is immediately hydrolyzed, the expected ketone is isolated in low yield.

(11)

The most unusual substrate that inserts into titanacyclobutenes is tetramethylguanidine. The insertion product, **6**, has two fluxional processes by NMR.[23] The higher-energy process coalesces at +15 °C at 90 MHz, yielding a $\Delta G^*=14.2\pm0.3$ kcal mol^{-1}. This process is attributable to hindered rotation of the $N(CH_3)_2$ groups. The lower-energy process coalesces at −47 °C, yielding a $\Delta G^*=10.9\pm0.3$ kcal mol^{-1}. This process is attributable to the inversion of the NH group bonded to the titanium. The nitrogen pair presumably interacts with the vacant LUMO on the metal (Eq. 12).[24] This interaction would lead to inequivalent η^5-cyclopentadienyl rings, if the rate were slowed below the NMR time scale.



(12)

The lack of carbonylation of **2a** is consistent with other titanium and zirconium alkyl alkoxide complexes. The lack of carbonylation is usually explained by invoking donation of the oxygen lone pair into the LUMO on the titanium. Dative interaction from the oxygen fills the orbital, which would be used for coordination of the CO. This π-donation from the oxygen of titanium alkoxides has been structurally verified.[25] Attempts to complex the oxygen to another Lewis acid failed. Dimethylaluminum chloride appeared to transmetallate the Ti–O bond, although the resulting complex did not react with CO.

Conclusion

Titanacyclobutenes readily insert ketones, aldehydes, and nitriles to form new organometalic complexes. These reactions proceed in good yield with titanacyclobutenes that have a phenyl grouped at the α-position. Titanacyclobutenes that have alkyl substituents at the α-position form unstable products.

The reaction is general for many ketones and highly selective for ketones and aldehydes over esters. Aldehydes yield two products, the predicted Ti–O bound isomer but also the Ti–C bound isomer. The product distribution is consistent with a π-bound carbonyl group at the rate-determining transition state. A detailed kinetics study of the insertion, including substituent effects, would be useful in understanding the mechanism.

Insertion of nitriles forms an analogous product; however, they are less stable than the ketone products.

The titanaoxacyclohexenes, **2**, may be hydrolyzed to the corresponding homoallylic alcohols in high yield. Unfortunately, the titanaoxacyclohexenes would not insert CO under any of the conditions used. Extensions of this work utilizing functionalized titanacyclobutenes and different Lewis acids may find use in organic synthesis.

Experimental

General Considerations. All manipulations were performed with the use of standard Schlenk techniques under argon or in a Vacuum Atmospheres Co. glovebox under nitrogen. Argon was purified by passage through columns of BASF R3-11 (Chemalog) and Linde 4 Å molecular sieves. Carbonylations were performed in Lab-Glass pressure bottles (60 or 100 mL) fitted with two inlet valves and a pressure gauge. Toluene, benzene, THF, and diethyl ether were vacuum-transferred from sodium benzophenone ketyl and stored in Teflon-valve sealed vessels under argon. Pentane and hexane were stirred over concentrated H_2SO_4, dried, vacuum-transferred from sodium benzophenone ketyl and stored in Teflon-valve sealed vessels under argon.

Methylene chloride was vacuum-transferred from P_2O_5 or CaH_2 and stored under argon. Benzene-d_6, toluene-d_8, and THF-d_8 were vacuum-transferred from sodium benzophenone ketyl. Carbon monoxide (CP) was obtained from Matheson. ^{13}C-enriched carbon monoxide (90% ^{13}C) was obtained from Monsanto-Mound Laboratories. Trimethylphosphine was obtained from Strem Chemicals. Acetylenes were obtained from Aldrich, Farchan Laboratory, or Wiley Organics and dried or distilled before use.

