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Synthesis, Structural Characterization, and Reactivity of Cp_2- and $(CpMe)_2$-Ligated Titanaaziridines and Titanaoxiranes with Fast Enantiomer Interconversion Rates

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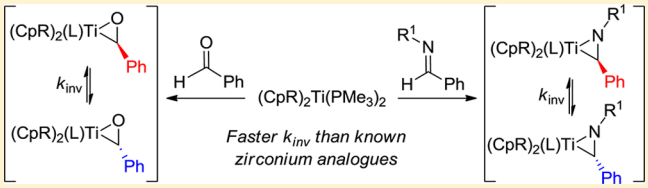
Supporting Information

ABSTRACT: A new synthetic route to $(CpR)_2$-ligated titanaaziridines and titanaoxiranes from stable Ti(II) precursors has been developed, and the enantiomer interconversion rate constants for chiral titanaaziridines and titanaoxiranes have been measured for the first time. The titanaaziridines $(CpR)_2Ti(\eta^2\text{-}N(R^1)CHPh)(L)$ (R = H (**10**), Me (**12**); R^1 = Ph (**a**), *o*-anisyl (**b**), $SiMe_3$ (**c**); L = PMe_3 (**a**, **c**), −OMe (**b**)) and titanaoxiranes $Cp_2Ti(\eta^2\text{-}Ph(R)CO)(L)$ (R = Ph (**14**), H (**15**); L = PMe_3) have been synthesized and characterized spectroscopically; titanaaziridine **10a** and titanaoxirane **14** have been characterized by X-ray crystallography. The enantiomer interconversion rate constants for the chiral titanaaziridines and titanaoxiranes have been measured by variable-temperature NMR; k_{inv} for **10b** is the fastest enantiomer interconversion rate constant reported for any metallaaziridine or metallaoxirane to date. Titanaaziridines **10** and **12** undergo exchange reactions with C═C and C═X bonds, whereas the titanaoxiranes **14** and **15** undergo insertions.

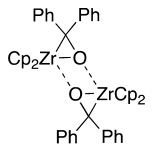


INTRODUCTION

Many η^2-imine complexes of transition metals[1] and lanthanides[2] ("metallaaziridines" or "azametallacyclopropanes") have been synthesized and used for the synthesis of new organic and organometallic compounds. In particular, the reactions of η^2-imine complexes of Nb, Ta, and Zr have produced (in some cases, asymmetrically) pyrroles,[3] α-amino alcohols,[4] α-amino acid esters,[5] α-amino amidines,[6] ureas,[4b] 1,2-diamines,[7] and allylic amines,[8] as well as structurally interesting organometallic compounds.[9] The abundance and low cost of early transition metals make their metallaaziridines especially attractive, as both stoichiometric and catalytic reactions are practical.

Many of the closely related (and isoelectronic) η^2-aldehyde and η^2-ketone complexes ("metallaoxiranes") have also been prepared, although these have been less used in organic synthesis. The η^2 and η^1 complexes of aldehydes[10] and ketones[11] with the middle transition-metal rhenium have been thoroughly investigated by Gladysz and his co-workers. Early transition-metal complexes of η^2-aldehydes and η^2-ketones are common. Niobocene complexes of ketene[12] and formaldehyde[13] have been prepared and structurally characterized by Bruno and his co-workers. Dimeric zirconaoxiranes with bridging ketone or aldehyde ligands, for example, $[Cp_2Zr(\eta^2\text{-}Ph_2CO)]_2$ (**1**), have been reported by the Erker group,[14] while a Zr_2 complex with a bridging acetone has been reported by the Norton group.[15] Ketone ligands that bridge Zr and Al have been reported by Waymouth, Clauser, and Grubbs,[16] while neutral and anionic η^2 aldehyde complexes of a single Zr have been made by Askham and his group.[17]

The isolation of *titana*aziridines and *titana*oxiranes has lagged behind that of *zircona*aziridines and *zircona*oxiranes, though



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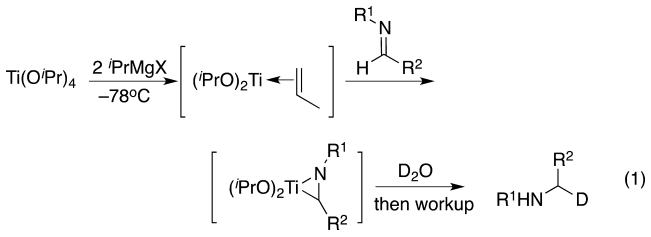
titanaaziridines have been invoked as intermediates in Ti-mediated cross-coupling reactions.[18] The most synthetically useful systems are those produced by the reaction of Sato's reagent, $Ti(O^iPr)_4/2^iPrMgCl$ (eq 1), with imines;[18a,19] treating



