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Preliminary communication

SILYL-TITANATION OF ACETYLENES AND 1,3-DIENES

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Summary

A Ti^{III}—Si active species, $Cp_2TiSiMe_2Ph$, is formed either by the reaction of Cp_2TiCl_2 with two equivalents of $PhMe_2SiLi$ or by the reaction of Cp_2TiCl with one equivalent of $PhMe_2SiLi$. Highly regio- and stereo-selective silyltitanation by this species has been observed with acetylenes and 1,3-dienes.

Hydro- [1] and carbo-titanation [2] reactions of unsaturated compounds have recently received much attention from the synthetic and mechanistic viewpoints. This report describes the first examples of silyl-titanation of acetylenes and 1,3-dienes. Transition metal-silicon complexes have been proposed and isolated, in some cases, as key intermediates for not only hydrosilylation, but also various types of addition reactions of organosilicon compounds to unsaturated compounds [3]. While this rapidly developing chemistry has been almost restricted to the Group VIII metal complexes, a few complexes containing titanium—silicon σ-bonds have been documented. Action of triphenylsilylpotassium on Cp_2TiCl_2 ($Cp = \eta^5$-C_5H_5) has been reported to form $Cp_2Ti(SiPh_3)_2$ [4], which has recently been called in question [5]. On the other hand, reaction between Cp_2TiCl_2 and trimethylsilyllithium resulted in reduction of Ti^{IV} to Ti^{II} species, $Cp_2Ti(THF)$, together with formation of $Me_3SiSiMe_3$ and Me_3SiH [6]. Quite recently, $Cp_2TiCl(SiMe_3)$ has been isolated [7].

We report herein the formation of a titanium(III)-silicon complex and its addition reactions to unsaturated compounds. Thus, to a suspension of Cp_2TiCl_2 (I) in THF was added 2 equivalents of a THF solution of $PhMe_2SiLi$ (II) [8] at 0°C, resulting in the formation of a red brown solution. After 10 min-stirring dibutylacetylene (III) was added at the same temperature, the color changing to greenish. After another 10 min-stirring the mixture was decomposed by addition of ethanol to give (*E*)-5-dimethylphenylsilyl-5-decene

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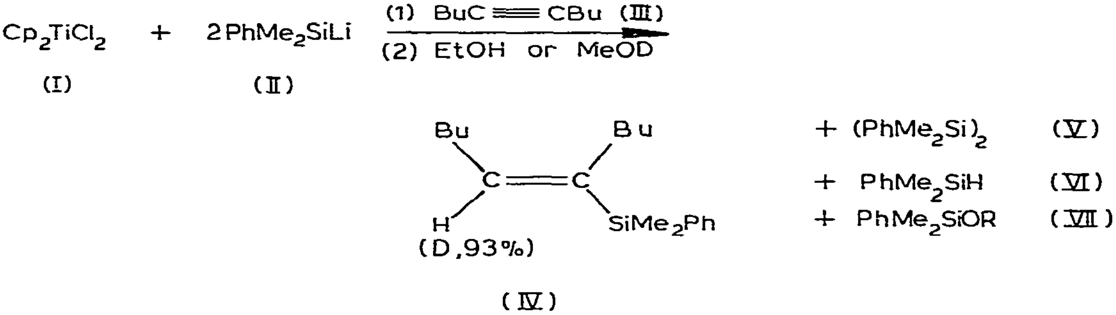
(IV) in 50% yield*, together with 1,2-diphenyltetramethyldisilane (V), phenyldimethylsilane (VI), and phenyldimethylethoxysilane (VII). No allenic product was formed**. Quenching with MeOD gave greater than 90% deuterium incorporation at the vinylic proton of IV.



In order to get information about the active species, we carried out the following quenching studies. Quenching a green reaction mixture of I and one equivalent of II with MeOD produced VI (48% yield) having ca. 30% D-incorporation and the disilane V in 8%. Quenching with MeOD a blue mixture obtained by addition of two equivalents of II afforded VI (100% yield) with a 50% D-incorporation, along with 13% yield of V. Quenching with Me_3SiCl gave no $PhMe_2SiSiMe_3$, indicative of the absence of free silyllithium.

Scheme 1 visualizes a plausible mechanism which is consistent with the above observations. Thus, the first one equivalent of silyllithium II acts as a reductant of the titanium(IV) to a titanium(III) species, Cp_2TiCl (VIII), most probably via a one-electron transfer process [9]. The resulting silyl radicals couple with each other to form disilane V or abstract a hydrogen atom from the solvent to give non-deuterated hydrosilane VI. Another equivalent of II couples with VIII to give a titanium(III)-silicon complex IX which should afford the deuteriosilane upon treatment with MeOD. The titanium(III)-silicon species II may add to an acetylene to give a silyltitanation product X, from which the observed silylolefin IV should be produced via protonolysis of the titanium—carbon bond.

