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Toward a Silicon Version of Metathesis: From Schrock-Type Titanium Silylidenes to Silatitanacyclobutenes

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Supporting Information

ABSTRACT: Olefin metathesis is one of the most important industrial processes for the production of alkenes. In contrast, silicon versions of metathesis are unknown given the lack of available silylene transition-metal complexes suitable for [2 + 2] cycloaddition with unsaturated substrates. Here, we report the synthesis of 18-electron titanium silylene complexes featuring different Lewis base ligands and classified on the basis of structural, computational, and reactivity studies as Schrock-type silylene complexes. Because of the presence of loosely bound Lewis base ligands, such silylene complexes readily undergo reaction with simple unsaturated hydrocarbons, such as alkynes, forming the corresponding [2 + 2] cycloaddition products.

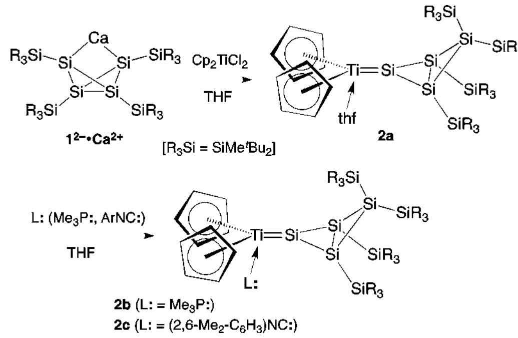
Alkenes are of paramount importance for the chemical industry; therefore, making carbon−carbon double bonds is one of the ultimate goals of organic chemistry processes. Alkene metathesis, as one such process first commercialized in petroleum reformation for the synthesis of higher alkenes from α-olefins, involves a transition-metal-catalyzed redistribution of the alkylidene fragments in the starting alkenes to form novel alkenes with a different substitution pattern.[1] Metallacyclobutanes, as the [2 + 2] cycloaddition products of alkenes and carbene complexes, are widely recognized as the key intermediates in this reaction.[2] The scope, limitations, and mechanism of alkene metathesis have been thoroughly studied by many research groups, first of all those led by Chauvin, Grubbs, and Schrock.[3]

Unsaturated compounds featuring multiple bonds to silicon have been known since 1981, including the first representatives of disilene[4] as a "heavy" alkene, disilynes[5] as "heavy" alkynes, tetrasilabuta-1,3-diene[6] as a "heavy" 1,3-diene, and trisilaallene[7] as a "heavy" allene. However, despite the large number of stable organometallic derivatives, featuring silicon atoms doubly bonded to either main group elements or transition metals,[8] there are very few general approaches for their synthesis, and the metathesis process is not among them. Moreover, unlike transition-metal carbene complexes, for which [2 + 2] cycloaddition with alkenes and alkynes, forming metallacyclobutanes and metallacyclobutenes as the key intermediates of the metathesis process, is well established, reactions of this type are unprecedented in the chemistry of transition-metal silylene complexes.[9] There is only one report of the formal [2 + 2] cycloaddition of the highly polarized isocyanate substrate and cationic ruthenium silylene complex, proceeding through a different stepwise mechanism, initiated by the coordination of the isocyanate nitrogen lone pair to the electrophilic silicon and involving polar intermediates.[10] Here we report our approach to the synthesis of rare examples of Schrock-type silylidenes, featuring loosely bound and readily removable Lewis base ligands (THF, phosphine, isocyanide), thus providing a vacant site for coordination of terminal alkynes and resulting in the formation of unprecedented silatitanacyclobutenes as the "frozen" intermediates of the silicon version of the metathesis process.

The target silicon analogues of the Schrock-type alkylidenes were readily available by a straightforward procedure: reaction of the Ca salt $\mathbf{1}^{2-}\cdot\mathbf{Ca}^{2+}$ of the tetrasilabicyclo[1.1.0]butane-2,4-diide[11] with the group 4 metallocene dichlorides (Scheme 1).[12]

The reaction is quite general and proceeds smoothly for all group 4 metals (Ti, Zr, Hf) bearing both unsubstituted (η^5-C_5H_5) and Et-substituted (η^5-C_5H_4Et) cyclopentadienyl ligands. In this work the formation of the titanium silylene complexes will be discussed as the most representative and challenging example.[13] The initially formed **2a** represents an

Scheme 1. Synthesis of the Schrock-Type Titanium Silylene Complexes 2a−c



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18-electron titanium silylene complex featuring a THF ligand bound to the titanium center. Although stable in the solid state for a limited period, THF complex **2a** undergoes decomposition in solution, most probably involving initial loss of the loosely bound THF ligand followed by dissociation of the titanium−silicon double bond in the resulting 16-electron complex. Indeed, use of stronger Lewis bases, such as trimethylphosphine and xylyl isocyanide, allowed isolation of the titanium silylene complexes **2b** and **2c** that are indefinitely stable, both in the solid state and in solution (Scheme 1).