(1)

them with aqueous acid gives the corresponding amines (eq 1),[19h] as expected. These systems can produce homoallylic and allylic amines,[19h,20] γ-lactams,[21] α-amino ketones and allenes,[19g] amino alcohols,[22] and N-containing heterocycles, such as pyrroles,[23] piperidines,[22b,24] and quinolizidines/indolizidines.[25] Regio- and stereoselective versions of some of these reactions have been developed,[19g,h,20a,21b,22b,25,26] and their generation by

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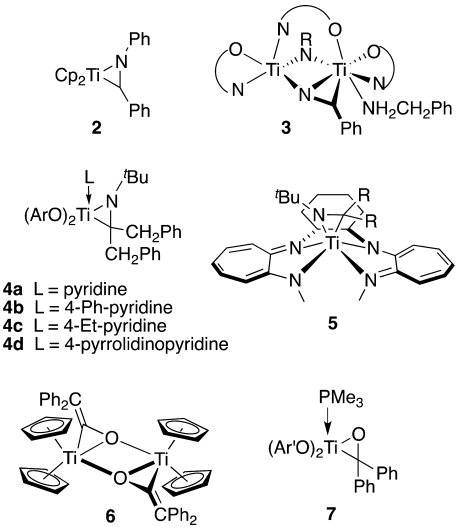
reducing agents other than RMgX has been investigated.[27] Titanaaziridines have also been implicated as intermediates in other synthetically attractive reactions.[28]

A few titanaaziridines that have been *isolated* are shown in Chart 1. The Cp_2-ligated titanaaziridine **2**[29] was prepared by

Chart 1. Isolable Titanaaziridines and Titanaoxiranes



the reaction of Cp_2TiMe with *N*-benzylidene aniline; methane was evolved via intermolecular hydrogen atom abstraction from a Cp ligand, reducing the maximum yield to 50%. The amidate-ligated bridging titanaaziridine **3** was formed by C−H bond activation, followed by amine elimination.[30] The monomeric bis(aryloxy)- and aminotroponiminate-ligated titanaaziridines **4**[31] and **5**[32] arose from alkyl migrations to bound isocyanides. These syntheses have not proven general enough to produce a variety of substituted titanaaziridines for synthetic applications.

Two titanaoxiranes that have been isolated and characterized by X-ray crystallography are also shown in Chart 1. The dimer $[Cp_2Ti(Ph_2C_2O)]_2$ **6** was prepared by Floriani from $Cp_2Ti(CO)_2$ and diphenylketene.[33] The monomer $(Ar'O)_2Ti(\eta^2\text{-}Ph_2CO)(PMe_3)$ (Ar′O = 2,6-diphenylphenoxide) **7** was prepared by Rothwell by an indirect route from the corresponding propylene complex and benzophenone.[34]

The reactivity of these isolable titanaaziridines and titanaoxiranes in synthetically useful transformations has not been thoroughly investigated. Several redox, substitution, and decomposition reactions of titanaaziridines **2** and **4** have been reported, but they do not produce useful organic products.

We have sought a general method for the preparation of Cp_2-ligated titanaaziridines and titanaoxiranes. We have structurally characterized these complexes and investigated their ability to undergo insertion reactions that lead to useful organic products. Furthermore, because the configurational lability of chiral Cp_2 zirconaaziridines has made them useful for dynamic kinetic asymmetric transformations (DYKAT's),[5c,9] we have measured the rates at which the enantiomers of Cp_2-ligated titanaaziridines and titanaoxiranes interconvert.

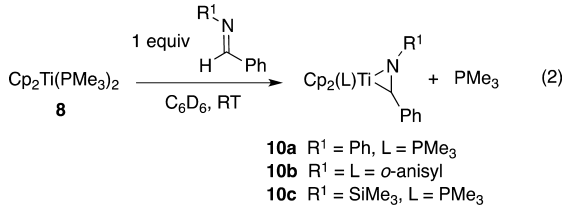
RESULTS AND DISCUSSION

Preparation of Titanaaziridines. In the Buchwald synthesis of Cp_2 zirconaaziridines,[3b,5b] methyl amide complexes $Cp_2Zr(Me)(N(CH_2R^2)R^1)$ eliminate methane to form zirconaaziridines $Cp_2Zr(\eta^2\text{-}N(R^1)CHR^2)(L)$. Unfortunately, the analogous reaction of $Cp_2TiMe(OTf)$[35] with $LiN(Ph)CH_2Ph$ yields the comproportionation products Cp_2TiMe_2 and $Cp_2Ti(N(Ph)CH_2Ph)_2$ rather than a titanaaziridine.[36]

Ti(II) Precursors. Sato's Ti(II) reagent (eq 1) is produced by reducing a Ti(IV) precursor with an organometallic reducing agent.[18a,37] Although this method is suitable for effecting organic transformations, it has drawbacks as a method for producing pure titanaaziridines. The organometallic reducing agents—Grignards or organolithiums—produce stoichiometric quantities of metal salts that are difficult to remove, and can undergo side reactions. Furthermore, the Sato reagent is unstable at room temperature.

