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Preparation of Tungsten Alkyl Alkylidene Alkylidyne Complexes and Kinetic Studies of Their Formation

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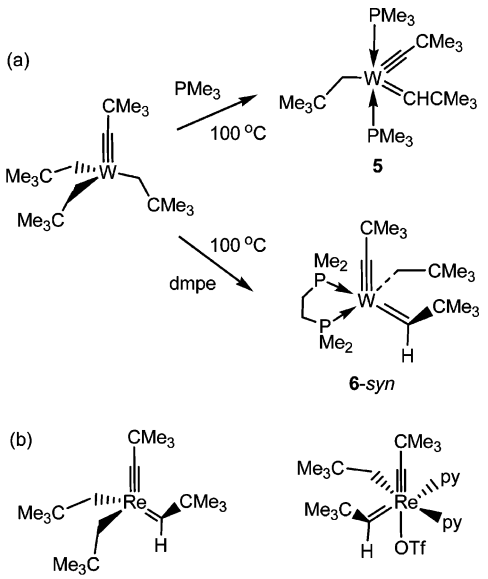
Abstract: An equilibrium mixture of alkyl alkylidyne $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PMe_3)$ (**1a**) and its bis(alkylidene) tautomer $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**) has been found to undergo an α-hydrogen abstraction reaction in the presence of PMe_3 to form alkyl alkylidene alkylidyne $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_3)_2$ (**2**). In the presence of PMe_3, the formation of **2** follows first-order kinetics, and the observed rate constant was found to be independent of the concentration of PMe_3. The activation parameters for the formation of **2** are $\Delta H^{\ddagger} = 28.3(1.7)$ kcal/mol and $\Delta S^{\ddagger} = 3(5)$ eu. In the presence of PMe_2Ph, an equilibrium mixture of $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PMe_2Ph)$ (**3a**) and its bis(alkylidene) tautomer $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_2Ph)$ (**3b**) was similarly converted to $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (**4**). The observed rate of this reaction was also independent of the concentration of PMe_2Ph. These observations suggest a pathway in which the tautomeric mixtures **1a,b** and **3a,b** undergo rate-determining, α-hydrogen abstraction, followed by phosphine coordination, resulting in the formation of the alkyl alkylidene alkylidyne complexes **2** and **4**.

Alkyl alkylidene alkylidyne complexes are unique compounds containing single, double, and triple bonds to one atom in a single molecule. The first such complex, $W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)(PMe_3)_2$ (**5**, Scheme 1a), reported by Clark and Schrock, was prepared through α-hydrogen abstraction by heating a solution of alkyl alkylidyne complex $W(CH_2CMe_3)_3(\equiv CCMe_3)$ in liquid PMe_3 at 100 °C.[1] The crystal structure of an analogous complex, $W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)$(dmpe) (**6**) containing a chelating phosphine ligand dmpe ($Me_2PCH_2CH_2PMe_2$), was reported by Churchill and Youngs.[2] **6**, unlike the bis-PMe_3 complex **5**, exhibits cis coordination of the chelating phosphine with the alkylidyne ligand in the axial position (Scheme 1a). It is hypothesized that the phosphine ligands in **5** are coordinated trans to one another, and the other ligands occupy the equatorial sites in a trigonal bipyramidal configuration. Rhenium alkyl alkylidene alkylidyne complexes $Re(CH_2CMe_3)_2(=CHCMe_3)(\equiv CCMe_3)$ and $Re(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)(py)_2(OTf)$, as well as their derivatives, have also been reported (Scheme 1b).[3]

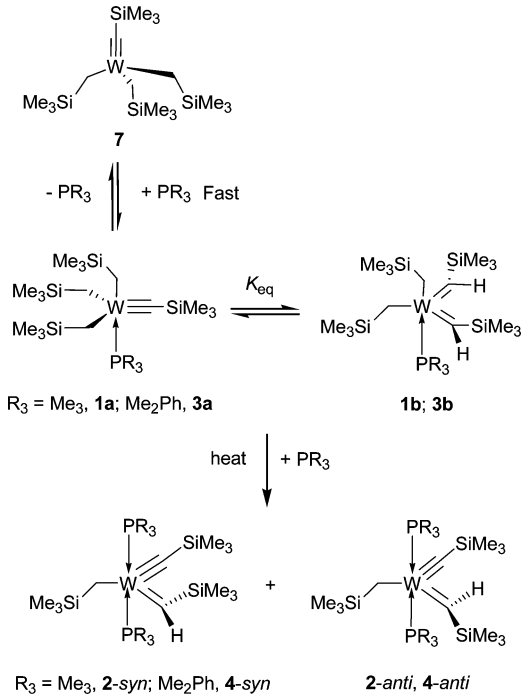
Earlier we had found unusual reactions of d^0 tantalum bis(alkylidene) complexes, such as $Ta(CH_2SiMe_3)(=CHSiMe_3)_2(PMe_3)_2$, with silanes.[4] The reactivities of the d^0 tungsten complexes containing $Me_3SiCH=$ and $Me_3SiC\equiv$ ligands toward silanes were of interest to us. We thus attempted to prepare $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_3)_2$ (**2**) and $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (**4**), the β-Si analogs of **5**. In these studies, we reported that $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**) reacts with PMe_3 and PMe_2Ph, forming adducts $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PR_3)$ ($R_3 = Me_3$, **1a**, and Me_2Ph, **3a**).[5] These adducts subsequently undergo α-hydrogen migration to give bis(alkylidene) tautomers $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PR_3)$ ($R_3 = Me_3$, **1b**, and Me_2Ph, **3b**) and reach equilibria,

Scheme 1

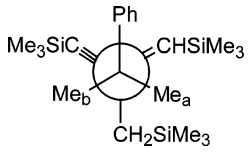


(1) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.
(2) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.
(3) (a) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505. (b) LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.
(4) (a) Diminnie, J. B.; Xue, Z.-L. *J. Am. Chem. Soc.* **1997**, *119*, 12657. (b) Diminnie, J. B.; Blanton, J. R.; Cai, H.; Quisenberry, K. T.; Xue, Z.-L. *Organometallics* **2001**, *20*, 1504.
(5) (a) Morton, L. A.; Zhang, X.-H.; Wang, R.; Lin, Z.; Wu, Y.-D.; Xue, Z.-L. *J. Am. Chem. Soc.* **2004**, *126*, 10208. (b) Morton, L. A.; Wang, R.; Yu, X.; Campana, C. F.; Guzei, I. A.; Yap, G. P. A.; Xue, Z.-L. *Organometallics* **2006**, *25*, 427.

