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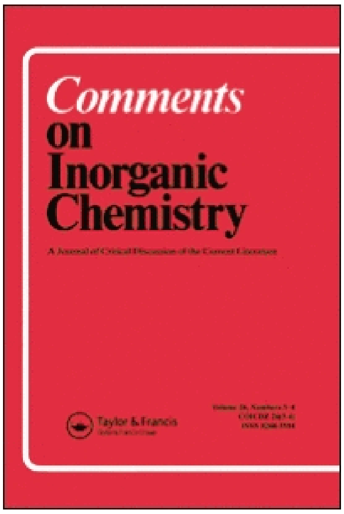

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Early-Transition-Metal Silyl Complexes Free of Anionic π-Ligands. A Comparison of Alkyl and Silyl Ligands

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Early-Transition-Metal Silyl Complexes Free of Anionic π-Ligands. A Comparison of Alkyl and Silyl Ligands*

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Received January 27, 1996

A new family of silyl complexes, $(RCH_2)_3MSiR'_3$ (M = Ti, Zr), $(RCH_2)_2Ta(=CHR)SiR'_3$ and $(RCH_2)_2W(\equiv CR)SiR'_3$, which are free of cyclopentadienyl (Cp) or other supporting anionic π-ligands, have been prepared and characterized. The silyl ligands are found to be more reactive than the alkyl ligands in the silyl alkyl and silyl alkylidene complexes. Silane ($HSiR'_3$) elimination to form metal–carbon multiple bonds is preferred over alkane (RCH_3) elimination. In the formation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ from the reaction of $(Me_3SiCH_2)_3TaCl_2$ with 2 equiv of $Li(THF)_3Si(SiMe_3)_3$, an intermediate $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ was identified. The first step in the conversion of this intermediate to $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ is a silane $[HSi(SiMe_3)_3]$ elimination reaction to form "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$". The dimer of "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$", $(Me_3SiCH_2)_4(Cl)_2Ta_2(=CHSiMe_3)_2$, was observed in the formation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ and in the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$. Subsequent Cl^- substitution by $Si(SiMe_3)_3^-$ leads to the formation of the silyl alkylidene complex. In comparison, the first step in the reaction of $(RCH_2)_4TaCl$ (R = CMe_3, $SiMe_3$) with $LiCH_2R$ to form alkyl alkylidene complexes $(RCH_2)_3Ta{=}CHR$ is Cl^- substitution by CH_2R^- to form $Ta(CH_2R)_5$. Subsequent alkane

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*Dedicated to Professor Herbert D. Kaesz, a scientist, mentor and friend.

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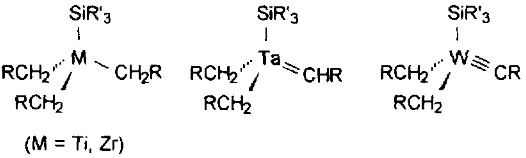
elimination gives $(RCH_2)_3Ta{=}CHR$. The kinetic and mechanistic studies of these processes will be discussed.

Key Words: *silyl complexes, early transition metals, alkyl, alkylidene, alkylidyne complexes, α-hydrogen abstraction*

INTRODUCTION

Transition-metal silyl chemistry has been a subject of intense study for four decades, since the report in 1956 of the preparation of (η^5-Cp)$(CO)_2FeSiMe_3$ (Cp = cyclopentadienyl) by Wilkinson and co-workers, the first compound known to contain a transition metal–silicon bond.[1] The family of transition-metal silyl compounds now includes almost all of the transition elements.[2] The large majority of these silyl complexes are those of late-transition-metal elements; many coordinatively saturated, electron-rich transition-metal silyl complexes are quite stable. The chemistry of electron-poor early-transition-metal silyl compounds is, however, comparatively young.[2] The studies in this area have been focused mostly on silyl compounds supported by Cp or analogous anionic π-ligands; the work of many researchers has laid a solid foundation in this area.[2a,3] The presence of such ligands in, e.g., $Cp_2Zr(SiR_3)R'$,[4a] $Cp_2Ta(=CH_2)SiH^tBu_2$[4b] and $Cp_2W(\eta^2\text{-}Me_2Si{=}SiMe_2)$,[4c] is believed to contribute to the enhanced stabilities of these silyl compounds. The few known Cp-free early-transition-metal silyl complexes, such as $V(CO)_6SiH_3$,[5]$(Me_3CO)_3MSi(SiMe_3)_3$(M = Zr, Hf)[6] and $(Me_3P)_3W(H)_2I(SiMe_3)$,[7] usually contain carbonyls, alkoxides or phosphines as ancillary ligands.[8]

We began studying the following new family of Cp-free early-transition-metal silyl complexes (Scheme 1) in 1993. Our initial interest in these alkyl, alkylidene and alkylidyne silyl complexes originated from our proposal to investigate the reactions between silane SiH_4 and $M(CH_2R)_4$, $(RCH_2)_3M{=}CHR$, or $(RCH_2)_3M{\equiv}CR$, and the chemistry involved in these processes. The novel silyl complexes in Scheme 1 were proposed as models for the possible intermediates in these reactions. Realizing that these complexes offered unique opportunities to compare the reactivities of alkyl and silyl ligands free of the influence of Cp or other ancillary ligands, we subsequently concentrated our efforts in this area. The aim of this *Comment* is to discuss: (1) the synthesis, characterization and structural features of these Cp-free silyl complexes; (2) a comparison, through kinetic and mechanistic studies, of the formation of M=CHR bonds in a



SCHEME 1

silyl alkylidene complex $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ and in alkyl alkylidene complexes $(RCH_2)_3Ta{=}CHR$ (R = CMe_3, $SiMe_3$).

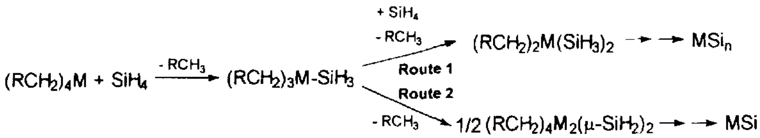
1. Cp-FREE SILYL COMPLEXES AND THE REACTIONS OF SiH_4 WITH ALKYL, ALKYLIDENE AND ALKYLIDYNE COMPOUNDS

Our preliminary results show that silane SiH_4 reacts with $Ti(CH_2CMe_3)_4$, $(Me_3CCH_2)_3Ta{=}CHCMe_3$, or $(Me_3CCH_2)_3W{\equiv}CCMe_3$; the gaseous product is neopentane CMe_4.[9] We have been studying these σ-bond metathesis reactions to explore novel molecular routes to metal silicides MSi_n, an important class of microelectronic, high-temperature and IR detector materials.[10]

Alkyl ligands in metallocenes Cp_2MR_2 (M = Ti triad) and $TiMe_2(dmpe)_2$ have been found to undergo, among other processes, similar σ-bond metathesis with silanes $H_xSiR'_{4-x}$ (Eq. (1)).[3a,11,12]

$$\begin{gathered} M'{-}R + H{-}Si \rightarrow M'{-}Si + H{-}R \\ [M' = Cp_2MR{-}\text{and } (dmpe)_2TiMe] \end{gathered} \tag{1}$$