In contrast, the "masked titanocene" $Cp_2Ti(PMe_3)_2$ (**8**),[38] first prepared by Rausch, can be stored for months under Ar at room temperature. Complex **8** is synthesized by the reduction of Cp_2TiCl_2 with Mg^0 in the presence of excess PMe_3; in solution, it is in equilibrium with $Cp_2Ti(PMe_3) + PMe_3$, with **8** favored at room temperature.[38] The reaction of PhC≡CPh with **8** yields a stable η^2-acetylene complex, $Cp_2Ti(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)$ (**9**).[39] We sought to use the stable Ti(II) precursor **8** in analogous reactions with imines to form stable, isolable η^2-imine complexes of titanocene.

Cp_2 Titanaaziridines. When **8** is treated with 1 equiv of *N*-benzylidene aniline in C_6D_6, the color changes from dark



brown to dark red over 3 h (eq 2). The Cp peak at δ 4.57 in the ^1H NMR of **8** disappears, and two new Cp resonances (assigned to **10a**) grow in at δ 5.11 and δ 5.20. The PMe_3 singlet remains broad, but shifts upfield from δ 0.84 in **8** to δ 0.74 in **10a**. The singlet at δ 8.13 due to the imine proton of free *N*-benzylidene aniline disappears, and a broad 1H singlet (also assigned to **10a**) grows in at δ 2.87 (near the chemical shift, δ 2.47, of the methine proton in the analogous zirconaaziridine, $Cp_2Zr(\eta^2\text{-}N(Ph)CHPh)(PMe_3)$[3b,8a]). A new peak appears in the ^{13}C NMR at δ 52.5, near the peak (δ 46.8) of the imine carbon in the known zirconaaziridine. Both the inequivalence of the Cp peaks and the new N(Ph)*CH*Ph peaks indicate that the *N*-benzylidene aniline in **10a** has an η^2 coordination mode, with an accompanying reduction in its C−N bond order.

The IR spectrum of a mixture of **8** and 1 equiv of *N*-benzylidene aniline in benzene initially shows a band at 1627 cm^{-1}, from the C=N stretch of the free *N*-benzylidene aniline. Over the course of 2 h, this band disappears as **10a** forms; no new C=N band appears in this region, indicating a reduction in the C−N bond order as the imine becomes bound.

At 298 K, the $^{31}P\{^1H\}$ NMR of **10a** in THF-d_8 shows a broad singlet at δ 13.9, which sharpens and shifts slightly downfield on cooling. The PMe_3 peak in the ^1H NMR of **10a** in THF-d_8 at 298 K shifts from δ 1.29 to δ 1.00, toward that of free PMe_3 (δ 0.95), when 1 equiv of free PMe_3 is added. These results make it clear that the coordinated PMe_3 in **10a** dissociates and thus exchanges with free PMe_3.

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Complex **10a** decomposes in solution without excess PMe_3. However, impure samples of **10a** can be precipitated from the reaction mixture and stored in the solid state under an inert atmosphere at −20 °C. Single crystals suitable for X-ray analysis were obtained by allowing a solution of **10a** in benzene with 1 equiv of free PMe_3 to stand at room temperature overnight. The crystal structure of **10a** is shown in Figure 1.

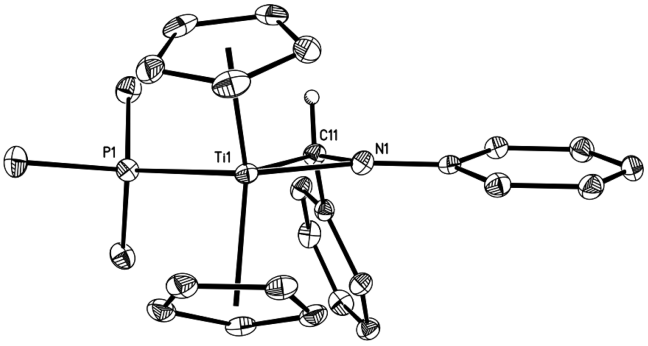

Figure 1. ORTEP view of $Cp_2Ti(\eta^2\text{-}N(Ph)CHPh)(PMe_3)$ (**10a**). Thermal ellipsoids drawn at 30% probability level. Select hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Ti(1)−N(1), 1.9923(19); Ti(1)−C(11), 2.302(2); C(11)−N(1), 1.382(2); Ti(1)−P(1), 2.5759(8); C(11)−Ti(1)−N(1), 36.65(8); C(11)−Ti(1)−P(1), 76.95(6); N(1)−Ti(1)−P(1), 113.55(6).

