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Tungsten Alkyl Alkylidyne and Bis-alkylidene Complexes. Preparation and Kinetic and Thermodynamic Studies of Their Unusual Exchanges

Laurel A. Morton,[†] Ruitao Wang,[†] Xianghua Yu,[†] Charles F. Campana,[‡] Ilia A. Guzei,[§] Glenn P. A. Yap,[⊥] and Zi-Ling Xue*[,†]

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996, Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin 53711, Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706, and Department of Chemistry & Biochemistry, The University of Delaware, Newark, Delaware 19716

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Preparation and characterization of novel alkyl alkylidyne $(Me_3SiCH_2)_3W(\equiv CSiMe_3)(PMe_3)$ (**1a**) and bis-alkylidene $(Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_3)$ (**1b**) and studies of the exchange between alkylidyne **1a** and bis-alkylidene **1b** are reported. An adduct between PMe_3 and alkyl alkylidyne $(Me_3SiCH_2)_3W\equiv CSiMe_3$ (**2a**), $(Me_3SiCH_2)_3W(\equiv CSiMe_3)(PMe_3)$ (**1a**), was found to undergo a rare reversible transformation to its bis-alkylidene tautomer $(Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_3)$ (**1b**). The X-ray crystal structure of **1b** has been determined. The bis-alkylidene tautomer **1b** is favored in the **1a** $\rightleftharpoons$ **1b** equilibrium with K_{eq} ranging from 12.3(0.2) at 278(1) K to 9.37(0.12) at 303(1) K, giving the thermodynamic parameters for the equilibrium: $\Delta H° = -1.8(0.5)$ kcal/mol and $\Delta S° = -1.5(1.7)$ eu. The α-H exchange between **1a** and **1b** follows first-order reversible kinetics. The activation parameters are $\Delta H^‡ = 16.2(1.2)$ kcal/mol and $\Delta S^‡ = -22(4)$ eu for the forward reaction (**1a** → **1b**) and $\Delta H^‡ = 18.0(1.3)$ kcal/mol and $\Delta S^‡ = -21(4)$ eu for the reverse reaction (**1b** → **1a**). An adduct between $(Me_3SiCH_2)_3W\equiv CSiMe_3$ and PMe_2Ph, $(Me_3SiCH_2)_3W(\equiv CSiMe_3)(PMe_2Ph)$ (**3a**), was found to undergo a similar reversible transformation to its bis-alkylidene tautomer $(Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_2Ph)$ (**3b**). The **3a** $\rightleftharpoons$ **3b** equilibrium is shifted more to the alkyl alkylidyne adduct **3a** [$K_{eq}' = 4.65(0.11)$ at 303 K] than the **1a** $\rightleftharpoons$ **1b** equilibrium. The forward **3a** → **3b** conversion in the PMe_2Ph complexes is slower than the **1a** → **1b** conversion at 303 K, whereas the reverse **3b** → **3a** conversion is slightly faster than the **1b** → **1a** conversion.

