

- tions.
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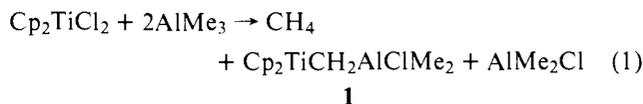
## Olefin Homologation with Titanium Methylene Compounds

Sir:

A family of methylene-bridged compounds,  $\text{Cp}_2\text{Ti-CH}_2\text{AlXR}_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) has been prepared. These compounds are versatile methylene transfer reagents for homologation of olefins and for conversion of ketones to terminal olefins. Under certain conditions the compounds react with olefins to generate cyclopropanes in low yield.

Although  $\text{Cp}_2\text{TiCH}_2\text{AlClMe}_2$  (**1**) is the first well-characterized compound of this type,  $\alpha$ -elimination from  $\text{CH}_3\text{TiCl}_3$  to give a transient methylene species was proposed<sup>1</sup> as early as 1961. More recently Sinn and coworkers conducted detailed studies of methane formation from mixtures of  $\text{AlMe}_3$  and  $\text{Cp}_2\text{TiCl}_2$ .<sup>2</sup> Several  $\text{TiCH}_2\text{Al}$  species were postulated as co-products, and in one case an isolated solid was assigned the formula  $\text{Cp}_2\text{TiCH}_2\text{AlCl}_2\text{Me}$ .<sup>2</sup> Stimulated by reports of tantalum alkylidene compounds<sup>3</sup> and of the role of tungsten methylene compounds in olefin metathesis,<sup>4</sup> we investigated the titanium-aluminum-methyl system to determine the nature of isolated products.

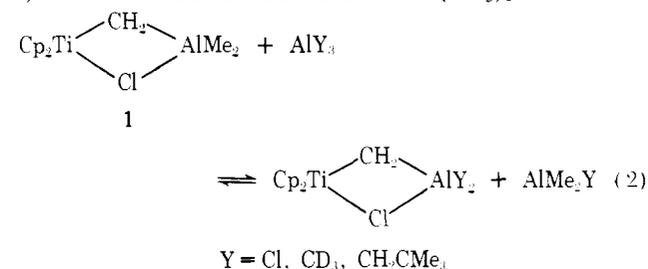
The reaction of 2 equiv of  $\text{AlMe}_3$  with  $\text{Cp}_2\text{TiCl}_2$  produces **1** and methane according to the equation



In a preparative experiment, a solution of 62 g of  $\text{Cp}_2\text{TiCl}_2$  and 48 mL of  $\text{Me}_3\text{Al}$  in 250 mL of toluene was allowed to stand 60 h at room temperature. The nonvolatile products were recrystallized from toluene to produce 35 g of crude **1** (80–90% pure). Recrystallization from a solution of  $\text{Me}_3\text{Al}$  in toluene and from pentane gave analytically pure<sup>5</sup> reddish orange crystals of **1**. The same product is formed by reaction of  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$  with  $\text{AlMe}_2\text{Cl}$ . Similarly,  $\text{Cp}_2\text{TiMe}_2$  reacts slowly with  $\text{AlMe}_3$  to produce  $\text{Cp}_2\text{TiCH}_2\text{AlMe}_3$  (**2**) and methane. Although **2** is always contaminated with  $\text{Cp}_2\text{TiMe}_2$ , its  $^1\text{H}$  NMR spectrum<sup>6</sup> confirms a structural analogy with **1**. The persistence of  $\text{Cp}_2\text{TiMe}_2$  is significant because it decomposes autocatalytically with loss of Cp hydrogens<sup>8</sup> in the absence of alkylaluminum compounds. It seems likely that a weak complex such as  $\text{Cp}_2\text{TiMe}_2\text{-AlMe}_3$  stabilizes the system and is an intermediate in the formation of the methylene compound.

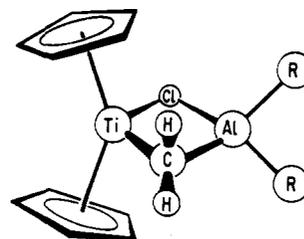
Dimethylzinc and  $\text{Cp}_2\text{TiMe}_2$  or  $\text{Cp}_2\text{TiCl}_2$  react to yield methane and products which we believe contain the  $\text{TiCH}_2\text{Zn}$  group, based on the appearance of low-field  $^1\text{H}$  NMR resonances<sup>6</sup> in the region characteristic of  $\text{TiCH}_2\text{Al}$  and their reactivity with ketones (see below). The  $\text{Cp}_2\text{TiMe}_2$  reaction is slow and we have not obtained isolable amounts of product. The  $\text{Cp}_2\text{TiCl}_2$  reaction proceeds at a convenient rate and yields products whose solubility characteristics change with time. In a typical reaction, 0.515 g (2.07 mmol) of  $\text{Cp}_2\text{TiCl}_2$  with 0.28 mL (4.1 mmol) of  $\text{Me}_2\text{Zn}$  in 5 mL of  $\text{C}_6\text{D}_6$  yielded 2.7 mmol of  $\text{CH}_4$  after 4 h at room temperature.

