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Generation of a Low-Valent Titanium Species from Titanatrane and its Catalytic Reactions: Radical Ring Opening of Oxetanes

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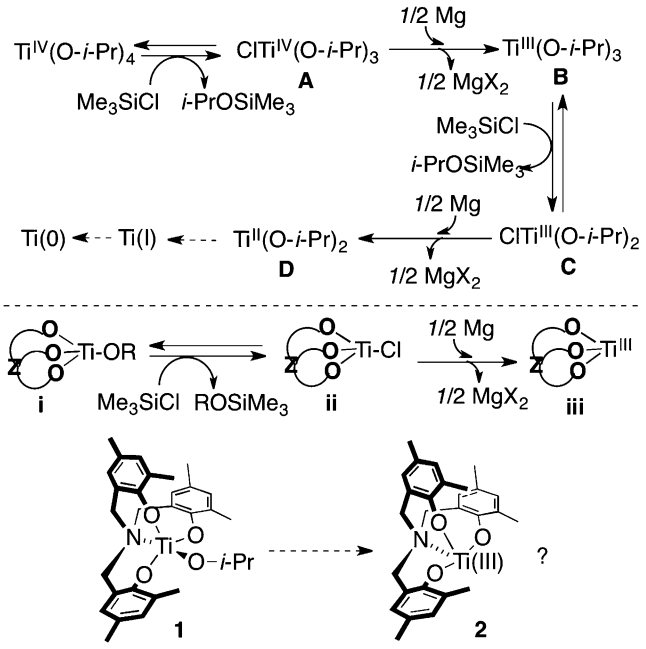
Abstract: Treatment of a titanatrane complex with trimethylsilyl chloride and magnesium powder in tetrahydrofuran generated a low-valent titanium species. This species catalyzed the radical ring opening of epoxides and oxetanes to produce the corresponding less substituted alcohols. The reagent also catalyzed the deallylation and depropargylation of allylic and propargylic ethers, respectively, to provide the parent alcohols.

Keywords: homogeneous catalysis; low-valent titanium; oxetanes; radical reactions; reduction; regioselectivity; tripodal ligands

Recently, amine triphenolate metal complexes [tripodal aminetris(aryloxide) complexes] have attracted significant attention for their synthesis, structure, and use in catalytic reactions.[1] The titanium complexes (titanatranes), one of the most investigated classes of complexes, are characterized by a propeller-like arrangement of the ligand around the titanium when viewed along the titanium–nitrogen axis. These complexes have been used as Lewis acid catalysts for lactide polymerization[2] and aza-Diels–Alder reactions[3] and for oxidations of amines and sulfides.[4] The C_3-chiral complexes have been used as a chiral shift agent for NMR analysis[5] and as an asymmetric oxidation catalyst.[6] Here we report the first examples of the use of a titanatrane complex as a precursor for a low-valent titanium (LVT) catalyst and its application in organic transformations.[7]

Previously, we had developed a new, mild method for the generation of an LVT[8,9] species by using Ti(O-*i*-Pr)$_4$, Me$_3$SiCl (or MgCl$_2$), and Mg powder in THF (Scheme 1).[10] Thus, the LVT reagent catalyzed the deallylation and depropargylation of allylic and propargylic ethers, respectively, to the corresponding parent alcohols. The intermolecular and intramolecular [2+2+2]cycloaddition of alkynes to substituted benzenes could be also catalyzed by the reagent. The McMurry coupling (olefination) reaction of aryl aldehydes and imino-pinacol coupling under mild homogeneous conditions have also been mediated by an LVT. Recently, we found that the reagent cleaved the N–S or O–S bond of sulfonamides and sulfonyl esters to give the corresponding amines and alcohols, respectively. The reagent could regioselectively cleave the C–O bond of epoxides to provide less substituted alcohols.