It would be of interest to study how such metathesis would occur in our *proposed* reactions of $M(CH_2R)_4$, $(RCH_2)_3M{=}CHR$, or $(RCH_2)_3M{\equiv}CR$ with SiH_4, where all the $M{-}CH_2R$, $M{=}CHR$ and $M{\equiv}CR$ bonds are expected to react with the Si–H bonds. In the reaction between $M(CH_2R)_4$ and SiH_4, the first step in the reaction might give $(RCH_2)_3M{-}SiH_3$. Then there are several possible routes by which this intermediate could further react. The *proposed* reactions are shown in Scheme 2. $(RCH_2)_3M{-}SiH_3$ could react with *another* SiH_4 (Route 1) to form $(RCH_2)_2M(SiH_3)_2$ (Si/M ratio = 2) and eventually *silicon-rich* MSi_n ($n \geq 2$). It could also go through *intramolecular* σ-bond metathesis (Route 2) to form $(RCH_2)_2M{=}SiH_2$ or, *more likely*, a dimer

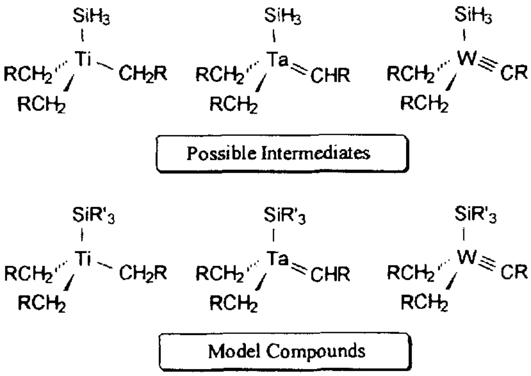


SCHEME 2

$(RCH_2)_4M_2(\mu\text{-}SiH_2)_2$. Route 2 may lead to MSi which retains M/Si = 1 as in $(RCH_2)_3M\text{–}SiH_3$. A key question is what factors control the reactivities of the intermediate $(RCH_2)_3M\text{–}SiH_3$.

In the reactions of $(RCH_2)_3M{=}CHR$ or $(RCH_2)_3M{\equiv}CR$ with SiH_4, similar pathways may exist with $(RCH_2)_2M({=}CHR)SiH_3$ or $(RCH_2)_2M({\equiv}CR)SiH_3$ as the possible intermediates.

We proposed to use $(RCH_2)_3MSiR'_3$, $(RCH_2)_2M({=}CHR)SiR'_3$ and $(RCH_2)_2M({\equiv}CR)SiR'_3$ (R′ = H, alkyl) as models for the possible intermediates (Scheme 3). Besides the potential relevance of these model compounds to the possible intermediates, we were also interested in the chemistry of these model compounds since, except for a few silyl complexes with CO, alkoxides, or phosphine ligands, chemistry of Cp-free early-transition-metal silyl complexes was an unexplored area. With such a two-fold interest, we started the first step—preparation of these novel Cp-free silyl complexes.



SCHEME 3

2. SYNTHESES AND CHARACTERIZATION

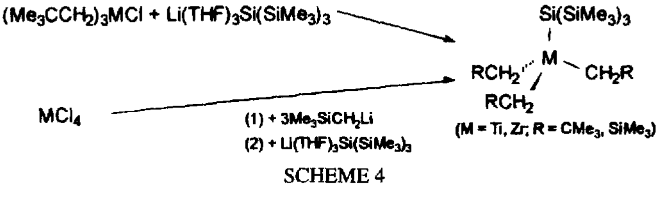
The primary method that we used to prepare these Cp-free silyl complexes was the substitution of a halide ligand such as Cl^- by a silyl anion $SiR'_3{}^-$.

2.1 Alkyl Silyl Compounds $(RCH_2)_3M{-}Si(SiMe_3)_3$ (M = Ti, Zr; R = CMe_3, $SiMe_3$) (Refs. 13 and 14)

The reactions used to synthesize these compounds are shown in Scheme 4. They are almost instantaneous at 23°C with the precipitation of LiCl.[15] These compounds are thermally stable in crystalline form, showing little or no degradation over several days in the dark at room temperature. The Zr complexes are significantly more stable than the Ti analogues. $(Me_3CCH_2)_3Zr{-}Si(SiMe_3)_3$ could be sublimed in darkness at 40°C without significant decomposition.

The two titanium complexes $(RCH_2)_3Ti{-}Si(SiMe_3)_3$ (R = CMe_3, $SiMe_3$) were characterized by X-ray diffraction; the molecular structure of the trimethylsilylmethyl compound is shown in Fig. 1. The crystal structures reveal threefold symmetry axes along the Ti–Si bonds with the alkyl groups on the metal center in staggered conformations with respect to the trimethylsilyl groups on the central silicon atom. The three alkyl and the silyl ligands present a pseudo-tetrahedral geometry around the metal centers. The coordination about the α-carbon atoms is greatly distorted from tetrahedral [Ti–C–C angle of 141.7(12)° (mean) in $(Me_3CCH_2)_3Ti{-}Si(SiMe_3)_3$ and Ti–C–Si angle of 130.4(4)° in $(Me_3SiCH_2)_3Ti{-}Si(SiMe_3)_3$]. No evidence of an agostic interaction was seen in their variable-temperature NMR spectra. The widening of the Ti–C–C (or Si) bond angles is probably caused by steric strain.

In comparison, the crystal structure of the similarly arranged alkoxy/silyl zirconium compound $(Me_3CO)_3ZrSi(SiMe_3)_3$[6] shows a mean O–Zr–O angle of 111.4(4)° and a mean O–Zr–Si angle of 107.6(3)°. The



SCHEME 4

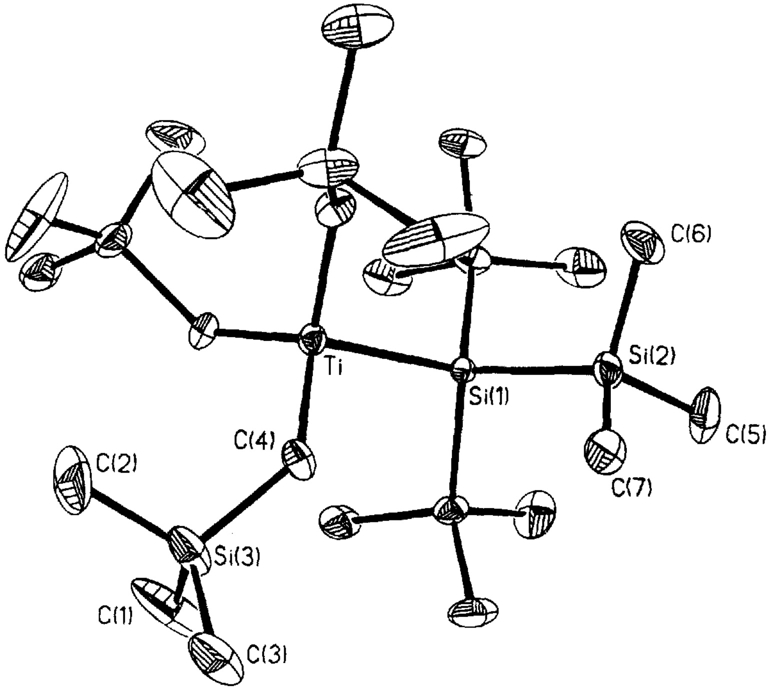
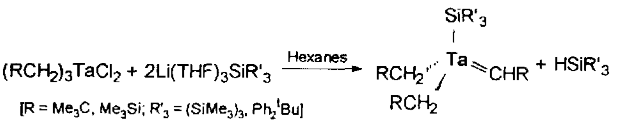


FIGURE 1 ORTEP diagram of $(Me_3SiCH_2)_3Ti{-}Si(SiMe_3)_3$ (Ref. 14).

