Articles

Radical Scission of Symmetrical 1,4-Dicarbonyl Compounds: C−C Bond Cleavage with Titanium(IV) Enolate Formation and Related Reactions

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Reaction of $Ti(NRAr^1)_3$ (**1**, R = $C(CH_3)_3$, Ar^1 = 3,5-$C_6H_3Me_2$) with 0.5 equiv of symmetrical 1,4-diketones $(ArCOCH_2)_2$ (Ar = *p*-Tol or *p*-$MeOC_6H_4$) in hydrocarbon solvents at ≤25 °C resulted in carbon−carbon bond cleavage with clean formation of titanium-bound enolates, **1**-$OC(CH_2)Ar$. Treatment of $Ti(NRAr^1)_3$ with esters or amides of succinic acid, under the same mild conditions, smoothly produced titanium(IV) compounds containing the corresponding amide or ester enolate moiety. The amide enolate condenses with benzaldehyde in an aldolic fashion. Differences in the observed reactivity of amido-enolate vs ketone-derived enolate toward aldol condensation were interpreted with the help of computational methods. Upon reaction with $Ti(NRAr^1)_3$, *para*-substituted acetophenones yielded equal amounts of enolate and alkoxide products. Under similar experimental conditions, acetophenone itself produced quantitatively a species whose proposed structure incorporates characteristics reminiscent of a Gomberg dimer. This intermediate decomposes cleanly to the expected enolate and alkoxide mixture upon heating. $Ti(NRAr^1)_3$ reductively complexes substrates such as *N*-methyl phthalimide. Treatment of $Ti(NRAr^1)_3$ with 0.5 equiv of *o*-bromophenyl allyl ether resulted in bromine atom abstraction followed by cyclization of the intermediate aryl radical to generate a titanium-bound 3-methylenedihydrobenzofuran product.

Introduction

The development of inorganic and organometallic compounds having applications in organic synthesis is an active area of chemical research.[1] Reductive coupling of ketones and aldehydes to produce vicinal diols or olefins is a useful method for carbon−carbon bond formation.[2−7] A variety of inorganic reagents based on low-oxidation-state transition metals or lanthanides has been utilized for such transformations. Heterogeneous and homogeneous reagents based on low-valent Ti, V, Ce, Nb, or Sm have been used for pinacolic or McMurry couplings.[5−7] The typical postulated mechanism for these reactions involves reduction of the carbonyl group to form an intermediate ketyl radical, which then undergoes coupling.[8] Insights into the nature of the ketyl radical intermediate came from the research of Wolczanski et al., where a sterically encumbered Ti(III) tris-silox (silox = $[OSi\text{-}t\text{-}Bu]_3$) complex was used to generate long-lived ketyl radicals.[9,10] These results highlight another major theme in the area of inorganic reagent design for applications in synthetic organic chemistry, namely, the use of steric control to tune or to alter completely the reactivity of organometallic compounds toward organic substrates. More recently, ketyl radicals generated by lanthanide centers have constituted the subject of intensive research.[11,12]

In this work we report on the reactions of $Ti(NRAr^1)_3$ (**1**, R = $C(CH_3)_3$, Ar^1 = 3,5-$C_6H_3Me_2$) with organic substrates containing carbonyl and/or halogen functionalities. Compound **1** contains a reducing and oxophilic d^1 metal center supported by sterically demanding amide ligands. Previous reports regarding its reactivity toward inorganic electrophiles show that **1** is a potent 1e reductant, making it suitable for studies with organic substrates.[13,14] Furthermore, **1** is easily accessible via

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(2) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *1*, 307.
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(11) Hou, Z.; Wakatsuki, Y. In *Lanthanides: Chemistry and Use in Organic Synthesis*; Kobayashi, S., Ed.; Springer-Verlag: Berlin, 1999.
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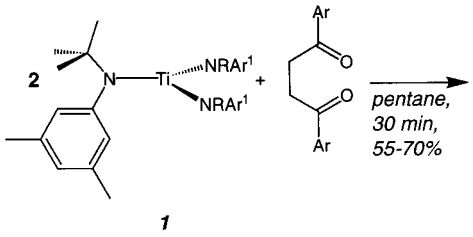
salt elimination upon reaction of $TiCl_3(THF)_3$ with 3 equiv of $Li(NRAr)(Et_2O)$ in the presence of TMEDA.[13]

Results and Discussion

Scission of *para*-Substituted 1,2-Dibenzoylethane Derivatives. Hoffmann et al. studied the SmI_2-mediated coupling of 1,4-diketones.[15] Samarium diiodide was found to promote classical pinacolic coupling of 1,4-diketones forming polycyclic compounds. Subsequent studies showed that treatment of certain carbonyl compounds with SmI_2 in the presence of HMPA (hexamethylphosphoramide) generates unexpected reaction products.[16−18] Ghosh et al. reported that addition of HMPA to the reaction mixture can promote scission of a carbon−carbon bond instead of ring formation for several types of polycyclic compounds containing the 1,4-diketone motif.[16] Since the types of compounds employed in these two studies involve quite different ring systems, it is difficult to interpret the observed differences in reactivity. A possible explanation is that intramolecular coupling of the intermediate ketyl radicals in the systems studied by Ghosh would engender a large energetic barrier due to ring strain.[16] An alternative interpretation bears on the fact that HMPA can coordinate to the metal centers and would sterically hinder combination of metal-coordinated ketyl radicals.[17] Recently, Williams et al. observed carbon−carbon bond fragmentation, in low yields, for unstrained 1,4-diketones when treated with SmI_2/HMPA.[17,18] The studies mentioned above[16−18] indicate that the use of certain bulky coordinating additives (HMPA) can induce carbon−carbon bond cleavage in the reduction of 1,4-diketones with SmI_2 and disfavor classical pinacol coupling. The role played by HMPA in these reactions is not very clear. A likely consequence of HMPA coordination is an increase of the steric bulk around the metal center.

Complex **1** sets the stage for an alternative scenario, namely, the use of a well-defined, sterically hindered metal center to control the reaction pathway rather than relying on uncertain steric attributes embedded in the reaction conditions. Acyclic 1,4-diketones were used in the studies described below (eq 1). A green toluene solution of **1** turns orange rapidly upon addition to a colorless suspension of the 1,4-diketone, indicating oxidation of titanium(III) to titanium(IV). The NMR spectrum of the reaction mixture reveals the presence of a single product exhibiting two singlets in the olefinic region corresponding to the methylene protons. Pinacol coupling products are not observed. Even though the conversion to the enolates is quantitative (^{1}H NMR), the isolated yields of orange crystalline products range from 55 to 70% due to the high lipophilicity of these compounds.

In the reaction presented here, a carbon−carbon single bond is cleaved reductively by 2 equiv of titanium-



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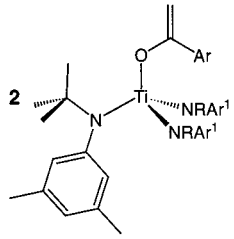

(1)

1-OC(CH$_2$)Ar^2 Ar^2 = *p*-tolyl

1-OC(CH$_2$)Ar^3 Ar^3 = 4-C$_6$H$_4$OMe

(III). Kinetic characterization of the system was attempted using UV−vis spectroscopy. Absorbance measurements were made at 792 and 645 nm, where the titanium(III) complex has molar absorption λ_{max} (ϵ = 223 (cm M)$^{-1}$ and 169 (cm M)$^{-1}$, respectively) and the enolate product has negligible absorption. Kinetic runs were performed after quick manual mixing of the reagents in a UV cell under inert atmosphere. Formation of a transient species was indicated by the time profile of the spectra, different from that expected for a simple decay of **1**. The UV spectra of the sample obtained by mixing solutions of $Ti(NRAr^1)_3$ and 1,2-di-*p*-methylbenzoylethane display a broad transient absorption around 670 nm. This absorption is consistent with the presence of a transient ketyl radical. Previously reported ketyl radicals supported by tris-silox titanium display absorption at 646 nm (for $OCPh_2$) and 692 nm ($OCTol_2$).[9]

Enolate **1**-OC(CH$_2$)Ar^2 was characterized structurally by single-crystal X-ray diffraction (Figure 1). The Ti(NRAr^1)$_3$ group displays pseudo-C_3 symmetry with the *tert*-butyl groups forming a pocket around the enolate ligand. From reported structural studies, organometallic titanium enolates involving compounds containing the titanocene motif display longer Ti−O distances (1.861(3)−1.903(2) Å) and smaller Ti−O−C angles (138.9(2)−147.3(2)°) compared to the values for **1**-OC(CH$_2$)Ar^2 (1.826(2) Å and 151.2(2)°).[19,20] These structural differences suggest stronger donation from the oxygen p orbitals into the metal d orbitals in the case of **1**-OC(CH$_2$)Ar^2. The carbon−carbon distance is similar to those reported previously.

Reactions of Complex 1 with *para*-Substituted Acetophenones. In the examples of the preceding section, complex **1** severs the linkage between two ArC(O)CH$_2$ groups. To expand the scope of this reaction, studies of Ti(NRAr^1)$_3$ reactivity toward acetophenones were performed. As anticipated, treatment of acetophenones with **1** induced disproportionation with formation of equal amounts of enolate and alkoxide Ti complexes (Scheme 1), according to ^{1}H NMR data. Pinacol condensation products were not observed. The data suggest that the proposed intermediate ketyl radical prefers to decompose via disproportionation, a typical radical annihilation fate.[9]

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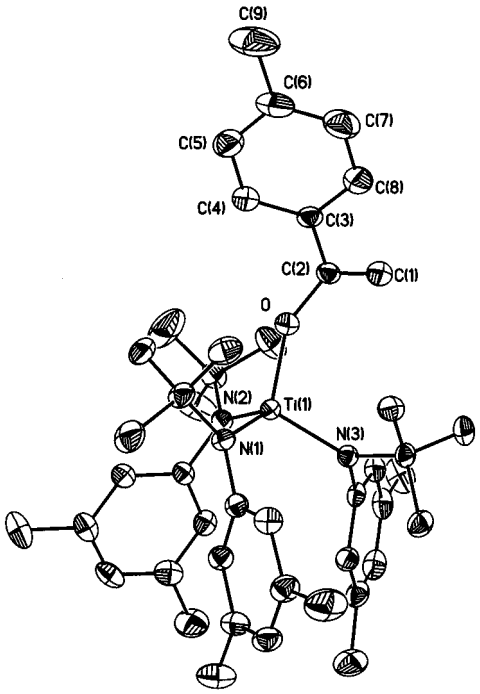
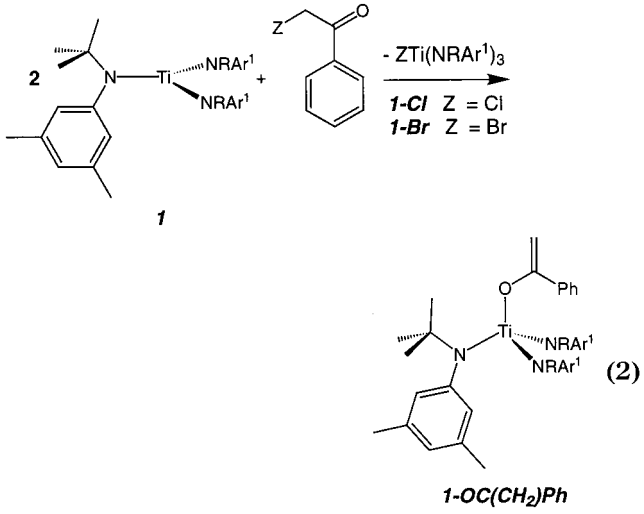


Figure 1. Structural drawing of **1**-OC(CH_2)Ar^2 with thermal ellipsoids at the 35% probability level. Selected bond distances (Å) and angles (deg): Ti−N(1) 1.943(3), Ti−N(2) 1.920(3), Ti−N(3) 1.904(3), Ti−O 1.826(2), O−C(2) 1.352(4), C(1)−C(2) 1.311(5), O−Ti−N(1) 109.36(11), C(2)−O−Ti 151.2(2), O−C(2)−C(1) 122.3(3).