Instrumentation. Infrared spectra were recorded on either a Beckman 4240, Shimadzu IR-435, or Perkin-Elmer 1310 spectrophotometer. ^1H NMR were recorded on a Varian EM-390, JEOL FX-90Q, Varian XL-200, JEOL GX-400, or Brüker WM-500 and referenced to residual solvent (C_6D_6, δ 7.15; C_7D_8, δ 2.09; THF-d_8, δ 3.58 or 1.73; $CDCl_3$, δ 7.24). $^{31}P\{^1H\}$ NMR were recorded on a JEOL FX-90Q and referenced to external 85% H_3PO_4 (positive δ, lower field). $^{13}C\{^1H\}$ NMR were recorded on a JEOL FX-90Q, Varian XL-200, or JEOL GX-400. Difference NOE spectra were recorded on a JEOL GX-400 or a Brüker WM-500 at the Southern California Regional NMR Facility located at the California Institute of Technology. Reaction kinetics were performed on the JEOL FX-90Q using an automated routine. Elemental analyses were performed by Dornis and Kolbe, Mulheim, West Germany, and the analytical facility of the California Institute of Technology.

Kinetics. The rates of the reaction were determined by NMR in septum capped tubes. At least 12 data points were taken by integration of the methylene signals in the starting material and products. The complex **1a** varied in concentration from 0.12 to 0.24 M and the acetone was always in excess varying from 0.17—0.34 M in C_6D_6. Probe temperature was determined at each temperature by a standard second order kinetic calculation.

Materials. Titanacyclobutenes were synthesized as previously described.[8] Ketones, aldehydes, and nitriles were purchased from Aldrich Chemical Co. and used as received. Tetramethylguanidine was obtained from Kodak and dried over 4 Å molecular sieves.

Insertion of Ketones into Titanacyclobutenes 1a and 1b. All reactions were performed by the same general procedure. A stirred solution or suspension of the titanacyclobutene (typically 0.5 M in toluene) was treated with the ketone. The mixture was stirred for 24—48 hours at room temperature, at which time the solution was clear orange. As an alternate method, the reaction mixture was heated to 80 °C for 10—15 minutes and cooled to room temperature. The orange solution was filtered and the volatiles removed, the solid washed with pentane or ether, and dried in vacuo to yield the product.

3,3-Dimethyl-5,6-diphenyl-2-oxa-titanocenecyclohex-5-ene, 2a. Yield: 93%. ^1H NMR (90 MHz, C_6D_6) δ=7.08—6.64 (m, 10H), 5.77 (s, 10H), 2.67 (s, 2H), 1.21 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=190.32, 154.32, 147.23, 134.30, 129.82, 127.55, 124.68, 122.87, 113.64 (Cp), 88.16, 58.79, 28.64. IR (KBr, cm^{-1}) 3010 (w), 2960 (m), 2920 (m), 1650 (w), 1155 (s), 995 (s), 800 (s). Anal. Calcd for $C_{28}H_{28}OTi$: C, 78.50; H, 6.59%. Found: C, 78.50; H, 6.72%.

3-Methyl-3,5,6-triphenyl-2-oxa-titanocenecylohex-5-ene, 2b. Yield: 87%. ^1H NMR (400 MHz, C_6D_6) δ=7.267—6.789 (m, 15H), 5.954 (s, 5H), 5.591 (s, 5H), 3.089 (d, J=15.4 Hz, 1H), 2.962 (d, J=15.4 Hz, 1H), 1.578 (s, 3H). Difference NOE experiments: irradiation of δ 5.954 enhances δ 7.220, 6.789, 5.591, 3.089; irradiation of δ 5.591 enhances δ 6.789, 5.954. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=190.7, 154.2, 150.6, 147.3, 133.9, 129.8, 128.3, 127.7, 126.4, 124.9, 123.1, 114.9 (Cp), 113.2 (Cp), 90.8, 58.3, 29.3. IR (KBr, cm^{-1}) 3025 (m), 2975 (m), 1600 (w), 1090 (s), 1068 (s), 1000 (s), 804 (s). Anal. Calcd for $C_{33}H_{30}OTi$: C, 80.81; H, 6.16%. Found: C, 79.70; H, 6.06%.

