

Silyl-substituted alkylidenes: preparation of the novel complexes and mechanistic studies of their formation from reactions of alkylidenes with silanes and silyl-to-alkyldyne migration[☆]

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Abstract

Alkylidene complexes $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)=\text{CHSiMe}_3$ (**1**) and $\text{Me}_3\text{SiCH}_2\text{Ta}(\text{PMe}_3)_2(=\text{CHSiMe}_3)_2$ (**3a**) were found to react with phenylsilanes $\text{H}_2\text{SiR}'\text{Ph}$ ($\text{R}' = \text{Me, Ph}$) and $(\text{PhSiH}_2)_2\text{CH}_2$ to give disilyl-substituted alkylidenes $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}=\text{C}(\text{SiMe}_3)(\text{SiHR}'\text{Ph})$ (**2**) and novel metallasilacyclobutadiene and metalladisilacyclohexadiene complexes. Silyl-substituted alkylidene complex $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{O})[\text{C}(\text{Bu}^t)(\text{SiPh}_2\text{Bu}^t)]$ (**5a**) was prepared from the reaction of O_2 with an equilibrium mixture $(\text{Bu}^t\text{CH}_2)\text{W}(=\text{CHBu}^t)_2(\text{SiPh}_2\text{Bu}^t)$ (**4b**) \rightleftharpoons $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiPh}_2\text{Bu}^t)$ (**4a**). Our recent studies of the preparation of these complexes and mechanistic pathways in the formation of these silyl-substituted alkylidene complexes are summarized.

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1. Introduction

Alkylidene and alkyldyne ligands in high-oxidation-state complexes are known to be highly reactive, and have been the subject of intense studies [1]. These Schrock-type ligands are, in general, nucleophilic, and undergo metathesis reactions with olefins [2] and alkynes [3]. Such activities have been widely used in, e.g., ring-opening metathesis polymerization (ROMP)

[2], acyclic diene metathesis (ADMET) polymerization [2], asymmetric synthesis [2], and cycloalkene synthesis by the ring-closing metathesis (RCM) process [2]. We recently found that d^0 Ta alkylidene complex $(\text{RCH}_2)_3\text{Ta}(\text{PMe}_3)=\text{CHR}$ ($\text{R} = \text{SiMe}_3$, **1**) reacted with silanes $\text{H}_2\text{SiR}'\text{Ph}$ ($\text{R}' = \text{Me, Ph}$) to give unusual disilyl-substituted alkylidene complexes $(\text{RCH}_2)_3\text{Ta}=\text{CR}(\text{SiHR}'\text{Ph})$ (**2**) [4]. Similar reactions between $\text{RCH}_2\text{Ta}(\text{PMe}_3)_2(=\text{CHR})_2$ ($\text{R} = \text{SiMe}_3$, **3a**) and these silanes yielded novel metallasilacyclobutadiene complexes [4]. D-labeling and kinetic studies were performed to elucidate the mechanism in the formation of these complexes. We were also surprised to find that a mixture of W silyl bis(alkylidene) and silyl