Scheme 2



Scheme 3



Diastereotopic **4**

leading to a rare case in which both alkyl alkylidyne complexes and their bis(alkylidene) tautomers were observed.[5−7]

We have recently found that heating the tautomeric equilibrium mixtures of **1a**/**3a** ⇌ **1b**/**3b** in the presence of phosphines leads to α-hydrogen abstraction and the formation of alkyl alkylidene alkylidyne complexes $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_3)_2$ (**2**) and $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (**4**) (Scheme 2). Both **2** and **4** exist as mixtures of two rotamers, **2**-*syn* and **2**-*anti* and **4**-*syn* and **4**-*anti*, as observed by NMR spectroscopy. Kinetic studies of the formation of **2** and **4** suggest that **1a**/**b** and **3a**/**b** undergo α-hydrogen abstraction, followed by the coordination of phosphine, to give the alkyl alkylidene alkylidyne complexes. In other words, the first phosphine PR_3 ligand coordinates to $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**), forming an adduct and its bis(alkylidene) tautomer **1a**/**b** (**3a**/**b**) (Scheme 2). This mixture then undergoes α-hydrogen abstraction to give an intermediate containing metal−carbon single, double, and triple bonds, prior to the coordination of the second phosphine ligand to give **2** (**4**). These studies offer the first direct insight into the formation of the unique alkyl alkylidene alkylidyne complexes. Our preparation and characterization of **2** and **4**, as well as kinetic studies of their formation, are reported here.

(6) To our knowledge, there is one other reported direct observation of an alkyl alkylidyne ⇌ bis(alkylidene) exchange: Chen, T.-N.; Wu, Z.-Z.; Li, L.-T.; Sorasaenee, K. R.; Diminnie, J. B.; Pan, H.-J.; Guzei, I. A.; Rheingold, A. L.; Xue, Z.-L. *J. Am. Chem. Soc.* **1998**, *120*, 13519.

Results and Discussion

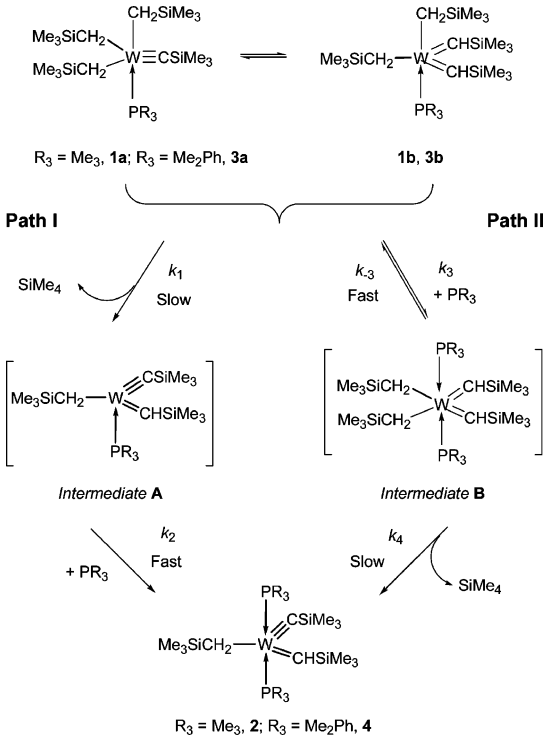
Synthesis and Characterization of 2 and 4. High-oxidation-state alkylidyne complexes such as $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**), highly electron deficient, are generally stabilized by the coordination of phosphine ligands. When PR_3 species (R_3 = Me_3, Me_2Ph) were added to solutions of $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**), phosphine adducts $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PR_3)$ (**1a**/**3a**) were observed. The alkyl alkylidyne phosphine complexes then undergo tautomerization to bis(alkylidenes) $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PR_3)$ (**1b**/**3b**).[5] The exchanges are reversible and reach equilibria (Scheme 2).

Upon heating of these equilibrium systems containing phosphines PMe_3 and PMe_2Ph, the mixtures were found to yield alkyl alkylidene alkylidyne complexes $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_3)_2$ (**2**) and $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (**4**), respectively, through α-hydrogen abstraction reactions (Scheme 2). The ^1H, ^{13}C, and ^{31}P NMR spectral analysis of **2** revealed two distinct rotamers, **2**-*syn* and **2**-*anti*, in solution.[3b,8,9] The ratio of the two is 7:1 on the basis of ^1H NMR integration. It is likely that **2**-*syn* is the major rotamer. In the **2**-*syn* rotamer, the $-SiMe_3$ group on the alkylidene ligand points toward the alkylidyne ligand. Such rotameric mixtures were also observed in alkylidene alkylidyne complexes $Re(=CHCMe_3)(\equiv CCMe_3)(OR)_2$.[9a] In the dmpe complex $W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)$(dmpe) (**6**), the only isomer observed in the X-ray crystal structure was the *syn* isomer (Scheme 1a).[2] One isomer of octahedral $Re(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)(py)_2(OTf)$ (Scheme 1b) was observed, and it was believed to be the *syn* isomer.[3b]

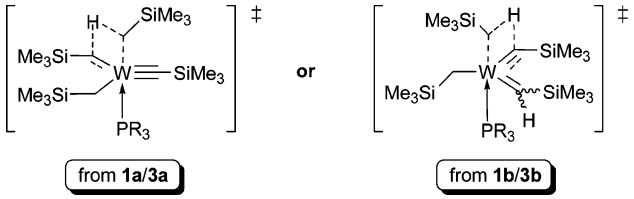
NMR spectroscopic characterization (^1H, ^{13}C, ^{31}P, ^{29}Si, ^1H-gated-decoupled ^{13}C, and HMQC) of the more abundant **2**-*syn* suggests that the PMe_3 ligands coordinate trans to one another. One resonance in the ^{31}P NMR spectrum for **2**-*syn* was observed at −2.21 ppm ($^1J_{P-W}$ = 124.7 Hz). The two *trans*-PMe_3 ligands exhibit virtual coupling and appear as a pseudotriplet in the ^1H and ^{13}C NMR spectra at 1.26 and 20.74 ppm, respectively.[10] Three singlet resonances of the $-SiMe_3$ groups were observed in the ^1H, ^{13}C, and ^{29}Si NMR spectra of **2**-*syn*. The ^1H resonances of the α-hydrogen atoms in $-CH_2SiMe_3$ appear as a triplet at −0.036 ppm with a large $^2J_{P-H}$ = 22.4 Hz. In the tantalum bis(alkylidene) bis(phosphine) complex $Ta(CH_2SiMe_3)(=CHSiMe_3)_2(PMe_3)_2$, where the phosphine ligands are trans to one another, a large coupling constant ($^2J_{P-H}$ = 19.8 Hz) was observed as well.[11] The resonance of the alkylidyne C atom in **2**-*syn* appears at 339.0 ppm as a triplet ($^2J_{P-C}$ = 11.1 Hz; $^1J_{W-C}$ = 161.8 Hz) due to its coupling with two equivalent P atoms, and it is upfield shifted from that (343.27 ppm) of $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**).[12] The alkylidene C and alkyl α-C atoms appear as triplets as well at 275.0 ppm ($^2J_{P-C}$ = 11.1 Hz; $^1J_{W-C}$ = 101.5 Hz) and 25.63 ppm ($^2J_{P-C}$ = 6.2 Hz, $^1J_{W-C}$ = 36.3 Hz), respectively. Most of the ^1H, ^{13}C, and ^{31}P

(7) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
(8) See Supporting Information. Additional mechanistic pathways in the formation of **2** and **4** have been considered to show the dependence of reaction rates on concentration of the phosphines PMe_3 and PMe_2Ph.
(9) (a) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 3367. (b) Toreki, R.; Vaughan, G. A.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1993**, *115*, 127.
(10) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, 2001.
(11) Diminnie, J. B.; Hall, H. D.; Xue, Z.-L. *Chem. Commun.* **1996**, 2383.
(12) Andersen, R. A.; Chisholm, M. H.; Gibson, J. F.; Reichert, W. W.; Rothwell, I. P.; Wilkinson, G. *Inorg. Chem.* **1981**, *20*, 3934.