Introduction

The reactivity of α-H atoms in alkyl ligands free of β-H atoms (e.g., Me_3CCH_2 and Me_3SiCH_2) has been studied due in part to their role in the formation of high-oxidation-state alkylidene and alkylidyne complexes.[1] d^0-Alkyl alkylidyne $(RCH_2)_3W\equiv CR'$ and alkylidene $(Bu^tCH_2)_3Ta=CDBu^t$ complexes are known to undergo α-H migrations among the α-C atoms.[1j,2] In previous work, bis-alkylidene complexes are believed to be intermediates in alkyl−alkylidyne scrambling through α-H transfer in alkylidyne complexes $(Bu^tCH_2)_3W\equiv{}^{13}CBu^t$ and $(Bu^tCH_2)_3W\equiv CSiMe_3$.[2] Such α-H exchanges in, for example, $(Bu^tCH_2)_3W\equiv{}^{13}CBu^t$ at 60 °C lead to scrambling of the ^{13}C-labeled atom between the alkyl and alkylidene ligands and the formation of $(Bu^tCH_2)_2(Bu^{t13}CH_2)W\equiv CBu^t$ (Scheme 1a). A statistical distribution of the ^{13}C-labeled α-C atoms in $(Bu^t{*}CH_2)_3W\equiv{*}CBu^t$ (*C: 25% ^{13}C) is reached in 24 h.[2c] In other words, the ^{13}C label is present in the α-C atoms in the $^{13}CH_2$:^{13}C groups in a 3:1 ratio. Another case of such alkyl−alkylidene scrambling has been reported in d^0 $(Bu^tCH_2)_3W\equiv CSiMe_3$, leading to the formation of $(Bu^tCH_2)_2(Me_3SiCH_2)W\equiv CBu^t$ (Scheme 1b). Deuterium-labeling studies using $(Bu^tCHD)_3W\equiv CSiMe_3$ and $(Bu^tCD_2)_3W\equiv CSiMe_3$ as well as kinetic studies of the α-H exchanges are consistent with unimolecular and stepwise transfer of two H atoms in one alkyl ligand to the alkylidyne ligand in $(Bu^tCH_2)_3W\equiv CSiMe_3$.[2a] A bis-alkylidene "$(Bu^tCH_2)_2W(=CHSiMe_3)(=CHBu^t)$" was proposed as an intermediate in the transfer (Scheme 1b), although it was not observed.[2a] It is reasonable to assume that there is a similar bis-alkylidene intermediate in the alkyl−alkylidyne scrambling in $(Bu^tCH_2)_3W\equiv{}^{13}CBu^t$ (Scheme 1a).[2c] In the d^2 Os bis-alkylidene complex $Os(=CHBu^t)_2(CD_2Bu^t)_2$, H/D atoms were found to

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* To whom correspondence should be addressed. E-mail: xue@utk.edu.

[†] The University of Tennessee.

[‡] Advanced X-ray Solutions, Bruker AXS Inc.

[§] The University of Wisconsin.

[⊥] The University of Delaware.

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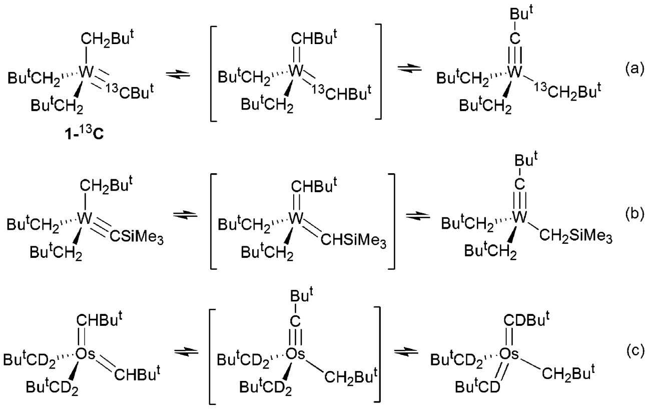
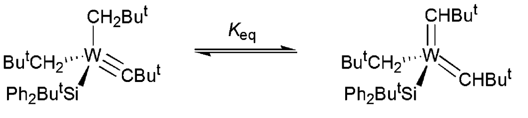
Scheme 1. Proposed Intermediates in Alkylidene/Alkylidyne Scrambling Processes[2,3]



scramble among the α-C atoms (Scheme 1c).[3] This exchange is believed to occur through the alkyl alkylidyne reactive intermediate "$(Bu^tCH_2)_3Os{\equiv}CBu^t$".

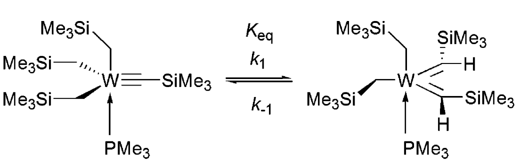
Although the exchange of α-H atoms is a fundamental dynamic process in these archetypical d^0 alkylidene and alkylidyne complexes, there is, to our knowledge, only one direct observation of such an exchange between bis-alkylidene and alkylidyne tautomers.[1a−j,4] Alkylidyne complex $(Bu^tCH_2)_2W({\equiv}CBu^t)(SiBu^tPh_2)$ (**4a**), a *silyl* analogue of $(Bu^tCH_2)_3W{\equiv}CBu^t$, was found to be in an equilibrium with its silyl bis-alkylidene tautomer $(Me_3CCH_2)W({=}CHCMe_3)_2(SiBu^tPh_2)$ (**4b**) (eq 1).[5] $(Bu^tCH_2)W({=}CHBu^t)_2(SiBu^tPh_2)$ (**4b**) is one of the rare known d^0 bis-neopentylidene complexes; the only other known examples involve Ta and Nb d^0 bis-neopentylidene complexes.[1i,3a,5b,6]