Reactions of Complex 1 with α-Halo-acetophenone. The goal of the experiments described in this section was to explore the possibility of activating linkages between $ArCOCH_2$ and halogens (Cl and Br, eq 2). Addition of 2 equiv of **1** to a solution of α-halo-

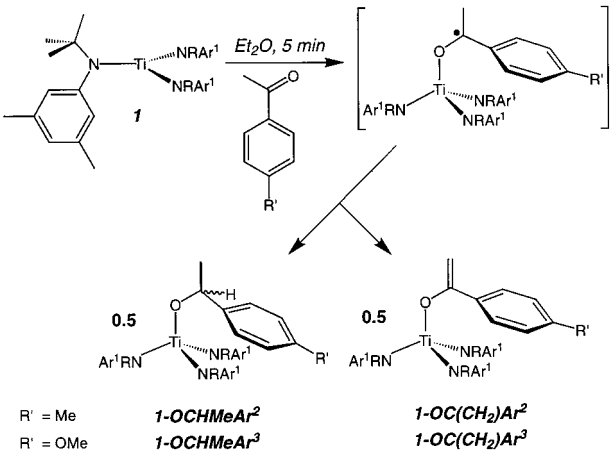


(2)

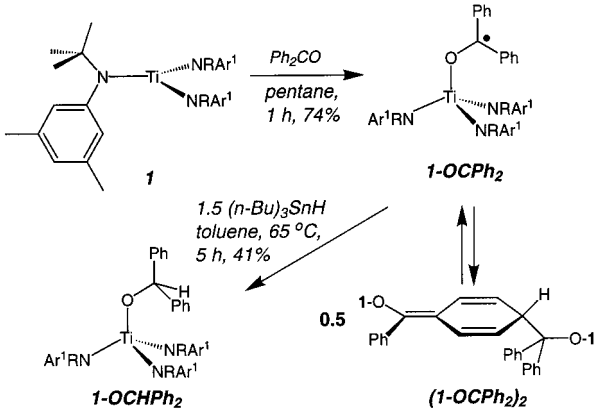
acetophenone affords clean formation of the titanium(IV) enolate (**1**-OC(CH_2)Ph) and the halide (**1**-Cl and **1**-Br). The experiments presented in the last two sections indicate facile activation of the bond positioned β to a carbonyl group and smooth enolate formation as the preferred reaction pathway.

Reaction of Ti(NRAr^1)$_3$ with Benzophenone. The reactions presented so far bear on the proposed formation of intermediate ketyl radicals that undergo radical decomposition by one of the available pathways: carbon−carbon bond cleavage, carbon−halogen bond cleavage, or disproportionation through hydrogen atom transfer. Attempts to observe the ketyl radical by EPR at low temperatures were unsuccessful due to its fast conversion to diamagnetic products. Stabilization of a ketyl radical was achieved by inhibiting the possible radical decomposition pathways. Taking advantage of the absence of β-linkages susceptible to radical fragmentation, reaction of **1** with benzophenone allowed generation of a stable ketyl-titanium complex **1**-$OCPh_2$ (Scheme 2). Treatment of a toluene solution of **1** with benzophenone at room temperature was accompanied by a color change from forest green to dark brown-green. Storage at −35 °C caused a reversible color change from dark brown-green to bright orange. This observation supports the idea of an equilibrium between the ketyl complex **1**-$OCPh_2$ and the diamagnetic dinuclear complex (**1**-$OCPh_2)_2$, reminiscent of the behavior of the trityl radical or of the ketyl radicals bound to metal centers supported by bulky ligands.[9,21,22] By analogy with the trityl radical case, pinacolic coupling is obviated by steric constraints. Steric hindrance in the asymmetric dinuclear complex along with the presence of radical species is invoked to account for the broadness and the number of ligand peaks displayed in the ^{1}H NMR

Scheme 1



Scheme 2



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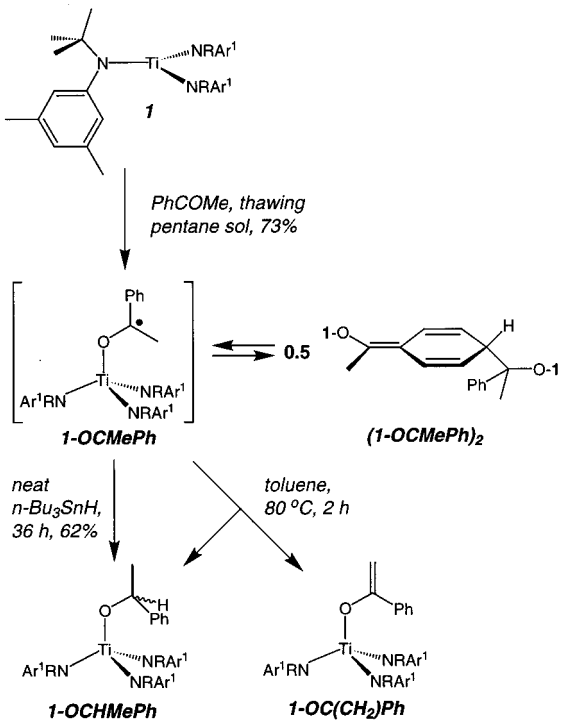
Scheme 3



spectrum of (**1**-OCPh$_2$)$_2$ at various temperatures. This species displays peaks around 5−6 ppm, peaks that increase in intensity at lower temperatures. This behavior indicates the presence of structures analogous to the dimer of the trityl radical (i.e., the Gomberg dimer).[9,23] EPR analysis of the system indicated the presence of a carbon-centered radical at room temperature ($g \approx 1.9925$ and sharp lines). Furthermore, a toluene solution of species (**1**-OCPh$_2$)$_2$ shows an absorption at 641 nm, in good agreement with previous spectroscopic reports for titanium-bound benzophenone ketyl radical.[9]

Chemical means were employed also to test the availability of the ketyl radical in a solution of the titanium-ketyl complex (Scheme 2). Complex (**1**-OCPh$_2$)$_2$ was stirred in toluene in the presence of *n*-Bu$_3$SnH to generate cleanly a diamagnetic compound displaying sharp peaks for a single NRAr ligand environment. The ^{1}H NMR spectrum thereby obtained is assignable to **1**-OCHPh$_2$, the product of H atom abstraction from the tin hydride.

Reaction of Ti(NRAr^1)$_3$ with Acetophenone. Treatment of acetophenone with a pentane solution of **1** at low temperatures induces, upon mixing, a color change from forest green to intense orange (Scheme 3). ^{1}H NMR spectroscopic analysis of the reaction mixture reveals, surprisingly, the absence of enolate and alkoxide peaks, compounds that formed cleanly in the case of *para*-substituted acetophenones. Instead, features quite similar to those observed in the ^{1}H NMR spectrum of **1**-OCPh$_2$ were in evidence. In particular, the peaks between 4 and 5 ppm were indicative of the 2,5-cyclohexadiene moiety as described by the structural drawing of (**1**-OCMePh)$_2$ in Scheme 3. Recrystallization from diethyl ether/pentane affords isolation of (**1**-OCMePh)$_2$ in 73% yield. Clean decomposition upon heating to the expected enolate (**1**-OC(CH$_2$)Ph and alkoxide (**1**-OCHMePh) substantiates the idea that (**1**-OCMePh)$_2$ is a resting state for a transient ketyl radical. Furthermore, slow reaction with *n*-Bu$_3$SnH generates the alkoxide **1**-OCHMePh as the major product. Notably, no significant conversion of (**1**-OCMePh)$_2$ to the corresponding enolate and alkoxide is observed, even after several weeks, if stored at −35 °C.

Formation of a Gomberg dimer-type species for the acetophenone ketyl radical raises two issues. First, the intermediate ketyl radicals couple to form a new carbon−carbon bond, but the coupling does not proceed in a pinacolic manner, even though a methyl rather than a phenyl abuts the ketone functionality. Massive steric bulk generated by the amido ligands in close proximity to the ketyl radical center may justify the observed behavior by compensating for the smaller size of the methyl substituent. Second, the intermediate ketyl radical does not decompose through the available pathway of β-hydrogen transfer. Bimolecular disproportionation through H atom transfer may likewise be disfavored for steric reasons. The ketyl radical clearly has more access to the *para* position of the phenyl ring than to the hydrogens on the methyl group. This kind of steric control has been used for synthetic organic applications in the SmI$_2$/HMPA system.[24,25] In such cases, benzaldehydes and acetophenones undergo activation of the *para* position when treated with SmI$_2$/HMPA to generate the phenyl−carbonyl coupling product, rather than the pinacolic coupling product.[24,25]

Reaction of Ti(NRAr^1)$_3$ with 1,2-Dibenzoylethane. Following a similar reactivity pattern, 1,2-dibenzoylethane, (PhCOCH$_2$)$_2$, reacts with **1** to generate a new compound ((**1**-OC(CH$_2$)Ph)$_4$, Scheme 4), displaying broad peaks in its ^{1}H NMR spectrum. The expected enolate is a minor product when the reaction is run at low temperatures. Compound (**1**-OC(CH$_2$)Ph)$_4$ can be precipitated selectively from an acetonitrile/diethyl ether mixture. The ^{1}H NMR spectrum of (**1**-OC(CH$_2$)Ph)$_4$ does not supply useful information regarding the molecular structure of this species, and crystals suitable for X-ray crystallography were not obtained. By analogy with the chemical reactivity of (**1**-OCMePh)$_2$, the structure of (**1**-OC(CH$_2$)Ph)$_4$ is proposed to be based on the Gomberg dimer-type motif. Oligomeric variants of (**1**-OC(CH$_2$)Ph)$_4$ containing the same head-to-tail coupling motif also are feasible. When heated in solution at 75 °C for 4 h, (**1**-OC(CH$_2$)Ph)$_4$ converts cleanly to expected enolate **1**-OC(CH$_2$)Ph. Hence, (**1**-OC(CH$_2$)Ph)$_4$ behaves as a resting state for the diketyl radical. The fact that (**1**-OC(CH$_2$)Ph)$_4$ can be observed spectroscopically and isolated suggests that the carbon−carbon cleavage reaction is facile if two titanium centers activate in concert the ketone groups (Scheme 4). If only one titanium(III) activates the carbon−carbon bond in a fast reaction, the intermediate monoketyl radical should split to form **1**-OC(CH$_2$)Ph and the [PhCOCH$_2$] radical, which would trap in turn another equivalent of **1** with no formation of byproduct (**1**-OC(CH$_2$)Ph)$_4$. However, if the monoketyl radical does not promote fast carbon−