Zr–O–C angle in the alkoxy complex [165(1)°] is larger than the mean Ti–C–C angle in $(Me_3CCH_2)_3Ti{-}Si(SiMe_3)_3$ and Ti–C–Si angle in $(Me_3SiCH_2)_3Ti{-}Si(SiMe_3)_3$, and is consistent with the assumption of some degree of O(pπ)–Zr(dπ) bonding in $(Me_3CO)_3ZrSi(SiMe_3)_3$.[6]

2.2 Alkylidene Silyl Compound $(RCH_2)_2Ta(=CHR)SiR'_3$ (Refs. 13 and 16)

The reactions used to synthesize these Schrock-type alkylidene compounds[17] are shown in Eq. (2).

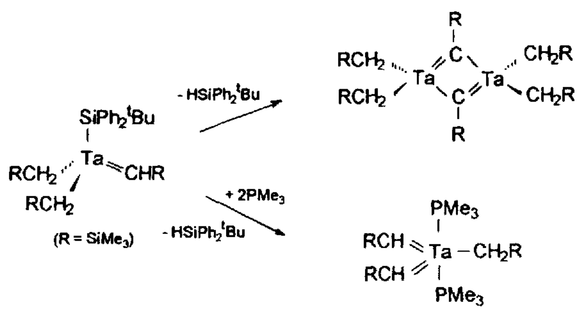


$$(RCH_2)_3TaCl_2 + 2Li(THF)_3SiR'_3 \xrightarrow{\text{Hexanes}} (RCH_2)_2Ta(=CHR)(SiR'_3) + HSiR'_3 \qquad (2)$$

$[R = Me_3C, Me_3Si;\ R'_3 = (SiMe_3)_3, Ph_2{}^tBu]$

The lithium silylating reagent $Li(THF)_3SiR'_3$ (2 equiv) reacts instantaneously with 1 equiv of the trialkyl tantalum dichloride to form the alkylidene silyl compounds and 1 equiv of the corresponding silane $HSiR'_3$ in high yield. α-Hydrogen abstraction reactions between the silyl groups and alkyl ligands led to the formation of the alkylidene bonds. The two complexes with $SiPh_2{}^tBu$ ligands, $(Me_3CCH_2)_2Ta(=CHCMe_3)SiPh_2{}^tBu$ and $(Me_3SiCH_2)_2Ta(=CHSiMe_3)SiPh_2{}^tBu$, were found to be unstable at 23°C; the latter undergoes α-hydrogen abstraction between the silyl group and the alkylidene ligand to form $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$, a bridging bis(alkylidyne) complex first reported by Wilkinson and co-workers[18] (Scheme 5). However, when phosphine (PMe_3) was added to $(Me_3SiCH_2)_2Ta(=CHSiMe_3)SiPh_2{}^tBu$, a phosphine adduct was formed; its NMR spectra are consistent with a formula $(Me_3SiCH_2)(Me_3SiCH=)_2Ta(PMe_3)_2$ with two alkylidene ligands.[19] It was perhaps formed through α-hydrogen abstraction between the silyl ligand and a hydrogen atom of one alkyl ligand. It may also be the product of the reaction between "$(Me_3SiCH_2)_2(Me_3SiC\equiv)Ta$" and PMe_3 with α-hydrogen transfers. In the absence of PMe_3, "$(Me_3SiCH_2)_2(Me_3SiC\equiv)Ta$" perhaps dimerizes to give the bridging bis(alkylidyne) complex.

There are large chemical shift differences between the diastereotopic H_a and H_b atoms of the RCH_aH_b groups in ^1H NMR [1.96 ppm for $(Me_3CCH_2)_2Ta(=CHCMe_3)Si(SiMe_3)_3$ and 1.15 ppm for $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$]. No evidence in favor of agostic interaction was seen in the variable-temperature ^1H or ^{13}C NMR of the complexes. It appears that the chemical shift differences are due to the diamagnetic anisotropy of the Ta=C bonds.



SCHEME 5

The molecular structures of $(RCH_2)_2Ta(=CHR)Si(SiMe_3)_3$ (R = CMe_3, $SiMe_3$) have been determined; the structure of the trimethylsilylmethyl complex is shown in Fig. 2. Crystallographically imposed threefold rotation axes containing the Si–Ta bonds in both complexes result in disorders between the alkylidene and the two alkyl ligands. The Ta–C bond lengths are 1.97(3) and 2.03(4) Å, respectively, in the two complexes. In comparison, the Ta–C and Ta=C bond length are 2.285(10)–2.299(10) and 1.932(9)–1.937(9) Å in $[Ta(=CHCMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$,[20] and 2.17(2) and 1.89(3) Å in $Ta(=CHSiMe_3)(CH_2SiMe_3)(OC_6H_3{}^tBu_2\text{-}2,6)_2$.[21] In both silyl complexes, the $-Si(SiMe_3)_3$ and the alkyl(alkylidene)–Ta moieties are arranged in a staggered conformation which is similar to those observed in $(RCH_2)_3TiSi(SiMe_3)_3$ (R = CMe_3 and $SiMe_3$) and $(Me_3CO)_3ZrSi(SiMe_3)_3$.[6] The Ta–Si distances of 2.680(15) and 2.611(7) Å in the two silyl complexes compare favorably with the Ta–Si distances of 2.624(2)–2.633(2) Å in $Cp_2Ta(H)(SiMe_2H)_2$,[22] 2.669(4) Å in $(C_5Me_5)Ta(SiMe_3)Cl_3$,[23] and 2.651(4) Å in $Cp_2Ta(H)_2SiPhMe_2$.[24]

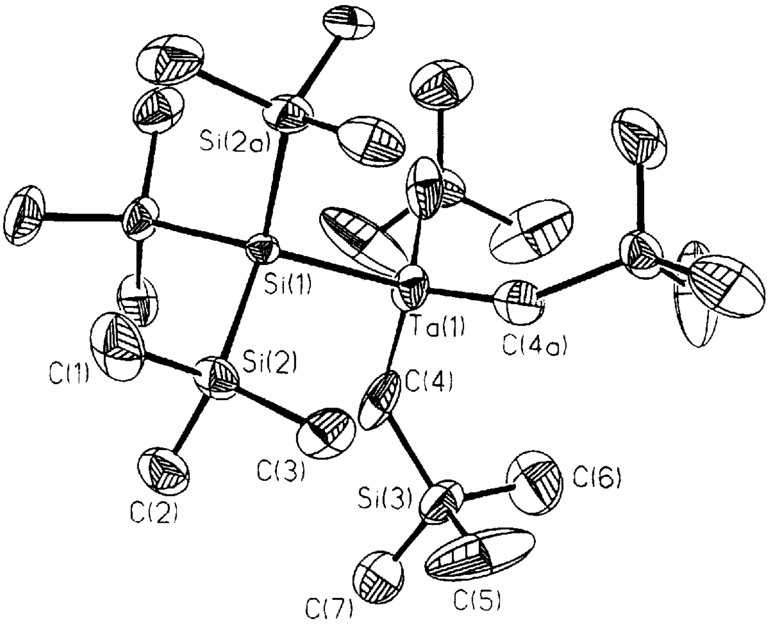


FIGURE 2 ORTEP diagram of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ (Refs. 13 and 16).

$(RCH_2)_2Ta(=CHR)Si(SiMe_3)_3$ (R = CMe_3 and $SiMe_3$) were found to react with 1 equiv of HCl at –78°C to form unstable purple complexes $(RCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (Eq.(3)).