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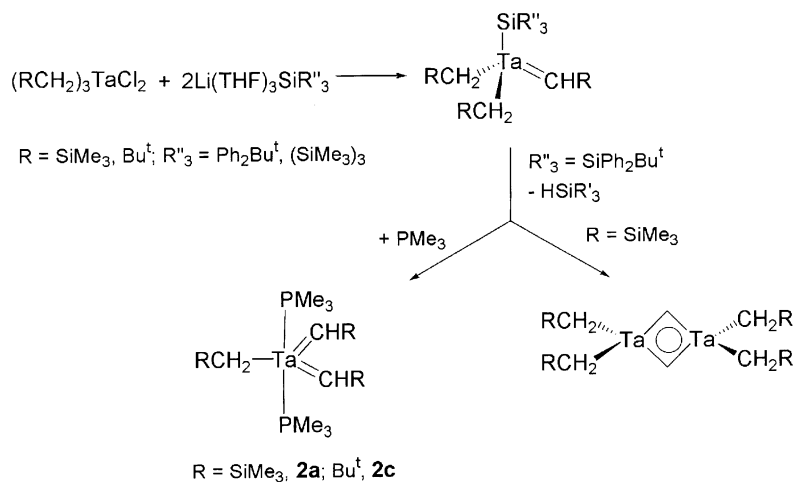
alkylidyne complexes $(\text{Bu}^t\text{CH}_2)\text{W}(=\text{CHBu}^t)_2(\text{SiPh}_2\text{-Bu}^t)$ (**4b**) \rightleftharpoons $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiPh}_2\text{Bu}^t)$ (**4a**) react with O_2 to give silyl-substituted alkylidene complex $(\text{Bu}^t\text{CH}_2)_2\text{W}(=\text{O})[\text{C}(\text{Bu}^t)(\text{SiPh}_2\text{Bu}^t)]$ (**5a**) [5]. The W-bonded silyl ligand in **4** has undergone an unusual migration to the alkylidyne ligand $\equiv\text{CBu}^t$ in the reaction. Experimental and theoretical studies have been conducted to understand this silyl migration. These recent studies of the Ta and W silyl-substituted alkylidene complexes and mechanistic pathways in their formation are summarized here.

2. Silyl alkylidene and alkylidyne complexes

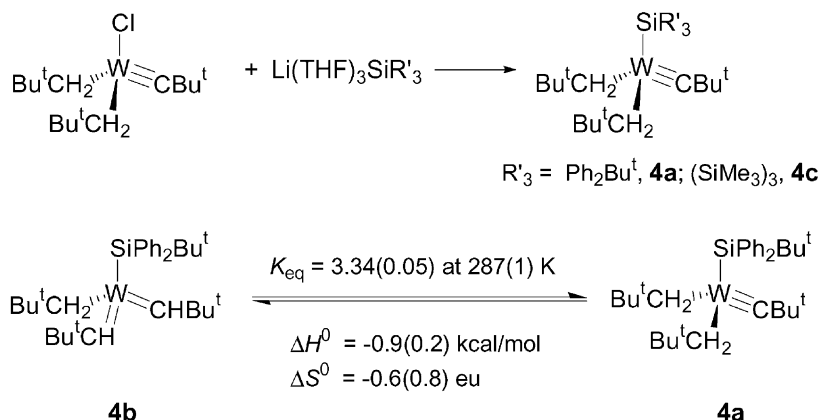
Our studies of the Ta and W silyl-substituted alkylidene complexes followed our work on Ta silyl alkylidene and W alkylidyne complexes. Ta silyl alkylidene complexes $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{SiR}''_3$ ($\text{R} = \text{Bu}^t, \text{SiMe}_3$; $\text{R}''_3 = \text{Ph}_2\text{Bu}^t$ and $(\text{SiMe}_3)_3$) were readily prepared from reactions of $(\text{RCH}_2)_3\text{TaCl}_2$ with silylating reagents $\text{Li}(\text{THF})_3\text{SiR}''_3$ (Scheme 1) [6]. These were the first isolated silyl alkylidene complexes [7]. The isolated yields of the tris(trimethylsilyl)silyl complexes $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{Si}(\text{SiMe}_3)_3$ are 72 to 73%. The diphenylbutylsilyl alkylidene complexes $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{SiPh}_2\text{Bu}^t$ are thermally unstable. The silyl ligand in $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(=\text{CHSiMe}_3)\text{-SiPh}_2\text{-Bu}^t$ undergoes α -H abstraction with the alkylidene ligand to give a dimeric, alkylidyne-