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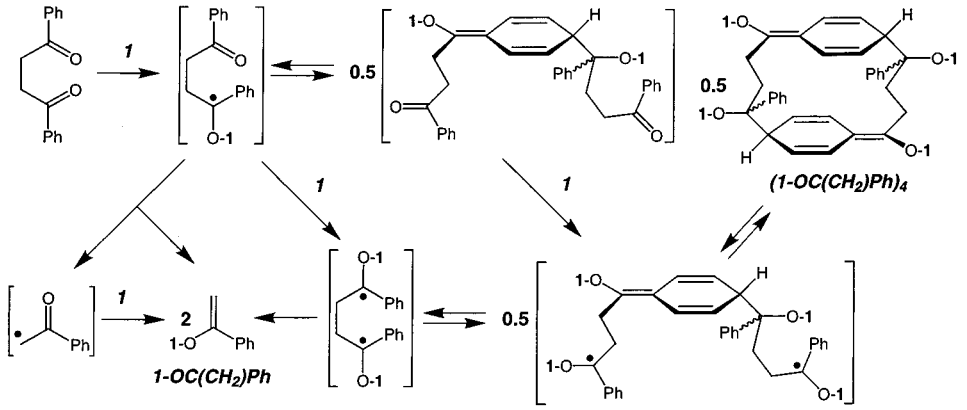
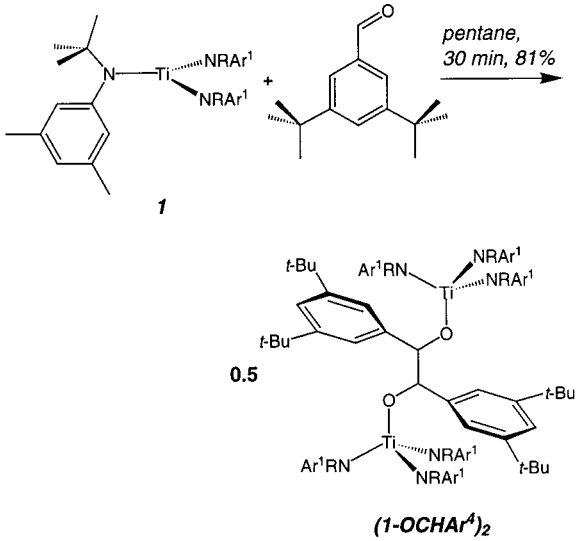
Scheme 4



carbon bond splitting, it would prefer to rest in structures similar to (**1**-OCMePh)$_2$ based on the arguments discussed in the preceding section. When the second ketone group of the substrate is reduced, carbon−carbon bond cleavage is not facile if the initial ketyl radical is coupled in the *para* position of a phenyl ring. Hence, the second ketyl radical will also rest in structures similar to (**1**-OCMePh)$_2$. Species with diketyl radical character are accessed upon heating and convert irreversibly to the enolate.

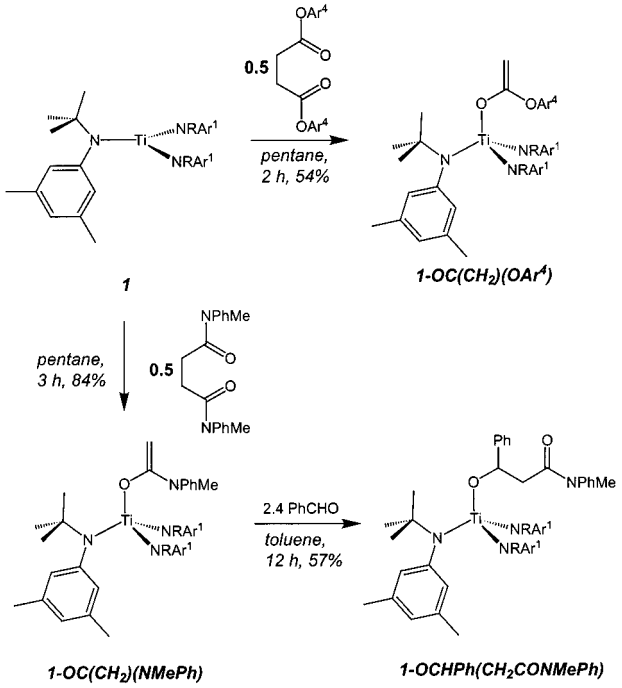
Reaction of Ti(NRAr^1)$_3$ with 3,5-Di-*tert*-butylbenzaldehyde. To investigate the extent to which the steric bulk of Ti(NRAr^1)$_3$ prohibits pinacol coupling, the reaction of **1** with an aldehyde was pursued (eq 3, Ar^4 = 3,5-C$_6$H$_3$(*t*-Bu)$_2$). Aromatic aldehydes provide access



(3)

to sterically more open ketyl radicals that do not contain β-linkages vulnerable to activation. On the basis of the color change of the toluene solution from green to yellow, the reaction is complete in a few seconds. The ^{1}H NMR spectrum of the reaction mixture shows clean conversion to a single product. However, the relatively broad peaks do not rule out the possibility of hydrogen abstraction from the solvent with formation of a benzyloxy ligand coordinated to **1**. In an additional experiment, no ^{2}H incorporation was observed when the reaction was performed in C$_6$D$_6$. This result substantiates the formation of the pinacol coupling product, (**1**-OCHAr^4)$_2$ (eq 3). The fact that pinacol coupling is not totally forbidden

Scheme 5



when Ti(NRAr^1)$_3$ is used as a reagent seems to indicate that a subtle interplay of steric factors governs the outcome of the reactions presented thus far. It is important to note that the benzaldehyde employed in this experiment cannot couple in the *para* position due to the voluminous *tert*-butyl groups in close proximity. Under similar reaction conditions, benzaldehyde gives a mixture of products presumably due to head-to-tail coupling besides pinacolic coupling.

Carbon−carbon Bond Cleavage in Esters and Amides of Succinic Acid. The previous sections have focused on reactions of **1** with substrates containing a carbonyl functionality. Extending the scope of these reactions by using carboxylic acid derivatives is very appealing (Scheme 5). Esters and amides of succinic acid have been treated with **1** under conditions similar to those employed for 1,4-diketones. The reaction is slower, but conversion to the ester and amide enolates is nearly quantitative in 2−3 h, based on ^{1}H NMR spectroscopy. Longer reaction times may be attributed to decreased oxidizing character of esters and amides as compared with ketones. Besides representing a novel type of carbon−carbon bond activation, the reactions presented

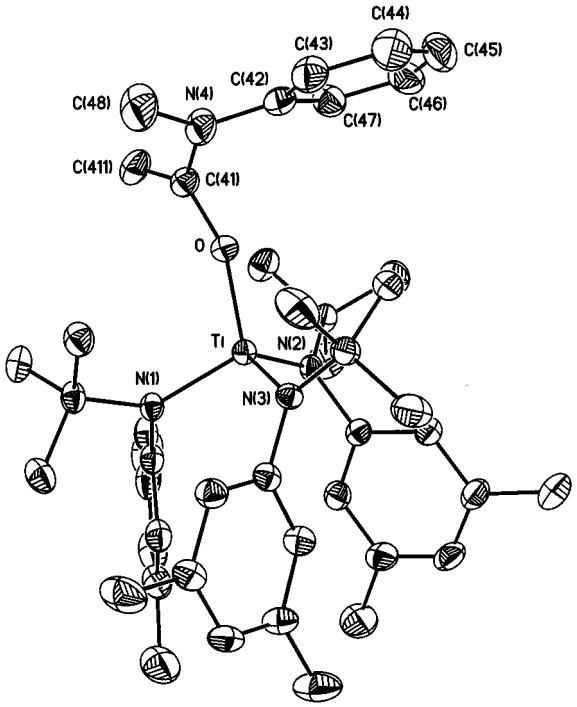


Figure 2. Structural drawing of **1**-OC(CH_2)NPhMe with thermal ellipsoids at the 35% probability level. Selected bond distances (Å) and angles (deg): Ti−N(1) 1.931(3), Ti−N(2) 1.936(3), Ti−O 1.847(3), O−C(2) 1.340(4), C(41)−C(411) 1.309(5), N(4)−C(41) 1.417(5), O−Ti−N(1) 110.59(12), C(41)−O−Ti 159.0(2), O−C(41)−C(411) 123.4(4), C(411)−C(41)−N(4) 122.1(4), O−C(41)−N(4) 114.5(3).

here have provided a novel synthetic pathway for accessing the ester **1**-OC(CH_2)OAr[4] and amide **1**-OC(CH_2)NPhMe enolates. While alternative routes involve strongly basic and polar reaction conditions, the syntheses presented here are performed under neutral conditions in nonpolar media.

Considering the paucity of structural data available for transition-metal amide enolates, an X-ray crystallographic study of **1**-OC(CH_2)NPhMe was performed (Figure 2). Comparison to the previously reported transition-metal amide enolate structure containing the zirconocene motif (Cp_2ZrCl[OC(CH_2)NPh_2]) revealed substantial similarity in the structural parameters; the N−C, C−O, and C−C distances are very similar in the two compounds.[26] Important features in the structure of **1**-OC(CH_2)NPhMe are the dihedral angles C(411)−C(41)−N(4)−C(48) and C(411)−C(41)−N(4)−C(42) (56° and 112°, respectively), which suggest that in the solid state there is no significant 4e repulsive interaction between the nitrogen lone pair and the carbon−carbon π bond.

Aldol Condensation of the Amide Enolate 1-OC(CH_2)NPhMe with Benzaldehyde. Amide enolates enjoy widespread use in synthetic organic chemistry particularly with regard to carbon−carbon bond formation.[27,28] The presence of increased steric bulk close to the amide enolate functionality is of interest also with respect to the effect on aldol condensation reactivity. Treatment of **1**-OC(CH_2)NPhMe with excess PhCHO in toluene at room temperature affords complete conversion to the aldol condensation product **1**-OCHPh(CH_2CONPhMe) within 12 h (Scheme 5). A strong band in the IR spectrum of **1**-OCHPh(CH_2CONPhMe) at 1659 cm^{-1} is diagnostic of an uncoordinated amide group. It is interesting to note that the sterically encumbered titanium center can be transferred from the enolate oxygen to the benzaldehyde oxygen, as required for aldol condensation.