The significant elongation of the C(11)−N(1) bond (1.382(2) Å) in **10a** compared with that in a free imine supports the description of **10a** as a titanaaziridine. The C(11)−N(1) bond length of **10a** is comparable to the C−N bond lengths in other isolated titanaaziridines, including **3** (1.368(4) Å), **4a**−**4d** (1.410(3)−1.421(7) Å), and **5** (1.417(4) Å). The Ti−N bond (1.9923(19) Å) in **10a** is slightly longer than the Ti−N bonds in **4a**−**4d** (1.846(4)−1.855(2) Å) and **5** (1.883(2) Å), which contain oxygen and nitrogen donor ligands; it is shorter than the analogous bond in the bridging, dinuclear titanaaziridine **3** (2.046(2) Å). The bond angles within the metallaaziridine ring of **10a** are comparable to those in Cp_2-ligated zirconaaziridines and to those in titanaaziridines **4b** and **4c**.[9]

The Ti−P bond length (2.5759(8) Å) is similar to that in Rothwell's bis(aryloxy)-ligated titanaoxirane **7**[34] (2.592(3) Å) and shorter than that in the closely related zirconaaziridine $Cp_2Zr(\eta^2\text{-}N(Ph)CHPh)(PMe_2Ph)$ (2.7227(3) Å).[40] Interestingly, the coordinated PMe_3 is closer to the carbon of the bound imine in **10a**, in an "outside" configuration.[9] Rothwell's bis(aryloxy) ligated titanaaziridines **4a**−**4d** similarly exhibit "outside" coordination of the stabilizing pyridine ligands. Though most zirconaaziridines exhibit a thermodynamic preference for "inside" coordination, with the stabilizing donor ligand closer to the nitrogen of the zirconaaziridine ring, the PMe_2Ph in $Cp_2Zr(\eta^2\text{-}N(Ph)CHPh)(PMe_2Ph)$ likewise exhibits "outside" coordination.[40]

In efforts to produce a titanaaziridine that is stable without excess phosphine ligand, we added an *o*-methoxy group (**10b**) and replaced the N*Ph* with an N(*TMS*) (**10c**). By ^1H NMR, the addition of *N*-benzylidene anisidine to **8** appeared to produce **10b** after 1 h (eq 2), with a methine resonance at δ 4.23 (near that in the Zr analogue, δ 3.82[5b]) and a methoxy resonance at δ 2.68 in the ^1H NMR. The upfield shift of the methoxy, from δ 3.37 in the free imine, implies that the methoxy oxygen is coordinated in **10b** and that the PMe_3 is not.

The analogous reaction with *N*-benzylidene trimethylsilylamine (eq 2) appears to result in the formation of **10c** (although its formation is much slower—12 h at room temperature—than that of **10a** and **10b**). The titanaaziridines **10b** and **10c** also decompose in solution without excess PMe_3, though they are stable in solution at room temperature for days with excess PMe_3.

$(CpMe)_2$ and Cp^*_2 Titanaaziridines. In an effort to make a more electron-rich Ti(II) precursor, we tried to prepare $(CpMe)_2Ti(PMe_3)_2$ (**11**) (eq 3). The reduction of

$$(CpMe)_2TiCl_2 \xrightarrow[\text{THF, 3 d}]{Mg^0,\ PMe_3} \underset{\mathbf{11}}{(CpMe)_2Ti(PMe_3)_2} \quad (3)$$

$(CpMe)_2TiCl_2$ with Mg^0 in the presence of excess PMe_3 over 3 days at room temperature appeared to give **11** as the only product. The ^1H NMR in C_6D_6 showed Cp resonances at δ 4.61 and 4.47, a PMe_3 peak at δ 0.85, and a broad Cp*Me* peak at δ 1.64.

The reactions of **11** with 1 equiv of *N*-benzylidene aniline, *N*-benzylidene anisidine, or *N*-benzylidene trimethylsilylamine appeared to produce (eq 4) the titanaaziridines $(CpMe)_2Ti(\eta^2\text{-}N(Ph)CHPh)(PMe_3)$ (**12a**), $(CpMe)_2Ti(\eta^2\text{-}N(o\text{-anisyl})CHPh)$ (**12b**), and $(CpMe)_2Ti(\eta^2\text{-}N(TMS)CHPh)(PMe_3)$ (**12c**). These titanaaziridines **12**, although stable in solution with excess PMe_3 (like **10a**−**10c**), decompose if the PMe_3 is removed (though more slowly than **10a**−**10c**).

$$\underset{\mathbf{11}}{(CpMe)_2Ti(PMe_3)_2} \xrightarrow[C_6D_6,\ RT]{Ph\ \ H\ \ N\ R^1} (CpMe)_2(L)Ti\langle N(R^1)Ph \quad (4)$$

12a R^1 = Ph, L = PMe_3
12b R^1 = L = *o*-anisyl
12c R^1 = $SiMe_3$, L = PMe_3

The "$Cp^*_2Ti(II)$" synthon is accessible in situ through the reduction of $Cp^*_2TiCl_2$ with 1% sodium amalgam.[41] We tried carrying out this reduction in the presence of *N*-benzylidene aniline, but by NMR data, the initially formed titanaaziridine $Cp^*_2Ti(\eta^2\text{-}N(Ph)CHPh)$ (**13**) decomposed within a few hours.