bridged complex $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\mu\text{-CSiMe}_3)_2\text{Ta}(\text{CH}_2\text{SiMe}_3)_2$ first reported by Mowat and Wilkinson [8]. Thermal decomposition of $(\text{Bu}^t\text{CH}_2)_2\text{Ta}(=\text{CH-Bu}^t)\text{SiPh}_2\text{Bu}^t$ gave unidentified species. However, in the presence of phosphine PMe_3 , the silyl ligand in both complexes $(\text{RCH}_2)_2\text{Ta}(=\text{CHR})\text{SiPh}_2\text{Bu}^t$ undergo μ -H abstraction with an alkyl ligand to give bis(alkylidene) complexes $(\text{RCH}_2)_2\text{Ta}(\text{PMe}_3)_2(=\text{CHR})_2$ (**3a**, **3c**, Scheme 1) [9]. $(\text{Bu}^t\text{CH}_2)_2\text{Ta}(\text{PMe}_3)_2(=\text{CH-Bu}^t)_2$ (**3c**) has been prepared by Schrock and co-workers [10] from the reaction of alkyl alkylidene $(\text{Bu}^t\text{CH}_2)_3\text{Ta}=\text{CHBu}^t$ with PMe_3 .

Silyl alkylidyne complexes $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)\text{-}(\text{SiR}_3)[\text{R}''_3 = \text{Ph}_2\text{Bu}^t, \text{4a}; (\text{SiMe}_3)_3, \text{4c}]$ were prepared in 58% (**4a**) and 90% (**4b**) isolated yields from the reactions of $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)\text{Cl}$ with $\text{Li}(\text{THF})_3\text{SiR}''_3$ (Scheme 2) [5,6]. The X-ray structures of both complexes were severely disordered, and the structure assignments and identification of the alkylidyne ligands in **4a** and **4c** were based on NMR and elemental analysis. **4a** was found to be in equilibrium with a silyl bis(alkylidene) tautomer **4b** (Scheme 2). α -H scrambling has been reported in d^0 alkyl and alkylidyne complexes $(\text{Bu}^t\text{CH}_2)_3\text{W}\equiv\text{C-R}$ ($\text{C-R}=\text{}^{13}\text{C-Bu}^t, \text{C-SiMe}_3$) [11] and a d^2 alkyl alkylidene complex $(\text{Bu}^t\text{CD}_2)_2\text{Os}(=\text{CHBu}^t)_2$ [12]. Such scrambling was proposed to proceed through bis(alkylidenes) and alkylidynes such as “ $(\text{Bu}^t\text{CH}_2)_2\text{-W}(=\text{CHBu}^t)_2$ ” and “ $(\text{Bu}^t\text{CH}_2)_3\text{Os}\equiv\text{CBu}^t$,” respectively. The equilibrium between **4a** and **4b** was the



Scheme 1.



Scheme 2.

first directly observed exchange between alkyl alkylidene and bis(alkylidene) complexes. Density functional molecular orbital calculations suggest that the large π -accepting ability of silyl ligands increases the relative stability of the bis(alkylidene) tautomer [13].

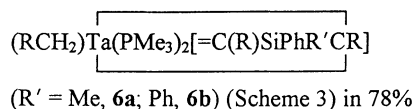
3. Reactions of alkylidene complexes with silanes

