

ORGANOMETALLICS

Volume 19, Number 21, October 16, 2000

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American Chemical Society

Communications

Reactivity of a Well-Characterized Titananorbornadiene (η^6 -Arene) Complex with Ketones and Aldehydes

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Received May 15, 2000

Summary: The reaction between the titananorbornadiene complex $[(DMSC)Ti(\eta^6-1,2,4-(Me_3Si)_3C_6H_3)]$ (**2**) and ketones or aldehydes proceeds by insertion of a ketone or aldehyde molecule into a Ti–C bond of **2**, yielding 2,5-dioxatitanacyclopentane or 2-oxatitanacycloheptene compounds. The intermediacy of a 2-oxatitanacycloheptene species en route to arene loss from **2** and the formation of 2,5-dioxatitanacyclopentane compounds are indicated.

While the chemistry of low-valent early-transition-metal metallocenes and related organometallics has been the focus of some investigation,^{1–12} well-character-

ized low-valent group 4 metal complexes supported by noncyclopentadienyl ligands have received little attention.^{13–28} Our research has focused on the application of calix[4]arene-derived bis(aryloxy) ligands in early-transition-metal chemistry.^{29–31} Previously, we reported

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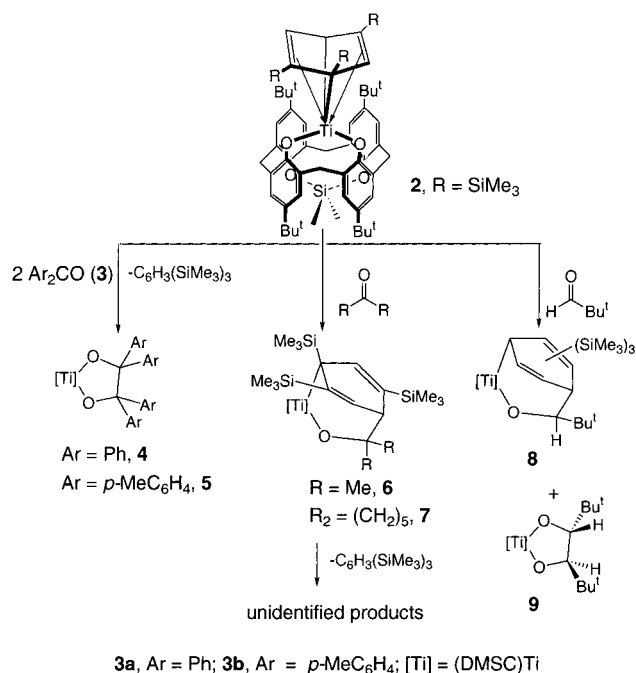
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Scheme 1



that reduction of (DMSC)TiCl₂ (**1**; DMSC = 1,2-alternate dimethylsilyl-bridged *p*-*tert*-butylcalix[4]arene)³² with activated Mg in the presence of Me₃SiC≡CH led to isolation of the titanaborbornadiene (η^6 -arene) complex [(DMSC)Ti(1,2,4-(Me₃Si)₃C₆H₃)] (**2**), which was fully characterized including by X-ray crystallography.²⁹ To the best of our knowledge, the only other well-characterized titanaborbornadiene was reported by Arnold et al.,¹⁶ but no studies of its reactivity have so far appeared. We have reported that **2** catalyzes highly regioselective cyclotrimerization of terminal alkynes to yield 1,2,4-substituted benzenes;²⁹ the high regioselectivity can be explained by the directing influence of the DMSC ligand.^{29,30} Remarkably, **2** is the resting state of the catalyst in the cyclotrimerization of Me₃SiC≡CH and functions essentially as a source of (DMSC)Ti^{II}. We saw advantage in employing **2** to further explore the reactivity of Ti- η^6 -arene complexes since it is conveniently synthesized and handled. The potential of **2** as a (DMSC)Ti^{II} synthon was also of interest because few stable X₂M^{II} synthons (X = monoanionic ligand, M = Ti, Zr) are available.^{11,12} Synthetic protocols to base-free X₂M^{II} usually involve unstable metal species generated at low temperatures.^{9,10,33–36} Herein we describe results from our preliminary study of the reactions between **2** and aldehydes and ketones.