Scheme 1. Postulated mechanism for the generation of an LVT from Ti(O-*i*-Pr)$_4$/Me$_3$SiCl/Mg and a proposal for the selective formation of a Ti(III) species from titanium complex **1**.

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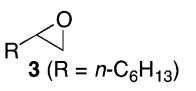
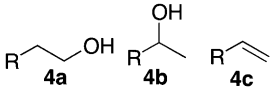
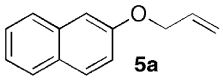
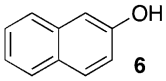
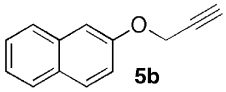
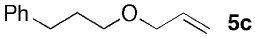
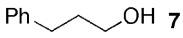
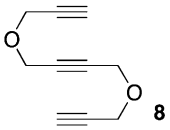
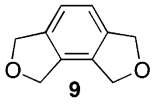
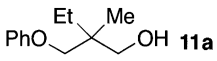
Table 1. Ti(O-*i*-Pr)$_4$- or complex **1**-catalyzed reactions of various substrates.[a]

Run	Ti complex (equiv.)	Substrate	Time [h]	Product(s)	Yield
1	Ti(O-*i*-Pr)$_4$ (1.2)	 **3** (R = *n*-C_6H_{13})	12	 **4a** **4b** **4c**	76% (98:2:0)[10b]
2	Ti(O-*i*-Pr)$_4$ (0.05)	**3**	12	**4a**+**4b**	24% (98:2:0) (64% recovered)
3	**1** (0.05)	**3**	12	**4a**+**4b**+**4c**	50% (76:10:14)
4	**1** (0.05)	**3**+CHD (10 equiv.)[b]	12	**4a**+**4b**+**4c**	87% (75:20:5)
5	Ti(O-*i*-Pr)$_4$ (0.05)	 **5a**	12	 **6**	95%[10a]
6	**1** (0.05)	**5a**	12	**6**	>99%
7	Ti(O-*i*-Pr)$_4$ (0.05)	 **5b**	12	**6**	95%[10a]
8	**1** (0.05)	**5b**	12	**6**	>99%
9	**1** (0.05)	 **5c**	12	 **7**	92%
10	Ti(O-*i*-Pr)$_4$ (0.2)	 **8**	24	 **9**	60% (**8** was not recovered)[10a]
11	**1** (0.05)	**8**	24	**9**	5% (95% of **8** was recovered)
12	Ti(O-*i*-Pr)$_4$ (1.2)	 **10a**	12	 **11a**	84%
13	Ti(O-*i*-Pr)$_4$ (0.1)	**10a**	12	**11a**	78%
14	**1** (0.05)	**10a**	12	**11a**	66%
15	**1** (0.05)	**10a**+CHD (10 equiv.)[b]	12	**11a**	91%
16[c]	Cp_2TiCl_2 (2)+Mn (5)	**10a**+CHD (10 equiv.)[b]	24	no reaction	

[a] All reactions were performed with a Ti complex, Me_3SiCl and Mg powder (2–3 equiv.) in THF at 40–50 °C. For runs 1–4 and 12–16, 1.2 equiv. of Me_3SiCl were used, for runs 5–9, 0.15 equiv. was used, and for runs 10 and 11, 1.0 equiv. was used. For runs 1–15, the reactions did not proceed in the absence of a titanium compound.

[b] 1,4-Cyclohexadiene.

[c] We checked the reaction of a mixture of **10a** and 1,2-epoxyoctane with a Cp_2TiCl_2/Mn/CHD reagent in THF in another vessel and found that the epoxide was converted to 1-octanol (42% yield), but **10a** was recovered (98%).