3.1. Preparation of novel metallasilacyclobutadiene and metalladisilacyclohexadiene complexes

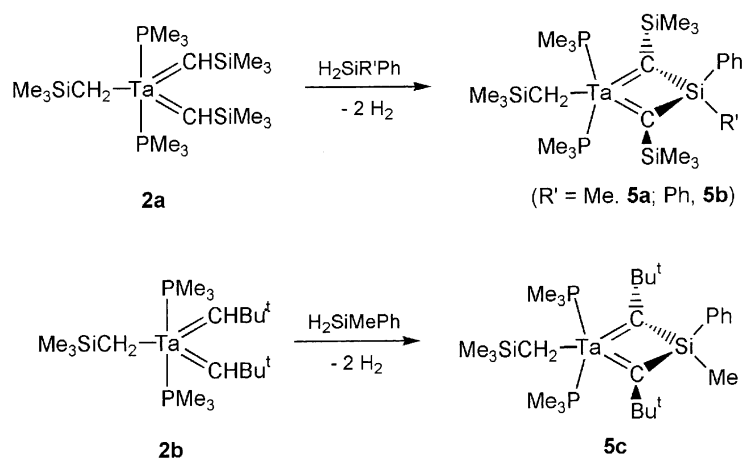
We have been interested in the reactions of coordinated ligands with silanes to investigate the nature of such reactions and their potential applications in elucidating the mechanistic pathways in the formation of solid-state materials [14]. Before we obtained the alkylidene complexes with phosphine ligands $(\text{RCH}_2)_2\text{Ta}(\text{PMe}_3)_2(\text{C}=\text{CHR})_2$ ($\text{R} = \text{SiMe}_3$, **3a**; Bu^t , **3c**), we had investigated the reactions of $(\text{Bu}^t\text{CH}_2)_3\text{Ta}=\text{CHBu}^t$ with silanes. $(\text{Bu}^t\text{CH}_2)_3\text{Ta}=\text{CHBu}^t$ was found to react with SiH_4 to give amorphous solids which contained both Ta and Si. Trapping of the volatiles from the reaction and analysis by NMR showed neopentane (CMe_4) to be among the reaction products [15]. Reactions of $(^t\text{BuCH}_2)_3\text{Ta}=\text{CHBu}^t$ with substituted silanes H_3SiPh and H_2SiPh_2 in benzene- d_6 were also investigated, but the reactions were found to be very slow and only unidentified products were obtained. Addition of $(^t\text{BuCH}_2)_3\text{Ta}=\text{CHBu}^t$ to neat H_3SiPh

resulted in an immediate vigorous reaction with gas evolution and the formation of an intractable black tar.

In order to further study the reaction of alkylidene complexes with silanes, we turned to alkylidene complexes containing phosphine ligands, in the hope that such ligands would help stabilize the resulting reaction products. The first reactions tested were those between $(\text{RCH}_2)_2\text{Ta}(\text{PMe}_3)_2(\text{C}=\text{CHR})_2$ ($\text{R} = \text{SiMe}_3$, **3a**) and $\text{H}_2\text{SiR}'\text{Ph}$ ($\text{R}' = \text{Me}, \text{Ph}$). Smooth reactions in benzene- d_6 at 23 °C were observed with the evolution of gaseous H_2 and the formation of novel 1,1'-metalla-3-silacyclobutadiene complexes



(6a) and 44% **(6b)** isolated yields. The amount of H_2 yielded in the reaction was not measured, and it is reasonable to assume the amount is one equivalent based on the nearly quantitative yields of $(\text{RCH}_2)_3\text{Ta}=\text{CR}(\text{SiHR}'\text{Ph})$ (**2**) from the reactions of $(\text{RCH}_2)_3\text{Ta}(\text{PMe}_3)(\text{C}=\text{CHR})$ (**1**) with $\text{H}_2\text{SiR}'\text{Ph}$ [4]. Preferential reactions with the alkylidene ligands were observed, and the products were inert to excess silane. We then probed whether such a preference was general. $(\text{Me}_3\text{SiCH}_2)_2\text{Ta}(\text{PMe}_3)_2(\text{C}=\text{CHBu}^t)_2$ (**3b**) containing mixed ligands was prepared, and found to react with H_2SiMePh to generate H_2 and a metallasilacyclobutadiene complex **6c** in 38% isolated yield



Scheme 3.