Reaction of Cyclohexanone with 1a, 2c. Yield: 90%. ^1H NMR (400 MHz, C_6D_6) δ=7.029 (m, 6H), 6.883 (t of t, J=7.0, 2.0 Hz, 1H), 6.767 (m, 3H), 5.775 (s, 10H), 2.646 (s, 2H), 1.710 (m, 2H), 1.472 (m, 5H), 1.349 (m, 2H), 1.239 (m, 1H). Difference NOE experiments: irradiation of δ 5.775 enhances δ 6.767, 2.646, 1.710; irradiation of δ 2.646 enhances δ 5.775, 1.349. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δ=189.4, 154.7, 147.6, 133.6, 129.9, 128.3, 124.6, 122.8, 113.5 (Cp), 89.9, 57.1, 37.8 (×2), 26.6, 23.6 (×2). IR (KBr, cm^{-1}) 3030 (m), 2925 (s), 1068 (s), 995 (s), 800 (s).

Reaction of 2-Cyclohexen-1-one with 1a, 2d. Yield: 57%. ^1H NMR (400 MHz, C_6D_6) δ=7.062—7.046 (m, 6H), 6.868 (m, 1H), 6.804 (m, 3H), 6.044 (d, J=10.0 Hz, 1H), 5.841 (s, 5H), 5.742 (s, 5H), 5.74 (d, overlapping Cp, 1H), 2.838 (d, J=15.4 Hz, 1H), 2.750 (d, J=15.4 Hz, 1H), 1.932—1.755 (m, 3H), 1.641—1.518 (m, 3H). Difference NOE experiments: irradiation of δ 5.841 enhances δ 6.84, 2.838; irradiation of δ 5.742 enhances δ 6.044, 2.750. $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6) δ=190.7, 154.2, 147.2, 133.3, 133.6, 129.9, 128.7, 128.3, 127.8, 124.8, 122.9, 113.9 (Cp), 113.7 (Cp), 87.4, 57.8, 36.6, 25.9, 25.4, 20.3. IR (KBr, cm^{-1}) 3015 (w), 2920 (m), 1068 (s), 993 (s), 805 (s).

3-Cyclopropyl-3,5,6-triphenyl-2-oxa-titanocenecyclohex-5-ene, 2e. Yield: 77%. ^1H NMR (400 MHz, C_6D_6) δ=7.23—6.76 (m, 15H), 5.842 (s, 5H), 5.673 (s, 5H), 3.381 (d, J=15.4 Hz, 1H), 3.283 (d, J=15.4 Hz, 1H), 1.472 (m, 1H), 0.430 (m, 2H), 0.295 (m, 1H), 0.198 (m, 1H). Difference NOE experiments: irradiation of δ 5.842 enhances δ 7.06, 6.77, 3.28; irradiation of 5.673 enhances δ 6.77, 1.47, 0.43, 0.198. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=189.3, 154.4, 147.6, 146.7, 133.7, 130.1, 127.5, 127.7, 126.4, 124.9, 123.0, 115.1 (Cp), 112.8 (Cp), 91.7, 57.1, 22.8, 2.19, 1.47. IR (KBr, cm^{-1}) 3010 (m), 2930 (w), 1030 (s), 810 (s).

Reaction of α-Tetralone with 1a, 2f. Yield: 96%. ^1H NMR (400 MHz, C_6D_6) δ=7.940 (d, J=7.6 Hz, 1H), 7.237 (m, 1H), 7.108 (m, 1H), 7.044 (m, 8H), 6.860 (m, 2H), 6.796 (m, 1H), 5.998 (s, 5H), 5.673 (s, 5H), 3.150 (d, J=16.1 Hz, 1H), 2.920 (s, J=16.1 Hz, 1H), 2.643 (m, 1H), 2.588 (m, 1H), 2.320 (m, 1H), 1.923 (m, 1H), 1.815 (m, 2H). Difference NOE experiments: irradiation of δ 5.998 enhances δ 7.940, 6.860, 5.673, 3.150; irradiation of δ 5.673 enhances δ 6.860, 5.998, 2.920, 1.923.

Reaction of β-Tetralone with 1a, 2g. Yield: 77%. ^1H NMR (400 MHz, C_6D_6) δ=7.236—6.911 (m, 14H), 5.961 (s, 1H), 5.561 (s, 5H), 3.270 (d, J=16.3 Hz, 1H), 2.942 (m, 1H), 2.920 (d, J=15.6 Hz, 1H), 2.880 (d, J=16.6 Hz, 1H), 2.722 (d, J=15.6 Hz, 1H), 1.825 (m, 1H), 1.780 (m, 1H). Difference NOE experiments: irradiation of δ 5.961 enhances δ 6.91, 5.561, 2.920; irradiation δ 5.561 enhances δ 6.91, 5.961, 3.270.