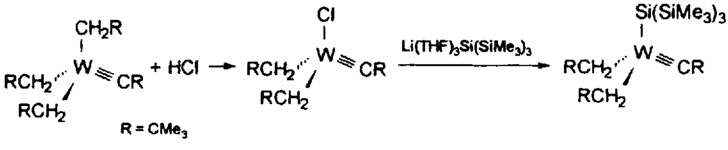
$$(RCH_2)_2Ta(=CHR)Si(SiMe_3)_3 + HCl \rightarrow (RCH_2)_3Ta(Cl)Si(SiMe_3)_3 (R = CMe_3, SiMe_3) \tag{3}$$

When $(Me_3SiCH_2)_2TaCl_2$ reacted with $Li(THF)_3Si(SiMe_3)_3$ at –78°C, the purple complex $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ was observed. The reactions of the purple complex with $Li(THF)_3Si(SiMe_3)_3$ and $LiCH_2SiMe_3$ form $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ and $(Me_3SiCH_2)_3Ta=CHSiMe_3$,[17d,25] respectively. Detailed kinetic and mechanistic studies will be presented in Section 3.

2.3 Alkylidyne Silyl Compound $(Me_3CCH_2)_2W(\equiv CCMe_3)Si(SiMe_3)_3$ (Ref 13)

This first silyl alkylidyne compound, a model for $(RCH_2)_2W(\equiv CR)SiH_3$, was prepared by the reactions shown in Scheme 6. The starting Schrock-type alkylidyne complex[26] contains a $W\equiv CCMe_3$ moiety, which is retained during synthesis. In comparison, the Ta=CHR bonds are formed through α-hydrogen abstraction during the formation of the alkylidene silyl complexes. There is a large chemical shift difference (4.56 ppm) between the diastereotopic H_a and H_b atoms of the RCH_aH_b groups in ^1H NMR as a result of the diamagnetic anisotropy of the W≡C bond.

In our studies of $(Me_3SiCH_2)_3W\equiv CSiMe_3$ and our attempt to prepare "$(Me_3SiCH_2)_2W(\equiv CSiMe_3)Si(SiMe_3)_3$" by reactions similar to those in Scheme 6, we were surprised by the difference in reactivity between $(Me_3SiCH_2)_3W\equiv CSiMe_3$ and the neopentyl analog $(Me_3CCH_2)_3W\equiv CCMe_3$.[26] The reaction of $(Me_3SiCH_2)_3W\equiv CSiMe_3$ with HCl does *not* lead to the elimination of $SiMe_4$ and our target compound "$(Me_3SiCH_2)_2W(\equiv CSiMe_3)Cl$". Instead, the reaction, through an addition of HCl to the $W\equiv CSiMe_3$ bond, produces a thermally unstable alkylidene



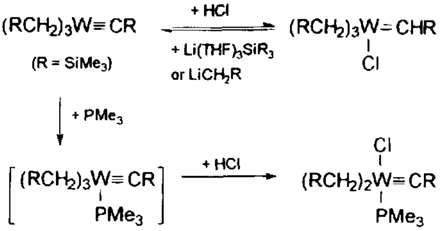
SCHEME 6

compound with a formula consistent with $(Me_3SiCH_2)_3W(=CHSiMe_3)Cl$ from its NMR spectra. The addition of $Li(THF)_3Si(SiMe_3)_3$ or $LiCH_2SiMe_3$ to this alkylidene compound gives $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ back with the elimination of $HSi(SiMe_3)_3$ or $SiMe_4$. It is not clear if $Si(SiMe_3)_3^-$ directly attacks the alkylidene hydrogen atom or replaces the Cl^- ligand first before undergoing α-hydrogen abstraction to form the $W{\equiv}CSiMe_3$ bond. In the reaction of HCl with $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ in the presence of PMe_3, an alkylidyne product was isolated, which has been tentatively assigned to be $(Me_3SiCH_2)_2W(\equiv CSiMe_3)(Cl)(PMe_3)$. However, the reaction of this chloro alkylidyne compound with $Li(THF)_3Si(SiMe_3)_3$ does not lead to the replacement of the chloride ligand. Some unknown products form in the process. The reactions of $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ discussed here are summarized in Scheme 7.

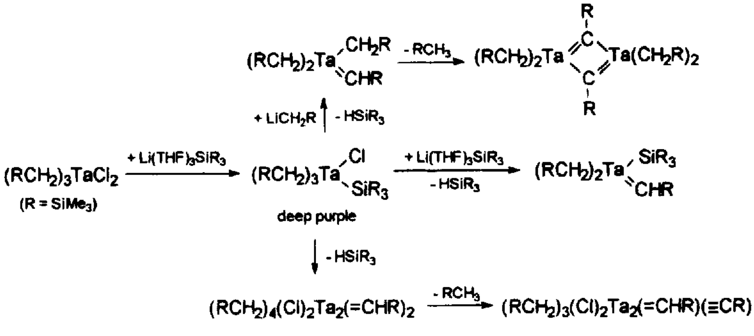
3. SILANE AND ALKANE ELIMINATION—A COMPARISON OF REACTIVITIES OF SILYL AND ALKYL LIGANDS IN THE FORMATION OF ALKYLIDENE BONDS

3.1 Preferential Silane Elimination in α-Hydrogen Abstraction Reactions

It is interesting to note that, in the quantitative formation of $(RCH_2)_2Ta(=CHR)SiR_3$ (Eq. (2)), there is an unprecedented *preferential* silane $[HSi(SiMe_3)_3]$ elimination through α-hydrogen abstraction to give the silyl alkylidene complex. Similar preferential silane eliminations have also been observed in other reactions summarized in Scheme 8. The unsta-



SCHEME 7



SCHEME 8

ble deep purple alkyl silyl intermediate $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ undergoes *silane elimination* in its reaction with $LiCH_2SiMe_3$ to form a Schrock-type alkyl alkylidene complex $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$. *Subsequent alkane elimination* (to be discussed in Section 3.3) converts $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$ into the bridging alkylidyne compound $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$.[18] In the presence of $Li(THF)_3Si(SiMe_3)_3$, the alkyl silyl intermediate $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ is converted to the silyl alkylidene complex $(Me_3SiCH_2)_2Ta({=}CHSiMe_3)Si(SiMe_3)_3$. $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ decomposes, *through silane elimination*, to form an unstable bis(alkylidene) complex $(Me_3\ SiCH_2)_4(Cl)_2Ta_2({=}CHSiMe_3)_2$. This silane elimination is then followed by *alkane elimination* to form an alkylidene alkylidyne complex $(Me_3SiCH_2)_3(Cl)_2Ta_2({=}CHSiMe_3)({\equiv}CSiMe_3)$.

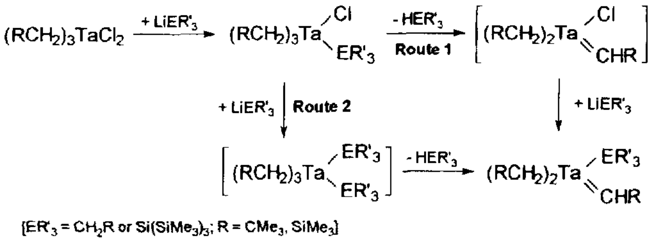
The reason for such preferential silane elimination is not clear. Experimental and theoretical studies of Si–X and C–X bond strengths reveal that the substituents with electronegativities closer to silicon tend to form stronger bonds to carbon than to silicon, due to higher ionic character in the C–X bonds.[27] If this principle applies to Si–Ta and C–Ta bond strengths, an analysis of electronegativities (Ta: 1.50; Si: 1.90; C: 2.55)[28] indicates that the Ta–C bonds are more polar and stronger than Ta–Si bonds. However, our *ab initio* quantum mechanics calculations[29] of the reactivities of $MCl_x(CH_3)_y(SiH_3)_z$ (M = Nb, Ta) show that CH_4 elimination is usually thermodynamically more favorable than SiH_4 elimination. The weaker M–Si bond in $MCl_x(CH_3)_y(SiH_3)_z$ may not be the reason for the preference for silane elimination. Such preference could be attributed to a kinetic effect; the calculated activation free energy is lower for silane elimination than for methane elimination by about 4–5 kcal/mol.[29]

3.2 Kinetic and Mechanistic Studies of the Formation of a Silyl Alkylidene Complex $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ (Ref. 16)

The principal difference between the structures of $(Me_3SiCH_2)_3Ta=CHSiMe_3$ and $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ is that the former contains three alkyl ligands and the latter is composed of two alkyl and one silyl ligands. These two complexes make an ideal case to compare the differences in reactivities between alkyl and silyl ligands.