(Scheme 3). However, the reaction of the neopentyl analog of **3a**, $(^t\text{BuCH}_2)\text{Ta}(\text{PMe}_3)_2(\text{=CHBu}^t)_2$ (**3c**), with H_2SiMePh was found to give H_2 , CMe_4 , PMe_3 , and a mixture of unidentified complexes. It is not clear why this reaction did not give a metallasilacyclobutadiene complex. β - SiMe_3 groups in $-\text{CH}_2\text{SiMe}_3$ and $=\text{C}(\text{SiMe}_3)-$ ligands in **6a–c** perhaps help stabilize the metal-carbon bonds in these complexes [16]. In addition, the reaction of $(^t\text{BuCH}_2)\text{Ta}(\text{PMe}_3)_2(\text{=CHBu}^t)_2$ (**3c**) with H_2SiMePh may give a product too sterically crowded to be stable.

We further investigated the reaction of **3a** with disilylmethane $(\text{H}_2\text{PhSi})_2\text{CH}_2$ [4a,17], and obtained a metalladisilacyclohexadiene complex **7** in 10% isolated yield (Scheme 3). No further products could be isolated from the reaction mixture. The X-ray structure of crystalline **7** revealed it is the meso-isomer, in which both phenyl rings on the two stereogenic Si atoms occupy pseudo-equatorial positions on the metalladisilacyclohexadiene ring.

3.2. Kinetic and mechanistic studies of the reactions between alkylidene complexes and silanes

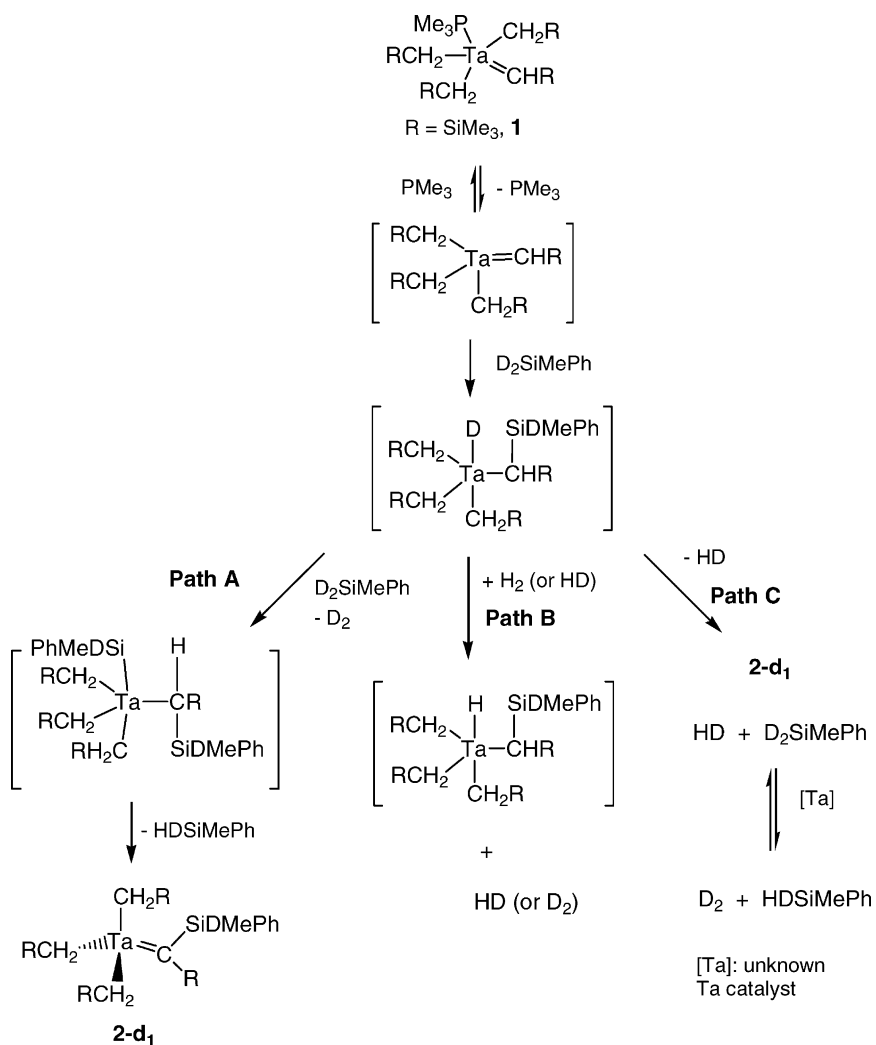
The unexpected formation of metallasilacyclobutadiene and metalladisilacyclohexadiene complexes prompted us to study the mechanism of the reactions between d^0 alkylidenes and silanes. The reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)=\text{CHSiMe}_3$ (**1**) with 2.1 eq. of D_2SiMePh gave $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}[\text{C}(\text{SiMe}_3)\text{SiD}-$