Preparation of Titanaoxiranes from Ketones/Aldehydes. When 1 equiv of benzophenone is added to a solution of $Cp_2Ti(PMe_3)_2$ (**8**) at room temperature in C_6D_6, the color changes quickly from dark brown to purple as the titanaoxirane **14** is formed (eq 5). The NMR spectra of **14** vary with

$$\underset{\mathbf{8}}{Cp_2Ti(PMe_3)_2} \xrightarrow[C_6D_6,\ RT]{Ph\ \ Ph\ \ O} \underset{\mathbf{14}}{Cp_2Ti\langle O(Ph)Ph} \quad (5)$$

temperature in a complex way, suggesting (but not proving) that **14** dimerizes at low temperatures. (Recall that **1**, the Zr analogue of **14**, is a dimer.) Single crystals of **14** were grown from a toluene solution at −20 °C, and its structure determined by X-ray crystallography (Figure 2).

It is instructive to compare the structure of **14** with that of the known titanaoxirane dimer $[Cp_2Ti(PhC_2O)]_2$[16] (**6**) and that of the titanaoxirane monomer $(Ar'O)_2Ti(\eta^2\text{-}Ph_2CO)(PMe_3)$[34] (**7**). In **14**, in contrast with **7**, C(11), O(1), and P(1)

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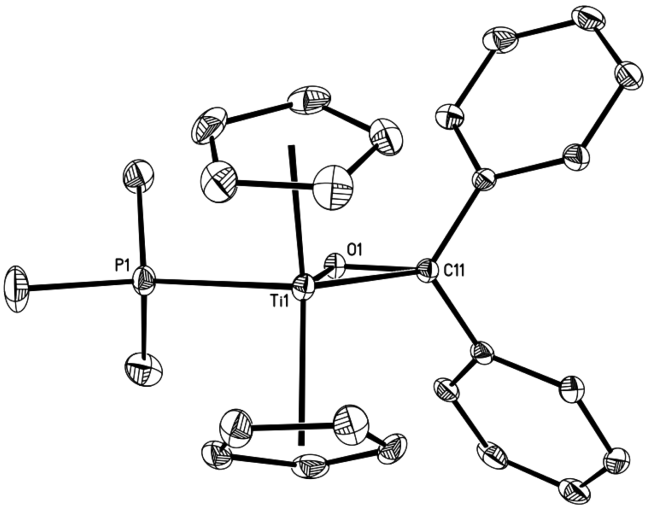
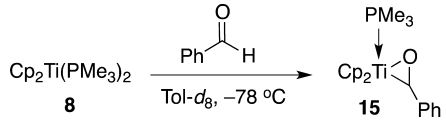


Figure 2. ORTEP view of $Cp_2Ti(\eta^2\text{-}Ph_2CO)(PMe_3)$ (**14**). Thermal ellipsoids drawn at 20% probability level. Selected bond lengths (Å) and bond angles (deg): Ti(1)−O(1), 2.0057(14); Ti(1)−C(11), 2.2477(19); C(11)−O(1), 1.360(2); Ti(1)−P(1), 2.590(9); C(11)−Ti(1)−O(1), 36.75(6); C(11)−Ti(1)−P(1), 107.39(6); O(1)−Ti(1)−P(1), 70.63(5).

lie in a plane probably because of the greater bulk of the phenylphenoxide ligands in **7**. The coordinated PMe_3 in **14** is close to the oxygen of benzophenone, showing "inside" coordination, as observed for most Cp_2-ligated zirconaaziridines;[5b] the PMe_3 in **7** is "outside". The C−O distance in **14** (1.360(2) Å) is slightly shorter than that in **7** (1.397(8) Å), but longer than that of **6** (1.311(4) Å), and is characteristic of a C−O single bond. The Ti−C(11) distance (2.2477(19) Å) is slightly longer than the values for **7** and **6** (2.150(7) and 2.099(3) Å, respectively). The Ti−O distance of 2.0057(14) Å is slightly longer than the value in **7** (1.849(5) Å) and slightly shorter than that in **6** (2.037(2) Å). The C(11)−Ti−O bond angle of 36.75(6)° is comparable with the angle in **6** (36.9(1)°) and **7** (40.0(2)°).