For these reactions, we assume that the LVT can be generated from Ti(O-*i*-Pr)$_4$, Me_3SiCl and Mg by a mechanism illustrated in Scheme 1: Ti(O-*i*-Pr)$_4$ reacts with Me_3SiCl to yield ClTi(O-*i*-Pr)$_3$ (**A**), which can be reduced by the reaction with Mg powder to generate Ti(O-*i*-Pr)$_3$ (**B**) and/or its equivalents (the polymeric and/or solvated compounds). Repeating a similar process might give an LVT species such as Ti(II), Ti(I), and Ti(0). We anticipated that a Ti(III) trialkoxide (**iii**) could be selectively generated when titanium alkoxide (**i**) derived from an appropriate triol, such as a titanatrane complex **1**,[11] was used instead of Ti(O-*i*-Pr)$_4$. It can be expected that steric shielding by *ortho*-methyl substituents in titanatrane **1** may prevent over-reduction through further O–Cl exchange of **2**.

With this idea in mind, reactions of complex **1** with various substrates in the presence of Me_3SiCl and Mg were investigated. We found that complex **1** reacted with Me_3SiCl/Mg to generate the corresponding LVT species and catalyzed several reactions. In addition, during these studies, we found that LVT alkoxides catalyzed the radical ring-opening reaction of oxetanes.

Table 1 summarizes and compares the results of the reactions of various substrates with titanium complex Ti(O-*i*-Pr)$_4$ or **1** in the presence of Me_3SiCl and Mg powder in THF.

The reaction of epoxide **3** with a stoichiometric amount of Ti(O-*i*-Pr)$_4$ selectively gave less substituted alcohol **4a** in good yield (run 1);[10b,12] however, the catalytic use of titanium (5 mol%) resulted in lower conversion (run 2). On the other hand, complex **1** (5 mol%) could catalyze the reduction of epoxide **3**, but in lower conversion and with lower selectivity, where the deoxygenation product **4c** was co-produced (run 3). In the Ti(O-*i*-Pr)$_4$-promoted reactions, we reported that the β-titanoxy radical intermediate **iv** intramolecularly abstracts a hydrogen from the *i*-Pr group of the titanium complex (Figure 1).[10b] However, complex **1** has no hydrogen at the titanium β posi-

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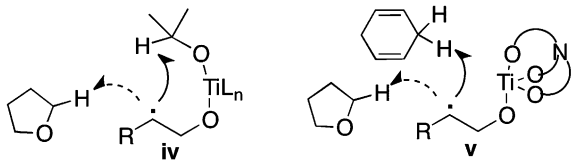


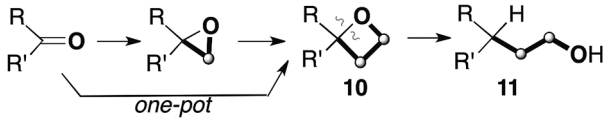
Figure 1. Hydrogen abstraction by β-titanoxy radicals.

tion; therefore, in the **1**-catalyzed reaction, the titanoxy radical intermediate **v** intermolecularly abstracts a hydrogen from a solvent (THF) or undergoes deoxygenation through a β-titanoxy alkyltitanium intermediate. When excess of 1,4-cyclohexadiene (CHD) was used as a hydrogen source in the **1**-catalyzed reaction, a higher yield of the alcohols **4a** and **4b** was attained (run 4).

Both titanium complexes Ti(O-*i*-Pr)$_4$ and **1** smoothly catalyzed the deallylation of allylic ethers **5a** and **5c** and the depropargylation of propargylic ether **5b** to quantitatively give the corresponding alcohol (runs 5–9). By contrast, complex **1** exhibited marginal activity for the cyclotrimerization of triyne **8** (run 11), but Ti(O-*i*-Pr)$_4$ catalyzed the reaction (run 10). These results allow us to conclude that the reaction of complex **1** with Me_3SiCl and Mg generated the corresponding LVT species that have distinct reactivities from Ti(O-*i*-Pr)$_4$. To the best of our knowledge, these are the first examples of the use of complex **1** as a precursor for an LVT catalyst.