A summary of the reactions of [(DMSC)Ti(1,2,4-(Me₃Si)₃C₆H₃)] (**2**) with aldehydes and ketones is presented in Scheme 1. Reaction between **2** and Ar₂CO (**3a**, Ar = Ph; **3b**, Ar = *p*-C₆H₅Me) furnished good yields of the corresponding 2,5-dioxatitanacyclopentane derivative [(DMSC)Ti(OCR₂CR₂O)] (**4**, R = Ph; **5**, R = *p*-C₆H₅Me). The reaction can be carried out in aliphatic or aromatic

solvents. It proceeds to completion in 3 h at 80 °C or in ~3 days at 22 °C, without forming any DMSC-containing side products.³⁷ Conversely, multiple DMSC-containing products are formed in the reaction of **2** with less bulky PhCOMe or PhCHO.³⁸

2,5-Dioxatitanacyclopentanes **4** and **5** are thermally stable, air- and moisture-sensitive, diamagnetic yellow solids. Both dissolve well in aromatic and ethereal solvents but are only modestly soluble in aliphatic solvents. ¹H and ¹³C NMR data for **4** and **5** are consistent with C_s symmetry in solution and the existence of the DMSC ligand in a 1,2-alternate conformation.^{29,38} The *endo*-SiMe group (inside the calixarene cavity) is strongly shielded, showing a signal at δ -1.36 ppm for both **4** and **5**. In ¹³C NMR, the Ph₂C(Tol)₂C carbons of **4** (**5**) appear at δ 111.1 (111.2) and 110.1 (109.6) ppm, similar to the values reported for related X₂Ti(OCPh₂CPh₂O) complexes.^{18,22} Two sets of resonances are observed for the Ph (Tol) substituents of the five-membered titanacycle, suggesting the solution structure is an average of the structures of two or more conformers that exist in rapid equilibrium.

The solid-state structure of [(DMSC)Ti(OCPh₂CPh₂O)] (**4**) was determined by X-ray crystallography. Two independent molecules are contained within the unit cell. Both molecules have similar bond distances and angles. One of the molecules is shown in Figure 1. The geometry about Ti can be described as pseudotetrahedral, the small O5–Ti–O6 angle being the result of constraints imposed by the 2,5-dioxatitanacyclopentane ring. All Ti–O distances fall within the range 1.795–1.827 Å, the expected range for a Ti–O distance in a four-coordinate Ti(IV) complex. Notably, this structure demonstrates the absence of correlation between the Ti–O distance and the angle at the oxygen atom.^{39,40} Steric repulsion between the 2,5-dioxatitanacyclopentane *endo*-phenyl groups (located near the calixarene cavity) and the DMSC framework results in distortion of the DMSC ligand. The interesting structural feature of **4** is the long C47–C48 bond (1.628(6) and 1.652(5) Å), most likely a consequence of steric repulsion between CPh₂ units. Lippard et al. have reported L₂Ti(OCPh₂–CMe₂O) (L = *N,N*-dimethylaminotroponimine) with a similar metallacyclic C–C distance of 1.610(2) Å.¹⁸

Surprisingly, the reaction of **2** with aliphatic ketones (acetone or cyclohexanone) occurred via formal insertion into a Ti–C bond. Addition of acetone or cyclohexanone to C₆D₆ or pentane solutions of **2** initially produced the 2-oxatitanacycloheptene compounds [(DMSC)Ti{C₆H₃–(SiMe₃)₃Me₂CO}] (**6**) and [(DMSC)Ti{C₆H₃(SiMe₃)₃–C₆H₁₀O}] (**7**), respectively (Scheme 1).⁴¹ The reaction is faster with acetone (~20 min) than with cyclohexanone

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(37) In a typical reaction, [(DMSC)Ti{C₆H₃(SiMe₃)₃}] (**2**; 1.05 g, 1.00 mmol) and Ph₂CO (0.364 g, 2.00 mmol) were dissolved in 15 mL of heptane. This mixture was stirred for 3 h at 80 °C under an N₂ atmosphere. The color of the solution gradually changed from yellow-brown to light yellow. Volatile materials were removed in vacuo, and the residue was recrystallized from 5 mL of pentane to give a yellow crystalline precipitate. The supernatant was decanted and the product dried in vacuo to give 0.82 g (74% yield) of (DMSC)Ti(Ph₂CO)₂ (**4**).