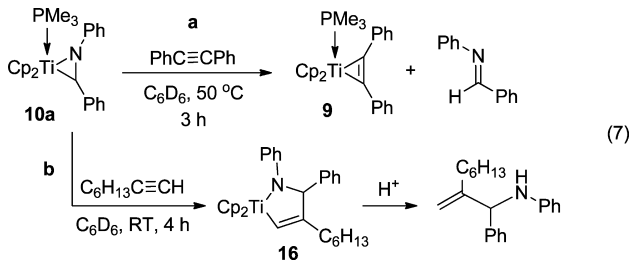
To prepare a titanaoxirane with a chiral center, we added an equivalent of benzaldehyde in cold toluene-d_8 to a solution of **8** in the same solvent at −78 °C and obtained a dark red solution that appeared to contain the titanaoxirane $Cp_2Ti(\eta^2\text{-}PhCHO)(PMe_3)$, (**15**) (eq 6). The upfield ^{13}C NMR chemical shift (δ 79.1, C_6D_6) and ^1H NMR chemical shift (δ 4.15, tol-d_8) of the methine confirm the η^2-coordination mode of benzaldehyde in **15**.[19h]



(6)

Reactivity of Titanaaziridines. Constrained geometry[40] (cg) and Cp_2 zirconaaziridines insert C═C, C≡C, and C═X bonds,[1a,7,8,42] forming zirconacycles that can be hydrolyzed to isolate organic products. However, a few attempts to carry out similar reactions with titanaaziridines have led to coordination of the C═C or C═X in place of the coordinated imine (vide infra).[31,32,43]

The titanaaziridines that we have prepared also undergo exchange rather than insertion in most cases. The reaction of **10a** with PhC≡CPh proceeds slowly at room temperature (or over 3 h at 50 °C) to form free *N*-benzylidene aniline and the known complex $Cp_2Ti(\eta^2\text{-}PhC{\equiv}CPh)(PMe_3)$ (**9**, eq 7a).[39] In contrast, the reaction of **10a** with 1-octyne (eq 7b) proceeds to



(7)

completion (by ^1H NMR) over 4 h at room temperature, forming a mixture of insertion products that is predominantly **16**. The reactions of **10a** with ethylene carbonate, substituted alkenes, isocyanates, carbodiimides, and ketones, however, result in displacement of the imine rather than insertion. The titanaaziridines appear to undergo insertion of some less-hindered C═C and *terminal* C≡C bonds, but, in general, undergo exchange reactions with C═X bonds and substituted C═C/internal C≡C bonds.

These results are in sharp contrast to those obtained with the "$(^i\text{PrO})_2$Ti(II) + imine" system, in which *proposed, but not isolated,* titanaaziridine intermediates appear to undergo insertion reactions. It is apparent that the nature of the metal center in the $(CpR)_2M(II)$ system differs significantly from that in the $(^i\text{PrO})_2$Ti(II) system, though their ligand sets are nominally isoelectronic.[44] We have demonstrated that the imines in Cp_2-ligated titanaaziridines **10** and **12** are bound in the η^2 mode and that **10** and **12** are monomeric in solution (as are the related zirconaaziridines), though they do not undergo insertions with most unsaturated bonds. Hydrolysis experiments imply that the $(^i\text{PrO})_2$Ti(II) system also binds imines in the η^2 mode, but further information about the structure of the resulting complexes is not available. The reactive intermediates in this system are not necessarily monomeric; such structural differences could have a significant role in determining exchange versus insertion reactivity.

Reactivity of Titanaoxiranes. The Ti−C bond of the titanaoxirane **14** inserts C═C and C═X bonds (Scheme 1).

The addition of 1 equiv of benzaldehyde to **14** at RT results in an immediate color change from purple to bright red and the formation of the stable insertion product **18**; acidolysis of **18** yields 1,2-triphenylethane-1,2-diol (>99%). The reaction of methyl acrylate with **14** is complete after 5 min at room temperature, forming **19** as the only regioisomer; acidolysis of **19** yields methyl 3-hydroxy-2-methyl-3,3-diphenylpropanoate (99%). The reaction of **14** with excess ethylene carbonate results in a color change from purple to brown within 5 min; ^1H NMR suggests that conversion to the insertion product **17** is complete in 30 min. Unfortunately, **17** decomposes over several hours at room temperature.

The reaction with ethylene, in contrast with the C═O insertions, is slow. When ethylene is in excess, formation of **20** is complete only after 4 h at 50 °C. Similar conditions are required for the insertion of styrene into **14**, which forms **21** as a single regioisomer. The preference for the 2,1 insertion product has precedent in the reaction of titanaoxirane **7** with excess propylene, which yields an oxatitanacyclopentane with the Me substituent on the carbon α to the Ti as the major product.[34,45] Earlier,[46] Negishi and co-workers demonstrated that the favored metallacycle from the reaction of Cp_2ZrBu_2