In addition to the aforementioned reactions, we found that LVT alkoxides could reduce oxetanes to the corresponding alcohols (runs 12–15). Thus, a stoichiometric or catalytic amount of Ti(O-*i*-Pr)$_4$ with Me_3SiCl and Mg reduced oxetane **10a** to primary alcohol **11a** in good yield (runs 12 and 13, respectively). Similarly, complex **1** catalyzed the reduction of **10a**, and a high yield was attained when excess CHD was used (runs 14 and 15). This high yield was attributed to a higher reagent potential for reduction compared with cyclopentadienyl (Cp)-based reagents such as Cp_2TiCl and its dimer because the Cp_2TiCl_2/Mn/CHD reagent did not react with oxetane **10a** (run 16).[13]

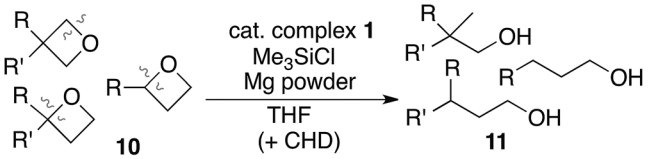
Since oxetanes **10** are readily available from epoxides or carbonyl compounds by a one-step reaction with $Me_2S^+(=O)CH_2^-$ reagent,[14] their reduction to alcohols **11** may be synthetically versatile as a formal one- or two-carbon homologation reaction (Scheme 2).



Scheme 2. Formal one- or two-carbon homologation.

However, when comparing with the ring opening of epoxides, the ring opening of oxetanes is much slower because of the reduced ring strain of their larger ring size.[15] Nevertheless, several examples of oxetane cleavage have been demonstrated. Oxetane ring-opening mediated by an organolithium species (4,4′-di-*tert*-butylbiphenylide) has been developed by Cohen et al. where the regiochemistry of the C–O bond cleavage changes in the presence of a Lewis acid such as $AlEt_3$.[16] Thus, in the absence of any Lewis acid the C–O bond cleavage occurs at the less substituted carbon for the alkyl-substituted oxetanes.[16a] In contrast, in the presence of $AlEt_3$ C–O bond cleavage occurs at the more substituted carbon.[16b] These reactions yield the corresponding γ-lithioalkoxides, which can be utilized as nucleophiles and for transmetallation to cerium and chromium derivatives.[17] Recently, Gansäuer, Grimme et al. reported the reductive opening of oxetanes promoted by a Cp_2TiCl reagent, the reaction of which proceeds by a radical reaction pathway. Calculation results suggested that non- or mono-substituted oxetanes at the 2 position might be barely cleaved under these conditions, thereby limiting the reaction to 2,2-disubstituted oxetanes.[13]

The results shown in Table 1 prompted us to investigate the Ti(O-*i*-Pr)$_4$- and **1**-catalyzed reductions of oxetanes (Scheme 3) because of their higher reducing



Scheme 3. Complex-**1** catalyzed reduction of oxetanes **10** to alcohols **11**.

potency than a Cp_2TiCl reagent. The results of the reaction of representative oxetanes **10b–10j** are summarized in Table 2.

As revealed from Table 2, the present method could indeed reduce non- and mono-substituted oxetanes at the 2 position; therefore, it is more general in terms of the substrate structure than the Cp_2TiCl-promoted reaction. In addition to **10a** (Table 1), 3,3-disubstituted oxetanes **10b** and **10c** were cleanly reduced to the corresponding alcohols **11b** and **11c**, respectively, without any loss of benzyloxy and silyloxy functionalities (runs 1 and 2 in Table 2). The ring opening reactions of 2-mono-aryl- and mono-alkyl-substituted oxetanes **10d**[18] and **10e**[19] occurred smoothly at the 2 position to give the corresponding primary alcohol (runs 3–8). 2,2-Disubstitued oxetanes **10f** and **10g** and spiro compounds **10h** and **10i** were also reduced to the corresponding primary alcohol