$\text{MePh}]$ (**2-d**₁) with H incorporation into excess D_2SiMePh to yield HDSiMePh and H_2SiMePh . When a large excess of D_2SiMePh (>10 equivalents) was used, only HDSiMePh was found. Additional studies ruled out the possibility that H incorporation into D_2SiMePh is the result of exchanges between D_2SiMePh and $-\text{CH}_2\text{SiMe}_3$ ligands in **1** or the residual hydrogen in the NMR solvent toluene- d_8 .

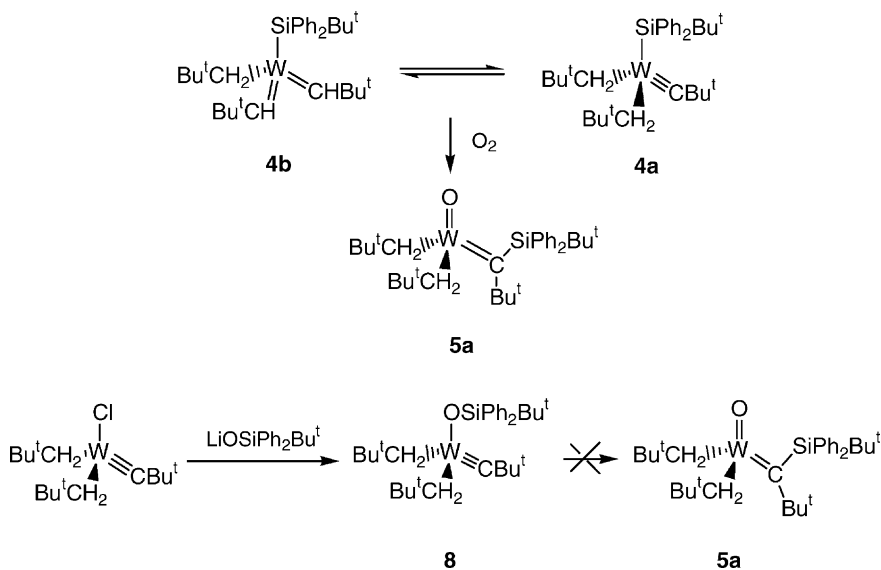
Analysis of the gaseous products from the reaction of $(\text{Me}_3\text{SiCH}_2)_3\text{Ta}(\text{PMe}_3)=\text{CHSiMe}_3$ (**1**) with D_2SiMePh by mass spectrometry showed that D_2 was the major product in the reaction, and the ratios of D_2 , HD, and H_2 changed slightly when $\text{D}_2\text{SiMePh}/\mathbf{1}$ ratios varied from ca. 1 to 5. When this reaction with D_2SiMePh was conducted in the presence of added H_2 , the products and H_2 were found to undergo hydrogen scrambling. Kinetic studies of the reactions of **1** with H_2SiMePh and D_2SiMePh showed that the reaction with D_2SiMePh was slower than that with H_2SiMePh with a kinetic isotope effect value of 1.87. Results of the kinetic studies are consistent with a pathway involving the loss of a PMe_3 ligand to open a coordination site on the Ta center, followed by rate-determining addition of the silane to the Ta=C bond possibly through nucleophilic attack on the silane by the π -electron density of the alkylidene bond, leading to the formation of a product in which a new carbon-silicon bond is formed. Similar attacks of silanes by alkyl or amido ligands to