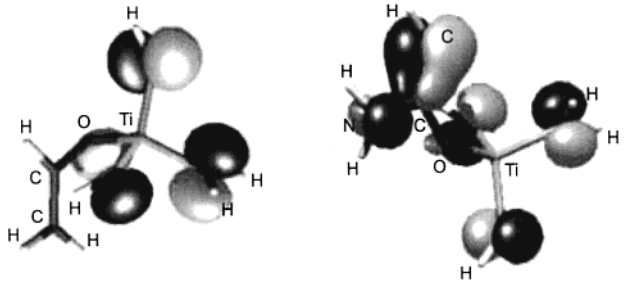


Figure 3. HOMOs of **2**-OCHCH$_2$ (left) and **2**-OC(NH_2)-CH_2 (right).

Theoretical Investigation of Titanium Enolates. After successful aldol condensation of benzaldehyde with amide enolate **1**-OC(CH_2)NPhMe, extension of the same procedure to the ketone-derived enolate **1**-OC(CH_2)Ar[2] was attempted. However, under identical conditions, enolate **1**-OC(CH_2)Ar[2] showed no reactivity toward benzaldehyde. The decreased nucleophilicity of the ketone-derived enolate compared to the amide enolate may be invoked to account for the difference. To detail the electronic differences between the ketone-derived and the amide titanium enolates, a density functional theory computational study was performed on the model compounds **2**-OCHCH$_2$ (**2** = Ti(NH_2)$_3$) and **2**-OC(NH_2)CH_2.[29−32] Local C_{3v} symmetry was imposed for fragment **2**. Calculated structural parameters for the model compounds were in good agreement with the experimental ones (see Supporting Information for details). Hirshfeld charge analysis shows a significantly higher electron density on the methylene carbon in the case of the amide enolate (−0.178) as compared with the unsubstituted enolate (−0.124), this being in agreement with the predictions of valence bond theory.[33] Furthermore, an analysis of the frontier molecular orbitals shows that the HOMO of **2**-OC(NH_2)CH_2 enjoys a large contribution from the carbon−carbon π bond, while the HOMO of **2**-OCHCH$_2$ is only a ligand-based orbital comprised of amido nitrogen lone pairs (Figure 3). Also, the orbitals containing π electron density on the carbon atoms are higher in energy for **2**-OC(NH_2)-CH_2. Although the X-ray study of **1**-OC(CH_2)NPhMe indicated that in solid state there is no significant interaction between the nitrogen lone pair and the carbon−carbon π bond, the computational study pro-

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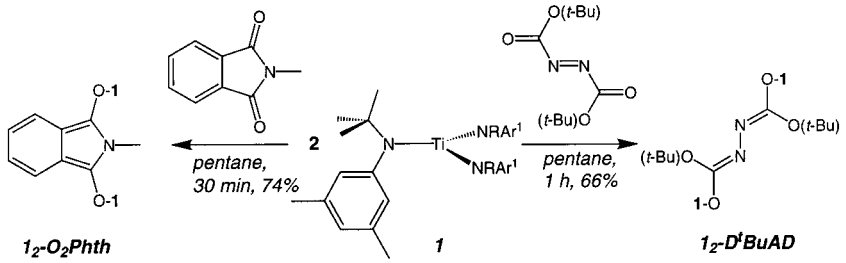
(32) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. *J. Theor. Chem. Acc.* **1998**, *99*, 391.
(33) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; an Introduction to Modern Structural Chemistry*; Cornell University Press: Ithaca, NY, 1960.

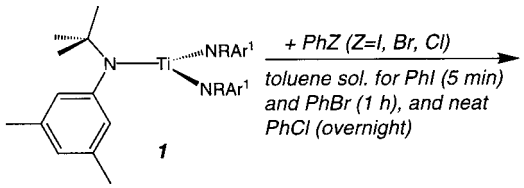
Scheme 6



vides an elegant explanation for the observed solution-phase reactivity.

Reactions of Ti(NRAr^1)$_3$ with Substrates Containing Conjugated π Systems. The reactions described in the foregoing sections document the ability of **1** to sever σ bonds positioned β to a carbonyl group. An extension to these reactions would be to use substrates incorporating a π bond β to a carbonyl group. The experiments depicted in Scheme 6 portray 2 equiv of Ti(NRAr^1)$_3$ acting in concert to effect 2e reduction. In the case of *N*-methylphthalimide (O_2Phth), reduction with **1** disrupts the aromaticity of the six-membered ring, cleanly affording **1**$_2$-O_2Phth. The *iso*-indole motif displayed by **1**$_2$-O_2Phth previously has been accessible only in low yields, under a special electrolytic procedure.[34] Interesting to note is that treatment of **1** with di-*tert*-butylazodicarboxylate (D*t*-BuAD) led to reorganization of the π framework rather than *tert*-butyl radical loss.[13]

Halogen Abstraction from Halobenzenes. In the previous sections, **1** has been used for facile 1e reduction of carbonyl groups, causing the cleavage or formation of other bonds via radical pathways. A relatively unreactive functionality prone to activation by Ti(NRAr^1)$_3$ is the aryl-Z bond (eq 4). Treatment of **1** with stoichio-

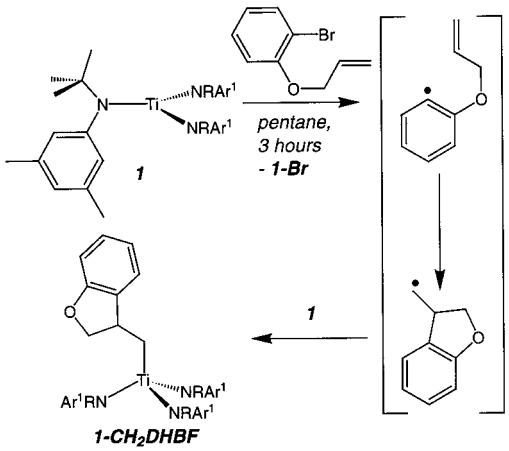


(4)

1-Cl Z = Cl
1-Br Z = Br
1-I Z = I

metric amounts of iodo- or bromobenzene generates cleanly the titanium(IV) halide complexes within less than an hour at room temperature. Activation of chlorobenzene is considerably slower. Conversion of **1** to **1**-Cl is complete after stirring overnight in neat chlorobenzene. A kinetic study of the halogen abstraction reactions was performed using UV−vis spectroscopy. Decay of **1** was monitored at 792 nm. Large concentrations of halobenzenes were employed in order to provide pseudo-first-order conditions for kinetic analysis. The reaction was found to obey a second-order kinetic law, first order in both reagents ($r = k$[Ti(NRAr^1)$_3$][PhZ]) for activation of iodobenzene ($k = (6.6 \pm 0.5) \times 10^{-1}$ (s M)$^{-1}$) and bromobenzene ($k = (9.3 \pm 0.1) \times 10^{-3}$ (s M)$^{-1}$). Chlorine atom abstraction from chlorobenzene displays first-order kinetics with respect to **1**. The order in PhCl could not be determined accurately due to the small variations in the employed concentrations of PhCl. Very high concentrations of PhCl were used (almost neat) in order to promote the reaction on a reasonable time scale. The pseudo-first-order rate constant (k_{obs}) was found to be $(1.8 \pm 0.3) \times 10^{-4}$ s^{-1}. No significant decay of **1** in neat fluorobenzene solution was observed by UV−vis spectroscopy over 10 h. **1**-F was prepared independently for spectroscopic characterization by XeF_2 fluorination of **1**.

Scheme 7



Reaction of Ti(NRAr^1)$_3$ with *o*-Bromophenyl Allyl Ether. Halogen atom abstraction by **1** from halobenzenes is thought to occur with generation of a transient phenyl radical. For substantiation of this hypothesis, the reaction of **1** with *o*-bromophenyl allyl ether was investigated (Scheme 7). This substrate offers the opportunity for a transient aryl radical to undergo cyclization.[35] Examination of the reaction mixture by ^{1}H NMR revealed two NRAr^1 ligand environments, one corresponding to **1**-Br and the other assigned to **1**-CH_2DHBF (DHBF = dihydrobenzofuranyl). The inequivalence of the methylene protons vicinal to the oxygen atom (two peaks at 4.15 and 4.29 ppm) is indicative of formation of a ring-closure product. Although attempts to separate **1**-CH_2DHBF from the bromotitanium byproduct were not successful, exhaustive hydrolysis of **1**-CH_2DHBF was found to generate 3-methyldihydrobenzofu-

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ran,[36] consistent with the structural assignment for **1**-CH_2DHBF displayed in Scheme 7.

Conclusions

In this paper the chemical reactivity of Ti(NRAr[1])$_3$ with a series of organic substrates, especially carbonyl compounds, has been elucidated. Complex **1** has been shown to activate a variety of σ and π bonds situated β to carbonyl groups. The presence of steric bulk in proximity to the generated ketyl radical has been shown dramatically to influence the outcome of the reactions. Disproportionation, pinacol coupling, carbon−carbon bond cleavage, and activation of the *para* position of phenyl-substituted ketyl radicals were all observed depending on the nature of the substrate. The synthetic strategies developed in this context afforded clean preparation of ester and amide enolates in neutral nonpolar media via symmetrical scission of succinic acid derivatives. The amide enolate synthesized through this novel C−C bond cleavage pathway was shown to undergo aldol condensation with benzaldehyde. Ti(NRAr[1])$_3$ was found to abstract atomic halogen from halobenzenes. In the case of *o*-bromophenyl allyl ether, the intermediate aryl radical undergoes ring closure with formation of the dihydrobenzofuran moiety. Activation of a bond β to a ligating functional group continues to be a dominant feature of the chemistry of three-coordinate **1**, a reactive and potent hydrocarbon-soluble 1e reductant.

Experimental Section

General Considerations. Unless stated otherwise, all operations were performed in a Vacuum Atmospheres drybox under an atmosphere of purified nitrogen or using Schlenk techniques under an argon atmosphere. Anhydrous diethyl ether was purchased from Mallinckrodt; pentane, *n*-hexane, and tetrahydrofuran (THF) were purchased from EM Science. Diethyl ether, toluene, benzene, pentane, and *n*-hexane were dried and deoxygenated by the method of Grubbs.[37] THF was distilled under nitrogen from purple sodium benzophenone ketyl. Distilled solvents were transferred under vacuum into vacuum-tight glass vessels before being pumped into a Vacuum Atmospheres drybox. Hexamethyldisiloxane was degassed and dried over 4 Å sieves. C_6D_6 and $CDCl_3$ were purchased from Cambridge Isotopes and were degassed and dried over 4 Å sieves. The 4 Å sieves, alumina, and Celite were dried in vacuo overnight at a temperature just above 200 °C. Ti(NRAr[1])$_3$,[13] 1,4-diketones,[38] *o*-bromophenyl allyl ether,[39] esters, and amides of succinic acid[40] were synthesized according to literature procedures. Other chemicals were used as received. Solution infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR using KBr plates. UV−vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer. Room-temperature X-band EPR spectra were recorded on a Bruker EMX spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-300, Mercury 300, or Varian INOVA-501 spectrometers at room temperature, unless indicated otherwise. Chemical shifts are reported with respect to internal solvent: 7.15 and 128.38 (t) ppm (C_6D_6); 7.27 ppm, and 77.23 (t) ppm ($CDCl_3$), for ^{1}H and ^{13}C data. CHN analyses were performed by H. Kolbe Mikroanalytisches Laboratorium (Mülheim, Germany).