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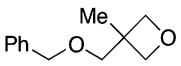
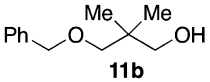
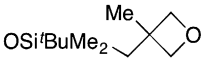
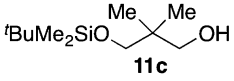
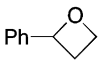
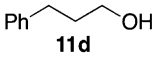
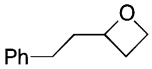
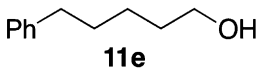
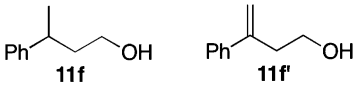
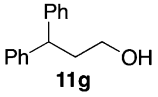
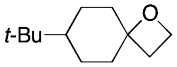
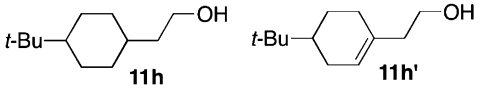
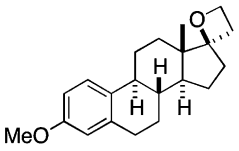
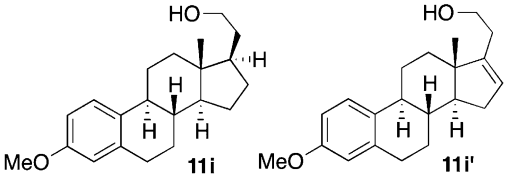
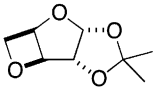
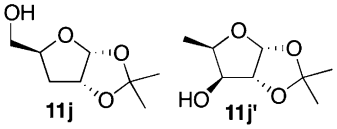
Table 2. Reductive ring-opening reactions of oxetanes **10** catalyzed by a complex **1**/Me_3SiCl/Mg reagent.

Run	Oxetane **10**	**10**	Ti complex[a]	Time [h]	Product(s)	Yield
1		**10b**	**1**+CHD[b]	12	 **11b**	76%
2		**10c**	**1**+CHD[b]	12	 **11c**	58%
3		**10d**	**1**	12	 **11d**	62%
4		**10d**	**1**+CHD[b]	12	**11d**	74%
5		**10d**	Ti(O-*i*-Pr)$_4$[c]	12	**11d**	72%
6		**10e**	**1**	12	 **11e**	90%
7		**10e**	**1**+CHD[b]	12	**11e**	99%
8		**10e**	Ti(O-*i*-Pr)$_4$[c]	12	**11e**	61%
9		**10f**	**1**	12	 **11f** **11f'**	total 65% (**11f**:**11f'** = 92:8)
10		**10f**	**1**+CHD[b]	12	**11f**	80%
11		**10f**	Ti(O-*i*-Pr)$_4$[c]	12	**11f**	81%
12		**10g**	**1**+CHD[b]	12	 **11g**	98%
13		**10h**[d]	**1**	24	 **11h** **11h'**	total > 99%[d] (**11h**:**11h'** = 74:26)
14		**10h**	**1**+CHD[b]	24	**11h**	89%[d]
15		**10h**	Ti(O-*i*-Pr)$_4$[e]	24	**11h**	45% (80% conversion)[d]
16		**10i**	**1**	24	 **11i** **11i'**	total 96% (**11i**:**11i'** = 73:27), *dr* of **11i** = > 99:1
17		**10i**	**1**+CHD[b]	24	**11i**	96%, *dr* > 99:1
18		**10j**	**1**	24	 **11j** **11j'**	total 81% (**11j**:**11j'** = 60:40)
19		**10j**	**1**+CHD[b]	24	**11j**+**11j'**	total 99% (**11j**:**11j'** = 70:30)
20		**10j**	Ti(O-*i*-Pr)$_4$[e]	24	**11j**+**11j'**	total 19%[f] (**11j**:**11j'** = 61:39)
21		**10j**	Ti(O-*i*-Pr)$_4$[g]	60	**11j**+**11j'**	total 99% (**11j**:**11j'** = 58:42)