give metal hydride complexes and alkylsilanes or amidosilanes have recently been reported [14,18]. The three processes in Scheme 4 are consistent with the results of these kinetic and D-labeling studies. The mechanism shown in Path A accounts for the preferential formation of D₂ and the H incorporation into the unreacted D₂SiMePh to give HDSiMePh in the D-labeling studies. It should be noted that Path A first requires H-SiHMePh addition to the Ta=C bond to give the H-Ta-C'-Si moiety (C'=CHR), and at the last step requires the elimination of H-SiDMePh from an intermediate with the Si-Ta-C'-H moiety

[C'=C(SiDMePh)R] of opposite regiochemistry. Paths B and C are consistent with the observations of H scrambling in products when H₂ was added. In Path B, an intermediate with a deuteride ligand undergoes σ-bond metathesis with H₂ (or HD) to give HD (or D₂). Path C in Scheme 4, followed by the exchange HD + D₂SiMePh ⇌ D₂ + HDSiMePh, may explain the observed hydrogen scrambling process. Another process that may occur is a σ-bond metathesis reaction involving the α-C and H atoms of the Ta=CHSiMe₃ ligand in **1** and the incoming D₂SiMePh yielding HD and **2-d₁** as products.



Scheme 4.



Scheme 5.

4. Silyl migration to give a silyl-substituted alkylidene complex

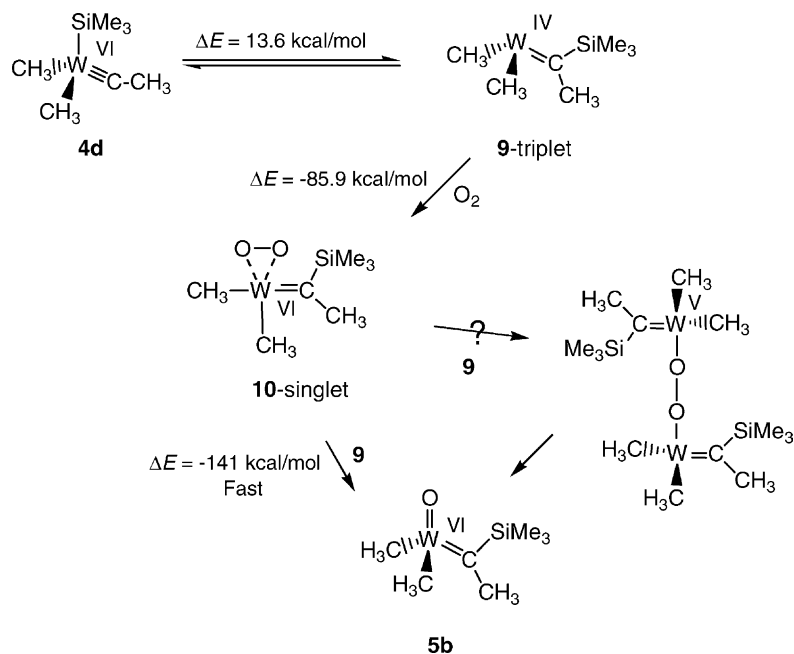
When a yellow-orange solution of an equilibrium mixture of $(\text{Bu}^t\text{CH}_2)_2\text{W}(\text{=CHBu}^t)_2(\text{SiPh}_2\text{Bu}^t)$ (**4b**) \rightleftharpoons $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiPh}_2\text{Bu}^t)$ (**4a**) was exposed to gaseous O_2 , a rapid reaction occurred to give a silyl-substituted alkylidene complex $(\text{Bu}^t\text{CH}_2)_2\text{W}(\text{=O})[\text{C}(\text{Bu}^t)(\text{SiPh}_2\text{Bu}^t)]$ (**5a**, Scheme 5). **5a** was characterized by NMR, single-crystal X-ray diffraction, and elemental analysis [5]. In benzene- d_6 with 1 eq. of O_2 at 23°C , 32% of **4** reacted with O_2 within 20 min, and 68% of **4** still remained in the reaction mixture. The silyl ligand in $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{SiPh}_2\text{Bu}^t)$ (**4a**) migrated to the alkylidyne ligand to give a silyl-substituted alkylidene ligand $(\text{=C}(\text{Bu}^t)(\text{SiPh}_2\text{Bu}^t))$ in **5a**. To our knowledge, this is the first observation of such a silyl migration to give a silyl-substituted alkylidene ligand. Ahn and Mayr [19] have reported a formal insertion of an alkylidyne group into a W–N bond in the reaction of Br_2 with $\text{TpW}(\text{=CHPh})(\text{=X})\text{Br}$ (Tp = tris(pyrazolyl)borate; X = NR, O).