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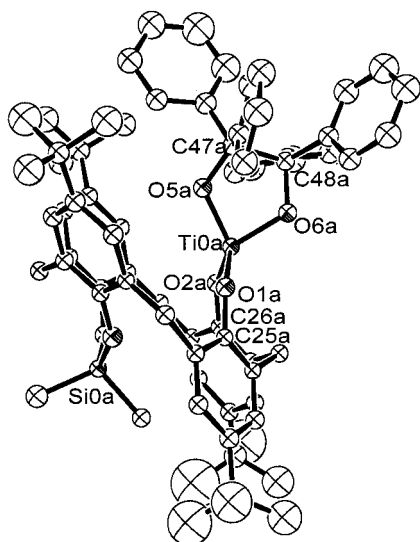


Figure 1. Molecular structure of **4**, molecule **A** (50% probability ellipsoids). There are 1.5 C_7H_8 molecules per Ti, which are omitted for clarity. Selected bond distances (Å) and angles (deg): Ti0a–O1a, 1.803(3); Ti0a–O2a, 1.827(2); Ti0a–O5a, 1.804(3); Ti0a–O6a, 1.817(3); C47a–C48a, 1.652(5); C25a–O1a–Ti0a, 140.9(2); C26a–O2a–Ti0a, 143.9(2); C47a–O5a–Ti0a, 119.0(2); C48a–O6a–Ti0a, 117.7(2); O1a–Ti0a–O2a, 106.65(12); O5a–Ti0a–O6a, 85.40(11). Crystal data: $C_{82.50}H_{90}O_6SiTi$, triclinic, $P1$, $Z = 2$, $a = 14.121(2)$ Å, $b = 14.554(2)$ Å, $c = 19.098(3)$ Å, $\alpha = 77.80(1)^\circ$, $\beta = 73.23(1)^\circ$, $\gamma = 74.16(1)^\circ$, $T = 173(2)$ K, $R1 = 0.059$ $wR2 = 0.146$ (all data).

(~1 h). 1H NMR analysis of the reaction mixtures revealed that **6** and **7** are the predominant products (>90%). Rothwell et al. have similarly observed insertion of aliphatic ketones and aldehydes into a related tungstanorbornadiene.⁴² The very high solubility of **6** and **7** hampers their isolation. However, the pure compounds can be obtained in low and poorly reproducible yields (15–30%) by prolonged cooling of saturated pentane solutions. Solution NMR data for **6** and **7** are consistent with their C_1 symmetry, revealing inequivalent Me_3Si groups. The three hydrogens that originally belonged to the η^6 -arene ring of **2** appear as one singlet (**6**, δ 6.32 ppm; **7**, δ 6.37 ppm) and two doublets (**6**, δ 6.06, 3.42 ppm; **7**, δ 5.91, 4.05 ppm) in 1H NMR. One of the doublets is considerably shifted to high field from its position in **2**, indicative of a change in the hybridization of the carbon atom from sp^2 to sp^3 and consistent with insertion of the ketone into a Ti–CH bond. The vicinal arrangement of the CH group at δ 3.42 (4.05) ppm and the CH group at δ 6.06 (5.91) ppm in **6** (**7**) can be deduced from the magnitude of the coupling constant ($^3J = 5.5$ Hz) between the two protons.