Synthesis of 1-OC(CH$_2$)Ar: General Procedure. A cold toluene solution of Ti(NRAr[1])$_3$ (**1**, 2 equiv) was added to a thawing suspension of 1,4-diketone (1 equiv) in toluene. Upon addition to the colorless suspension, the forest green solution of **1** gradually turns orange. After 30 min of stirring, volatile materials are removed in vacuo, providing an orange oily residue containing pure product as assigned by ^{1}H NMR spectroscopy. No diketone starting material is present on the basis of NMR data. Recrystallization from pentane or diethyl ether resulted in the isolation of the orange crystalline enolate product in 55−70% yield.

1-OC(CH$_2$)Ar^2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (s, 27H, C(CH_3)$_3$), 2.27 (s, 18H, ArCH_3), 2.41 (s, 3H, enolate aryl-CH_3), 4.70 and 4.77 (singlets, 2H, CH_2), 6.24 (br s, 6H, aryl *o*-*H*), 6.74 (s, 3H, aryl *p*-*H*), 7.15 and 7.51 (doublets, 4H, enolate aryl *o*- and *m*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6 (enolate *p*-*C*H$_3$), 21.8 (*m*-*C*H$_3$), 30.8 (C(*C*H$_3$)$_3$), 61.8 (*C*(CH$_3$)$_3$), 94.4 (=*C*H$_2$), 115.5 (aryl), 125.9 (aryl), 126.5 (aryl), 127.7 (aryl), 128.4 (aryl), 137.4 (aryl), 151.8 (aryl), 166.2 (O*C*=C). Anal. Calcd for $TiN_3OC_{45}H_{63}$: C, 76.14; H, 8.93; N, 5.92. Found: C, 76.03; H, 9.10; N, 5.99.

1-OC(CH$_2$)Ar^3. ^{1}H NMR (300 MHz, C_6D_6): δ 1.32 (s, 27H, C(CH_3)$_3$), 2.25 (s, 18H, ArCH_3), 3.32 (s, 3H OCH_3), 4.94 and 5.00 (singlets, 2H, CH_2), 6.48 (br s, 6H, aryl *o*-*H*), 6.72 (s, 3H, aryl *p*-*H*), 6.86 and 7.71 (doublets, 4H, enolate aryl *o*- and *m*-*H*). ^{13}C NMR (75 MHz, C_6D_6): 22.2 (*m*-*C*H$_3$), 31.4 (C(*C*H$_3$)$_3$), 55.2 (O*C*H$_3$), 62.4 (*C*(CH$_3$)$_3$), 94.8 (=*C*H$_2$), 113.9 (aryl), 126.9 (aryl), 128.6 (aryl), 132.5 (aryl), 136.9 (aryl), 152.7 (aryl), 160.4 (aryl), 167.1 (O*C*=C). Anal. Calcd for $TiN_3O_2C_{45}H_{63}$: C, 74.46; H, 8.75; N, 5.78. Found: C, 74.44; H, 8.80; N, 5,71.

Reaction of Ti(NRAr[1])$_3$ with 1,2-Dibenzoylethane. A cold toluene solution (10 mL) of **1** (550 mg, 0.95 mmol, 2 equiv) was added to a thawing suspension of (PhCOCH$_2$)$_2$ (113.5 mg, 0.47 mmol, 1 equiv) in toluene (5 mL). Evacuation of volatile material was started immediately after addition. The reaction mixture turns dark brown-red, then intense orange. The ^{1}H NMR spectrum of the oily solid obtained upon removal of volatile material displays sharp peaks corresponding to the titanium enolate as well as broad peaks attributed to (**1**-OC(CH$_2$)Ph)$_4$. The oily solid was dissolved in the minimum amount of diethyl ether, and acetonitrile was added to cause precipitation of an orange solid collected on a sintered glass frit. The isolated orange powder (236 mg) contains (**1**-OC(CH$_2$)Ph)$_4$ along with 20% enolate **1**-OC(CH$_2$)Ph. ^{1}H NMR (300 MHz, C_6D_6, tentative assignments): 1.09−1.43 (br m, C(CH_3)$_3$), 2.06−2.45 (br m, ArCH_3), 5.4−8.30 (br m, olefin and aryl C*H*).

Synthesis of 1-OC(CH$_2$)Ph. A cold toluene solution (5 mL) of **1** (110 mg, 0.19 mmol, 2 equiv) was added to a thawing suspension of (PhCOCH$_2$)$_2$ (22.7 mg, 0.095 mmol, 1 equiv) in toluene (2 mL) and stirred for 1 h to reach room temperature and then heated at 75 °C with stirring for four additional hours. The reaction mixture was allowed to cool to room temperature, followed by removal of volatile material in vacuo. The oily residue contained pure Ti enolate as assigned by ^{1}H NMR spectroscopy. Recrystallization from pentane resulted in the isolation, in two crops, of the orange crystalline enolate product in 65% yield (86 mg, 0.12 mmol). ^{1}H NMR (300 MHz, C_6D_6): δ 1.30 (s, 27H, C(CH_3)$_3$), 2.25 (s, 18H, ArCH_3), 4.94 and 4.99 (singlets, 2H, CH_2), 6.46 (br s, 6H, aryl *o*-*H*), 6.71 (s, 3H, aryl *p*-*H*), 7.15 (1H, phenyl *p*-*H*), 7.21 (t, 2H, phenyl *m*-*H*) and 7.73 (d, 2H, phenyl *o*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): 21.7 (*m*-*C*H$_3$), 30.7 (C(*C*H$_3$)$_3$), 61.8 (*C*(CH$_3$)$_3$), 94.9 (=*C*H$_2$), 115.5 (aryl), 125.9 (aryl), 126.6 (aryl), 127.8 (aryl), 136.2 (aryl), 139.0 (aryl), 151.8 (aryl), 166.1 (O*C*=C). Anal. Calcd for $TiN_3OC_{44}H_{61}$: C, 75.95; H, 8.83; N, 6.04. Found: C, 75.86; H, 8.90; N, 5.96.

Reaction of Ti(NRAr[1])$_3$ with ArCOCH$_3$: General Procedure. A diethyl ether solution of **1** (1 equiv) was added to a suspension of ArCOCH$_3$ (1 equiv) in diethyl ether, at room

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(40) Weygand, C.; Hilgetag, G. *Preparative Organic Chemistry*; Wiley-Interscience: New York, 1972.

temperature. Upon mixing of the reagents, the color of the reaction mixture turned dark green-brown, then orange. After 5 min of stirring, volatile material was removed in vacuo. The ^{1}H NMR spectra of the crude reaction mixture indicated formation of two products in equal amounts, one of the products being the enolate, the other being the corresponding alkoxide.

1-OCHMeAr^3. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.28 (s, 27H, C(CH_3)$_3$), 1.71 (br s, 3H, CHCH_3), 2.25 (s, 18H, ArCH_3), 3.35 (s, 3H, OCH_3), 5.71 (br s, 1H, CH$_3$C*H*), 6.30 (br s, 6H, aryl *o*-*H*), 6.71 (s, 3H, aryl *p*-*H*), 6.92 and 7.45 (app doublets, 4H, alkoxide aryl *o*- and *m*-*H*). ^{13}C (125.8 MHz, C_6D_6): δ 22.2 (*m*-CH_3), 27.7 (OCH*C*H$_3$), 31.7 (C(*C*H$_3$)$_3$), 55.1 (O*C*H$_3$), 60.9 (*C*(CH$_3$)$_3$), 85.1 (O*C*H), 114.3 (aryl), 126.5 (aryl), 129.0 (aryl), 129.1 (aryl), 136.7 (aryl), 139.0 (aryl), 153.5 (aryl), 160.0 (aryl).

1-OCHMeAr^2. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.15 (s, 27H, C(CH_3)$_3$), 1.63 (br s, 3H, CHCH_3), 2.29 (s, 18H, ArCH_3), 2.43 (s, 3H, alkoxide aryl-CH_3), 5.62 (br s, 1H, CH$_3$C*H*), 6.14 (br s, 6H, aryl *o*-H), 6.77 (s, 3H, aryl *p*-*H*), 7.22 (d) and 7.39 (br s, 4H, alkoxide aryl *o*- and *m*-*H*). ^{13}C (125.8 MHz, $CDCl_3$): δ 21.7 (*m*-*C*H$_3$), 27.3 (OCH*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$), 60.3 (*C*(CH$_3$)$_3$), 84.6 (O*C*H), 126.0 (aryl), 127.0 (aryl), 128.5 (aryl), 128.9 (aryl), 136.0 (aryl), 138.8 (aryl), 143.4 (aryl), 152.7 (aryl).

Reaction of Ti(NRAr^1)$_3$ with α-Halo-acetophenones. A diethyl ether solution (5 mL) of **1** was added to a suspension of α-Br or α-Cl acetophenone in diethyl ether (2 mL) at room temperature. Upon mixing the reagents, the color of the reaction mixture turned dark brown, then orange. After 15 min of stirring, volatile material was removed in vacuo. The ^{1}H NMR spectra of the reaction mixture showed formation of the titanium tris-anilide halide (**1**-Cl and **1**-Br) and enolate (**1**-OC(CH$_2$)Ph).

Reaction of Ti(NRAr^1)$_3$ with Benzophenone. At room temperature, a pentane solution (5 mL) of **1** (104 mg, 0.18 mmol, 1 equiv) was added to a suspension of benzophenone (33 mg, 0.18 mmol, 1 equiv) in pentane (3 mL). The color turned brown-green upon mixing. The reaction mixture was stirred for 1 h at room temperature. During that time copious precipitation of a yellow solid was observed. Volatile material was removed under reduced pressure to leave a yellow residue, which was partially soluble in pentane. Addition of pentane generated a brown-green solution, the color of which turned reversibly orange upon cooling to −35 °C. Compound (**1**-OCPh$_2$)$_2$ precipitated as a yellow powder (101.2 mg, 0.067 mmol, 74% yield). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, tentative assignments): δ 0.47 (v br), 1.18 (s), and 1.59 (v br) assigned to C(CH_3)$_3$, 2.28 (s) and 2.40 (br s) assigned to ArCH_3, 5.0 (br s) and 5.92 (br s) assigned to the olefinic protons, 6.76 (s), 6.99−7.03 (m), 7.24 (t), 7.31 (br s), 7.49 (d), 8.02, 8.24, 8.40 (br singlets) assigned to aryl C*H*. At lower temperatures, in toluene-d_8, the broad peaks become sharper and split. UV−vis (toluene, RT): λ_{max} 541, 641 nm. Anal. Calcd for $TiN_3OC_{49}H_{64}$: C, 77.48; H, 8.43; N, 5.53. Found: C, 76.91; H, 8.37; N, 5.11.