Scheme 4. Two Proposed Pathways in the Formation of **2** and **4**



Scheme 5. Cyclometalation Transition States in the Formation of **2** and **4**



resonances of **2**-*anti* are shifted only slightly from those of **2**-*syn*. One exception in the ^{1}H NMR spectrum is that the alkylidene proton, W=C*H*SiMe$_3$, is significantly shifted in **2**-*anti* to 13.46 ppm from 10.54 ppm for **2**-*syn*. Likewise, the W*C*H$_2$SiMe$_3$ resonance in the ^{13}C{^{1}H} NMR spectrum at 34.0 ppm is shifted in **2**-*anti* from 25.6 ppm in **2**-*syn*.

Synthesis and Characterization of 4. PMe$_2$Ph is bulkier than PMe$_3$, and the phenyl group often acts as an electron-withdrawing group. In the presence of PMe$_2$Ph, its adduct, W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$)(PMe$_2$Ph) (**3a**) and W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PMe$_2$Ph) (**3b**) also undergo α-hydrogen abstraction, yielding the alkyl alkylidene alkylidyne complex W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_2$Ph)$_2$ (**4**). As for **2**, there are **4**-*syn* and **4**-*anti* rotamers in solution (Scheme 2) in a ratio of **4**-*syn*:**4**-*anti* = 27:1 on the basis of the ^{1}H NMR spectrum.

The methyl groups on the PMe$_2$Ph ligand in **4** are diastereotopic, as shown in the Newman projection down a W−P bond in Scheme 3. In addition, the two phosphine ligands show virtual coupling. The *Me*−P groups of **4**-*syn* thus appear as two pseudotriplets in the ^{1}H and ^{13}C NMR spectra.[8] One ^{1}H NMR resonance of the *Me*−P groups on **4**-*anti* overlaps with those of **4**-*syn*.[8]

Attempts were made to prepare compounds analogous to **3** and **4** using PCy$_3$ or PPh$_3$. Addition of these bulky phosphines to solutions of W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**) in toluene-d_8, and their subsequent heating at 100 °C for 2 days yielded no products. No complexation was observed between PPh$_3$ or PCy$_3$ and W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**). Perhaps the bulkiness of PCy$_3$ and PPh$_3$ prevents them from coordinating to **7** to form adducts, a prerequisite for the formation of their alkyl alkylidene alkylidyne derivatives.

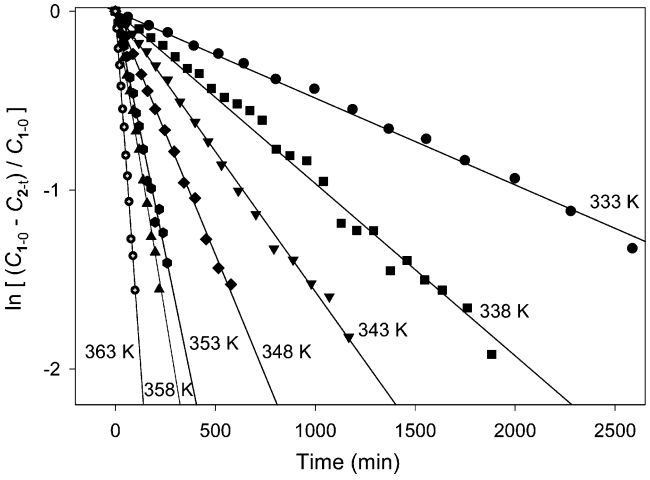


Figure 1. Kinetic plots for the conversion of **1a**,**b** to **2**. C_{1-0} and C_{2-t} are concentrations of **1a,b** (total) at time = 0 and in **2** (total) at time = *t*, respectively.

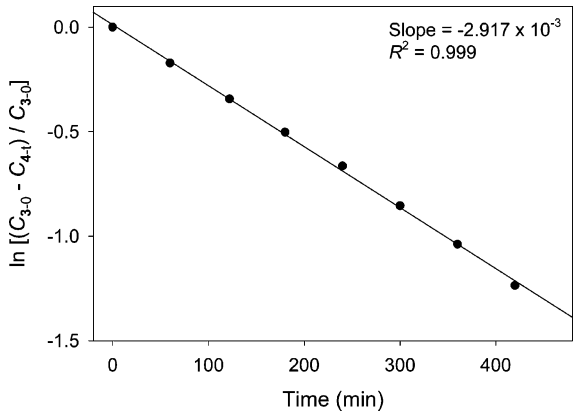


Figure 2. Kinetic plot for the formation of **4** at 348.2 K (ratio = [PMe$_2$Ph]/[**3a,b**] = 13.5). C_{3-0} and C_{4-t} are the concentrations of **3a,b** (total) at time = 0 and **4** (total) at time = *t*, respectively.

Kinetic Study of the Conversion of 1a,b to 2 and 3a,b to 4. In the presence of phosphines, kinetic studies of the α-H abstraction reactions to yield **2** and **4** (Scheme 2) have been conducted. The conversion of **1** to **2** was found to follow first-order kinetics (eq 1),[8,13] as revealed by the ^{1}H NMR spectra of the reaction between 333.2(0.1) and 358.2(0.1) K (Figure 1). The observed rate constant k_{obs} [1.5(0.2) × 10^{-5} s^{-1}] at 338 K was found to be independent of PMe$_3$ concentrations, when C_{PMe_3} ranged from 1.51 to 3.06 M (PMe$_3$ in 12−30-fold excess):[8]

$$dC_1/dt = -k_{obs}C_1 \qquad (1)$$

C_1: concentration of **1a,b**

The kinetics of the reaction to give **4** was also studied at 348.2 K by a kinetic equation similar to eq 1. These kinetic studies with different $C_{PMe_2Ph}/C_{\mathbf{3}}$ ratios yielded the observed rate

Table 1. Observed Rate Constants (k_{obs}) in the Formation of **2**[a]