Unfortunately, neither VIII and IX has yet been isolated from the present reaction system. However, formation of IX could be confirmed by the reaction of authentic Cp_2TiCl (VIII). Thus, brown-green complex VIII, prepared by the Cp_2TiCl_2/Et_2AlCl method [10], was allowed to react with one equivalent of II at −30°C and the mixture was then quenched with DCl/D_2O to give VI-D (72% D-incorporation by NMR). Treatment with dibutylacetylene (III)

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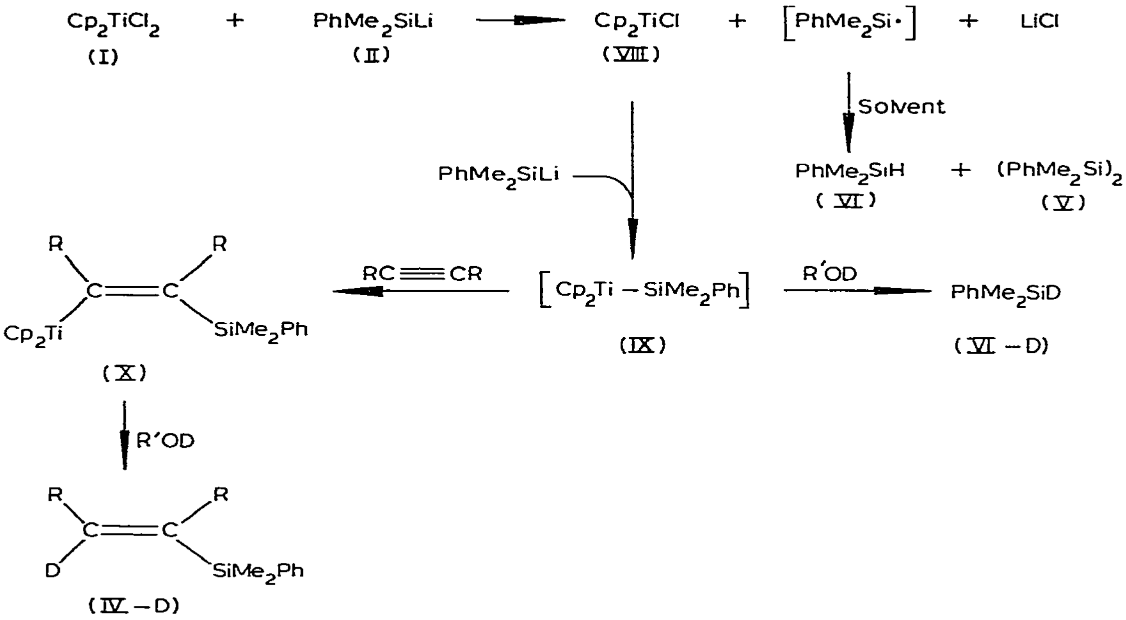
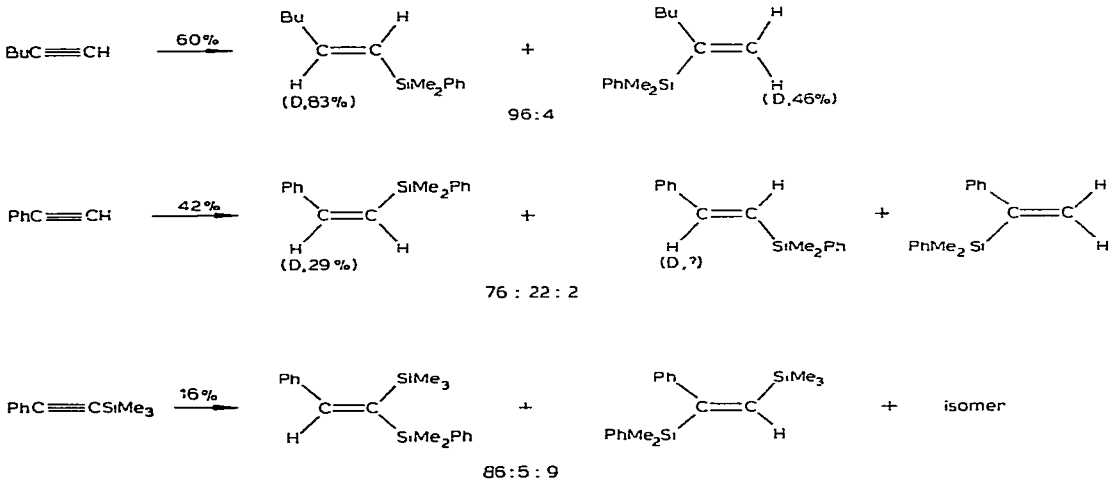
*Unless otherwise stated, yields were determined by GLC based on I; organic products were isolated by preparative GLC after hydrolysis (diluted HCl), extraction, evaporation, and passing through a short Silica Gel column (hexane as an eluent), and characterized by GLC, ^1H NMR, IR, and mass spectroscopy and/or analysis.

**When the silyllithium solution was added to a mixture of I and III, the formation of a silylallene derivative, $BuC(SiMe_2Ph)=C=CHC_3H_7$, also occurred. The formation of allenic products in carbotitanation has been reported [2c].