3-Methyl-5,6-diphenyl-3-vinyl-2-oxa-titanocenecylohex-5-ene, 2h. Yield: 62%. ^1H NMR (400 MHz, C_6D_6) δ=7.03—6.76 (m, 10H), 5.97 (d of d, J=10.5, 17.1 Hz, 1H), 5.938 (s, 5H), 5.612 (s, 5H), 5.100 (d of d, J=17.1, 2.2 Hz, 1H), 4.970 (d

of d, J=10.5, 2.2 Hz, 1H), 2.910 (d, J=15.4 Hz, 1H), 2.58 (d, J=15.4 Hz, 1H), 1.34 s 3. Difference NOE experiments: irradiation of δ 5.940 and 5.970 enhances δ 6.76, 5.61, 2.91; irradiation of δ 5.61 enhances δ 6.76, 5.94; irradiation of δ 1.34 enhances 7.02, 5.97, 5.61, 5.10, 2.58. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=190.7, 154.3, 147.0, 146.1, 133.4, 129.9, 127.6, 124.8, 123.0, 114.5, 113.4, 110.3, 89.7, 57.0, 26.2. IR (KBr, cm^{-1}) 3005 (m), 2910 (s), 1015 (s), 987 (s), 800 (s).

Reaction of Ethyl Levulinate with 1a. Synthesis of 2m. ^1H NMR (400 MHz, C_6D_6) δ=7.02—6.69 (m, 6H), 6.88 (t of t, J=7.0, 2.0 Hz, 1H), 6.75 (m, 3H), 5.901 (s, 5H), 5.596 (s, 5H), 4.010 (m, 2H), 2.720 (d, J=15.4 Hz, 1H), 2.460 (d, J=15.4 Hz, 1H), 2.315 (m, 2H), 2.138 (m, 1H), 2.01 (m, 1H), 1.77 (m, 1H), 1.134 (s, 3H), 1.020 (t, J=7.1 Hz, 3H). Difference NOE experiments: irradiation of δ 5.901 enhances δ 6.75 and 2.72; irradiation of δ 5.596 enhances δ 6.75. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ 190.52, 173.51, 154.27, 147.18, 133.85, 129.84 (CH), 127.62 (CH), 124.75 (CH), 122.96 (CH), 114.19 (Cp), 113.59 (Cp), 89.38 (quat), 60.07 (CH_2), 57.52 (CH_2), 37.53 (CH_2), 30.11 (CH_2), 24.64 (CH_3) 14.34 (CH_3).

Reaction of *l*-Carvone with 1a. Synthesis of 2j. Major isomer: ^1H NMR (400 MHz, C_6D_6) δ=7.31—6.75 (m, 10H), 6.076 (s, 5H), 5.441 (s, 5H), 5.32 (br s, 1H), 5.05 (t, J=1.0 Hz, 1H), 4.91 (t, J=1.0 Hz, 1H), 3.16 (d of d, J=15.8, 1.7 Hz, 1H), 2.70 (m, 1H), 2.69 (d, J=15.8 Hz, 1H), 2.50 (m, 2H), 1.95 (m, 1H), 1.83 (br s, 3H), 1.79 (s, 3H). Difference NOE experiments: irradiation of δ 6.074 enhances δ 6.880, 5.441, 3.16; irradiation of δ 5.441 enhances δ 6.076. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ 190.95, 154.22, 149.51, 147.45, 140.13, 134.34, 130.11, 129.95, 127.67, 125.94, 125.40, 124.08, 123.18, 123.07, 113.37 (Cp), 114.51 (Cp), 109.71, 93.33, 53.68, 40.89, 39.27, 31.89, 20.52, 19.22.