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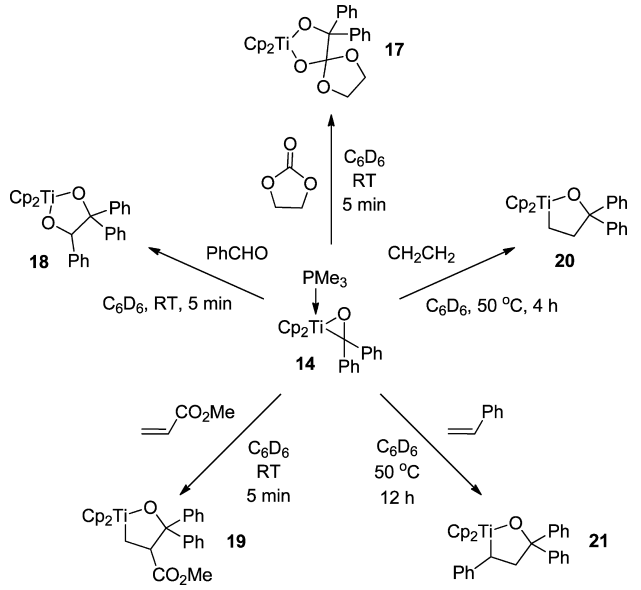
Scheme 1. Reactivity of Titanaoxirane 14



with excess styrene is the zirconacyclopentane $Cp_2Zr(\kappa^2$-$CH(Ph)CH_2CH(Et)CH_2)$, which has the phenyl substituent α to the Zr.

Thus, Cp_2-ligated *titanaoxiranes*, unlike the titanaaziridines we have prepared herein from $(CpR)_2Ti(II)$, *do* readily insert substituted C═C and C═X bonds.

Rates of Interconversion of Titanaaziridine Enantiomers. The η^2 binding of an aldimine or an unsymmetrically substituted ketimine to $(CpR)_2M(II)$ (M = Ti, Zr) produces either of two enantiomeric metallaaziridines, depending upon which face of the ligand is coordinated (Scheme 2). The insertion of an *enantiopure* C═X compound leads to a dynamic kinetic asymmetric transformation, or DYKAT, if the enantiomers of a metallaaziridine interconvert more rapidly than they insert a C═X, that is, if $k_{inv} > k_R[C{=}X]$ and $k_S[C{=}X]$ in a system like that in Scheme 2.[5c,e,9] Faster enantiomer interconversion enables us to add the insertion reagent more quickly and still obtain the maximum diastereomer ratio (k_R/k_S). For many zirconaaziridines, k_{inv} have been measured and used to effect DYKATs with diastereomer ratios up to 95:5.[5c]

To see how the enantiomer interconversion rates of Ti complexes compare with those of their Zr analogues, we have measured k_{inv} for the titanaaziridines **10** and **12**. In either enantiomer of a chiral metallaaziridine, the two cyclopentadienyl ligands are *inequivalent*. However, if the enantiomers interconvert quickly on the NMR time scale, the cyclopentadienyl ligands (and their NMR resonances) become *equivalent*. In the room-temperature ^{1}H NMR spectra of the Cp titanaaziridines **10a** and **10c**, there are two peaks for the Cp protons; in the room-temperature ^{1}H NMR spectra of the CpMe titanaaziridines **12a** and **12c**, there are two peaks for the Cp*Me* protons. However, at 298 K, there is a *single* Cp peak for **10b** and a *single* Cp*Me* peak for **12b**, indicating that these titanaaziridines have fast enantiomer interconversion rates at that temperature.

At 234 K, **12b** has two distinct C_5H_4Me peaks and eight distinct C_5H_4Me peaks, showing that the two CpMe ligands are inequivalent at that temperature and that enantiomer interconversion is slow on the NMR time scale. The Cp*Me* peaks of **12b** coalesce at approximately 257 K (Figure S1, Supporting Information), implying a k_{inv} of 51(1) s^{-1} and a $\Delta G^{\ddagger}$ of 12.9 kcal mol^{-1} at that temperature.

We have similarly measured k_{inv} for the titanaaziridines **10a**–**10c** and **12a**,**12c** at the coalescence temperatures of their Cp and Cp*Me* peaks. These results are in Table 1, along with previously reported[5c] values of k_{inv} measured at 298 K for comparable zirconaaziridines.

It seems clear that the *o*-anisyl titanaaziridines **10b** and **12b** undergo enantiomer interconversion more rapidly than any metallaaziridines examined to date. We have estimated k_{inv} and $\Delta G^{\ddagger}$ at 298 K for the titanaaziridine **10b** by measuring the widths of its C_5H_5 peaks as a function of temperature (see Table S1 in the Supporting Information). The results, $k_{inv,298} \approx 4 \times 10^4$ s^{-1} and $\Delta G^{\ddagger}_{298} = 11$ kcal mol^{-1}, show that the enantiomers of **10b** interconvert *orders of magnitude faster* than those of the analogous zirconaaziridine, $Cp_2Zr(\eta^2$-N(*o*-anisyl)-CHPh) ($k_{inv} = 5.3 \times 10^{-6}$ s^{-1} and $\Delta G^{\ddagger} = 24.6$ kcal mol^{-1} at 298 K[5c]).