4a **4b**

(1)

We recently observed that $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_3)$ (**1a**), an adduct between PMe_3 and $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**2a**), undergoes an exchange with its bis-alkylidene tautomer $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_3)$ (**1b**, eq 2).[7]



1a **1b**

(2)

In the *absence* of the phosphine, the bis-alkylidene tautomer "$(Me_3SiCH_2)_2W({=}CHSiMe_3)_2$" (**2b**) was not observed. Unlike the exchange involving *silyl* alkylidyne and bis-alkylidene complexes **4a** and **4b**, this is an unusual phosphine-induced exchange. Assuming $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**2a**) undergoes an alkyl−alkylidyne scrambling involving "$(Me_3SiCH_2)_2W({=}CHSiMe_3)_2$" (**2b**) as an intermediate similar to that in Scheme 1b, the current work suggests that PMe_3 coordination making $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_3)$ (**1b**) significantly stabilizes **2a** to make its phosphine adduct **1b** observable at room temperature. The synthesis of analogues $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_2Ph)$ (**3a**) and $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_2Ph)$ (**3b**) was also studied, and the tautomeric mixture was found to undergo a similar exchange or equilibrium. Our preparation and characterization of **1a**, **1b**, **3a**, and **3b** as well as thermodynamic and kinetic studies of their exchanges are reported here.

Results and Discussion

Synthesis and Characterization of the W Alkyl Alkylidyne Complex $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_3)$ (1a). Addition of PMe_3 to a solution of $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**2a**) in toluene-d_8 leads to an immediate color change from yellow to red and the formation of the PMe_3 adduct $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_3)$ (**1a**). NMR spectroscopic characterization [^1H, ^{13}C, ^{31}P, ^{29}Si,^1H-gated-decoupled ^{13}C,[8] and HMQC] of **1a** at −50 °C suggests that the PMe_3 ligand coordinates *cis* to the alkylidyne ligand. Two alkyl resonances were observed in the ^1H (in a 1:2 ratio), ^{13}C, and ^{29}Si NMR spectra of **1a** at −50 °C, as expected from the structure of **1a** in eq 2. The coupling constant $^2J_{P-C-axial}$ of 36.5 Hz for the axial $-CH_2R$ ligand is, as expected, larger than $^2J_{P-C-equatorial}$ of 7.2 Hz for the equatorial $-CH_2R$ ligand. The resonance of the alkylidyne C atom in the PMe_3 adduct $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_3)$ (**1a**) at 358.81 ppm appeared as a doublet ($^2J_{P-C} = 14.5$ Hz) in both ^{13}C and ^1H-gated-decoupled ^{13}C NMR spectra and is downfield shifted from that of $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**2a**) at 343.27 ppm.[8]

Synthesis and Characterization of the W Bis-alkylidene Complex $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_3)$ (1b). Upon warming the solution of **1a** in toluene-d_8 to room temperature, **1a** was found to undergo alkyl-to-alkylidyne α-H migration to give bis-alkylidene $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_3)$ (**1b**), which was characterized by ^1H,[8] ^{13}C,[8] ^{31}P, ^{29}Si, ^1H-gated-decoupled ^{13}C,[8] and HMQC NMR spectroscopy. The two tautomers are found to be in equilibrium (**1a** $\rightleftharpoons$ **1b**). The two alkylidene ligands are inequivalent; the alkylidene C resonances in **1b** are observed *as a doublet of doublets* at 256.43 ($^1J_{C-H} = 123.5$ Hz) and 254.71 ppm ($^1J_{C-H} = 102.6$ Hz) in the ^1H-gated-decoupled ^{13}C NMR spectrum at −50 °C.[8] The coupling constants $^2J_{P-C-axial}$ and $^2J_{P-C-equatorial}$ of 32.3 and 0 Hz for the axial and equatorial $-CH_2R$ ligands, respectively, and $^2J_{P-C}$ of 11.8 and 12.6 Hz for the two alkylidene ligands suggest that the two alkylidene and one alkyl ligand coordinate *cis* to the PMe_3 ligand. The ^1H NMR resonances of the alkylidene H atoms in **1b** were observed as doublets at 7.985 ($^3J_{P-H} = 5.6$ Hz) and 7.1982 ($^3J_{P-H} = 4.0$ Hz) ppm, respectively. The presence of two inequivalent alkylidene ligands suggests that