All titanium silylene complexes showed the distinctive extreme deshielding of their sp^2-Si centers, whose resonances were observed at 322.4 ppm (**2a**), 350.6 ppm (**2b**), and 401.4 ppm (**2c**).[9] One can note a remarkable increase in the chemical shift values, especially on going from **2b** to **2c**, which correlates with the substantial increase in the same direction of the π-acceptor power of the Lewis base ligand. This trend may be explained in terms of a remarkable decrease in the HOMO(π)−LUMO(π^*) energy gap, primarily caused by the lowering of the LUMO energy levels (because of the stronger π-acceptance), resulting in an enhanced paramagnetic contribution, which is well-known to be responsible for the overall low-field isotropic chemical shift[14] [$\Delta E(\pi-\pi^*)$ in eV and ^{29}Si NMR in ppm (experimental/calculated)]: 2.75 and 350.6/381.5 (for **2b**); 2.47 and 401.4/435.9 (for **2c**) (computational details in Supporting Information, SI).[15]

Both phosphine and isocyanide complexes **2b** and **2c** were crystallographically characterized, and the structural features of the isocyanide complex are discussed below.[12] The titanium center in **2c** is coordinated to the four ligands, giving rise to the total count of 18 electrons associated with the transition metal (Figure 1). The formulation of **2c** as the heavy analogue of the alkylidene complexes is supported by the remarkable shortening of its titanium−silicon bond. Thus, the Ti1−Si1 bond of 2.5039(6) Å is notably shorter than the known Ti−Si single bonds in silyltitanium complexes of 2.59−2.70 Å[16] (~3.5−7.4% shortening). The Si center in the bicyclic silylidene ligand of **2c** features a nearly ideal planar geometry, with the sum of the bond angles being 359.6°. The peculiar geometrical features of **2c** allow for the diagnostic d(Ti)−p(Si) $\pi-\pi$ interaction, as a manifestation of the Ti═Si double bond, which can be seen in the frontier molecular orbitals of **2c**. Thus, its HOMO and LUMO represent mostly the bonding and antibonding π-interactions between the titanium 3d- and silicon 3p-orbitals with some contribution from the π^*-orbital of the C═N bond and the σ-orbital of the bridging Si−Si bond of the bicyclic Si_4 fragment (Figure 2).

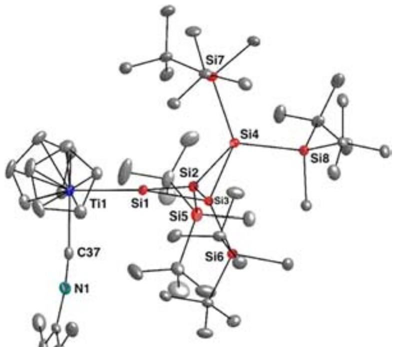


Figure 1. ORTEP view of the titanium−silylene complex with the isocyanide ligand **2c** (thermal ellipsoids are given at the 30% probability level, hydrogen atoms are not shown). Selected bond lengths (Å): Ti1−Si1 = 2.5039(6), Si1−Si2 = 2.3398(8), Si1−Si3 = 2.3393(7), Si2−Si4 = 2.3792(8), Si3−Si4 = 2.3614(7), Si2−Si3 = 2.4036(8), Ti1−C37 = 2.090(2), C37−N1 = 1.177(3).

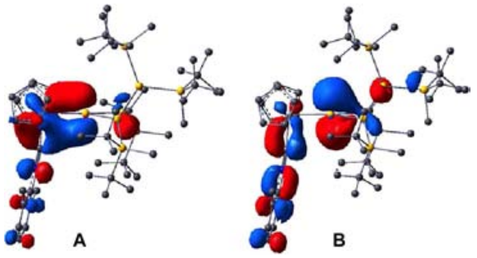


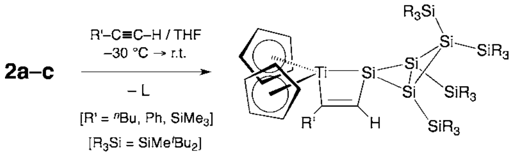
Figure 2. Frontier molecular orbitals (A) HOMO, (B) LUMO of the silylene complex **2c**.