The molecular structure of $[(DMSC)Ti\{C_6H_3(SiMe_3)_3-C_6H_{10}O\}]$ (**7**), depicted in Figure 2, confirmed the insertion mode proposed on the basis of solution NMR

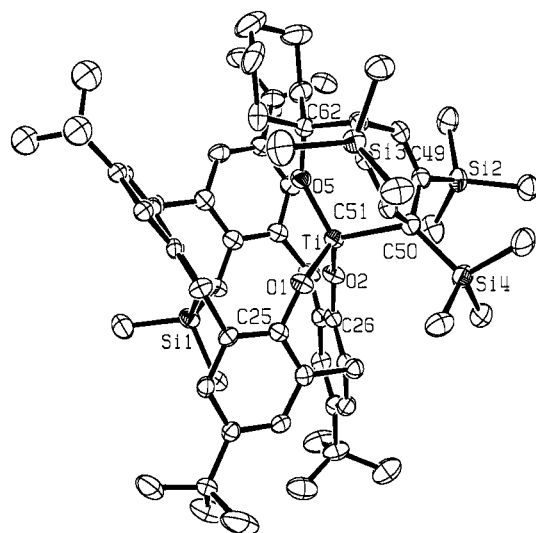


Figure 2. Molecular structure of **7** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ti–O1, 1.812(2); Ti–O2, 1.818(2); Ti–O5, 1.783(2); Ti–C50, 2.132(3); Ti–C51, 2.539(3); Ti–C49, 2.773(3); C25–O1–Ti, 141.80(18); C26–O2–Ti, 150.32(19); C62–O5–Ti, 138.59(18); O5–Ti–C50, 108.65(11); O1–Ti–O2, 102.91(9). Crystal data: $C_{67}H_{98}O_5Si_4Ti$, triclinic, $P1$, $Z = 2$, $a = 13.1290(10)$ Å, $b = 14.3440(10)$ Å, $c = 20.898(2)$ Å, $\alpha = 79.411(10)^\circ$, $\beta = 78.2750(19)^\circ$, $\gamma = 81.334(10)^\circ$, $T = 173(2)$ K, $R1 = 0.0842$, $wR2 = 0.1647$ (all data).

studies. That the insertion occurs selectively at the *endo*-CH carbon of the η^6 -arene is likely due to steric reasons; that is, insertion occurs at the less substituted *endo*-CH. This occurs despite the fact that steric interaction between the DMSC framework and *endo* substituents generally disfavors reaction at the *endo* face.^{29–31} The cyclohexadienyl fragment is coordinated to Ti in an η^2 fashion. The Ti–C50 distance of 2.132(3) Å is comparable to the corresponding Ti–C distance of 2.142(3) Å in **2**. The Ti–C51 distance of 2.539(3) Å is indicative of a weak bonding interaction, similar to that in η^2 -benzyl compounds.⁴³

In C_6D_6 , **6** and **7** decompose over time with release of 1,2,4- $(Me_3Si)_3C_6H_3$ to give unidentified DMSC-based products. Decomposition occurs more slowly for **6** ($t_{1/2} \approx 2$ days, 22 °C) than for **7** ($t_{1/2} \approx 3$ h, 22 °C).⁴⁴ A possible decomposition pathway for **6** and **7** is depicted in Scheme 2. **6** (**7**) may rearrange into the allylic isomer **A**, followed by the cleavage of the C–C bond and release of $C_6H_3(SiMe_3)_3$. The formation of the free arene and relief of steric repulsion in **6** (**7**) is presumably the driving force behind the decomposition. Possibly, reactions of **2** with aromatic ketones (or aldehydes) proceed via an unobserved intermediate similar to **6** or **7**, which rapidly decomposes to a Ti– η^2 -ketone (or aldehyde) species (e.g. **B** or **C**); such species will most likely be unstable and undergo further reaction.⁴⁵ Accordingly, when the decomposition of **6** or **7** was carried out in the

(41) In a typical experiment, cyclohexanone (0.041 mL, 0.40 mmol) was dissolved in 3 mL of pentane. To this solution was added solid $[(DMSC)Ti\{C_6H_3(SiMe_3)_3\}]$ (**2**; 0.418 g, 0.400 mmol), and the mixture was stirred for 45 min, during which time a clear reddish orange solution formed. The solution was cooled at -15 °C in the glovebox freezer; reddish crystals precipitated after 2 days. The supernatant was decanted, and the crystals were washed with cold pentane (1 mL) and dried in vacuo to give 0.18 g (37% yield) of $[(DMSC)Ti\{C_6H_3(SiMe_3)_3-C_6H_{10}O\}]$ (**7**).