The methyl groups in **1** exchange with certain aluminum alkyls and halides, but the methylene group is unreactive (eq 2). The NMR of **1** after reaction with  $\text{Al}(\text{CD}_3)_3$  is consistent



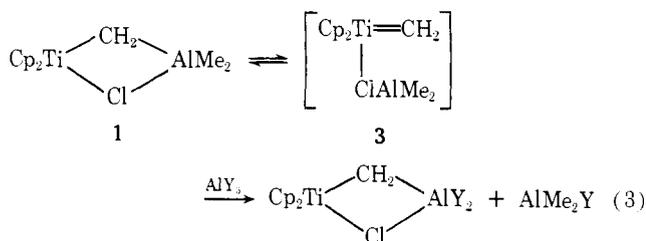
with statistical scrambling of methyl groups between free and titanium-bound aluminum alkyl, with no deuterium incorporation in the Cp or  $\text{CH}_2$  positions.<sup>9</sup> Partial exchange of the methyl groups of **1** with  $\text{Al}(\text{CH}_2\text{CMe}_3)_3$  or  $\text{AlCl}_3$  produces the unsymmetrical species  $\text{Cp}_2\text{TiCH}_2\text{AlClMeY}$  ( $\text{Y} = \text{CH}_2\text{CMe}_3$  or  $\text{Cl}^2$ ) which exhibits nonequivalent methylene and Cp protons in its  $^1\text{H}$  NMR spectrum.<sup>6</sup> Pure  $\text{Cp}_2\text{TiCH}_2\text{AlCl}(\text{CH}_2\text{CMe}_3)_2$  has been obtained by repeated exchange with  $\text{Al}(\text{CH}_2\text{CMe}_3)_3$ . A small amount of **2** is produced by the exchange of **1** with  $\text{AlMe}_3$ .

The geometry of the chloride containing derivatives, from  $^1\text{H}$  NMR spectra,<sup>6</sup> is that of a heterocycle which contains Ti,



CH<sub>2</sub>, Al, and Cl members. It seems likely that **2** has a similar structure in which a methyl group, rather than Cl, bridges Ti and Al. The <sup>1</sup>H NMR spectrum of **2** shows nonequivalent methyl groups in a 1:2 ratio<sup>6</sup> which are assigned to bridging and terminal methyl groups, respectively. Alkyl groups bridging titanium and aluminum are frequently postulated<sup>10</sup> for Ziegler-Natta olefin polymerization catalysts, but there are few examples based on structural data. Recently Cp<sub>2</sub>Ti-Me<sub>2</sub>AlMe<sub>2</sub>, which has two bridging methyl groups, has been reported.<sup>11</sup> Titanium and aluminum bridged by cyclopentadienyl carbon (TiC<sub>5</sub>H<sub>4</sub>Al) has been established for two compounds by x-ray studies.<sup>12,13</sup>

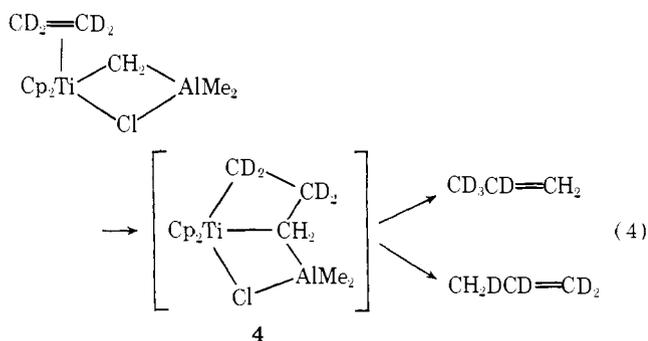
It is likely that exchange reactions between AlY<sub>3</sub> and **1** or **2** proceed via partial dissociation of the heterocycle. One possible mode of dissociation and exchange is shown in eq 3.