Calculations suggest that the enantiomers of Cp_2 zirconaaziridines interconvert via η^1 intermediates (Scheme 3),[5c] a mechanism like that established for aromatic η^2 aldehydes coordinated to Re.[47] The same mechanism is likely for titanaaziridines like **10** and **12**.

Rate of Interconversion of the Enantiomers of the Titanaoxirane 15. At 298 K, the ^{1}H NMR of the benzaldehyde adduct **15** in toluene-d_8 shows a single broad Cp peak. At lower temperatures two distinct Cp peaks are observed (Figure 3). The peaks coalesce at 295 K, giving a k_{inv} of 168(1) s^{-1} and a $\Delta G^{\ddagger}$ of 14.2 kcal mol^{-1} at that temperature. This rate constant is faster than any measured for a zirconaaziridine to date and within the range found for the various titanaaziridines **10** and **12** (Table 1).

CONCLUSION

We have prepared Cp_2- and $(CpMe)_2$-ligated titanaaziridines and titanaoxiranes from stable Ti(II) precursors and imines or aldehydes/ketones; the reaction tolerates a variety of substituents and proceeds at room temperature. The new titanaaziridines and titanaoxiranes have faster enantiomer interconversion rates than those previously reported for other metallaaziridines or metallaoxiranes, and likely interconvert via η^1-coordinated intermediates. The titanaaziridines exchange their imine ligands with most C═C, C≡C, and C═X, whereas their zirconaaziridine and titanaoxirane analogues insert such multiple bonds.

Scheme 2. Reaction of Enantiopure Substrate with a Racemic Zirconaaziridine

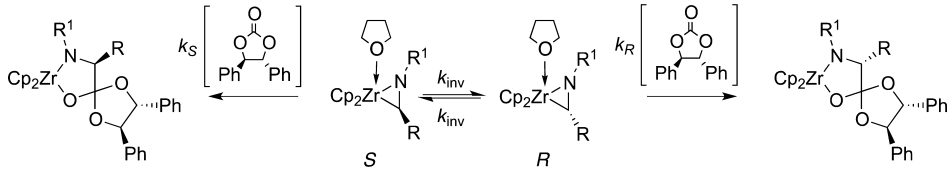


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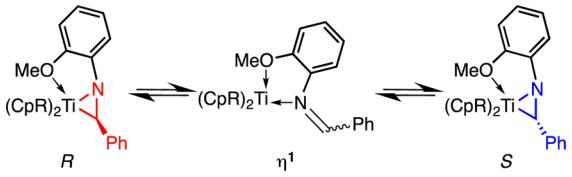
Table 1. Enantiomer Interconversion Rate Constants of Metallaaziridines $(C_5H_4R)_2M(\eta^2\text{-}N(R^1)CHPh)(L)$

R^1	compd. or ref	L	R	M	k_{inv} (s^{-1})[a]	$\Delta G^{\ddagger}$(kcal/mol)[a]	T (K)
o-anisyl	ref 5c	−OMe	H	Zr	$5.3(7) \times 10^{-6}$	24.6	298
	10b	−OMe	H	Ti	310(1)	11.5	260
	12b	−OMe	Me	Ti	51(1)	12	257
TMS	ref 5c	THF	H	Zr	$9.1(1) \times 10^{-3}$	20.2	298
	10c	PMe_3	H	Ti	40.5(5)	18.8	364
	12c	PMe_3	Me	Ti	378(3)	19.1	372
Ph	ref 5c	THF	H	Zr	$7(2) \times 10^{-3}$	20.4	298
	10a	PMe_3	H	Ti	59.7(3)	18.8	371
	12a	PMe_3	Me	Ti	351(2)	18.6	357

[a]Measured at temperature T.

Scheme 3. Proposed Enantiomer Interconversion Mechanism



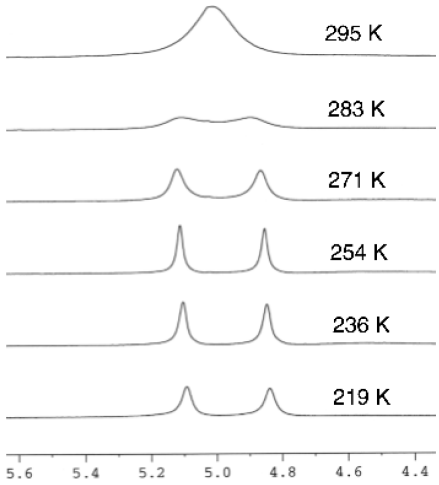


Figure 3. Temperature dependence of the C_5H_5 ^{1}H NMR resonances in **15** (toluene-d_8, 300 MHz).

■ ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, NMR spectra, crystallographic and structural results, and details for the VT-NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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