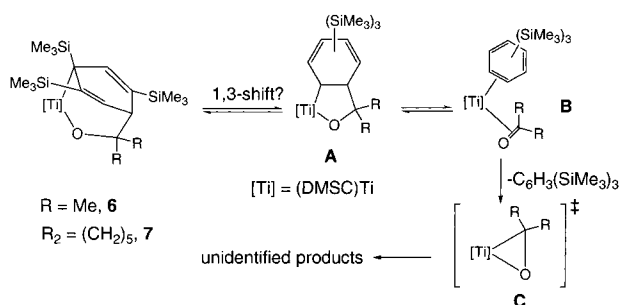
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(43) See for example: Tsukahara, T.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1997**, *16*, 3303 and references therein.

(44) The faster formation and slower decomposition of **6** can be explained on the basis of steric effects. The approach of acetone to **2** should be less hindered than that of more bulky cyclohexanone. The bulkier cyclohexanone moiety in **7** would more effectively facilitate arene release by inducing greater reduction in the steric strain of **7**.

(45) Rothwell et al. have structurally characterized $[(ArO)_2Ti(\eta^2\text{-benzophenone})(PMe_3)]$ ($Ar = 2,6\text{-Ph}_2C_6H_3$),²⁶ but no ligand-free $(RO)_2Ti(\eta^2\text{-ketone})$ complexes are known.

Scheme 2



presence of an excess of the corresponding ketone, the appropriate diols (pinacols) were detected by GC-MS after protolysis.

Interestingly, **2** reacted with Bu^tCHO to yield [(DMSC)Ti{C₆H₃(SiMe₃)₃Bu^tCHO}] (**8**) and [(DMSC)Ti{OCH(Bu^t)CH(Bu^t)O}] (**9**)⁴⁶ (Scheme 1). ¹H NMR showed that both **8** and **9** are present in solution throughout the course of the reaction. Upon exhaustion of **2**, the product ratio (**8**:**9** = 30:70) did not change over time (7 days, 22 °C) in the presence of excess Bu^tCHO. Hence, **8** is not converted to **9** and is stable at ambient temperature. The stability of **8** contrasts with that

(46) **8** was characterized by ¹H NMR in solution. Compound **9** could be isolated easily due to its poor solubility in pentane. [(DMSC)Ti{C₆H₃(SiMe₃)₃}] (**2**; 0.366 g, 0.350 mmol) was dissolved in 7 mL of pentane. Next, Bu^tCHO (0.115 mL, 1.05 mmol) was introduced. The solution was allowed to stand at ambient temperature for 24 h, during which time a yellow precipitate separated. The suspension was filtered, and the precipitate was washed with small portions of pentane until the washings were colorless. The pale yellow powder was dried in vacuo to give 0.190 g of product (58%). NMR and microanalysis data support the formulation given. The small (³J ≈ 1 Hz) coupling between C³H and C⁴H suggests that the Bu^t groups are trans to each other, as might be expected.

observed for **6** and **7** under analogous conditions. If the insertion of Bu^tCHO into a Ti–C bond of the titanaborbornadiene **2** occurs exclusively at the less substituted *endo*-CH, as was observed for the formation of **6** and **7** (vide supra), then two diastereomers can be formed.⁴⁷ Apparently, of the two possible isomers only **8** is stable. Presumably, the other isomer reacts with another molecule of Bu^tCHO to yield **9**.

In summary, these preliminary results are consistent with the intermediacy of a 2-oxatitanacycloheptene species en route to arene loss from **2** and the formation of 2,5-dioxatitanacyclopentane compounds. Further studies of the reactivity of these and related complexes are in progress in our laboratory.

Acknowledgment. Thanks are expressed to the Kentucky National Science Foundation EPSCoR Program (Grant No. EPS-9452895) for partial support of this work. Also, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supporting Information Available: Text giving preparation and chemical characterization data for **4–9** and tables giving a summary of crystallographic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **4** and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(47) The Bu^t group may be situated *endo* or *exo* (inside or outside of the calix[4]arene cavity).