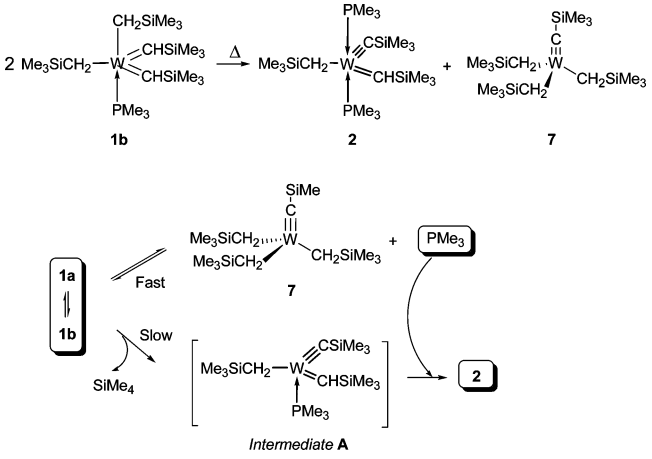
T (K)	$10^5 k_{obs}$ (s^{-1})[b]	T (K)	$10^5 k_{obs}$ (s^{-1})[b]
333.2(0.1)	0.73(0.08)	353.2(0.1)	9.7(0.5)
338.2(0.1)	1.4(0.2)	358.2(0.1)	15.6(0.7)
343.2(0.1)	2.3(0.3)	363.2(0.1)	25.7(1.2)
348.2(0.1)	5.0(0.5)		

[a] Solvent: toluene-d_8. [b] The largest random uncertainty is $\delta k_{ran}/k = 0.2/1.4 = 0.14$. The total uncertainty $\delta k/k = 0.15$ was calculated from $\delta k_{ran}/k$ and the estimated systematic uncertainty $\delta k_{sys}/k = 0.05$ by $\delta k/k = [(\delta k_{ran}/k)^2 + (\delta k_{sys}/k)^2]^{1/2}$.

Table 2. Activation Parameters in Reactions through Cyclometalation Transition States

reacns	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
$CpTaCl_2(CH_2CMe_3)_2 \rightarrow CpTaCl_2(=CHCMe_3)$[14]	21(2)	−4(10)
$W(CH_2CMe_3)_3(\equiv CSiMe_3) \rightarrow W(CH_2CMe_3)_2(CH_2SiMe_3)(\equiv CCMe_3)$[15]	27.5(0.6)	−2.0(1.7)
$W(CH_2CMe_3)_2(CH_2SiMe_3)(\equiv CCMe_3) \rightarrow W(CH_2CMe_3)_3(\equiv CSiMe_3)$[15]	25.4(0.8)	−9.5(1.9)
$Ta(CH_2SiMe_3)_5 \rightarrow Ta(CH_2SiMe_3)_3(=CHSiMe_3)_2$[16]	21.6(1.4)	−5(5)

Scheme 6



constant $k_{obs}' = 5.1(0.2) \times 10^{-5}$ s^{-1} at 348.2(0.1) K for the formation of **4**. The observed rate constant (k_{obs}) of $1.5(0.2) \times 10^{-5}$ s^{-1} at 348.2(0.1) K for the PMe_3 complexes **1a,b** is smaller than that involving bulkier PMe_2Ph complexes **3a,b**.

The observations that k_{obs} for the formation of $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_3)_2$ (**2**) and k_{obs}' for the formation of $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (**4**) are independent of phosphine concentrations suggest that the coordination of the second phosphine molecule is *not* the rate-determining step. Two paths were considered.[8] In path I (Scheme 4), tautomeric alkyl alkylidyne−bis(alkylidene) mixtures **1a,b** and **3a,b** undergo a rate-determining, α-hydrogen abstraction to give monophosphine, alkyl alkylidene alkylidyne intermediates **A** which then bind PR_3 to give the bisphosphine products **2** and **4**. In this pathway, the α-hydrogen abstraction is a spontaneous process in the penta-coordinated **1a,b** and **3a,b** to yield tetracoordinated intermediates **A**. In the second step, phosphine coordinates to **A** to give **2** and **4**. The rates of the reactions are thus functions of the concentrations of **1a/b** or **3a/b** and are independent of C_{PR_3}.

In path II, phosphine coordination to **1a,b** and **3a,b**, yielding hexacoordinated intermediates **B**, precedes the α-hydrogen abstraction. Kinetic analyses of path II are given in the Supporting Information. In path II, both the steady-state or preequilibrium approaches show that the observed rates of the reactions are functions of concentrations of both **1a,b** (or **3a,b**) and PR_3. Two additional pathways in the formation of **2** were considered: both show the dependence of observed reaction rates on the concentration of PMe_3.[8]

Thus, the observations that the rates of the formation of alkyl alkylidene alkylidyne complexes **2** and **4** are independent of concentrations of PR_3 suggest that it follows path I in Scheme 4. A review of the crystal structure of the bis(alkylidene) complex $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**)[5b] supports this view. A space-filling drawing of the molecular structure of the pentacoordinated complex **1b** (Figure 3) suggests that there is little open space around the W atom in **1b** for the coordination of a second PMe_3 ligand, as would be required via path II. In path I, α-hydrogen abstraction eliminates a ligand as $SiMe_4$, converting *pentacoordinated* **1a,b** and **3a,b** to *tetracoordinated* intermediates **A**. The *tetracoordinated* **A** readily accepts the coordination of a second phosphine ligand, yielding the pentacoordinated products **2** and **4**. Additional studies were conducted involving the reaction of **1b** with 1 equiv of PMe_2Ph and the thermal conversion of **1b** to **2** in the absence of added phosphine. Both, discussed below, are consistent with path I.

The observed rate constants for the **1a/b** → **2** conversion between 333.2(0.1) and 363.2(0.1) K were calculated from

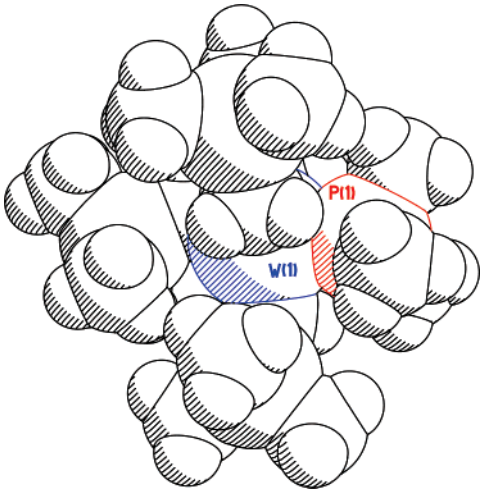


Figure 3. Space-filling drawing of the molecular structure of **1b**, looking down an equatorial axis.

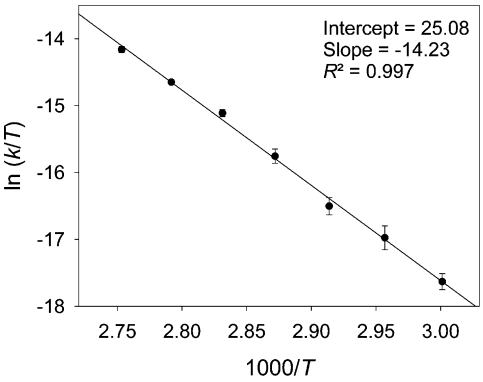


Figure 4. Eyring plot for the **1a,b** → **2** conversion.

(13) See, e.g.: Espenson, J. H. *Chemical Kinetics and Reaction Mechanism*, 2nd Ed.; McGraw-Hill: New York, 1995; pp 46−49.