The pioneering work of Schrock and others has laid solid foundations in the areas of alkylidene and alkylidyne complexes.[17,26] The discovery of a purple intermediate $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ in the formation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ prompted us to investigate the mechanistic pathways to the silyl alkylidene complex. We also studied the mechanistic pathways to alkyl alkylidene complexes $(RCH_2)_3Ta=CHR$ ($R = CMe_3$, $SiMe_3$).[30] We were surprised by the different pathways $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ and $(RCH_2)_4TaCl$ followed to form $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ and $(RCH_2)_3Ta=CHR$, respectively. Discussed below are the results of these studies and a comparison of reactivities of alkyl and silyl ligands.

Two possible pathways for the reactions of $(RCH_2)_3Ta(Cl)ER'_3$ [$ER'_3 = CH_2R$, $Si(SiMe_3)_3$, $R = CMe_3$, $SiMe_3$] with $LiER'_3$ to form $(RCH_2)_2Ta(=CHR)ER'_3$ are listed in Scheme 9. Such pathways have been postulated for the reaction of $(Me_3CCH_2)_3TaCl_2$ with $LiCH_2CMe_3$



[$ER'_3 = CH_2R$ or $Si(SiMe_3)_3$; $R = CMe_3$, $SiMe_3$]

SCHEME 9

to form $(Me_3CCH_2)_3Ta{=}CHCMe_3$.[17] Currently there is no firm conclusion in the literature regarding the mechanisms of the formation of $(RCH_2)_2Ta(=CHR)ER'_3$. In Route 1, the first step is an α-hydrogen abstraction reaction by the ER'_3 ligand to eliminate HER'_3 and form an intermediate "$(RCH_2)_2Ta(=CHR)Cl$" containing an alkylidene bond. Subsequent Cl^- substitution by ER'^-_3 leads to the formation of the alkyl alkylidene or silyl alkylidene complex $(RCH_2)_2Ta(=CHR)ER'_3$. In other words, the alkylidene bond forms *before* the Cl^- substitution in Route 1. In Route 2, the first step is the Cl^- substitution to form a penta-coordinated $(RCH_2)_3Ta(ER'_3)_2$, followed by an α-hydrogen abstraction reaction to form $(RCH_2)_2Ta(=CHR)ER'_3$. The alkylidene bond is formed *after* the Cl^- substitution in Route 2.

In Route 1 (Scheme 9), if the first step in the reaction of $(RCH_2)_3Ta(Cl)ER'_3$ (α-hydrogen abstraction) is rate-determining, the reaction would follow first-order kinetics. The rate constants should be the same as the rates of the decomposition of $(RCH_2)_3Ta(Cl)ER'_3$, and independent of the concentrations of $LiER'_3$. If Route 2 is the pathway to $(RCH_2)_2Ta(=CHR)ER'_3$, the reaction probably would not follow first-order kinetics. Thus the reactivities of $(RCH_2)_3Ta(Cl)ER'_3$ and kinetic studies of its decomposition and reactions with $LiER'_3$ would provide information regarding the formation of the alkylidene complex.

We therefore studied the kinetics of the reactions of thermally unstable $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$. The decomposition of this purple intermediate was monitored by variable-temperature ^1H and ^{13}C NMR, and was found to follow first-order kinetics. Plots of $\ln(C/C_0)$ vs t and an Eyring plot of $\ln(k_1/T)$ vs T are shown in Figs. 3 and 4, respectively, from which the activation parameters for the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ [$\Delta H_1^{\neq} = 17.2(1.0)$ kcal/mol, $\Delta S_1^{\neq} = -4.2(4.0)$ eu] could be derived. Furthermore, the reaction of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ with $Li(THF)_3Si(SiMe_3)_3$ to form $(Me_3SiCH_2)_3Ta(=CHSiMe_3)Si(SiMe_3)_3$ and $HSi(SiMe_3)_3$ is kinetically identical to the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$; the rates of the two reactions are the same.

We further discovered that the decomposition of $(Me_3SiCH_2)_3$ $Ta(Cl)Si(SiMe_3)_3$ led to the formation of an unstable bis(alkylidene) complex $(Me_3SiCH_2)_2(Cl)_2Ta_2(=CHSiMe_3)_2$ which could be regarded as the dimer of "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$." This dimeric complex was also observed in the reaction of $(Me_3SiCH_2)_3TaCl_2$ with 2 equiv of $Li(THF)_3Si(SiMe_3)_3$. It was identified by its ^1H and ^{13}C NMR and

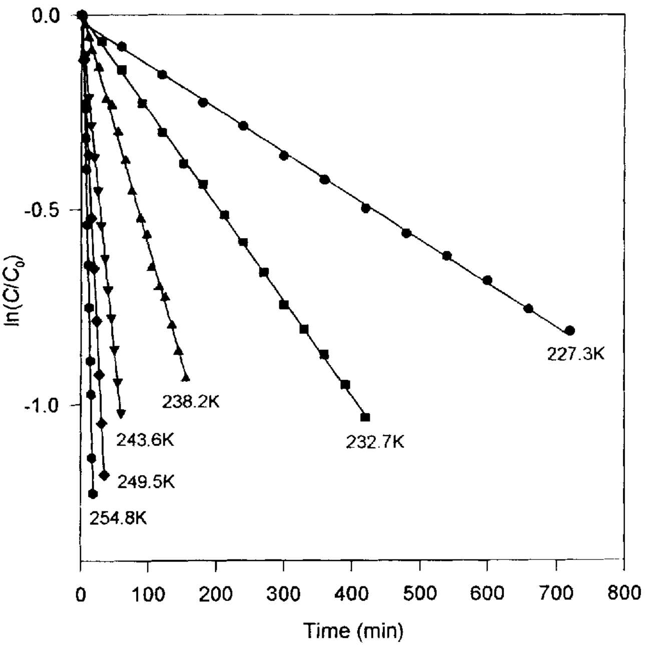


FIGURE 3 Kinetics plots of the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (Ref. 16).

independently synthesized by the reaction of $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ with 2 equiv of HCl (see Section 3.4 for details).

These results point to Route 1 in Scheme 9 as the pathway to the silyl alkylidene complex $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$. The alkylidene bond Ta=CHR is formed before the Cl^- substitution. The intermediate "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)Cl$" either reacts with $Li(THF)_3Si(SiMe_3)_3$ to form $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$, or dimerizes to give $(Me_3SiCH_2)_4(Cl)_4Ta_2(=CHSiMe_3)_2$ which reacts with $Li(THF)_3Si(SiMe_3)_3$ to form $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (see Section 3.4 for details). This bridging bis(alkylidyne) complex was observed as a byproduct in the formation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)Si(SiMe_3)_3$ from the reaction of $(Me_3SiCH_2)_3TaCl_2$ with $Li(THF)_3Si(SiMe_3)_3$. Thus our results here show that the formation of the silyl alkylidene complex and the byproduct $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ follow the pathways in Scheme 10.