Minor isomer: ^1H NMR (400 MHz, C_6D_6) δ=7.31—6.75 (m, 10H), 6.032 (s, 5H), 5.665 (s, 5H), 5.44 (br d, J=12 Hz, 1H), 5.01 (t, J=1.0 Hz, 1H), 4.89 (t, J=1.0 Hz, 1H), 3.35 (d, J=15.6 Hz, 1H), 2.41 (d, J=15.6 Hz, 1H), 2.70 (m, 1H), 2.50 (m, 2H), 1.95 (m, 1H), 1.88 (br s, 3H), 1.78 (s, 3H). Difference NOE experiments: irradiation of δ 6.032 enhances δ 6.75, 5.665, 3.35; irradiation of δ 5.665 enhances δ 6.75, 6.032. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=190.14, 154.44, 149.78, 147.12, 137.86, 134.23, 130.11, 129.95, 127.67, 125.94, 125.40, 124.08, 123.18, 123.07, 114.51 (Cp), 113.48 (Cp), 109.64, 91.00, 56.06, 41.81, 38.72, 32.33, 20.95, 19.54. (Some signals of the isomers overlap.)

Reaction of Norcamphor with 1a. Synthesis of 2k. ^1H NMR (400 MHz, C_6D_6) δ=7.05—6.99 (m, 6H), 6.86 (t of t, J=7.1, 2.0 Hz, 1H), 6.78 (m, 3H), 5.825 (s, 5H), 5.692 (s, 5H), 2.84 (d, J=15.4 Hz, 1H), 2.73 (d, J=15.4 Hz, 1H), 2.18—2.15 (m, 2H), 1.81 (m, 1H), 1.73 (m, 1H), 1.53 (m, 1H), 1.35—1.15 (m, 4H), 0.93 (m, 1H). Difference NOE experiments: irradiation of δ 5.825 enhances δ 6.78, 5.692, 2.84; irradiation of δ 5.692 enhances δ 6.78, 5.825, 2.73, 1.35. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=190.30, 154.92, 147.34, 134.12, 129.90, 127.62, 127.51, 124.70, 122.85, 113.59 (Cp), 113.48 (Cp), 97.45, 57.52, 48.26, 45.44, 38.24, 37.42, 29.29, 22.85.

Reaction of *d*-Camphor with 1a. Synthesis of 2l. ^1H NMR (400 MHz, C_6D_6) δ=7.14—6.99 (m, 6H), 6.86—6.78 (m, 4H), 5.961 (s, 10H), 5.641 (s, 10H), 2.940 (d, J=15.4 Hz, 1H), 2.360 (d, J=15.4 Hz, 1H), 2.195 (d of t, J=12.9, 1.5, 1H), 1.72 (t, J=4.6 Hz, 1H), 1.68 (d, J=13.2 Hz, 1H), 1.56 (m, 2H), 1.32 (m, 2H), 1.017 (s, 3H), 0.932 (s, 3H), 0.852 (s, 3H). Difference NOE experiments: irradiation of δ 5.961 enhances δ 5.641, 2.96, 1.72, 0.932; irradiation of δ 5.641 enhances δ 5.961, 2.360, 2.195, 1.017. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ 190.57, 154.82, 147.77, 134.39, 129.95, 128.49, 127.67, 127.57, 124.75, 122.96, 113.64 (Cp), 113.37 (Cp), 100.80, 54.65, 54.43, 49.40, 45.88, 31.57, 27.51, 21.55, 21.39, 12.12.

Reaction of 2-Methylcyclohexanone with 1a. Synthesis of 2i. First isomer: ^1H NMR (400 MHz, C_6D_6) δ=7.06—6.75 (m, 10H), 6.000 (s, 5H), 5.644 (s, 5H), 2.80 (d, J=15.6 Hz, 1H), 2.56 (d, J=15.6 Hz, 1H), 2.01 (m, 1H), 1.56—1.10 (m, 8H), 0.995 (d, J=6.6 Hz, 3H). Second isomer: ^1H NMR (400 MHz, C_6D_6) δ=7.06—6.75 (m, 10H), 5.943 (s, 5H), 5.601 (s, 5H), 2.96 (d, J=15.6 Hz, 1H), 2.53 (d, J=15.6 Hz, 1H), 2.01 (m, 1H), 1.56—1.04 (m, 8H), 0.950 (d, J=7.1 Hz, 3H). Difference NOE experiments: irradiation of δ 6.000 enhances δ 6.75, 2.80; irradiation of δ 5.943 enhances δ 6.75, 2.96; irradiation of δ 5.664 enhances δ 6.75, 2.56, 2.01, 1.53; irradiation of δ 5.601 enhances δ 6.75, 2.53, 2.01. $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ 189.60, 189.27, 154.82, 154.55, 147.94, 147.61, 134.45, 134.28, 129.95, 127.62, 124.75, 122.91, 114.19, 114.02, 113.32, 113.05, 93.4, 92.52, 55.68, 50.15, 41.76, 41.43, 35.25, 31.79, 24.53, 24.42, 24.09. 23.94, 16.46.