Figure 1, and they are given in Table 1. The Eyring plot (Figure 4) gives the activation parameters of the reaction: $\Delta H^{\ddagger} = 28.3(1.7)$ kcal/mol and $\Delta S^{\ddagger} = 3(5)$ eu. It is not clear whether alkyl alkylidyne **1a**, bis(alkylidene) **1b**, or both undergo α-hydrogen abstraction reactions to give **3a,b**. The process may involve a cyclometalation transition state (Scheme 5). The activation parameters of the conversion $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (near zero) are similar to other reported reactions through cyclometalation transition states for complexes containing $-CH_2CMe_3$ and/or $-CH_2SiMe_3$ ligands (Table 2).[14−16]

Thermal Conversion of 1b to W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_3$)$_2$ (2) and W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (7) in the Absence of PMe$_3$. W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PMe$_3$) (**1b**) dissolved in toluene-d_8 was heated at ca. 68(4) °C for 23 h. After cooling of the sample to room temperature, the ^{1}H NMR spectrum of the mixture revealed the formation of alkyl alkylidene alkylidyne complex **2** and phosphine-free **7**, along with unreacted **1a,b**. ^{1}H NMR spectra before and after the heating are given in the Supporting Information. This observation is consistent with the equilibrium involving **7**, PMe_3, and **1a** (Scheme 6) that leads to partial PMe_3 dissociation from **1a** to provide the free phosphine. At the same time, **1a,b** undergoes the α-hydrogen abstraction to give the *intermediate* **A** (Scheme 4), which then picks up the free PMe_3, forming bisphosphine complex **2**. The ratio of **1** vs **2** is ca. 0.63:1.00. The *estimated* rate constant for the formation of **2** using eq 1 and this ratio is ca. 1.2×10^{-5} s^{-1}. In comparison, the rate constant at 65.0(0.1) °C is $1.4(0.2) \times 10^{-5}$ s^{-1} (Table 1). It should be noted that there was *no* added free PMe_3 in the current reaction. The PMe_3 ligand that reacts with **1a,b** to give **2** comes from the dissociation of **1a,b**. The fact that the estimated rate constant for this reaction is close to that obtained for systems with added PMe_3 (Table 1) is consistent with path I in Scheme 4. **1a,b** readily dissociates PMe_3 but undergoes a slow, rate-determining α-hydrogen abstraction. The intermediate **A** then quickly picks up PMe_3 dissociated from **1a,b** (Scheme 6) to give **2**.

Reaction of W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PMe$_3$) (1b) with 1 equiv of PMe$_2$Ph. A mixture of W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PMe$_3$) (**1b**) and 1 equiv of PMe_2Ph in toluene-d_8 was heated at ca. 68(4) °C for 39 h. The solution was cooled to −20 °C, and its ^{1}H NMR spectrum revealed the formation of W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_3$)$_2$ (**2**), W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_2$Ph)$_2$ (**4**), and a new mixed diphosphine complex, W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_3$)(PMe$_2$Ph) (**8**). The alkylidene proton resonances in the ^{1}H NMR spectrum of the reaction mixture is shown in Figure 5. This observation is consistent with the mechanistic pathways in Scheme 7. PMe_3 dissociates from **1b**, yielding **7**, which then reacts with PMe_2Ph to give an equilibrium mixture of W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$)(PMe$_2$Ph) (**3a**) ⇌ W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PMe$_2$Ph) (**3b**). Both **1** and **3** undergo the α-hydrogen abstraction reactions to give the intermediates, which then react with PMe_3 or PMe_2Ph to give the three alkyl alkylidene alkylidyne complexes **2**, **4**, and **8**.

Concluding Remarks

The equilibrium mixtures W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$)(PR$_3$) (**1a/3a**) ⇌ W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PR$_3$) (**1b/3b**) have been shown to convert to alkyl alkylidene alkylidyne complexes W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PR$_3$)$_2$ (**2** and **4**). In other words, **1a/3a** ⇌ **1b/3b** are intermediates in the reactions of W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**) with PR_3 to give **2** and **4**. The kinetic studies, the first such studies of the formation of the complexes containing alkyl alkylidene alkylidyne ligands, show that the α-H abstraction reaction to form **2** follows first-order kinetics. These results suggest that the equilibrium mixture **1a** ⇌ **1b** undergoes a rate-determining, α-hydrogen abstraction reaction to give W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_3$) (intermediate **A**), followed by fast coordination of PMe_3 to give **2**.

It is interesting to note the difference in the reactivities of W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**) and its analogue W(CH$_2$CMe$_3$)$_3$(≡CCMe$_3$) toward PMe_3. W(CH$_2$CMe$_3$)$_3$(≡CCMe$_3$) reacts with neat PMe_3 in a sealed tube at 100 °C, giving the alkyl alkylidene alkylidyne complex W(CH$_2$CMe$_3$)(=CHCMe$_3$)(≡CCMe$_3$)(PMe$_3$)$_2$ through α-H abstraction and CMe_4 elimination, as Schrock and Clark reported (Scheme 1).[1] When ca. 1 equiv of PMe_3 was added to W(CH$_2$CMe$_3$)$_3$(≡CCMe$_3$) in benzene-d_6 at room temperature, a similar reaction giving W(CH$_2$CMe$_3$)(=CHCMe$_3$)(≡CCMe$_3$)(PMe$_3$)$_2$ and CMe_4 occurred.[5] *No adduct between alkylidyne W(CH$_2$CMe$_3$)$_3$(≡CCMe$_3$) and PMe$_3$ was observed*. In comparison, PR_3 (R_3 = Me_3, Me_2Ph) coordinates readily to W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**) to give the phosphine alkylidyne adducts W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$)(PR$_3$) (**1a** and **3a**). These phosphine alkylidyne adducts then undergo α-hydrogen migration to give the bis(alkylidene) tautomers W(CH$_2$SiMe$_3$)$_2$(=CHSiMe$_3$)$_2$(PR$_3$) (**1b** and **3b**). An α-hydrogen abstraction, followed by PR_3 coordination, gives the alkyl alkylidene alkylidyne complexes **2** and **4**. Thus, in the current case involving the $-CH_2SiMe_3$ and ≡CSiMe$_3$ ligands, there are intermediates [observed alkyl alkylidyne−PR$_3$ ⇌ bis(alkylidene)−PR$_3$ tautomeric mixtures and likely intermediate **A**] before the formation of two rare alkyl alkylidene alkylidyne complexes **2** and **4**. The current work exemplifies the differences in $-CH_2CMe_3$ and $-CH_2SiMe_3$ ligand systems.[4]

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere with the use of either a glovebox or standard Schlenk techniques. Solvents were purified by distillation from potassium benzophenone ketyl. NMR solvents were dried and stored over 5 Å molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AC-250 or AMX-400 spectrometer and referenced to solvent (residual protons in the ^{1}H spectra). ^{31}P, ^{29}Si, and HMQC (heteronuclear multiple quantum coherence) spectra were recorded on a Bruker AMX-400 spectrometer. ^{29}Si chemical shifts were referenced to $SiMe_4$.