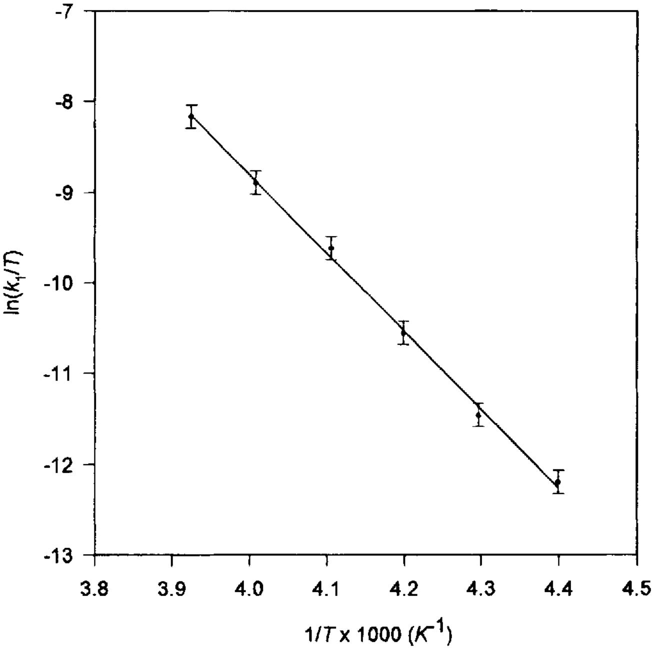
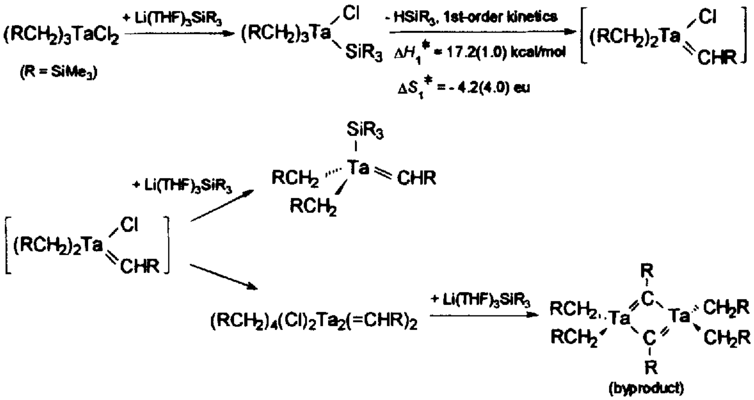


FIGURE 4 Eyring plot of the decomposition of $(Me_3SiCH_2)_3Ta(Cl)Si(SiMe_3)_3$ (Ref. 16).



SCHEME 10

3.3 Kinetic and Mechanistic Studies of the Formation of Alkyl Alkylidene Complexes $(RCH_2)_3Ta{=}CHR$ ($R = CMe_3$, $SiMe_3$) (Ref. 30)

Our pursuit of an unexpected result led us to the studies here. We soon realized the importance of these studies in demonstrating the striking differences in the reactivities of alkyl and silyl complexes.

The preparation of the first Schrock-type alkylidene complex $(Me_3CCH_2)_3Ta{=}CHCMe_3$ was reported in 1974.[17] The mechanistic pathways to the alkylidene complexes are not clear. Several thermally unstable pentaalkyl derivatives of tantalum, $Ta(CH_2R)_5$ (R = H,[31–33] Ph,[32,33] 4-methylbenzyl[34]), have been reported, which decompose via α-hydrogen abstraction to give unidentified residues and methane, toluene and *p*-xylene, respectively.[31–34]

As stated earlier, the bridging bis(alkylidyne) complex $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$, first reported in 1973,[18] was found as a byproduct in our synthesis of $(Me_3SiCH_2)_2Ta({=}CHSiMe_3)Si(SiMe_3)_3$. In the preparation of this bridging bis(alkylidyne) compound to confirm its presence in our systems, two peaks in the ^1H and ^{13}C NMR, which disappeared with time, caught our attention. Further studies confirmed that they were those of an unstable pentaalkyl intermediate $Ta(CH_2SiMe_3)_5$. $Ta(CH_2SiMe_3)_5$ was found to undergo α-hydrogen abstraction to first form a Schrock-type alkylidene complex $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$, then $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ as shown in Fig. 5 and Scheme 11.[30]

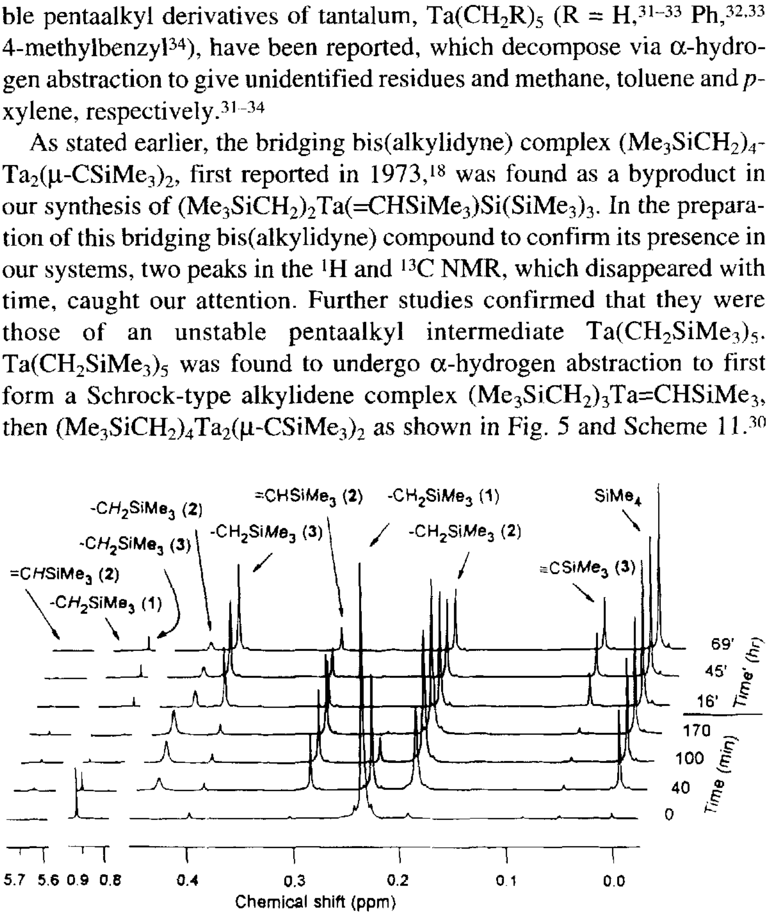
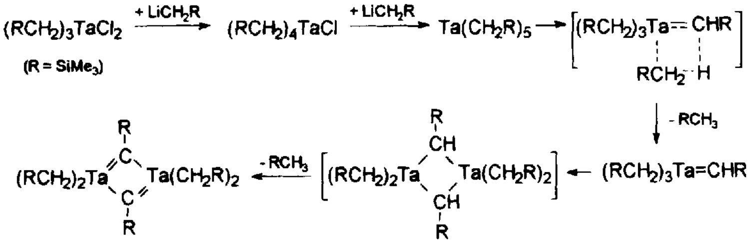


FIGURE 5 ^1H NMR (toluene-d_8) spectra of the conversions $(Me_3SiCH_2)_5Ta$ (**1**) → $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$ (**2**) → $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ (**3**) (Ref. 30).