Synthesis of 1-OCHPh$_2$. A pentane solution (10 mL) of **1** (254 mg, 0.44 mmol, 1 equiv) was added to a diethyl ether suspension (5 mL) of benzophenone (80 mg, 0.44 mmol, 1 equiv). The reaction mixture was stirred for 30 min. After evacuating volatile material, the orange residue was dissolved in toluene (5 mL), and *n*-Bu$_3$SnH (200 mg, 0.69 mmol, 1.5 equiv) was added to the solution. The reaction mixture was placed in a 25 mL Schlenk tube and stirred at 65 °C for 5 h. The color of the mixture gradually changed from dark green-brown to dark red and then to bright orange. Volatile material was removed in vacuo. Upon crystallization from pentane at −35 °C, 136 mg of yellow crystalline **1**-OCHPh$_2$ were obtained in two crops (0.18 mmol, 41% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 1.22 (s, 27H, C(CH_3)$_3$), 2.26 (s, 18H, ArCH_3), 6.52 (br s, 6H, aryl *o*-*H*), 6.63 (br s, 1H, OC*H*), 6.71 (s, 3H, aryl *p*-*H*), 7.07 (t, 1H, phenyl *p*-*H*), 7.22 (t, 2H, phenyl *m*-*H*), 7.57 (br s, 2H, phenyl *o*-*H*). ^{13}C NMR (125.8 MHz, C_6D_6): δ 22.1 (*m*-*C*H$_3$), 31.4 (C(*C*H$_3$)$_3$), 61.4 (*C*(CH$_3$)$_3$), 91.1 (Ph$_2$*C*H), 126.7 (aryl), 127.7 (aryl), 128.7 (aryl), 128.9 (aryl), 136.8 (aryl), 146.2 (aryl), 153.1 (aryl). Anal. Calcd for $TiN_3OC_{49}H_{65}$: C, 77.38; H, 8.55; N, 5.52. Found: C, 77.75; H, 8.85; N, 5.02.

Reaction of Ti(NRAr^1)$_3$ with Acetophenone. A cold pentane solution (5 mL) of **1** (140 mg, 0.24 mmol, 1 equiv) was added to a thawing solution of acetophenone (29 mg, 0.24 mmol, 1 equiv) in pentane (3 mL). Upon addition, the color of the mixture changed to intense orange. Volatile material was removed in vacuo while the solution was cold. Crystallization from pentane at −35 °C afforded 125 mg of orange solid (**1**-OCMePh)$_2$ (0.09 mmol, 73% yield). Stored at −35 °C, compound (**1**-OCMePh)$_2$ does not decompose significantly to enolate **1**-OC(CH$_2$)Ph and alkoxide **1**-OCHMePh even over several weeks. ^{1}H NMR (300 MHz, C_6D_6, tentative assignments): δ 1.24 (s), 1.36 (s), and 1−1.5 (br) assigned to C(CH_3)$_3$, 1.86, 2.02, 2.06, and 2.12 (broad singlets) assigned to OCCH_3, 2.25 (s), 2.31 (s), and 2.39 (br s) assigned to ArCH_3, 4.57 and 4.79 (br s) assigned to the olefinic protons, 6.23 (br app d), 6.55, 6.63, 6.74, 6.77, 6.80 (br app s), 6.88−7.10 (br m), 7.28−7.35 (br m), 7.50, 7.73 (br s) assigned to aryl C*H*. ^{13}C NMR (125.8 MHz, $CDCl_3$): after 6 h of data collection a considerable quantity of **1**-OC(CH$_2$)Ph and **1**-OCHMePh was formed based on ^{1}H NMR analysis. The corresponding peaks in the ^{13}C NMR spectrum were shifted 0.4 ppm downfield. Peaks assigned to (**1**-OCMePh)$_2$ (tentative assignments): δ 14.8 (alkyl *C*H$_3$), 19.8 (alkyl *C*H$_3$), 22.3 (*m*-*C*H$_3$), 23.0 (*m*-*C*H$_3$), 31.3 (C(*C*H$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$), 61.2 (*C*(CH$_3$)$_3$), 61.8 (*C*(CH$_3$)$_3$), 62.3 (*C*(CH$_3$)$_3$), 93.3 (O*C*Ph$_2$R), 117.5 (aryl), 118.0 (aryl), 116.0 (aryl), 124.0−129.7 (aryl), 136.7 (aryl), 151.9 (aryl).

Thermal Decomposition of (1-OCMePh)$_2$. Thawing toluene solutions of **1** (65.4 mg, 0.11 mmol, 1 equiv) and acetophenone (13.6 mg, 0.11 mmol, 1 equiv) were mixed and volatile material was removed before the mixture reached room temperature. The intense orange residue was dissolved in toluene (5 mL) and heated at 80 °C with stirring. Within 30 min the color of the solution turned yellow-orange. Volatile material was removed in vacuo after a total of 2 h of stirring. ^{1}H NMR spectroscopic analysis of the yellow-orange residue revealed the presence of **1**-OC(CH$_2$)Ph and **1**-OCHMePh in a 1:1 ratio.

Synthesis of 1-OCHMePh. Thawing pentane solutions of **1** (90 mg, 0.16 mmol, 1 equiv) and acetophenone (18.7 mg, 0.16 mmol, 1 equiv) were mixed and solvent was removed in vacuo before the mixture reached 25 °C. The intense orange residue was dissolved in 2 mL of *n*-Bu$_3$SnH and allowed to stir at room temperature for 36 h. The color of the reaction mixture gradually turned yellow from intense orange. Excess tin hydride was removed by distillation under reduced pressure. The ^{1}H NMR spectrum of the resulting oily residue showed (*n*-Bu$_3$Sn)$_2$, the alkoxide product **1**-OCHMePh, and trace amounts of enolate **1**-OC(CH$_2$)Ph. The residue was dissolved in pentane and cooled to −35 °C. The yellow precipitate was collected on a sintered glass frit and washed with a small amount of hexamethyldisiloxane. Alkoxide **1**-OCHMePh obtained in this manner (67 mg, 0.10 mmol, 62%) was contaminated with a small amount of enolate, from which it could not be separated by recrystallization. Not performing the reaction in neat *n*-Bu$_3$SnH or heating it for fast completeness formed considerable amounts of enolate. ^{1}H NMR (500 MHz, C_6D_6): δ 1.29 (s, 27H, C(CH_3)$_3$), 1.63 (br s, 3H, CHCH_3), 2.25 (s, 18H, ArCH_3), 5.66 (br s, 1H, CH$_3$C*H*), 6.32 (br s, 6H, aryl *o*-*H*), 6.74 (s, 3H, aryl *p*-*H*), 7.14 (t, 1H, alkoxide phenyl *p*-*H*), 7.27 (t, 2H, alkoxide phenyl *m*-*H*), 7.48 (app d, alkoxide phenyl *o*-*H*). ^{13}C NMR (125.8 MHz, C_6D_6): δ 21.0 (*m*-*C*H$_3$), 27.5 (OCH*C*H$_3$), 31.6 (C(*C*H$_3$)$_3$), 60.9 (*C*(CH$_3$)$_3$), 85.5 (O*C*H), 126.5 (aryl), 127.6 (aryl), 127.9 (aryl), 128.8 (aryl), 129.1 (aryl), 136.7 (aryl), 146.8 (aryl), 153.3 (aryl). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 21.7 (*m*-*C*H$_3$), 27.2 (OCH*C*H$_3$), 31.0 (C(*C*H$_3$)$_3$), 60.3 (*C*(CH$_3$)$_3$), 84.7 (O*C*H), 125.6 (aryl), 127.1 (aryl), 127.3 (aryl), 128.3 (aryl), 128.5 (aryl), 136.0 (aryl), 146.5 (aryl), 152.6 (aryl).

Reaction of Ti(NRAr[1])$_3$ with 3,5-Di-*tert*-butylbenzaldehyde. At room temperature, a pentane solution (5 mL) of **1** (127 mg, 0.22 mmol, 1 equiv) was added to a pentane solution (3 mL) of 3,5-di-*tert*-butylbenzaldehyde (48 mg, 0.22 mmol, 1 equiv). Upon addition, the color turned briefly dark brown-green, then yellow. After 30 min, solvent was removed in vacuo and the yellow residue was crystallized from a diethyl ether/THF mixture at −35 °C. The yellow crystalline precipitate was collected on a sintered glass frit and washed with pentane. In this manner, 142 mg (0.18 mmol, 81% yield) of yellow (**1**-OCHAr$_4$)$_2$ were obtained in two crops. ^{1}H NMR examination after performing the reaction in C_6D_6 showed clean formation of the same product, while the ^{2}H NMR spectrum showed no evidence of ^{2}H incorporation. It would be reasonable to propose the formation of a single product vs a mixture of diastereomers. The ^{1}H NMR spectrum is not of much help in making this kind of decision because the broadness of the peaks can be due to a mixture of diatereomers as well as to hindered rotation of the substituents. The spectroscopic data do not give conclusive information regarding the stereochemistry of this pinacolic coupling reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.96 (br s, 27H, NC(C*H*$_3$)$_3$), 1.45 (br s, 18H, ArC(C*H*$_3$)$_3$), 2.18 (br s, 18H, ArC*H*$_3$), 5.8 (v br s, 6H, aryl *o*-*H*), 6.68 (s, 3H, N-aryl *p*-*H*), 6.91, 7.49 (br singlets, 1H each, OC*H* and alkoxide aryl *p*-*H*), 7.64 (v br s, 2H, alkoxide aryl *o*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.9 (*m*-*C*H$_3$), 31.4 (C(*CH*$_3$)$_3$), 32.2 (C(*C*H$_3$)$_3$), 35.4 (aryl-*C*(CH$_3$)$_3$), 60.4 (N*C*(CH$_3$)$_3$), 124.4 (aryl), 125.8 (aryl), 127.8 (aryl), 135.6 (aryl), 153.9 (aryl). Anal. Calcd for $Ti_2N_6O_2C_{102}H_{152}$: C, 77.09; H, 9.57; N, 5.29. Found: C, 76.98; H, 9.65; N, 4.99.

Reaction of Ti(NRAr[1])$_3$ with Di(3,5-bis[*t*-Bu]phenyl)-succinate. A cold pentane solution (10 mL) of **1** (273 mg, 0.47 mmol, 2 equiv) was added to a thawing suspension of the succinic acid ester (117 mg, 0.23 mmol, 1 equiv) in pentane (5 mL). The reaction mixture was allowed to stir for 2 h. The color gradually changed from forest green to orange-brown. Removal of volatile material in vacuo provided an oily residue, which was inspected by ^{1}H NMR spectroscopy. As determined by ^{1}H NMR spectroscopy, the major component in the mixture is the ester enolate, but some *tert*-butyl-3,5-dimethylaniline was found also to be present. Recrystallization from pentane resulted in the isolation of the orange crystalline ester-enolate product **1**-OC(CH$_2$)OAr^4 (210 mg, 0.25 mmol) in 54% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 27H, NC(C*H*$_3$)$_3$), 1.37 (s, 18H, aryl C(C*H*$_3$)$_3$), 2.24 (s, 18H, ArC*H*$_3$), 3.46 and 3.76 (doublets, 2H, C*H*$_2$), 5.87 (br s, 6H, aryl *o*-*H*), 6.74 (s, 3H, aryl *p*-*H*), 7.08 (d, 2H, enolate aryl *o*-*H*), 7.08 (t, 1H, enolate aryl *p*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8 (*m*-*C*H$_3$), 30.6 (NC-(*C*H$_3$)$_3$), 31.8 (aryl-C(*C*H$_3$)$_3$), 35.2 (aryl-*C*(CH$_3$)$_3$), 61.9 (N*C*(CH$_3$)$_3$), 68.9 (=*C*H$_2$), 114.3 (aryl), 117.7 (aryl), 125.9 (aryl), 127.5 (aryl), 136.1 (aryl), 152.2 (aryl), 152.3 (aryl), 155.4 (aryl), 166.6 (O*C*=). Anal. Calcd for $TiN_3O_2C_{52}H_{77}$: C, 75.79; H, 9.42; N, 5.10. Found: C, 75.73; H, 9.41; N, 5.10.