Preparation of W(CH$_2$SiMe$_3$)(=CHSiMe$_3$)(≡CSiMe$_3$)(PMe$_3$)$_2$ (2). W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**, 0.050 g, 0.0942 mmol) was dissolved in toluene (0.5 mL) in a Schlenk flask (50 mL). PMe_3 (ca. 10 equiv, 0.966 mmol) was added via a syringe to the vigorously stirred solution at −40 °C. The mixture was then stirred at room temperature for 24 h, followed by heating at 80 °C for another 24 h. All volatiles were removed in vacuo at room temperature, the residue was extracted with Et_2O, and the mixture was filtered. The filtrate was put in a freezer at −32 °C and then filtered to remove a small amount of a white solid impurity. After this second filtration, the volatiles in the solution were removed in vacuo to give **2** a dark brown solid (0.252 g, 45% yield).

(14) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.
(15) Caulton, K. G.; Chisholm, M. H.; Streib, W. E.; Xue, Z.-L. *J. Am. Chem. Soc.* **1991**, *113*, 6082.
(16) Li, L.; Hung, M.; Xue, Z.-L. *J. Am. Chem. Soc.* **1995**, *117*, 12746.

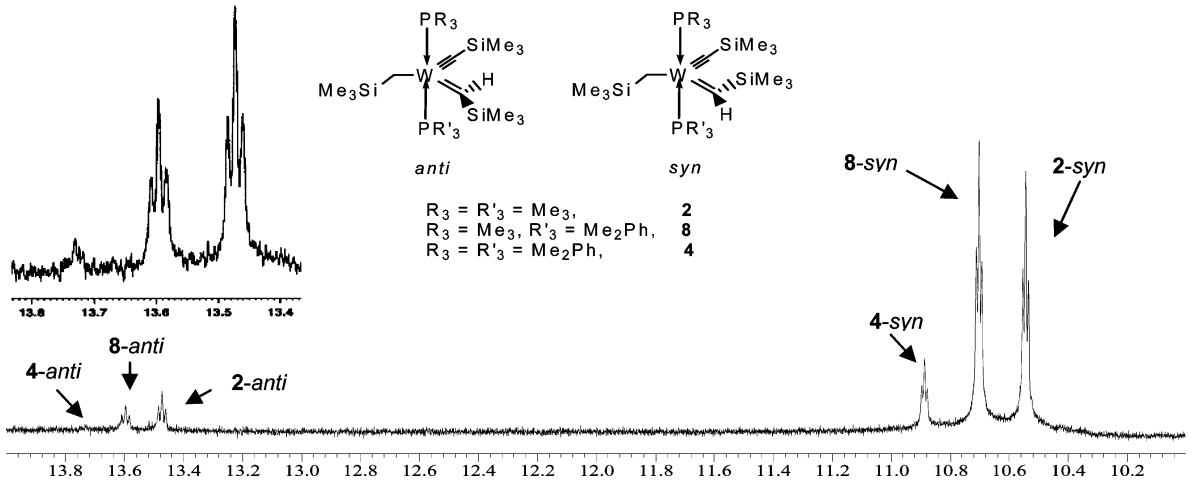


Figure 5. ^{1}H NMR spectra (−20 °C) of a solution of $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**) and 1 equiv of PMe_2Ph in toluene-d_8 after heating at ca. 68(4) °C for 39 h. This alkylidene proton region shows the formation of **2**, **4**, and mixed diphosphine alkyl alkylidene alkylidyne complex **8**.

2-*syn*: ^{1}H NMR (toluene-d_8, 399.97 MHz, 23 °C, *J* in Hz) δ 10.54 (t, 1H, $=CH$SiMe$_3$, $^3J_{P-H} = 4.2$), 1.26 (t, 18H, P*Me*$_3$, $^2J_{P-H} = 3.6$), 0.33 (s, 9H, −Si*Me*$_3$), 0.23 (s, 9H, −Si*Me*$_3$), 0.19 (s, 9H, −Si*Me*$_3$), −0.04 (t, 2H, $-CH_2$SiMe$_3$, $^3J_{P-H} = 22.4$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, 23 °C, *J* in Hz) δ 339.0 (t, $\equiv C$SiMe$_3$, $^2J_{P-C} = 11.1$, $^1J_{W-C} = 161.8$), 275.0 (t, $=C$HSiMe$_3$, $^2J_{P-C} = 11.1$, $^1J_{W-C} = 101.5$), 25.6 (t, $-CH_2$SiMe$_3$, $^2J_{P-C} = 6.2$, $^1J_{W-C} = 36.3$), 20.7 (t, P*Me*$_3$, $^1J_{P-C} = 14.5$), 5.2 (s, −Si*Me*$_3$), 3.7 (s, −Si*Me*$_3$), 2.4 (s, −Si*Me*$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 161.92 MHz, 23 °C, *J* in Hz) δ −2.2 (s, $^1J_{W-P} = 249$); ^{29}Si{^{1}H} NMR (toluene-d_8, 79.46 MHz, −23 °C, *J* in Hz) δ −2.1 (s, $-CH_2Si$Me$_3$), −4.7 (s, $=$CH*Si*Me$_3$), −23.1 (s, $\equiv$C*Si*Me$_3$). ^{1}H and ^{13}C assignments were confirmed by DEPT, HMQC, and ^{1}H-gated-decoupled−^{13}C NMR. **2**-*anti*: ^{1}H NMR (toluene-d_8, 399.97 MHz, 23 °C, *J* in Hz) δ 13.46 (t, 1H, $=CH$SiMe$_3$, $^3J_{P-H} = 5.6$), 1.29 (t, 18H, P*Me*$_3$, $^2J_{P-H} = 3.2$), 0.32 (s, 9H, −Si*Me*$_3$), 0.22 (s, 9H, −Si*Me*$_3$), 0.06 (s, 9H, −Si*Me*$_3$), −0.37 (t, 2H, $-CH_2$SiMe$_3$, $^3J_{P-H} = 21.4$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, 23 °C, *J* in Hz) δ 343.5 (t, $\equiv C$SiMe$_3$, $^2J_{P-C} = 10.5$), 273.8 (t, $=C$HSiMe$_3$, $^2J_{P-C} = 11.1$) 34.0 (t, $-CH_2$SiMe$_3$, $^2J_{P-C} = 6.2$), 20.7 (t, overlapping with **2**-*syn* and toluene-d_8 peaks, P*Me*$_3$), 6.4 (s, −Si*Me*$_3$), 3.1 (s, −Si*Me*$_3$), 2.0 (s, −Si*Me*$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 161.92 MHz, 23 °C, *J* in Hz) δ −2.4 (s). Anal. Calcd: C, 36.36; H, 8.14. Found: C, 36.43; H, 8.17.