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[3] (a) LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 4802. (b) There is no H/D scrambling among the neopentyl and neopentylidene ligands in $Re({\equiv}CBu^t)({=}CHBu^t)(CD_2Bu^t)_2$ at 80 °C in toluene-d_8. LaPointe, A. M.; Schrock, R. R. *Organometallics* **1995**, *14*, 1875.

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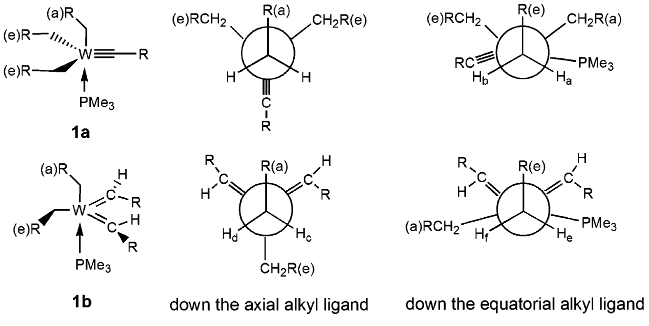
[8] See Supporting Information for details.

Chart 1. Newman Projections of 1a and 1a Showing Diastereotopic Protons



R = SiMe$_3$; (a) = axial; (e) = equatorial

1b adopts an *anti*, *syn* configuration (eq 2), and it is unlikely that the two ligands are involved in a fast rotation about the W═C bonds. (RCH$_2$)(R′CH═)$_2$Ta(PMe$_3$)$_2$, bis-phosphine Ta analogues of **4b**, have been reported.[6,9] The prochiral W atom in **1a** gives rise to diastereotopic α-H atoms (CH_aH_b-SiMe$_3$) for the equatorial alkyl ligands observed as a doublet of doublets at 0.751 ppm (both $^2J_{\mathrm{Ha-Hb}}$ and $^3J_{\mathrm{P-H}} = 14.4$ Hz) and 0.213 ppm ($^3J_{\mathrm{P-H}} = 28.2$ Hz) in its ^{1}H NMR spectrum at −50 °C.[8] The presence of the prochiral W atom in **1b** similarly leads to diastereotopic α-H atoms (CH_eH_f-SiMe$_3$, Chart 1) for the equatorial alkyl ligand observed as a doublet of doublets at 0.917 ($^3J_{\mathrm{P-H}} = 17.7$ Hz, $^2J_{\mathrm{Ha-Hb}} = 11.3$ Hz) and 0.876 ($^3J_{\mathrm{P-H}} = 32.2$ Hz) ppm in the ^{1}H NMR spectrum at −50 °C. The chemical shift difference between the diastereotopic H$_a$ and H$_b$ atoms in **1a** (0.538 ppm) is larger than that (0.041 ppm) in **1b**. The chemical shift difference in alkylidyne **1a** is, however, smaller than 4.56 ppm in pseudo-tetrahedral silyl alkylidyne complex (Me$_3$CCH$_2$)$_2$W(≡CSiMe$_3$)[Si(SiMe$_3$)$_3$].[1o]

The equilibrium mixture of **1a** and **1b** is stable in solution for several days, and cooling the solution to −30 °C yielded crystals of **1b** that were suitable for X-ray diffraction studies. A representation of the molecular structure, crystallographic refinement data, and selected bond distances and angles of **1b** are given in Figure 1 and Tables 1 and 2, respectively.[8] Low-temperature ^{1}H NMR spectra of the crystals showed that the crystals are those of **1b**, indicating that **1b** preferentially crystallized from the mixture. Elemental analysis of the crystals is consistent with the composition of **1b** (or **1a**). The X-ray crystal structure of **1b** was found to be severely disordered with a crystallographically imposed 3-fold axis through the Si(2), W(1), and P(1) atoms. The C(6) atom was located in three equivalent positions: C(6), C(6a), and C(6b), each with a partial occupancy of 1/3. Only C(6) is shown in the ORTEP view of **1b** (Figure 1).