We have conducted additional experimental and theoretical studies to elucidate the mechanistic pathway in the formation of the unusual silyl-substituted alkylidene **5a**. Siloxy complex $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv$

$\text{CBu}^t)(\text{O-SiPh}_2\text{Bu}^t)$ (**8**) [20] was prepared from the reaction of $(\text{Bu}^t\text{CH}_2)_2\text{W}(\equiv\text{CBu}^t)(\text{Cl})$ and $\text{LiO-SiPh}_2\text{Bu}^t$ [21]. This thermally stable complex does not convert to $(\text{Bu}^t\text{CH}_2)_2\text{W}(\text{=O})[\text{C}(\text{Bu}^t)(\text{SiPh}_2\text{Bu}^t)]$ (**5a**, Scheme 5). This rules out **8** as an intermediate in the formation of **5a**. In other words, it is unlikely that the $-\text{SiPh}_2\text{Bu}^t$ ligand migrates to the alkylidyne ligand in **8** to give **5a**.

Ab initio quantum chemical calculations at the B3LYP/HW3 level were performed for a model complex $(\text{CH}_3)_2\text{W}(\equiv\text{C-CH}_3)(\text{SiMe}_3)$ (**4d**) [20]. These studies revealed a likely pathway, shown in Scheme 6, in the formation of the silyl-substituted alkylidene complexes. The silyl ligand in **4d** migrates to the alkylidyne ligand to give a d^2 , triplet **9**. In this process, the formal oxidation state of Si has changed from +2 in **4d** to +4 in **9**,¹ leading to W reduction from VI to IV. Complex **9** then reacts with O_2 to form an O_2 adduct (**10**). Further reaction of this O_2 adduct **10** with another molecule of **9** gives the product $(\text{CH}_3)_2\text{W}(\text{=O})[\text{C}(\text{CH}_3)(\text{SiMe}_3)]$ (**5b**). The first step, silyl migration, is endothermic. However, the next two steps, an oxidation of the oxophilic, d^2 W by O_2

¹ Carbon is more electronegative than silicon (the Pauling electronegativities of carbon and silicon are 2.55 and 1.90, respectively). Si–C bond is thus polarized ($\text{Si}^{\delta+}\text{-C}^{\delta-}$).



Scheme 6.

from the formal oxidation state of IV to VI, are highly exothermic, driving the formation of the product.

Our studies of the preparation of disilyl- and silyl-substituted alkylidene complexes and the mechanistic studies of their formation demonstrate two examples of novel reactivities of Si-containing species which are not known for their carbon analogs. Still not clear about the reactions between the alkylidene complexes and silanes is the role of the phosphine ligands and phenyl groups in the silanes [4]. The scope of both the reactions of alkylidenes with silanes to give disilyl-substituted alkylidene complexes and silyl to alkylidyne migration deserves further studies.

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