Preparation of $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PMe_2Ph)_2$ (4). $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**7**, 0.050 g, 0.0942 mmol) was dissolved in toluene (0.5 mL) in a Schlenk tube (10 mL). PMe_2Ph (ca. 10 equiv, 0.970 mmol) was added with a syringe to the vigorously stirred solution at −42 °C. The mixture was then stirred at room temperature for 24 h, followed by heating at 78−79 °C for another 24 h. All volatiles were removed in vacuo at 57 °C for 6 h to give a viscous, dark brown liquid (0.475 g, 70% yield). **4**-*syn*: ^{1}H NMR (toluene-d_8, 399.97 MHz, 23 °C, *J* in Hz) δ 10.89 (t, 1H, $=CH$SiMe$_3$, $^3J_{P-H} = 3.7$), 7.4−7.0 (m, 5H, C_6H_5), 1.68 (t, 6H, $^2J_{P-H} = 3.6$, P*Me*$_a$Me$_b$Ph), 1.65 (t, 6H, $^2J_{P-H} = 3.6$, PMe$_a$*Me*$_b$Ph), 0.44 (s, 9H, −Si*Me*$_3$), 0.28 (s, 9H, −Si*Me*$_3$), −0.03 (t, 2H, $-CH_2$SiMe$_3$, $^3J_{P-H} = 21.5$), −0.23 (s, 9H, −Si*Me*$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, 23 °C, *J* in Hz) δ 341.6 (t, $\equiv C$SiMe$_3$, $^2J_{P-C} = 10.2$, $^1J_{W-C} = 162.7$), 277.7 (t, $=C$HSiMe$_3$, $^2J_{P-C} = 11.0$, $^1J_{W-C} = 103.5$), 138−124 (C_6H_5), 28.5 (t, $-CH_2$SiMe$_3$, $^2J_{P-C} = 5.6$, $^1J_{W-C} = 37.5$), 23.5 (t, $^1J_{P-C} = 15.3$, P*Me*$_a$Me$_b$), 20.6 (t, $^1J_{P-C} = 15.9$, PMe$_a$*Me*$_b$), 4.7 (s, −Si*Me*$_3$), 3.9 (s, −Si*Me*$_3$), 2.6 (s, −Si*Me*$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 161.92 MHz, 23 °C, *J* in Hz) δ 12.6 (s, $^1J_{W-P} = 250$); ^{29}Si{^{1}H} NMR (toluene-d_8, 79.46 MHz, −20 °C, *J* in Hz) δ −2.8 (s, $-CH_2Si$Me$_3$), −3.8 (s, $=$CH*Si*Me$_3$), −22.1 (s, $\equiv$C*Si*Me$_3$). ^{1}H and ^{13}C assignments were confirmed by HMQC experiments. **4**-*anti*: ^{1}H NMR (toluene-d_8, 399.97 MHz, 23 °C, *J* in Hz) δ 13.73 (t, 1H, $=CH$SiMe$_3$, $^3J_{P-H} = 4.8$), 7.4−7.0 (m, 5H, C_6H_5), 1.55 (t, 6H, P*Me*$_a$Me$_b$Ph, $^2J_{P-H} = 3.2$), 1.48 (t, 6H, PMe$_a$*Me*$_b$Ph, $^2J_{P-H} = 3.0$), 0.20 (s, 9H, −Si*Me*$_3$), 0.18 (s, 9H, −Si*Me*$_3$), 0.15 (t, 2H, $-CH_2$SiMe$_3$, $^3J_{P-H} = 21.6$), −0.05 (s, 9H, −Si*Me*$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, 23 °C, *J* in Hz) δ 344.6 (t, $\equiv C$SiMe$_3$, $^2J_{P-C} = 11.9$), 272.9 (t, $=C$HSiMe$_3$, $^2J_{P-C} = 8.5$), 138−124 (C_6H_5), 36.0 (t, $-CH_2$SiMe$_3$, $^2J_{P-C} = 4.9$), 19.7 (t, $^1J_{P-C} = 14.7$, P*Me*$_a$Me$_b$), 18.9 (t, $^1J_{P-C} = 13.8$, PMe$_a$*Me*$_b$), 6.0 (s, −Si*Me*$_3$), 3.1 (s, −Si*Me*$_3$), 1.9 (s, −Si*Me*$_3$); ^{31}P{^{1}H} NMR (toluene-d_8, 161.92 MHz, 23 °C, *J* in Hz) δ 10.9 (s, $^1J_{W-P} = 250$). Anal. Calcd: C, 46.79; H, 7.29. Found: C, 46.41; H, 7.19.

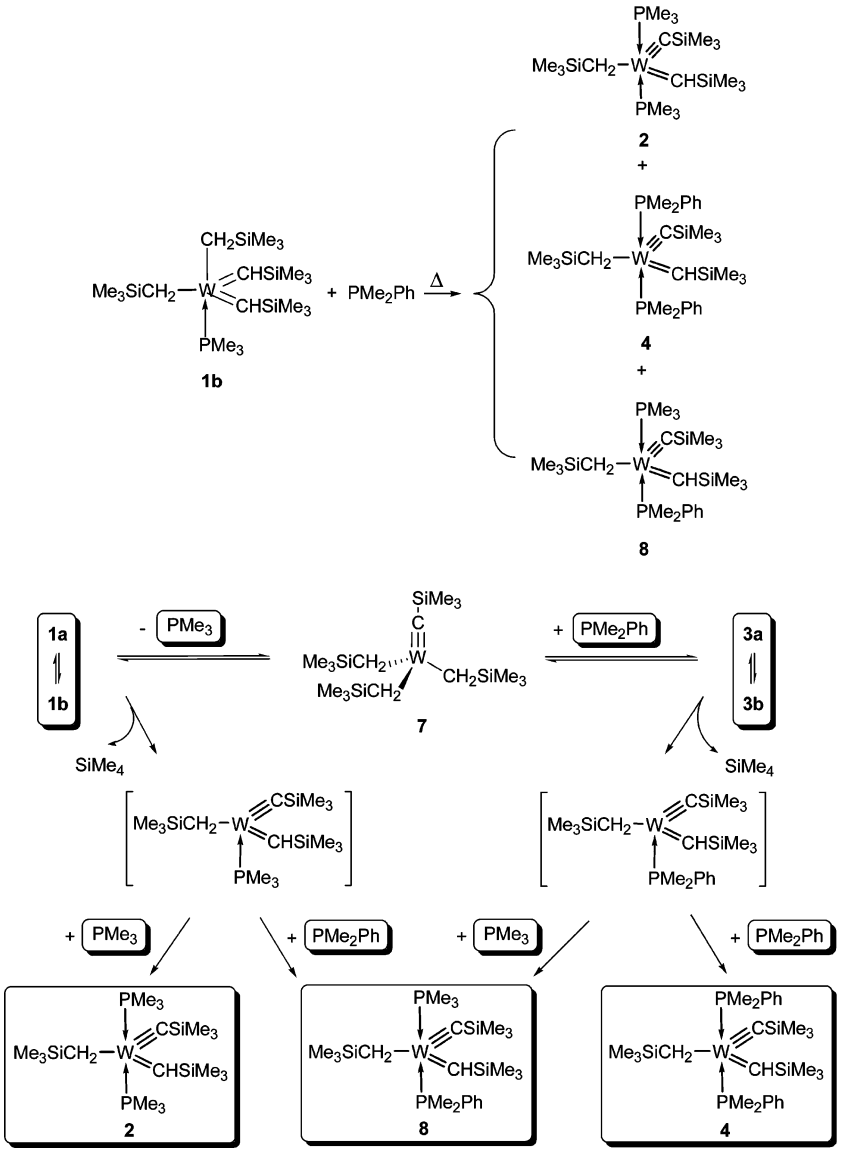
Thermal Conversion of $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (1b). $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**, 42 mg) was dissolved in toluene-d_8 (0.5 mL) in a J. Young NMR tube. The solution was heated at ca. 68(4) °C for 23 h. $W(CH_2SiMe_3)_3(\equiv CHSiMe_3)$ (**7**) and $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CHSiMe_3)(PMe_3)_2$ (**2**-*syn*, **2**-*anti*) were found as products in ca. 0.83:1.00 ratio along with decomposed $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**).[8]