As a hallmark feature of the Schrock-type carbene complexes,[17] which are exclusively found among the early transition metals, the Ti(IV) center in **2** is in its highest oxidation state (d^0), thus implying inherent Lewis basicity of the Si center in the silylidene ligand. This is further corroborated by the computational results of the natural population analysis (NPA) charge distribution in **2**: the Ti atom is positively polarized [+0.78 in **2a**, +0.52 in **2b**, +0.46 in **2c**], whereas the Si atom is polarized negatively [−0.13 in **2a**, −0.08 in **2b**, +0.01 in **2c**], indicative of the remarkable titanium−silicon bond polarization as a diagnostic feature of the Schrock alkylidenes.[17] In view of all the evidence discussed above, we can now reliably classify the titanium silylene complexes **2** as Schrock-type silylidenes, featuring a profoundly nucleophilic silicon center.[18] The very recently reported bis(silylene) titanium(II) derivatives exhibited completely different electronic properties.[19]

Having prepared and established the Schrock-type nature of the silylene complexes **2a−c**, we then focused on their utilization as the starting materials for [2 + 2] cycloadditions as a model reaction of the silicon variant of the metathesis process.[20] After the initial screening, we found that the reaction of the silylene complexes **2a−c** tolerates a variety of unsaturated substrates, of which the reactions with terminal alkynes were particularly selective and smooth, proceeding at very fast rates even at low temperatures and cleanly forming the desired silatitanacyclobutenes **3a−c** as the [2 + 2] cycloadducts between the Ti═Si and C≡C bonds, accompanied by the elimination of the free Lewis base ligand L (Scheme 2).[12]

Experimental observation of the extreme ease of the above-described cycloaddition reactions was backed by computations, which revealed a markedly exothermic reaction pathway (Gibbs

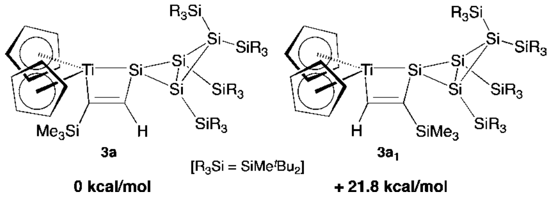
Scheme 2. Reaction of the Schrock-Type Silylene Complexes 2a−c with Terminal Alkynes



3 (a: R' = $SiMe_3$; b: R' = ^{n}Bu; c: R' = Ph) free-energy change $\Delta G = -14.6$ kcal/mol for **3a**), proceeding with an exceedingly low activation barrier of <2.0 kcal/mol (for the potential energy curve, see Figure S3). Moreover, in complete accord with our initial expectations, computations showed that as the silylene complex and the alkyne approach each other, the d(Ti)−π^*(C≡C) interaction between the transition metal and the alkyne begins to develop as the initial step of the reaction (visualized in the HOMOs of the reaction system formed upon the interaction of the silylene complex **2** (without ligand L) and trimethylsilylacetylene, forming metallacycle **3a**, see Figure S4). Such coordination of the alkyne at the transition metal is enabled by the preliminary elimination of the Lewis base ligand L from **2**, which provides a coordination site at the titanium center. Indeed, the [2 + 2] cycloaddition rate agrees well with the strength of the ligand L-to-titanium bonding: Complexes **2a**,**b** with the very loosely bound THF and moderately bound phosphine ligands react with alkynes instantly even at temperatures as low as −78 °C, whereas **2c** with the most strongly coordinating isocyanide ligand needs a couple of days at room temperature to complete the reaction.

Interesting to note that in all cases of the cycloaddition of terminal alkynes, only one regiosisomer of the silatitanacyclobutene is exclusively formed with the substituted fragment of the C═C bond bound to Ti and the unsubstituted fragment bound to Si. Computations revealed a clear free energy stabilization of 21.8 kcal/mol for the cycloadduct **3a**, compared with its regioisomer **3a$_1$** (Chart 1). Such thermodynamic preference can be attributed to the unfavorable steric repulsive interaction between the Me_3Si substituent on the silicon-bound sp^2-C atom and voluminous R_3Si groups at the bridgehead Si atoms of the tetrasilabicyclo[1.1.0]butane fragment in the regioisomer **3a$_1$**.