SCHEME 11

The conversion of $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$ to the bridging bis(alkylidyne) complex has been reported by Schrock and Rupprecht.[17d,25]

The conversion $Ta(CH_2SiMe_3)_5 \rightarrow (Me_3SiCH_2)_3Ta{=}CHSiMe_3$ was observed to follow first-order kinetics with the activation parameters $\Delta H_2^{\neq} = 21.6(1.4)$ kcal/mol and $\Delta S_2^{\neq} = -5(5)$ eu.[30] The conversion $(Me_3SiCH_2)_3Ta{=}CHSiMe_3 \rightarrow (Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ was found to follow second-order kinetics. The activation parameters for this second-order reaction are $\Delta H_3^{\neq} = 6.2(0.3)$ kcal/mol and $\Delta S_3^{\neq} = -61.6(0.8)$ eu.[30]

Small $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ values have been observed in *associative* reactions that follow second-order kinetics.[35] In the conversion from a monomeric $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$ to a dimeric $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ discussed here, the second-order kinetics observed, the small $\Delta H_3^{\neq}$ and the unusually large negative $\Delta S_3^{\neq}$ values suggest that dimerization of $(Me_3SiCH_2)_3Ta{=}CHSiMe_3$ to an intermediate "$(Me_3SiCH_2)_3Ta(\mu\text{-}CHSiMe_3)_2Ta(CH_2SiMe_3)_3$" is an integral part of the mechanism. This dimerization, followed by rate-determining α-hydrogen abstraction steps, constitutes one pathway, but rate-determining dimerization is more plausible in view of the characteristic activation parameters.

$Ta(CH_2CMe_3)_5$ was also observed as an intermediate in the reaction of $(Me_3CCH_2)_3TaCl_2$ with 2 equiv of $LiCH_2CMe_3$ to give the alkylidene complex $(Me_3CCH_2)_3Ta{=}CHCMe_3$ (Fig. 6).[30] $(Me_3CCH_2)_4TaCl$, previously reported by Schrock and Fellmann,[17b] was identified as an intermediate as well. The results presented here indicate the mechanistic pathway shown in Scheme 12 for the formation of the Schrock-type alkylidene complex $(Me_3CCH_2)_3Ta{=}CHCMe_3$.

In the alternate possible mechanistic pathway (Route 1, Scheme 9), a reasonable assumption is that forming "$(Me_3CCH_2)_2Ta({=}CHCMe_3)Cl$"

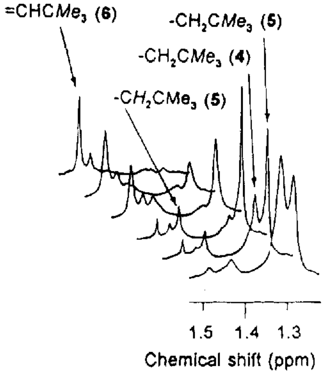
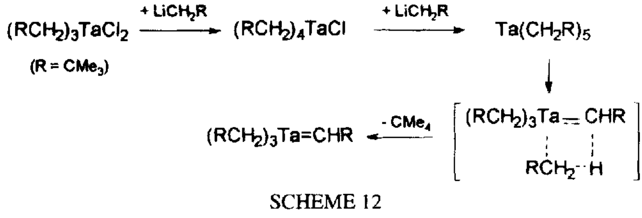


FIGURE 6 A portion of the ^{1}H NMR (toluene-d_8) spectra of the conversions $(Me_3CCH_2)_4TaCl$ (**4**) → $Ta(CH_2CMe_3)_5$ (**5**) → $(Me_3CCH_2)_3Ta{=}CHCMe_3$ (**6**) (Ref. 30).

is the first step in the thermal decomposition of $(Me_3CCH_2)_4TaCl$, which is observed to follow first-order kinetics with $\Delta H_4^{\neq} = 6.2(0.3)$ kcal/mol and $\Delta S_4^{\neq} = -61.6(0.8)$ eu.[30] This thermal decomposition is found to be much slower than the reaction of $(Me_3CCH_2)_4TaCl$ with Me_3CCH_2Li. The extrapolated half-life for the decomposition of $(Me_3CCH_2)_4TaCl$ at –40°C is 1.12×10^5 min. However, the reaction between Me_3CCH_2Li and $(Me_3CCH_2)_4TaCl$ at –40°C is virtually complete in about 80 min. The pathway involving "$(Me_3CCH_2)_2Ta(Cl)({=}CHCMe_3)$" (Route 2, Scheme 9) as the precursor to $(Me_3CCH_2)_3Ta{=}CHCMe_3$ is therefore unlikely.[36]

Thus the kinetic and mechanistic studies of the formation of $(Me_3SiCH_2)_2Ta({=}CHSiMe_3)Si(SiMe_3)_3$ show that the silyl alkylidene complex is formed by the pathway in Route 1 (Scheme 9) with the formation of the alkylidene bond preceding the Cl^- substitution. The formation of alkyl alkylidene complexes $(RCH_2)_3Ta{=}CHR$, on the other

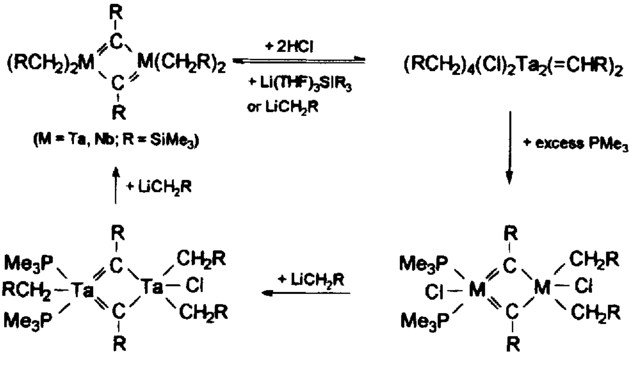


SCHEME 12

hand, adopts an alternative mechanism (Route 2, Scheme 9) where the Cl^- ligands are replaced before the formations of the alkylidene bonds. The reasons for such different reactivities are not clear. Steric factors perhaps play an important role here. The silyl ligand $Si(SiMe_3)_3$ is quite bulky, and may make Route 2 in Scheme 9 to "$(RCH_2)_3Ta[Si(SiMe_3)_3]_2$" unfavorable and Route 1 the low-energy and preferred pathway instead.