Reaction of $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (1b) with 1 equiv of PMe_2Ph. $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PMe_3)$ (**1b**, 42 mg) and 1 equiv of PMe_2Ph were dissolved in toluene-d_8 (0.5 mL) in a J. Young NMR tube. The mixture was heated at ca. 68(4) °C for 39 h. The reaction was found to give three products: $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CHSiMe_3)(PMe_3)_2$ (**2**-*syn*, **2**-*anti*); $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CHSiMe_3)(PMe_2Ph)_2$ (**4**-*syn*, **4**-*anti*); a new, mixed diphosphine alkyl alkylidene alkylidyne complex, $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CHSiMe_3)(PMe_3)(PMe_2Ph)$ (**8**). **8**-*syn*:[17] ^{1}H NMR (toluene-d_8, 399.97 MHz, 23 °C, *J* in Hz) δ 10.70 (t, 1H, $=CH$SiMe$_3$, $^3J_{P-H} = 3.8$), 7.6−7.0 (m, 5H, C_6H_5), 1.64 (d, 3H, $^2J_{P-H} = 8.0$ Hz, PMe$_A$*Me*$_B$Ph), 1.62 (d, 3H, $^2J_{P-H} = 8.0$ Hz, P*Me*$_A$Me$_B$Ph), 1.28 (d, 9H, $^2J_{P-H} = 8.4$ Hz, P*Me*$_3$), 0.46 (s, 9H, −Si*Me*$_3$), 0.28 (s, 9H, −Si*Me*$_3$), 0.02 (s, 9H, −Si*Me*$_3$), −0.13 (t, 2H, $-CH_2$SiMe$_3$, $^3J_{P-H} = 14.0$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, 23 °C, *J* in Hz) δ 339.8 (t, $\equiv C$SiMe$_3$, $^2J_{P-C} = 9.7$), 275.8 (t, $=C$HSiMe$_3$, $^2J_{P-C} = 8.8$), 151−124 (C_6H_5), 25.0 (t, $-CH_2$SiMe$_3$, $^2J_{P-C} = 6.5$), 23.4 (s, PMe$_3$), 9.0 (t, $^1J_{P-C} = 16.1$, P*Me*$_a$Me$_b$), 17.4 (t, $^1J_{P-C} = 19.6$, PMe$_a$*Me*$_b$), 4.3 (s, −Si*Me*$_3$), 3.1 (s, −Si*Me*$_3$), 3.0 (s, −Si*Me*$_3$).

Kinetic Studies of the Formation of 2 and 4. In the kinetic studies of the formation of **2**, at least a 10-fold excess of PMe_3 ($C_{PMe_3} = 1.42-2.31$ M) was added through vacuum transfer to a mixture of $W(CH_2SiMe_3)_3(\equiv CHSiMe_3)$ (**7**, 29.8−37.8 mg, 0.0562−0.0712 mmol, ca. 0.10−0.14 M), 4,4′-dimethylbiphenyl (an internal standard), and toluene-d_8 in a J. R. Young's NMR tube. The sample was kept at 23 °C overnight to establish the **1a** ⇌ **1b** equilibrium. The sample was then placed in a circulation bath between 60.0 (333.2 K) and 90.0 °C (363.2 K). After a measured period of time, the NMR tube was removed from the

(17) Several peaks of **2**, **4**, and **8** overlap in the NMR spectrum of the mixture (Supporting Information). **8**-*anti* was not fully identified.

Scheme 7



circulation bath and placed in a dry ice/ethanol bath at −78 °C, and ^{1}H NMR spectra were acquired at room temperature. Integration of the ^{1}H −P*Me*$_3$ resonances at 1.26−1.29 ppm for **2**-*syn* and **2**-*anti* versus an internal standard was used to give the kinetic plots in Figure 1. Both isomers were integrated together, since the peaks overlap in the ^{1}H NMR spectra. The average slope of at least two experiments was used to calculate k_{obs}. The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) were calculated from an unweighted nonlinear least-squares procedure. The uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were computed from the error propagation formulas developed by Girolami and co-workers.[18]

Similar to the kinetic studies of the conversion of **1a,b** to **2**, the conversion of **3a,b** to **4** was monitored by ^{1}H NMR. A mixture of W(CH$_2$SiMe$_3$)$_3$(≡CHSiMe$_3$) (**7**), PMe$_2$Ph, and 4,4′-dimethylbiphenyl (an internal standard) in toluene-d_8 (C_{3-0} = 0.123 M, C_{PMe_2Ph-0} = 3.79 M or C_{3-0} = 0.107 M, C_{PMe_2Ph-0} = 1.45 M) in a J. R. Young's NMR tube was heated in a circulation bath at 75.0 °C (348.2 K) for a measured amount of time. The reaction was then quenched in dry ice/ethanol bath at −78 °C. ^{1}H NMR spectra were acquired at room temperature, and the integration of the ^{1}H −P*Me*$_2$Ph resonances at 1.61−1.64 ppm for **4** versus an internal standard was used to give the first-order kinetic plot (Figure 2).

(18) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646.

Attempted Reactions of PCy$_3$ and PPh$_3$ with W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (7). Two separate experiments were conducted with W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**7**, 50 mg), 4,4′-dimethylbiphenyl (an internal standard), and toluene-d_8 in J. R. Young's NMR tubes. PCy$_3$ or PPh$_3$ respectively was added in at least a 10-fold excess. The solution was heated for 2 days at 100 °C. No reaction or adducts were observed by ^{1}H NMR spectroscopy.

Acknowledgment. Acknowledgment is made to the National Science Foundation (Grant CHE-0516928) for financial support. We thank a reviewer for suggesting the studies of the conversion of the **1a** ⇌ **1b** mixture to **2** and **7** in the absence of PMe$_3$ as well as the conversion of the **1a** ⇌ **1b** mixture to **2**, **4**, and **8** in the presence of PMe$_2$Ph. We also thank Michael D. Bleakley for assistance.

Supporting Information Available: NMR spectra of **2** and **4**, NMR spectra of the mixtures from the thermal conversion of **1b** in the absence of added phosphine, k_{obs} values at different C_{PMe_3} at 338.2(0.1) K, and considerations of alternative pathways to **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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