[a] Unless otherwise indicated, 5 mol% of a titanium complex, 1.2 equiv. of Me_3SiCl, and 3.0 equiv. of Mg powder were used.
[b] 10 equiv. of 1,4-cyclohexadiene were used.
[c] 0.1 equiv. of Ti(O-*i*-Pr)$_4$ was used.
[d] A mixture of diastereomers. Ratio of *cis*:*trans* was 70:30, 88:12, or 69:31 for run 13, 14, or 16, respectively.
[e] 1.2 equiv. of Ti(O-*i*-Pr)$_4$ were used.
[f] 78% of **10j** were recovered.
[g] 1.2 equiv. of Ti(O-*i*-Pr)$_4$ and 3.0 equiv. of Me_3SiCl were used.

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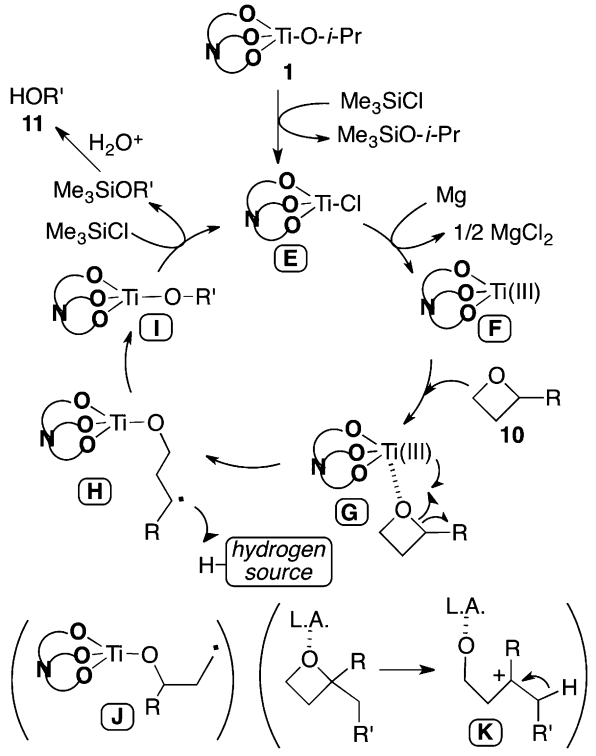
(runs 9–17), where the presence of excess CHD as a hydrogen source prevented the formation of the alkene by-product. It is noteworthy that the product **11i** was quantitatively obtained as a single diastereomer by the reduction of **10i**,[20] due to the selective hydrogen abstraction from the less hindered face of the intermediate γ-titanoxy radical (run 17). As shown in runs 18 and 19, the **1**-catalyzed reduction of bicyclic oxetane **10j**[21] derived from D- xylose smoothly proceeded and yielded 3-deoxyribose ketal **11j** as a major product, but a large amount of 5-deoxyxylose ketal **11j′** was co-produced. The presence of CHD led a better selectivity (run 19). Since the Ti(O-*i*-Pr)$_4$-based reaction was comparably slow, a stoichiometric amount of titanium with a longer reaction time was required for completion (runs 20 and 21). These results of regioselectivity were slightly disappointing, because we anticipated a higher selectivity considering the stability of the corresponding γ-titanoxy radical intermediates. The rationalization of the results must await further study.

In Scheme 4, we propose the reaction mechanism for the **1**-catalyzed reduction of oxetanes. Complex **1** can be converted to its chloride **E** by reaction with silyl chloride, which may immediately be reduced by Mg powder to generate a Ti(III) complex **F**. Complex **F** forms **G** by the coordination of an oxetane oxygen, followed by a single electron transfer. The generated γ-titanoxy radical **H** can abstract hydrogen from 1,4-cyclohexadiene (or solvent THF). The reaction of the resulting titanium alkoxide **I** with silyl chloride transforms **I** to the titanium chloride complex **E**. The regioselectivity of the ring-opening reaction, which generally gives less substituted alcohols, can be explained by assuming the stability of the γ-titanoxy radical intermediate **H** against **J**. However, as can be seen in the reduction of **10j** (runs 18–21 of Table 2) one may also be required to consider another factor such as a kinetic effect[22] arising from the independent substrate structure. The mechanism for the formation of the alkene by-product observed in several reactions is unclear. It is most likely due to a hydrogen atom abstraction from a radical by a radical (radical disproportionation).[23] Alternatively, it can be produced *via* a cationic intermediate **K** generated by activation with a Lewis acid such as titanium or a magnesium salt.