A transient species **3** formed by CH<sub>2</sub>-Al dissociation might be expected to be an energetic reagent for reaction with organic compounds. The formation of **3** might also be expected to be enhanced by the addition of Lewis bases (e.g., Me<sub>3</sub>N) which would complex with the aluminum in **3**.

Both expectations may be valid. Compound **1** reacts with ethylene at room temperature in toluene solution to form propylene (32% yield in 18 h) and with propylene to form isobutylene (59% yield), a trace of methylcyclopropane, and other C<sub>4</sub> hydrocarbons. Isobutylene is relatively unreactive alone, but, when tetrahydrofuran or trimethylamine is added, 1,1-dimethylcyclopropane and another C<sub>3</sub>H<sub>10</sub> compound are each formed in 2% yield, based on metal complex consumed. Most of the isobutylene is recovered. Addition of trimethylamine to the ethylene reaction leads to formation of a small amount of cyclopropane, a product not detected in the absence of the amine. The reactions seem to involve transfer of the methylene group specifically because Cp<sub>2</sub>TiCH<sub>2</sub>AlCl(CD<sub>3</sub>)<sub>2</sub> reacts with C<sub>2</sub>H<sub>4</sub> to form propylene-*d*<sub>0</sub>. The reaction of C<sub>2</sub>D<sub>4</sub> with **1** gives CD<sub>3</sub>CD=CH<sub>2</sub> and CH<sub>2</sub>DCD=CD<sub>2</sub> in a 1.4:1 ratio.<sup>14</sup>

By analogy with olefin metathesis mechanisms based on transient aluminum-stabilized tungsten carbene complexes,<sup>15</sup> we suggest metalocycle **4** as an intermediate in ethylene homologation (eq 4). The aluminum-free tungsten analogue of **4**, Cp<sub>2</sub>W(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), has been isolated.<sup>16</sup> Recently

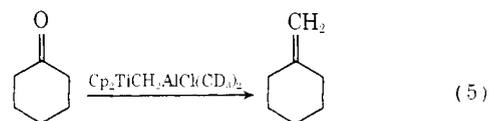


evidence was presented for the formation of a molybdenum methylene species in the reaction of Mo(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>(NO)<sub>2</sub> with Me<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, and for the incorporation of the methylene group in the products of a subsequent olefin metathesis reaction.<sup>17</sup>

Our representation of **4** includes the maximum probable number of metal-to-carbon and -chlorine interactions without assessment of their importance. The olefin products (eq 4) are consistent with β-deuterium transfer to either of the metal-bound methylene groups. It is unlikely that a metathesis process occurs prior to propylene formation because metathesis would scramble deuterium throughout the olefin. The formation of cyclopropanes could reflect a second mode of reaction of **4** in which reductive coupling occurs. At present, other mechanisms for cyclopropane synthesis cannot be excluded.

It is now possible to make a limited set of comparisons of the reactivity of olefins with isolated carbenoid species of group 4, 5, and 6 metals. The major product of reaction of ethylene with Cp<sub>2</sub>TiCH<sub>2</sub>AlClMe<sub>2</sub> and CpCl<sub>2</sub>Ta=CHCMe<sub>3</sub><sup>18</sup> is the homologous olefin, propylene and 4,4-dimethyl-1-pentene,<sup>18</sup> respectively. At present, this type of reactivity is unique for group 4 and 5 complexes. The titanium system produces small amounts of cyclopropanes, the amounts increasing with the Lewis basicity of the solvent and with substitution on the olefin in the series CH<sub>2</sub>=CH<sub>2</sub> < CH<sub>2</sub>=CHMe < CH<sub>2</sub>=CMe<sub>2</sub>. Olefins react with (CO)<sub>5</sub>W=CPh<sub>2</sub> (Ph = phenyl<sup>19a</sup> or tolyl<sup>19b</sup>) to give significant amounts of cyclopropanes as well as, uniquely, olefin metathesis products.<sup>19</sup>

The titanium-aluminum compounds react with certain organic carbonyls to produce olefins. For example, reaction of Cp<sub>2</sub>TiCH<sub>2</sub>AlClMe<sub>2</sub> with cyclohexanone in toluene solution at -15 °C to room temperature produces methylenecyclohexane in 65% yield. Only the methylene group is transferred as judged by reaction 5. The methylene reagent prepared by



reaction of Cp<sub>2</sub>TiCl<sub>2</sub> with Me<sub>2</sub>Zn reacts similarly. To the extent that we have examined this reaction,<sup>20</sup> **1** performs the methylene transfer with reactivity comparable to (Me<sub>3</sub>CCH<sub>2</sub>)<sub>3</sub>Ta=CHCMe<sub>3</sub>, which produces *tert*-butyl substituted olefins.<sup>21</sup>