Synthesis of 1-OC(CH$_2$)NPhMe. A pentane solution (10 mL) of **1** (585 mg, 1.01 mmol, 2 equiv) was added to a suspension of succinic acid amide (150 mg, 0.51 mmol, 1 equiv) in pentane (5 mL). The reaction mixture was allowed to stir for 3 h at 25 °C. The color changed gradually from forest green to yellow-brown. Analysis of the reaction mixture by ^{1}H NMR spectroscopy showed the presence of a single product. Abundant precipitation of a yellow solid was observed. The reaction mixture was stored at −35 °C for several hours and then filtered through a sintered glass frit. The collected yellow powder consisted of analytically pure amide enolate. The filtrate was concentrated and cooled at −35 °C to provide another crop of amide enolate. The solid amide enolate **1**-OC-(CH$_2$)NPhMe obtained using this procedure amounted to 608 mg (0.84 mmol, 84%). ^{1}H NMR (300 MHz, C_6D_6): δ 1.25 (s, 27H, C(C*H*$_3$)$_3$), 2.22 (s, 18H, ArC*H*$_3$), 3.13 (s, 3H, NC*H*$_3$) 4.46 and 4.60 (singlets, 2H, C*H*$_2$), 6.11 (v br s, 6H, aryl *o*-*H*), 6.73 (s, 3H, aryl *p*-*H*), 6.89 (t, 1H, phenyl *p*-*H*), 7.19 (d, 2H, phenyl *o*-*H*), 7.31 (t, 2H, phenyl *m*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8 (*m*-*C*H$_3$), 30.4 (C(*C*H$_3$)$_3$), 38.8 (N*C*H$_3$), 61.8 (*C*(CH$_3$)$_3$), 88.9 (=*C*H$_2$), 116.1 (aryl), 118.7 (aryl), 125.9 (aryl), 127.6 (aryl), 128.9 (aryl), 136.0 (aryl), 148.3 (aryl), 152.3 (aryl), 163.7 (O*C*=). Anal. Calcd for $TiN_4OC_{45}H_{64}$: C, 74.56; H, 8.90; N, 7.73. Found: C, 74.20; H, 9.07; N, 7.68. IR (C_6D_6, cm^{-1}): ν 2974 (s br), 2867 (br m), 1597 (m), 1586 (m), 1500 (m), 1289 (w), 1247 (s), 1177 (m), 1150 (w), 1118 (m), 1021 (m), 940 (m), 695 (m).

Reaction of 1-OC(CH$_2$)NPhMe with Benzaldehyde. Excess benzaldehyde (0.08 mL, 0.78 mmol, 2.4 equiv) was added via syringe to a toluene solution (5 mL) of **1**-OC(CH$_2$)-NPhMe (235 mg, 0.32 mmol, 1 equiv). The reaction mixture was stirred at 25 °C for 12 h. ^{1}H NMR interrogation of the reaction mixture showed complete consumption of the amido-enolate and clean formation of a single product. Volatile material was removed in vacuo. The yellow residue was recrystallized from diethyl ether at −35 °C, collected on a sintered glass frit, and washed with cold pentane. This procedure provided 152 mg (0.18 mmol, 57%) of **1**-OCHPh-(CH$_2$CONPhMe) in three crops. ^{1}H NMR (500 MHz, C_6D_6): δ 1.20 (s, 27H, C(C*H*$_3$)$_3$), 2.25 (s, 18H, ArC*H*$_3$), 2.85 (br, s, 2H, CHC*H*$_2$), 2.93 (s, 3H, NC*H*$_3$), 6.41 (br s, 9H, PhC*H*O, aryl *o*-*H* and phenyl *o*-*H*), 6.70 (s, 3H, aryl *p*-*H*), 6.93−6.98 (m, 3H, phenyl *p*-*H* and phenyl *m*-*H*), 7.14 (t, 1H, phenyl *p*-*H*), 7.25 (t, 2H, phenyl *m*-*H*), 7.59 (br s, 2H, phenyl *o*-*H*). ^{1}H NMR (500 MHz, C_6D_6, 60 °C): δ 1.18 (s, 27H, C(C*H*$_3$)$_3$), 2.24 (s, 18H, ArC*H*$_3$), 2.85 (br, app d, 2H, CHC*H*$_2$), 2.93 (s, 3H, NC*H*$_3$), 6.31 (br, app dd, 1H, PhC*H*O), 6.38 (br s, 6H, aryl *o*-*H*), 6.51 (d, 2H, phenyl *o*-*H*), 6.69 (s, 3H, aryl *p*-*H*), 6.96 (t, 1H, phenyl *p*-*H*), 7.00 (t, 2H, phenyl *m*-*H*), 7.14 (t, 1H, phenyl *p*-*H*), 7.24 (t, 2H, phenyl *m*-*H*), 7.56 (d, 2H, phenyl *o*-*H*). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 21.7 (*m*-*C*H$_3$), 30.8 (C(*C*H$_3$)$_3$), 37.2 (*C*H$_2$), 44.6 (N*C*H$_3$), 60.4 (C(*C*H$_3$)$_3$), 85.8 (O*C*Ph), 125.7 (aryl), 127.6 (aryl), 127.8 (aryl), 128.0 (aryl), 128.2 (aryl), 128.3 (aryl), 129.8 (aryl), 136.0 (aryl), 144.0 (aryl), 144.1 (aryl), 152.5 (aryl), 169.9 (O=*C*N(MePh)). Anal. Calcd for $TiN_4O_2C_{52}H_{70}$: C, 75.16; H, 8.49; N, 6.74. Found: C, 74.63; H, 8.50; N, 6.86. IR (C_6D_6, cm^{-1}): ν 3030 (br w), 2959 (br m), 2922 (br m), 2865 (w), 1659 (s, amide C=O stretch), 1596 (s), 1585 (s), 1495 (s), 1417 (w), 1376 (m), 1288 (m), 1185 (w), 1128 (s), 1092 (s), 1069 (s), 1028 (m), 968 (m), 701 (s).

Reaction of 1-OC(CH$_2$)Ar^2 with Benzaldehyde. A diethyl ether solution (5 mL) of **1** (50 mg, 0.088 mmol, 2 equiv) was added to a suspension of 1,4-diketone (11.6 mg, 0.044 mmol, 1 equiv) in diethyl ether (3 mL). The reaction mixture was stirred at room temperature for 30 min, and then volatile material was removed in vacuo. The oily residue was dissolved in toluene (5 mL), and benzaldehyde (22.2 mg, 0.21 mmol, 4.8 equiv) was added to the reaction mixture. After 12 h of stirring, the ^{1}H NMR spectrum of the reaction mixture displayed only the peaks for **1**-OC(CH$_2$)Ar^2 and benzaldehyde.

Reaction of Ti(NRAr[1])$_3$ with *N*-Methylphthalimide. A pentane solution (5 mL) of **1** (115 mg, 0.2 mmol, 2 equiv) was added to a suspension of *N*-methyl phthalimide (16 mg, 0.1 mmol, 1 equiv) in pentane (3 mL), at 25 °C. The color of the reaction mixture turned dark blue upon mixing. After 30 min of stirring, solvent was removed in vacuo. The ^{1}H NMR spectrum of the residue revealed formation of a single product. The oily residue was dissolved in diethyl ether. Upon addition of acetonitrile, a dark blue solid precipitated and was collected on a sintered glass frit and washed with cold pentane. Compound **1**$_2$-O$_2$Phth obtained in this fashion amounted to 97 mg (0.074 mmol, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 27H, C(C*H*$_3$)$_3$), 2.23 (s, 18H, ArC*H*$_3$), 3.26 (s, $_3$H, NC*H*$_3$), 6.50 (s, 6H, aryl *o*-*H*), 6.56 (br s, 2H phthalimide aryl *H*), 6.72 (s, 3H, aryl *p*-*H*), 7.56 (br s, 2H phthalimide aryl *H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (*m*-*C*H$_3$), 30.8 (C(*C*H$_3$)$_3$), 61.6 (*C*(CH$_3$)$_3$), 76.8 (N*C*H$_3$), 105.2 (aryl), 117.4 (aryl), 119.4 (aryl), 125.9 (aryl), 127.6 (aryl), 136.4 (aryl), 140.8 (aryl), 151.0 (aryl). Anal. Calcd for $Ti_2N_7O_2C_{81}H_{115}$: C, 74.04; H, 8.76; N, 7.47. Found: C, 73.88; H, 8.79; N, 7.28.

Reaction of Ti(NRAr[1])$_3$ with Di-*tert*-Butyl Azodicarboxylate. Cold pentane solutions of **1** (171 mg, 0.30 mmol, 2 equiv) and di-*tert*-butyl azodicarboxylate (34 mg, 0.15 mmol, 1 equiv) were mixed and allowed to stir for 1 h. The color of the reaction mixture turned orange. Solvent was removed in vacuo, leaving an oily orange residue. Crystallization from pentane at −35 °C afforded 135 mg of orange crystals of **1**$_2$-D*t*-BuAD (0.1 mmol, 66% yield). ^{1}H NMR (300 MHz, C_6D_6): δ 1.20 (s, 27H, NC(CH_3)$_3$), 1.69 (s, 18H, OC(CH_3)$_3$), 2.21 (s, 18H, ArCH_3), 5.94 (br s, 6H, aryl *o*-*H*), 6.73 (s, 3H, aryl *p*-*H*). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 22.0 (*m*-CH_3), 29.7 (C(CH_3)$_3$), 31.0 (C(CH_3)$_3$), 61.6 (N*C*(CH_3)$_3$), 80.1 (O*C*(CH_3)$_3$), 125.6 (aryl), 127.2 (aryl), 135.7 (aryl), 152.7 (aryl). Anal. Calcd for $Ti_2N_8C_{82}O_4H_{126}$: C, 71.17; H, 9.18; N, 8.09. Found: C, 70.75; H, 9.23; N, 8.15.