3.4 $(Me_3SiCH_2)_2(Cl)_2Ta_2(=CHSiMe_3)_2$ and Reaction Cycles Involving Bis(alkylidene), Nonsymmetric Bis(alkylidyne) and Symmetric Bis(alkylidyne) Complexes (Refs. 37 and 38)

The unstable bis(alkylidene) complex $(Me_3SiCH_2)_2(Cl)_2Ta_2(=CHSiMe_3)_2$, which is the dimer of an intermediate "$(Me_3SiCH_2)_2Ta(=CHSiMe_3)(Cl)$" in the formation of $(Me_3SiCH_2)_2Ta(=CHSiMe_3)$ $Si(SiMe_3)_3$, was first investigated as the product of HCl addition to the bridging bis(alkylidyne) complex $(Me_3SiCH_2)_4Ta(\mu\text{-}CSiMe_3)_2$. Our initial interest was its reaction with $Li(THF)_3Si(SiMe_3)_3$. In the reaction, the unstable bis(alkylidene) complex is converted back to the bridging bis(alkylidyne) complex, through either preferential silane elimination or a direct attack of the alkylidene hydrogen atoms by $Si(SiMe_3)_3^-$. A similar reaction occurs with $LiCH_2SiMe_3$. Interesting reaction cycles involving symmetric bis(alkylidyne), bis(alkylidene) and nonsymmetric bis(alkylidene) complexes are shown in Scheme 13.[39]



SCHEME 13

The addition of excess PMe_3 to the solution containing the bis(alkylidene) complex [or to the mixture from the reaction of $(Me_3SiCH_2)_4Nb_2(\mu\text{-}CSiMe_3)_2$ with 2 equiv of HCl] gives stable nonsymmetric bridging bis(alkylidyne) complexes $(Me_3P)_2(Cl)M(\mu\text{-}CSiMe_3)_2M(Cl)(CH_2SiMe_3)_2$. Interestingly the two PMe_3 molecules are both added to one metal atom in the reaction. The addition of phosphine to $(Me_3SiCH_2)_4(Cl)_2Ta_2(=CHSiMe_3)_2$ perhaps prompts α-hydrogen abstraction between the two Me_3SiCH_2 ligands from *the same* Ta atom and the α-hydrogen atoms of the alkylidene ligands, leading to the formation of the nonsymmetric bis(alkylidyne) bridges in $(Me_3P)_2(Cl)Ta(\mu\text{-}CSiMe_3)_2Ta(Cl)(CH_2SiMe_3)_2$.

The molecular structure of the Nb nonsymmetric bis(alkylidyne) complex, which is isomorphous to that of the Ta complex, is shown in Fig. 7.

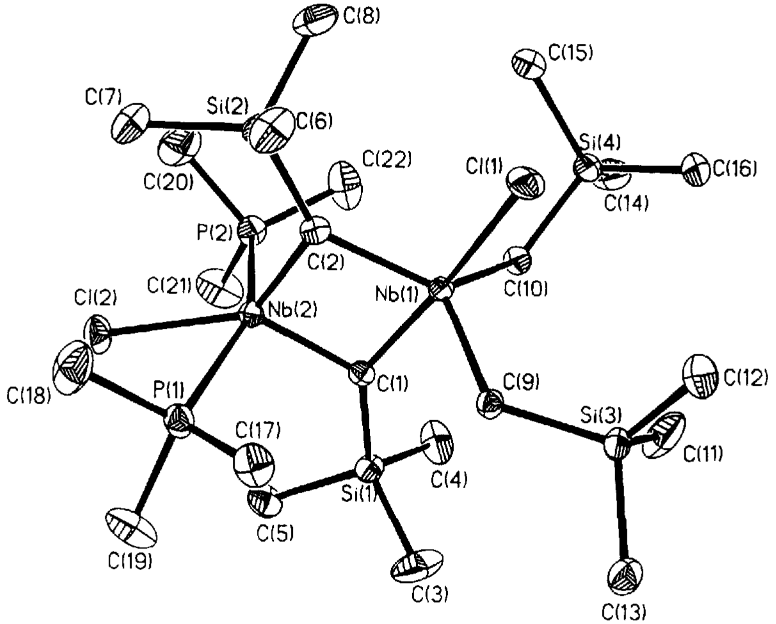


FIGURE 7 ORTEP diagram of $(Me_3P)_2ClNb(\mu\text{-}CSiMe_3)_2NbCl(CH_2SiMe_3)_2$ (Refs. 37 and 38).

The structures of the two complexes confirm the presence of nonsymmetric bis(alkylidyne) bridges. There is, to our knowledge, one other reported nonsymmetric bis(alkylidyne) complex $W_2(Me_3SiCH_2)_4(\mu\text{-}CSiMe_3)_2(\eta^2\text{-}PhC_2Me)$.[40]

The ligands on M(2) are arranged in slightly distorted trigonal bipyramidal geometry with C(1) and C(2) at axial and equatorial positions, respectively. These two bridging alkylidyne ligands were found to be involved in unusual axial–equatorial ligand exchange processes as seen in their $Me_3SiC\equiv$ resonances in variable-temperature ^1H and ^{13}C NMR spectra. The exchange processes of the two complexes were found to have similar kinetics with the activation enthalpies and entropies $\Delta H_5^{\neq} = 13.6(0.4)$ kcal/mol and $\Delta S_5^{\neq} = -5(2)$ eu in the Ta complex, and $\Delta H_6^{\neq} = 13.0(0.3)$ kcal/mol and $\Delta S_6^{\neq} = -5(1)$ eu in the Nb complex.[37,38] These exchanges perhaps take place through the conversion of the ground state trigonal bipyramid into a square pyramidal transition state, and back to a new trigonal bipyramidal structure. In comparison, the two axial and two of the three equatorial ligands are involved in an exchange in the Berry pseudorotation.[41]

The reaction of the Ta or Nb nonsymmetric bis(alkylidyne) complexes with 2 equiv of $LiCH_2SiMe_3$ leads to the replacement of the two chloride ligands and converts the nonsymmetric bis(alkylidyne) complexes back to $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ with elimination of two PMe_3 ligands (Scheme 13). The first $CH_2SiMe_3^-$ substitution occurs at the Ta atom containing two PMe_3 ligands to form a thermally unstable intermediate $(Me_3P)_2(Me_3SiCH_2)Ta(\mu\text{-}CSiMe_3)_2Ta(Cl)(CH_2SiMe_3)_2$. Subsequent $CH_2SiMe_3^-$ substitution of the remaining Cl^- ligand gives $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$. An interesting alkyl migration from one metal center to another might be involved in these conversions. After the first $CH_2SiMe_3^-$ substitution, subsequent $CH_2SiMe_3^-$ substitution at the other Ta atom, followed by an alkyl migration, leads to the formation of $(Me_3SiCH_2)_4Ta_2(\mu\text{-}CSiMe_3)_2$ with symmetric bis(alkylidyne) bridges. The migration of the $CH_2SiMe_3^-$ ligand in the conversions nicely completes the reaction cycles shown in Scheme 13. Alkyl migrations between metal centers have been observed in early-transition-metal complexes with direct metal–metal bonds.[42–45] However, unlike in these complexes, the rarely seen alkyl migration reported here involves two atoms that are not directly bonded.

4. CONCLUSIONS

Our studies discussed here demonstrate that early-transition-metal silyl complexes in Cp-free environments offer rich and interesting chemistry, and unusual chances to compare the reactivities of alkyl and silyl ligands. Alkyl, alkylidene and alkylidyne complexes containing silyl ligands could be prepared by substitution reactions analogous to the syntheses of alkyl, alkyl alkylidene and alkyl alkylidyne complexes. However, the silyl complexes often demonstrate reactivities different from those of corresponding alkyl compounds. More experimental and theoretical studies would help to give a better understanding of the origins of such differences and develop a more unified view of the alkyl and silyl chemistry.

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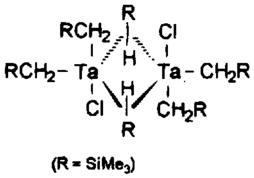
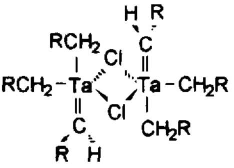
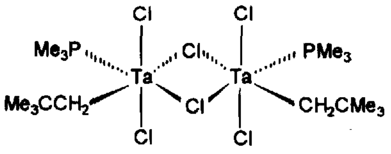




alkylidene complexes $[M(CHCMe_3)LX_3]_2$ (M=Nb, Ta; L=a tertiary phosphine; X = Cl, Br). Neutron diffraction studies have shown that $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ contains two bridging halide ligands:



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