These studies suggest some functions of aluminum alkyls as coreagents with transition metal complexes in olefin polymerization and metathesis catalysts. One of the major functions in the systems that we have studied<sup>12,13,22</sup> is to stabilize organometallic ligands which would otherwise decompose under reaction conditions. In the present case, AlMe<sub>3</sub> inhibits the catastrophic decomposition of Cp<sub>2</sub>TiMe<sub>2</sub>, and dictates the abstraction of hydrogen from methyl rather than Cp groups. The resulting methylene compound is stabilized by the presence of aluminum and the nucleophilicity of MCH<sub>2</sub> is reduced.

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- wt, 285. Found: C, 54.2; H, 6.3; Al, 9.3; Cl, 12.5; Ti, 16.9; mol wt, 310 (cryoscopic in benzene).
- (6) Characteristically the methylene hydrogens of **1** and its derivatives appear at low field in  $^1\text{H}$  NMR spectra. The methylene carbon is also shifted to low field, approaching the region for metal carbene complexes (e.g.  $\delta_{13\text{C}}$  204 ( $\text{Cp}_2\text{TiCH}_2\text{AlMe}_3$ ), 188 ( $\text{Cp}_2\text{TiCH}_2\text{AlClMe}_2$ ), vs. 228 ( $\text{Cp}_2\text{TaMe}(\text{=CH}_2)$ ).<sup>7</sup>  $^1\text{H}$  NMR data for **1** and its derivatives follow ( $\text{C}_6\text{D}_6$  solvent, 22 °C, 220-MHz spectrometer, measurements from  $\text{C}_6\text{D}_5\text{H}$   $\tau$  2.63):  $\text{Cp}_2\text{TiCH}_2\text{AlMe}_3$  (present with  $\text{Cp}_2\text{TiMe}_2$ ),  $\tau$  0.90 (2 H, s,  $\text{CH}_2$ ), 4.40 (10 H, s, Cp), 10.18 (6 H, s, AlMe), 11.36 (3 H, s, TiMeAl);  $\text{Cp}_2\text{TiCH}_2\text{AlClMe}_2$ ,  $\tau$  1.51 (2 H, s,  $\text{CH}_2$ ), 4.16 (10 H, s, Cp), 10.06 (6 H, s, Me);  $\text{Cp}_2\text{TiCH}_2\text{AlMeCH}_2\text{CMe}_3$ ,  $\tau$  1.51 (1 H, d,  $J = 6.7$  Hz,  $\text{TiCH}_2\text{Al}$ ), 1.57 (1 H, d,  $J = 6.7$  Hz,  $\text{TiCH}_2\text{Al}$ ), 4.12 (5 H, s, Cp), 4.15 (5 H, s, Cp), 8.57 (s, 9 H,  $\text{CMe}_3$ ), 9.28 (1 H, d,  $J = 13.8$  Hz,  $\text{AlCH}_2\text{CMe}_3$ ), 9.37 (1 H, d,  $J = 13.8$  Hz,  $\text{AlCH}_2\text{CMe}_3$ ), 10.04 (3 H, s, AlMe).  $^1\text{H}$  NMR data for the  $\text{TiCH}_2\text{Zn}$  species follow: product of  $\text{Cp}_2\text{TiMe}_2$  and  $\text{Me}_2\text{Zn}$ ,  $\tau$  1.32 (s,  $\text{TiCH}_2\text{Zn}$ ); product of  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Me}_2\text{Zn}$ ,  $\tau$  1.69 (s,  $\text{TiCH}_2\text{Zn}$ ).
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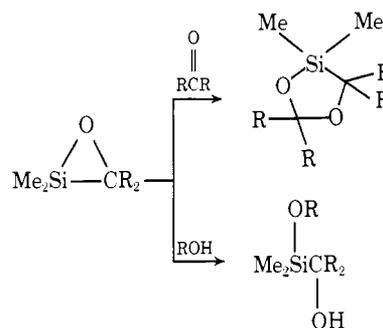
### Chemistry of Oxasilacyclopropane. 2.<sup>1</sup> Formations of Dioxasilacyclopentanes in the Reaction of Oxasilacyclopropane Derivatives with Adamantanone and Norbornone

Sir:

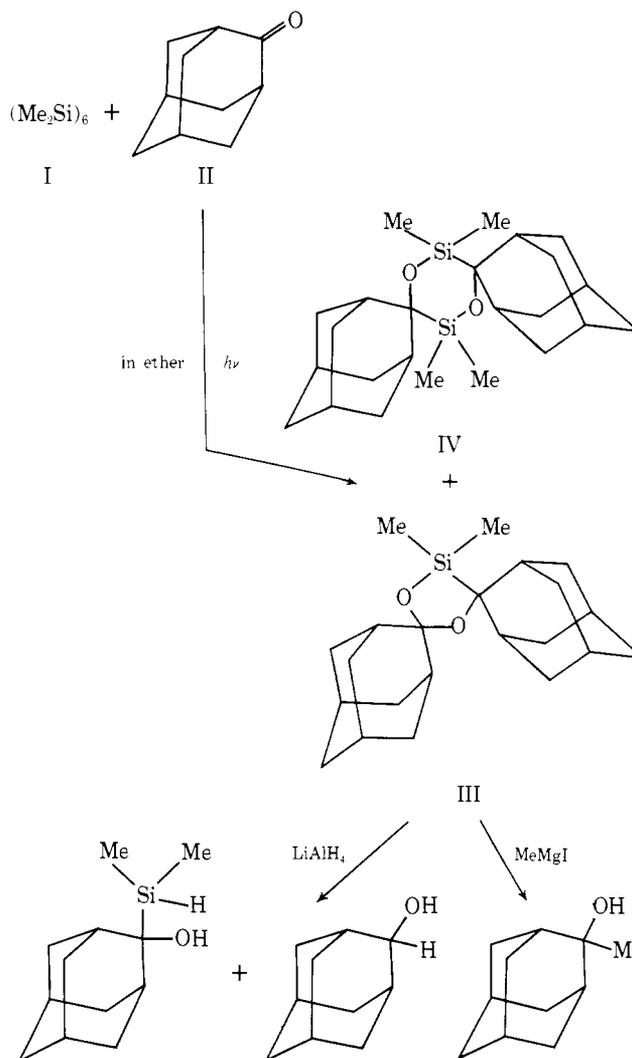
Interest has quickened over last few years in the chemistry of strained ring system containing a silicon atom. In contrast to rather extensive studies of chemistry of silacyclopropane,<sup>2,3</sup> and silacyclopentene,<sup>4,5</sup> very little is known about the chemistry of oxasilacyclopropane.<sup>1,6</sup> Recently, we reported that generation of dimethylsilylene by 1,2-dimethoxytetramethyldisilane pyrolysis in the presence of benzophenone gave 1,1-dimethyl-1-sila-2-oxa-3-phenyl-4,5-benzocyclopentene, which we can be best rationalized by assumption of oxasilacyclopropane intermediate followed by skeletal rearrangement via a cleavage of silicon-carbon bond.

We now report here the entirely new photochemical addition of silylene<sup>7</sup> to ketone in solution and study the intermolecular reactions of oxasilacyclopropane with ketones and alcohols.

An ether solution of dodecamethylcyclohexasilane (I, 0.3 mmol) and 2-adamantanone (II, 1.5 mmol) in quartz tube was irradiated with a low pressure mercury lamp for 4 h under a nitrogen atmosphere. Evaporation followed by GLC gave two main products, dispiro[adamantane-2,1'-(2',5'-dioxo-3'-



dimethylsilacyclopentane)-4',2''-adamantane] (III, mp 131–131.5 °C) and dispiro[adamantane-2,1'-(2',5'-dioxo-3',6'-tetramethyldisilacyclohexane)-4',2''-adamantane] (IV, mp 230–231 °C), in 165 and 18% yields, respectively (based on the number of moles of I). The assigned structure is com-



patible with spectral data of III, as well as the reaction with lithium aluminum hydride<sup>8</sup> to 2-adamantanol (70%) and 2-dimethylsilyl-2-adamantanol (78%), and the reaction with methylmagnesium iodide<sup>9</sup> to 2-methyl-2-adamantanol (47%). The mass spectrum (70 eV) of III showed a relatively strong molecular ion at  $m/e$  358, and no higher species, confirming that the five-membered ring was in hand. The  $^1\text{H}$  NMR spectra of III showed in  $\text{CDCl}_3$  a singlet for Si-Me at 0.25 (6 H) and broad adamantyl protons at 1.28–2.6 ppm (28 H). Its IR spectrum shows bands of medium intensity at 1090–1115 (Si-O and C-O bands) and at 1250  $\text{cm}^{-1}$  (Si-Me band).