Reaction of Ti(NRAr[1])$_3$ with PhBr. A pentane/bromobenzene (26 mg, 0.16 mmol, 1.1 equiv) mixture (3 mL) was added to a pentane solution (5 mL) of **1** (82 mg, 0.14 mmol, 1 equiv). The color of the solution turned intense orange in 1 h, and an orange powder precipitated out. Solvent was removed in vacuo. Crystallization from diethyl ether at −35 °C afforded 58 mg (0.087 mmol, 62% yield) of orange **1**-Br. ^{1}H NMR (300 MHz, C_6D_6): δ 1.38 (s, 27H, C(CH_3)$_3$), 2.22 (s, 18H, ArCH_3), 6.61 (br s, 6H, aryl *o*-*H*), 6.73 (s, 3H, aryl *p*-*H*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (s, 27H, C(CH_3)$_3$), 2.29 (s, 18H, ArCH_3), 6.46 (br s, 6H, aryl *o*-*H*), 6.83 (s, 3H, aryl *p*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (*m*-CH_3), 30.8 (C(CH_3)$_3$), 63.6 (*C*(CH_3)$_3$), 127.4 (aryl), 128.2 (aryl), 136.5 (aryl), 148.5 (aryl). Anal. Calcd for $TiN_3BrC_{36}H_{54}$: C, 66.46; H, 7.44; N, 6.46. Found: C, 66.35; H, 7.42; N, 6.39.

Reaction of Ti(NRAr[1])$_3$ with PhCl. Ti(NRAr[1])$_3$ (32.6 mg, 0.056 mmol, 1 equiv) was dissolved in neat PhCl (1.36 g, 12 mmol, 212 equiv). Upon overnight stirring, the color of the reaction mixture turned intense orange-red. The NMR spectrum of the reaction mixture revealed clean formation of **1**-Cl.[41]

Reaction of Ti(NRAr[1])$_3$ with PhI. Iodobenzene (0.020 mL, 0.18 mmol, 1 equiv) was added via syringe to a pentane solution of Ti(NRAr[1])$_3$ (103.3 mg, 0.18 mmol, 1 equiv). The color of the solution turned bright orange in less than 5 min, and precipitation of an orange solid was observed. The ^{1}H NMR spectrum of the reaction mixture indicated clean formation of **1**-I.[13]

Synthesis of 1-F. A benzene solution (5 mL) of **1** (100 mg, 0.173 mmol, 1 equiv) was added to a benzene suspension (3 mL) of XeF_2 (14.7 mg, 0.087, 0.5 equiv). After 1 h of stirring, the reaction mixture turned dark red. Solvent was removed in vacuo. ^{1}H NMR analysis of the residue showed clean formation of Ti(F)(NRAr)$_3$. The residue was crystallized from a THF/diethyl ether mixture at −35 °C, affording 82.3 mg (0.138 mmol, 80%) of bright orange crystals of **1**-F. ^{1}H NMR (300 MHz, C_6D_6): δ 1.38 (s, 27H, C(CH_3)$_3$), 2.17 (s, 18H, ArCH_3), 5.98 (br s, 6H, aryl *o*-*H*), 6.73 (s, 3H, aryl *p*-*H*). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 (s, 27H, C(CH_3)$_3$), 2.18 (s, 18H, ArCH_3), 5.72 (br s, 6H, aryl *o*-*H*), 6.76 (s, 3H, aryl *p*-*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.7 (*m*-CH_3), 30.2 (C(CH_3)$_3$), 60.6 (*C*(CH_3)$_3$), 127.2 (aryl), 127.5 (aryl), 136.4 (aryl), 151.5 (aryl). ^{19}F NMR (282 MHz, C_6D_6): δ −71.6. Anal. Calcd for $TiN_3FC_{36}H_{54}$: C, 72.46; H, 8.11; N, 7.04. Found: C, 71.86; H, 8.48; N, 6.95.

Reaction of Ti(NRAr[1])$_3$ with *o*-Bromophenyl Allyl Ether. A cold pentane solution (10 mL) of *o*-bromophenyl allyl ether (302 mg, 1.4 mmol, 1 equiv) was added to a thawing pentane solution (10 mL) of **1** (1.64 g, 2.8 mmol, 2 equiv). The color gradually turned orange-red, and orange **1**-Br precipitated out. The reaction mixture was stirred for 3 h, then concentrated and allowed to cool at −35 °C. Compound **1**-Br was collected partially on a sintered glass frit. The filtrate was concentrated to dryness in vacuo and analyzed by NMR spectroscopy. Subsequent recrystallizations did not provide the cyclization product **1**-CH_2DHBF free of **1**-Br. ^{1}H NMR (500 MHz, C_6D_6): δ 1.24 (s, 27H, C(CH_3)$_3$), 2.25 (s, 18H, ArCH_3), 4.15, 4.29 (app triplets, 2H, OCH_2), 6.71 (s, 3H, N-aryl *p*-*H*), 6.78−6.81 (m, 3H, aryl C*H*), 6.90−6.93 (m, 1H, aryl C*H*), 6.97 (s, 6H, N-aryl *o*-*H*). ^{13}C NMR (125.8 MHz, C_6D_6): δ 21.9 (*m*-CH_3), 31.2 (C(CH_3)$_3$), 45.5 (aliphatic *C*H), 62.2 (*C*(CH_3)$_3$), 80.3 (CH_2), 82.9 (CH_2), 110.0 (aryl), 120.6 (aryl), 123.9 (aryl), 127.6 (aryl), 130.7 (aryl), 137.5 (aryl), 137.7 (aryl), 147.6 (aryl), 160.2 (aryl). The filtrate obtained in the previous experiment was dissolved in 10 mL of THF in a 25 mL round-bottom flask capped with a septum and taken outside the box. Water (0.6 mL) was added via syringe. Immediate formation of a gray precipitate was observed. Upon overnight stirring the solution was colorless and an abundant gray precipitate was present. Exposure to air caused the gray precipitate to turn white. Volatile material was removed in vacuo, and the white residue was extracted with diethyl ether. Removal of solvent afforded a yellow oil. ^{1}H NMR and ^{13}C NMR analysis of this oil showed the presence of *tert*-butyl-3,5-dimethylaniline and 3-methyldihydrobenzofuran.[36]

Table 1. Crystallographic Data for and 1-OC(CH_2)NPhMe and 1-OC(CH_2)Ar[2]

	1-OC(CH_2)NPhMe	**1**-OC(CH_2)Ar[2]
formula	$C_{45}H_{64}N_4OTi$	$C_{45}H_{63}N_3OTi$
fw	724.90	709.88
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.0950(12)	15.3749(5)
b, Å	12.5053(12)	13.4837(2)
c, Å	16.003(2)	20.2826(6)
α, deg	88.924(2)	90
β, deg	85.898(2)	101.51
γ, deg	71.085(2)	90
V, Å^3	2095.1(4)	4120.2(2)
Z	2	4
cryst description	orange plate	orange plate
D_{calcd}, g·cm^{-3}	1.149	1.144
μ, mm^{-1}	0.241	0.243
F(000)	784	1536
GOF[a] on F^2	1.087	1.193
R_1 (F_o)[b] for $I > 2\sigma I$	0.0671	0.0659
wR_2 (F_o^2)[c] for $I > 2\sigma I$	0.1305	0.1470

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/[\sum w(F_c^2)^2]]^{1/2}$.

Kinetic Measurements: General Procedure. Stock solutions of **1**, halobenzenes, and diketones in toluene were used immediately after preparation or were stored at −35 °C. The reagents were mixed in the UV cell immediately prior to data collection. Compound **1** displays absorptions at 792 nm (ϵ = 223 (cm M)$^{-1}$) and 637 nm (ϵ = 169 (cm M)$^{-1}$). The decay of **1** was monitored at 792 nm.

Kinetics of Halogen Abstraction from Halobenzene. Concentrations in the range of 10^{-3}−10^{-2} M were used for **1**. Concentrations in the range 0.1−0.5 M were used for iodo- and bromobenzene. Measurements for rate constant determination were performed for various concentrations of **1** and halobenzene for at least 4 kinetic runs through 3 half-lives. k_{obs} corresponding to the pseudo-first-order decay of **1** was determined using an Origin curve-fitting to the equation $A = A_\infty + A_0[\exp(-k_{obs}t)]$. Variation of the original concentration of the halobenzene allowed determination of the order in PhZ (Z = Br or I). By dividing k_{obs} by the concentration of PhZ, second-order rate constants were determined ($(9.3 \pm 0.1) \times 10^{-3}$ (s M)$^{-1}$ for PhBr and $(6.6 \pm 0.5) \times 10^{-1}$ (s M)$^{-1}$ for PhI; 95% confidence interval). Large concentrations, in the range 6.5−8 M, were used for PhCl in order to ensure significant decay of **1** in a time period over which **1** does not independently decompose. The small variations in the concentration of PhCl did not allow an accurate determination of the order in PhCl. In this case, the pseudo-first-order rate constant (k_{obs}) was found to be $(1.8 \pm 0.3) \times 10^{-4}$ s^{-1}. No significant decay of **1**

(41) Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907.

was observed by UV−vis spectroscopy for a solution in neat fluorobenzene over an interval of 10 h.

Kinetics of 1,4-Dicarbonyl Scission: General Procedure. Concentrations in the range 10^{-3}−10^{-2} M were used for **1** and for 1,4-diketones. The measurements were performed after fast mixing. A new absorption, which decayed over time, was observed around 650−670 nm.

X-ray Crystal Data: General Procedure. Crystals grown from concentrated diethyl ether solutions at −35 °C were removed quickly from a scintillation vial to a microscope slide coated with Paratone N oil (an Exxon product). Samples were selected and mounted on a glass fiber in wax and Paratone N oil. Data collection was carried out at a temperature of 188 K on a three-circle goniometer Siemens Platform with a CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). The data were processed and refined by using the program SAINT supplied by Siemens Industrial Automation, Inc. The structures were solved by direct methods (SHELXTL v5.03, Sheldrick, G. M., and Siemens Industrial Automation, Inc., 1995) in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated ($d_{CH} = 0.96$ Å) positions. Some details regarding refined data and cell parameters are available in Table 1. Selected bond distances and angles are supplied in the captions of Figures 1 and 2.

DFT Calculations. Calculations were carried out with the ADF2000.01 package, employing scalar relativistic corrections for the non-hydrogen atoms in the context of the frozen core approximation. The local density approximation functional used was that of Vosko, Wilk, and Nusair, while the functionals for the generalized gradient approximations took the form of Becke (exchange) and Perdew (correlation).[29−32]

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Supporting Information Available: Tables with bond lengths, bond angles, atomic coordinates, and anisotropic displacement parameters for the structures of **1**-OC(CH_2)Ar^2 and **1**-OC(CH_2)NPhMe; solution EPR spectrum of **1**-$OCPh_2$; ^{1}H NMR spectra of (**1**-OCMePh)$_2$ and its disproportionation products; decay of **1** monitored by UV−vis spectroscopy; IR spectra of succinate diamide, **1**-OC(CH_2)NPhMe, and **1**-OCHPh-(CH_2CONPhMe); details of the DFT calculations; pictorial representations of the frontier molecular orbitals of **2**-$OCHCH_2$ and **2**-OC(NH_2)CH_2 as obtained from the DFT calculations. This information is available free of charge via the Internet at http://pubs.acs.org.

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