3,3-Bis(dimethylamino)-5,6-diphenyl-2-aza-titanocenecyclohex-5-ene, 6. Yield: 92%. ^1H NMR (90 MHz, C_7D_8) δ=7.30—6.24 (m, 10H), 5.72 (s, 10H), 2.56 (br s, 6H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_7D_8) δ=178.70, 161.09, 158.76, 150.15, 129.29, 127.88, 127.34, 127.07, 124.09, 121.71, 110.28 (Cp), 39.20 (br), 30.96. IR (KBr, cm^{-1}) 3060 (w), 3020 (w), 2920 (m), 2870 (m), 1570 (s), 1485 (s), 1455 (s), 1425 (s), 1360 (s), 1122 (s), 1022 (s), 805 (s). Anal. Calcd for $C_{30}H_{35}N_3Ti$: C, 74.21; H, 7.27; N, 8.65%. Found: C, 74.05; H, 7.18; N, 8.52%.

3,3,5-Trimethyl-6-phenyl-2-oxa-titanocenecyclohex-5-ene, 2n. Yield: 74%. ^1H NMR (90 MHz, C_6D_6) δ=7.38—6.87 (m, 5H), 5.74 (s, 10H), 2.26 (s, 2H), 1.64 (s, 3H), 1.13 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=186.8, 155.0, 123.0, 113.6, 88.0, 57.4, 28.5, 24.2. IR (KBr, cm^{-1}) 3020 (w), 2980 (m), 2910 (m), 1000 (s), 805 (s). Anal. Calcd for $C_{23}H_{26}OTi$: C, 75.41; H, 7.15%. Found: C, 75.16; H, 7.03%.

3,5-Dimethyl-3,6-diphenyl-2-oxa-titanocenecyclohex-5-ene, 2o. Yield: 85%. ^1H NMR (90 MHz, C_6D_6) δ=7.33—6.95 (m, 10H), 5.88 (s, 5H), 5.62 (s, 5H), 2.83 (d of d, J=15.3, 1.0 Hz, 1H), 2.42 (d, J=15.3 Hz, 1H), 1.70 (d, J=1.0 Hz, 3H), 1.42 (s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=187.05, 154.87, 150.81, 128.27, 126.54, 126.37, 124.91, 123.40, 114.67 (Cp), 113.10 (Cp), 90.78, 56.82, 28.64, 24.42. IR (KBr, cm^{-1}) 3060 (w), 2990 (m), 2890 (m), 1100 (s), 1070 (s), 808 (s).

Acidolysis of 2a. A stirred suspension of **2a** (115 mg, 0.268 mmol) in 2 ml of diethyl ether at 0 °C was treated with anhydrous HCl gas (15 ml, 0.67 mmol). The mixture immediately turned red and a red precipitate formed. The reaction was warmed to room temperature over 15 minutes, diluted with 10 ml more diethyl ether, filtered through a 1-inch plug of silica gel and the filtrate concentrated at reduced pressure to yield an orange residue. The residue was extracted with petroleum ether: ether (3:1), the extract filtered through glass wool, and concentrated at reduced pressure to yield the product 2-methyl-4,5-diphenyl-4-penten-2-ol (61 mg, 0.242 mmol, 90%) as yellowish crystals. ^1H NMR (400 MHz, $CDCl_3$) δ=7.279—7.198 (m, 5H), 7.100—7.052 (m, 3H), 6.940—6.921 (m, 2H), 6.522 (s, 1H),

2.768 (s, 2H), 1.497 (br s, 1H), 1.155 (s, 6H). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$) δ=141.41, 139.35, 137.13, 130.68, 129.00, 128.63, 127.82, 127.11, 126.35, 71.53, 53.71 (CH_2), 29.76 (CH_3).