Scheme 4. Proposed mechanism for **1**-catalyzed reduction with oxetanes.

We have demonstrated that the treatment of a titanatrane complex **1** with Me_3SiCl and Mg powder in THF generated a low-valent titanium species. This species catalyzed the deallylation of allylic ethers, the depropargylation of propargylic ethers, and the radical ring-opening reaction of epoxides and oxetanes. The reductive ring-opening reaction of epoxides and oxetanes gave the corresponding less substituted alcohols as major product. The Ti-catalyzed C–O bond cleavage of non- or mono-substituted oxetanes at the 2 position was achieved for the first time by the present low-valent titanium alkoxides.

The LVT derived from titanatrane **1** is a stronger reductant and more reactive than a Cp_2TiCl reagent but, therefore, less chemoselective. As a result, both reagents may complementarily be used.

Experimental Section

General

NMR spectra were recorded in $CDCl_3$ at 500 MHz for ^1H and 125 MHz for ^{13}C, respectively. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si ($\delta = 0.00$), residual $CHCl_3$ ($\delta = 7.26$ for ^1H NMR), or a center peak of $CDCl_3$ ($\delta = 77.0$ for ^{13}C NMR). IR spectra were recorded on an FT-IR spectrometer (JASCO FTIR-4100). High-resolution mass spectra (HR-MS) were measured on a JEOL Accu TOF T-100 system equipped with ESI ionization. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Dry solvents were purchased from Kanto Chemical Co., Inc. and were used as received. Ti(O-*i*-Pr)$_4$ was distilled and stored under an argon atmosphere. Me_3SiCl was stored over CaH_2 to remove HCl. Room temperature refers to 20–25 °C. Titanium complex **1**[11] was synthesized according to the reported procedures. Oxetane substrates **10b**,[17] **10d**,[18] **10e**,[19] **10f**,[13] **10g**,[13] **10h**,[13] **10i**,[20] and **10j**[21] were respectively prepared accord-

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ing to the reported procedures. Oxetane **10a** was a gift from Toagosei Co., Ltd.

tert-Butyldimethyl[(3-methyloxetan-3-yl)methoxy]-silane (10c)

Silane **10c** (907 mg) was prepared from (3-methyloxetan-3-yl)methanol (510 mg, 5.0 mmol) by the reaction with imidazole (748 mg, 11 mmol) and *t*-$BuMe_2SiCl$ (904 mg, 6.0 mmol) in DMF (10 mL) at room temperature for 12 h; yield: 84%. ^{1}H NMR: $\delta = 4.49$ (d, $J = 5.2$ Hz, 2H) 4.32 (d, $J = 5.8$ Hz, 2H) 3.63 (s, 2H) 1.27 (s, 3H) 0.90 (s, 9H) 0.06 (s, 6H); ^{13}C NMR: $\delta = 9.6$, 68.1, 40.9, 25.8, 18.3, −5.5; IR (neat): $\nu = 2950$, 2930, 2986, 1472, 1464, 1387, 1256 cm^{-1}; HR-MS: $m/z = 255.1185$, calcd. for $C_{11}H_{24}KO_2Si$ $[M+K]^+$: 255.1183.