Chart 1. Energetic Preferences for the Regioisomers 3a and 3a$_1$



The peculiar spectral and structural features of **3a** are noteworthy. Thus, a characteristic low-field resonance of +125.4 ppm was observed for the Ti-bound spiro-Si atom (calculated value 119.9 ppm). In the ^{13}C NMR spectrum of **3a**, the olefinic carbons were observed at +104.7 ppm (Si-bound olefinic C) and +221.1 ppm (Ti-bound olefinic C), with the latter signal being a diagnostic feature of the titanacyclobutene derivatives[21] (calculated values 103.9 and 218.5 ppm, respectively).

The structure of the tricyclic cycloadduct **3a** is rather interesting as it has a number of unusual features (X-ray analysis of metallacyclobutene **3b** revealed similar structural trends) (Figure 3). The Ti-bound Si1 atom manifests a remarkable inverted sp^3 geometry (so-called "umbrella" configuration), dictated by its peculiar position as the spiro-atom joining together cyclobutene and bicyclo[1.1.0]butane fragments. Moreover, the sum of the bond angles around Si1 (ignoring the C37 atom) comes to 357.1°, which is markedly closer to the sp^2 geometry, rather than the anticipated sp^3 configuration. The silatitanacyclobutene ring in **3a** is nearly planar, with the skeletal bond lengths shown in Figure 3. Although the Ti1−C38 bond length of 2.110(3) Å is in the normal range, the trend in the other bond distances is notable (geometrical parameters of the calculated real molecule agree very well with the experimental data). Thus, the Si1−C37 bond of 2.030(3) Å is slightly stretched, whereas the Ti1−Si1 bond of 2.4868(8) Å and the C37−C38 bond of 1.324(4) Å are slightly shortened. In fact, the Ti−Si bond distance in the cycloadduct **3a** is even marginally shorter than the Ti═Si double bond of its precursor silylene complex **2c**: 2.4868(8) vs 2.5039(6) Å. All of these structural peculiarities (along with the unusually strongly deshielded Ti-bound Si1 atom, see above) indicate the equally important (if not predominant) contribution of another structure to the overall composition of the [2 + 2] cycloadduct **3a**, which has the character of a titanium silylidene−alkyne π-complex (for representation of the two major contributions to the overall structure of **3a**, see Scheme S1). Moreover, the shape of the four-membered silatitanacyclobutene $SiTiC_2$ in **3a** resembles a distorted trapeze with a relatively short diagonal Ti1−C37 interatomic distance of 2.319(3) Å, indicative of their distant interaction and supporting the contribution of the π-complex form.

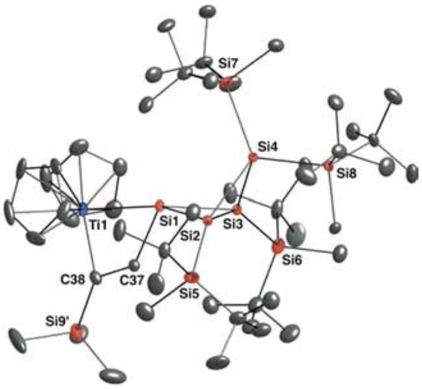


Figure 3. ORTEP view of the [2 + 2] cycloadduct **3a** synthesized by the reaction of the titanium−silylene complex **2** with trimethylsilylacetylene (thermal ellipsoids are given at the 30% probability level, hydrogen atoms are not shown). Selected bond lengths (Å): Ti1−Si1 = 2.4868(8), Si1−Si2 = 2.3427(10), Si1−Si3 = 2.3445(10), Si2−Si4 = 2.3795(10), Si2−Si3 = 2.3880(10), Si3−Si4 = 2.3789(10), Ti1−C38 = 2.110(3), Si1−C37 = 2.030(3), C37−C38 = 1.324(4), Ti1···C37 = 2.319(3).

The cycloadducts **3** are room temperature stable and even on heating up to 100 °C, the expected cycloreversion products Ti═C−C═Si were not observed but only partial decomposition of **3**. The search for other unsaturated substrates (including alkenes) that may form cycloadducts capable of the subsequent metathetical cycloreversion is our current focus.

In summary, in this contribution we presented our method for the synthesis of novel group 4 metal silylene complexes with loosely bound and readily removable Lewis base ligands that are reliably classified as the Schrock-type silylidenes, based on their structural, computational, and reactivity studies. Moreover, it was demonstrated that these titanium silylidenes smoothly react with the terminal alkynes forming unprecedented silatitanacyclobutenes as the [2 + 2] cycloaddition products, which may lead to the development of an alternative synthetic methodology for the design of novel organosilicon materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization data, and complete ref 15. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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