Reaction of *p*-Tolualdehyde with 1a. To a stirred suspension of titanacyclobutene **1a** (365 mg, 0.986 mmol) in 2 ml toluene at room temperature was added *p*-tolualdehyde (140 ml, 1.18 mmol). The mixture was stirred at room temperature for 12 hours, then the volatiles removed in vacuo to yield a red-orange form. The foam was triturated with diethylether, the yellow precipitate filtered from the red solution, and both fractions taken to dryness. The yellow fraction (150 mg, 0.307 mmol) was the insertion product **10a**: ^1H NMR (90 MHz, C_6D_6) δ=7.37—6.67 (m, 14H), 6.06 (s, 5H), 5.59 (s, 5H), 5.48 (m, 1H), 3.05 (s, 1H), 2.97 (d, J=3.2 Hz, 1H), 2.18 (s, 3H). ^1H NMR (400 MHz, C_6D_6) δ=7.29—6.95 (m, 10H), 6.89 (t of t, J=7.1, 0.8 Hz, 2H), 6.78 (t, of t, J=7.1, 0.8 Hz, 2H), 6.119 (s, 5H), 5.610 (s, 5H), 5.53 (d of d, J=10.1, 2.8 Hz, 1H), 3.07 (d of d, J=16.6, 2.9 Hz, 1H), 2.985 (d of d, J=16.6, 10.2 Hz, 1H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=191.44, 153.03, 146.71, 136.51, 136.29, 130.06, 129.08, 128.43, 127.62, 125.72, 124.97, 123.28, 114.35 (Cp), 113.86 (Cp), 88.67, 57.09, 21.11. The diethyl ether-soluble fraction revealed a 2:1 ration of products. The major product was the same as the yellow precipitate; the minor product had ^1H NMR η^5-cyclopentadienyl resonances at δ 5.91, 5.82.

Reaction of Acetaldehyde with 1a. To a stirred suspension of titanacyclobutene **1a** (320 mg, 0.864 mmol) in 3 ml of toluene at room temperature was added acetaldehyde (60 ml, 1.07 mmol) via syringe. The reaction vessel was wrapped in Al foil and the mixture stirred for 12 hours. The reaction mixture was taken to dryness and the red-orange solid was extracted with 2 ml toluene at −78 °C. Both fractions were dried in vacuo. The extract was red-orange and the residue was dark-red. The red-orange extract material was a 2:1 ratio of the Ti-O product. Orange isomer: ^1H NMR (90 MHz, C_6D_6) δ=7.34—6.57 (m, 10H), 5.98 (s, 5H), 5.60 (s, 5H), 4.66—4.29 (m, 1H), 2.70 (s, 1H), 2.64 (d, J=2.9 Hz, 1H), 1.06 (d, J=5.8 Hz, 3H). ^1H NMR (400 MHz, C_6D_6) δ=7.406—6.728 (m, 10H), 5.982 (s, 5H), 5.592 (s, 5H), 4.498 (m, 1H), 2.70 (d of d, J=16.4, 2.8 Hz, 1H), 2.60 (d of d, J=16.4, 9.5 Hz, 1H), 1.06 (d, J=5.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=191.11, 153.30, 136.18, 130.49, 130.06, 128.33, 127.57, 124.91, 123.12, 114.19 (Cp), 113.54 (Cp), 83.25, 55.95, 23.77. Red isomer: ^1H NMR (400 MHz, C_6D_6) δ=7.336—6.944 (m, 10H), 5.890 (s, 5H), 5.883 (s, 5H), 5.641 (q, J=6.35 Hz, 1H), 4.470 (d of d, J=10.0, 4.2 Hz, 1H), 1.48 (d, J=9.8 Hz, 1H), 1.215 (d, J=6.35 Hz, 3H). $^{13}C\{^1H\}$ NMR (22.5 MHz, C_6D_6) δ=181.76, 148.32, 146.09, 144.63, 143.06, 130.44, 130.00, 128.27, 127.57, 126.05, 125.67, 113.54 (Cp), 111.29 (Cp), 87.97, 59.42, 22.41.