General Procedure for Reductive Cleavage of Oxetanes Catalyzed by Complex 1 with Me_3SiCl and Mg powder (Table 2)

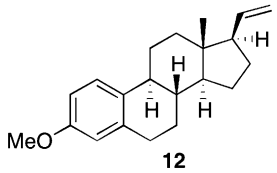
Under an argon atmosphere, to a mixture of an oxetane **10** (1.00 mmol), Mg powder (73 mg, 3.0 mmol), complex **1** (26.9 mg, 0.05 mmol), and 1,4-cyclohexadiene (0 or 10 mmol) in THF (5 mL) was added Me_3SiCl (0.15 mL, 1.2 mmol) at room temperature. The resulting mixture was stirred for 12–24 h (confirming the completion of the reaction by thin layer chromatography) at 40–50 °C. After addition of saturated aqueous $NaHCO_3$ (5 mL), the mixture was extracted with ethyl acetate. The organic layer(s) was washed with aqueous 0.1 M HCl and then saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with appropriate solvents (hexane/ether or hexane/ethyl acetate) to yield the ring-opening product **11**.

The structures of the products **9**,[24] **11b**,[25] **11c**,[26] **11d**,[27] **11e**,[28] **11f**,[29] **11g**,[13] **11h**,[30] **11j**,[31] and **11j′**[32] were confirmed by the comparison of their spectroscopic data with those reported.

2-Methyl-2-(phenoxymethyl)butan-1-ol (11a): ^{1}H NMR: $\delta = 7.28$ (t, $J = 6.6$ Hz, 2H), 6.95 (t $J = 6$ Hz, 1H), 6.91 (d, $J = 6.3$ Hz, 2H), 3.82 (d, $J = 7.5$ Hz, 1H), 3.78 (d, $J = 7.5$ Hz, 1H), 3.60 (dd, $J = 5.2$, 9.2 Hz, 1H), 3.57 (d, $J = 5.2$, 9.2 Hz, 1H), 1.96 (t, $J = 4.9$ Hz, 1H), 1.49 (q, $J = 6.3$ Hz, 2H), 0.95 (s, 3H), 0.90 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR: $\delta = 158.9$, 129.4, 120.9, 114.5, 73.6, 68.6, 38.8, 26.6, 18.3, 7.6; IR (neat): $\nu = 3353$, 2961, 2930, 1600, 1496, 1471, 1248, 1300 cm^{-1}; HR-MS: $m/z = 217.1204$, calcd. for $C_{12}H_{18}NaO_2$ $[M+Na]^+$: 217.1199.

2-[(8*S*,9*S*,13*R*,14*S*,17*R*)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl]ethanol (11i): ^{1}H NMR: $\delta = 7.25$ (s, 1H), 7.21 (d, $J = 8.6$ Hz, 1H), 6.71 (dd, $J = 2.9$, 8.6 Hz, 1H) 6.63 (d, $J = 2.9$ Hz, 1H), 3.78 (s, 3H), 3.75–3.60 (m, 4H), 2.92–2.79 (m, 2H), 2.35–2.15 (m, 2H), 1.95–1.75 (m, 5H), 1.49–1.21 (m, 9H), 0.63 (s, 3H); ^{13}C NMR: $\delta = 157.4$, 138.1, 132.9, 126.3, 113.8, 111.4, 62.6, 55.2, 54.7, 47.3, 44.1, 42.5, 38.8, 37.7, 33.7, 29.9, 28.4, 27.8, 26.4, 24.4, 12.6; IR (KBr): $\nu = 3568$, 2926, 2866, 2846, 2806, 1607, 1454, 1314 1287,1250 cm^{-1}; HR-MS: $m/z = 315.2314$, calcd. for $C_{21}H_{31}O_2$ $[M+H]^+$: 315.2319.

The stereochemistry of resulting **11i** was confirmed by its conversion to the known compound 3-methoxy-13-methyl-17-vinyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene (**12**)[33] by bromination of the alcohol with subsequent dehydrohalogenation and the comparison of the spectral data with reported data.[33]



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