SCHEME 1



SCHEME 2

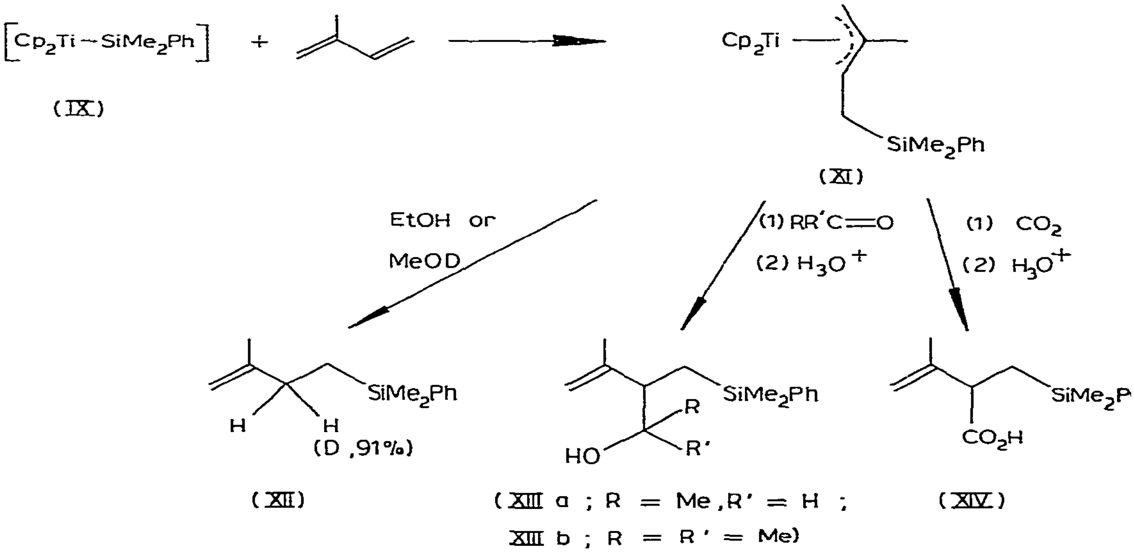
at 0°C prior to the DCl quenching afforded IV (D >99%). The titanium(III)-silicon species IX could also be formed by the silyllithium treatment of Cp_2TiCl (VIII) prepared in situ from I and one equivalent of i-PrMgX [11] or i-BuMgX [1d]. In these cases no disilane V was formed, supporting the above mechanism.

The aforementioned results indicate that the titanium(III)-silicon adds to an acetylene stereoselectively in a *cis* fashion and the resulting alkenyl—titanium bond is configurationally stable at least up to 0°C. The alkenyltitanium species did not react with ICl, CO_2, ketone, and Me_3SiCl.

The silyltitanation occurred also with terminal acetylenes and a silylacetylene, as shown in scheme 2. The last two results were obtained via I + i-BuMgBr + II.

There are several interesting features. The ethynylic proton is not metalated by the Ti—Si species. The silyl group is introduced onto the terminal carbon or the silyl group-bearing carbon atom predominantly. It seems of interest to note here that the regioselectivity of the present silyltitanation is opposite to that of recently developed carbotitanation of acetylenes [2g]. The *trans* addition product was formed mainly from $PhC{\equiv}CH$ with a rather low deuterium incorporation. The low deuterium incorporation suggests that a homolytic cleavage of the titanium—carbon bond followed by hydrogen abstraction from the medium or some other sources may be involved as one of competitive processes.

We have also observed silyltitanation of 1,3-dienes (Scheme 3). Thus, to a solution of the titanium(III)-silicon active species IX was added isoprene (1 equivalent) at 0°C. After 1 h stirring at 0°C quenching with EtOH gave 2-methyl-4-dimethylphenylsilyl-1-butene (XII) in 73% yield (via I + 2 equivalent of II) or in 50—60% yield (via I + i-PrMgBr + II). Quenching with MeOD gave 3-deuterated product (D 91%). The results may indicate the formation of silylated π-allyltitanium complex XI, analogous to the hydrotitanation of 1,3-dienes [1,12]. A mixture of (*E*)- and (*Z*)-1,3-pentadiene gave, under similar conditions, only the *E* isomer of 5-silyl-2-pentene in 82% yield, also supporting the formation of a π-allyltitanium complex [12].



SCHEME 3

π-Allyltitanium complexes have recently been reported to react with CO, CO$_2$, aldehydes and ketones [13]. The silylated π-allyltitanium species XI was allowed to react at 0°C for 1 h with acetaldehyde and acetone to give, upon hydrolysis and preparative TLC (Silica Gel; ethyl acetate/benzene = 1/2~3), alcohols XIIIa (58% isolated yield) and XIIIb (52% isolated yield), respectively. Carbon dioxide also reacted with XI to give XIV, but yields were low (<27% isolated yield).

Finally, we have observed no silylzirconation of an acetylene under similar conditions ($Cp_2ZrCl_2/PhMe_2SiLi/BuC{\equiv}CBu$) (cf. ref. 5), in accordance with Gladysz's recent observations using $Cp_2ZrCl(SiMe_3)$ [14].

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