Reaction of Benzonitrile with 1a. A solution of titanacycle **1a** (34 mg, 0.092 mmol) in 400 μL of C_6D_6 in an NMR tube was treated with benzonitrile (10 μL, 0.098 mmol). After 24 hours the solution was dark orange and NMR analysis revealed a new compound: ^1H NMR (90 MHz, C_6D_6) δ=7.50—6.80 (m, 15H), 5.64 (s, 10H), 4.03 (s, 2H).

Reaction of *p*-Tolunitrile with 1a. A solution of titanacyclobutene **1a** (38 mg, 0.103 mmol) in 400 μL of C_6D_6 in an NMR tube was treated with *p*-tolunitrile. After 18 hours the color had changed to dark-orange, and the NMR spectrum revealed the reaction as 90% complete: ^1H NMR (90 MHz, C_6D_6) δ=7.50—6.80 (m, 14H), 5.66 (s, 10H), 4.01 (s, 2H), 2.13 (s, 3H).

Reaction of α-Phenylpropionitrile with 1a. A solution of **1a** (38 mg, 0.103 mmol) in 400 μL of C_6D_6 in an NMR tube was treated with α-phenylpropionitrile (14 μL, 0.105 mmol) at room temperature. The color changed slowly over 24 hours from red to dark-orange. NMR analysis revealed a single product and some remaining starting materials: ^1H NMR (90 MHz, C_6D_6) δ=7.15—6.60 (m, 15H), 5.63 (s, 5H), 5.61 (s, 5H), 3.54 (br s, 2H), 3.08 (q, J=7.0 Hz, 1H), 1.32 (d, J=7.0 Hz, 3H).

Reaction of α-Methylpropionitrile with 1a. A solution of **1a** (38 mg, 0.103 mmol) in 400 μL of C_6D_6 in an NMR tube was treated with α-methylpropionitrile (10 μL, 0.11 mmol) at room temperature. The color changed slowly over 24 hours from red to dark-orange. NMR analysis revealed a single product and some remaining starting materials: ^1H NMR (90 MHz, C_6D_6) δ=7.15—6.60 (m, 10H), 5.60 (s, 10H), 3.51 (s, 2H), 1.94 (septet, J=7.1 Hz, 1H), 0.93 (d, J=7.1 Hz, 6H).

Reaction of Methacrylonitrile with 1a. A solution of **1a** (26 mg, 0.071 mmol) in 400 μL of C_6D_6 was treated with methacrylonitrile (6 μL, 0.071 mmol) at room temperature. After 12 hours the reaction was ca. 60% complete by NMR analysis: ^1H NMR (90 MHz, C_6D_6) δ=7.16—6.50 (m, 10H), 5.60 (s, 5H), 5.58 (s, 5H), 5.03 (m, 2H), 3.87 (s, 2H), 1.82 (br s, 3H).

Hydrolysis of the Insertion Product of 1a and *p*-Tolunitrile. To a stirred solution of metallacycle **1a** (200 mg, 0.54 mmol) in 3 ml of THF was added *p*-tolunitrile (75 μL, 0.627 mmol) at room temperature. The reaction was stirred at room temperature for 24 hours. The volatiles were removed in vacuo and the solid suspended in diethyl ether and hydrolyzed with 5% aqueous HCl for 30 minutes. The aqueous phase was separated and extracted with diethyl ether 3×5 ml, the organic phases combined, dried over $MgSO_4$, and concentrated in vacuo. The product was flash-chromatographed ($CHCl_3$) to yield 41 mg of the product ketone: ^1H NMR (90 MHz, $CDCl_3$) δ=7.80—7.00 (m, 14H), 6.55 (br s, 1H), 4.11 (d, J=1.2 Hz, 2H), 2.37 (s, 3H).

Reaction of *p*-Tolunitrile with 1b. A solution of metallacycle **1b** (97 mg, 0.315 mmol) in 500 μL of C_6D_6 was treated with *p*-tolunitrile (36 μL, 0.32 mmol) at room temperature. The reaction was complete within 4 hours to yield a dark-orange solution: ^1H NMR (90 MHz, C_6D_6) δ=7.50—6.80 (m, 9H), 5.70 (s, 10H), 3.68 (s, 2H), 2.20 (s, 3H), 1.65 (s, 3H).

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