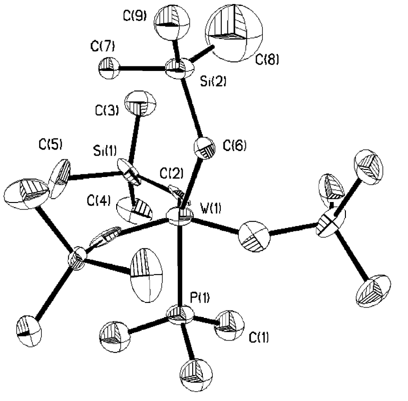


Figure 1. ORTEP view of bis-alkylidene **1b** showing 30% probability thermal ellipsoids. This is a disordered structure.

Table 1. Crystal Data and Structure Refinement for 1b

empirical formula (fw)	C$_{19}$H$_{53}$PSi$_4$W (608.79)
temperature	−100(2) °C
wavelength	0.71073 Å
cryst syst	hexagonal
space group	*P*6(3)
unit cell dimens	$a = 12.1310(5)$ Å, $\alpha = 90°$ $b = 12.1310(5)$ Å, $\beta = 90°$ $c = 12.1091(5)$ Å, $\gamma = 120°$
volume	1543.25(11) Å^3
Z	2
density (calcd)	1.310 g/cm^3
absorp coeff	3.953 mm^{-1}
F(000)	692
cryst size	0.35 × 0.25 × 0.25 mm^3
θ range for data collection	1.68 to 27.42°
index ranges	$-15 \le h \le 15$, $-15 \le k \le 15$, $-15 \le l \le 15$
no. of reflns collected	15 949
no. of indep reflns	2352 [*R*(int) = 0.0371]
completeness to $\theta = 27.42°$	100.0%
absorp corr	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2352/112/86
goodness-of-fit on F^2	1.205
final *R* indices [$I > 2\sigma(I)$]^a	$R_1 = 0.0624$, $wR_2 = 0.1233$
R indices (all data)^a	$R_1 = 0.0654$, $wR_2 = 0.1253$
absolute struct param	0.44(11)
largest diff peak and hole	1.878 and −2.405 e Å^{-3}

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$; $P = [2F_c^2 + \mathrm{Max}(F_o^2, 0)]/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1b

	Distances		
W(1)−C(2)	1.963(12)^a	Si(1)−C(5)	1.881(10)
W(1)−C(6)	2.042(18)	C(6)−Si(2)	1.890(19)
W(1)−P(1)	2.514(5)	Si(2)−C(9)	1.850(15)
P(1)−C(1)	1.86(2)	Si(2)−C(8)	1.874(15)
C(2)−Si(1)	1.861(13)	Si(2)−C(7)	1.855(15)
Si(1)−C(4)	1.868(13)	Si(1)−C(3)	1.861(13)
	Angles		
C(2)−W(1)−C(2a)	119.44(14)	C(1)−P(1)−W(1)	115.4(8)
C(6)−W(1)−P(1)	155.2(6)	C(2)−W(1)−P(1)	85.7(5)
C(2)−W(1)−C(6)	112.6(12)	Si(1)−C(2)−W(1)	135.1(7)
C(2a)−W(1)−C(6)	98.5(14)	Si(2)−C(6)−W(1)	128.2(12)
C(5)−Si(1)−C(2)	111.2(6)	C(7)−Si(2)−C(6)	108.7(12)
C(5)−Si(1)−C(3)	108.7(7)	C(7)−Si(2)−C(8)	108.5(10)

[a] This is the average of one W═CHR and two W−CH$_2$R bonds in the disordered structure.

1b adopts a pseudo-trigonal bipyramidal structure with C(6) and P(1) in the axial positions and the C(6)−W(1)−P(1) angle of 155.2(6)°. The 3-fold disorder leads to an average of the three equatorial W−C bond distances [W(1)−C(2)] of 1.963(12) Å. This average is smaller than the W(1)−C(6) bond distance of 2.042(18) Å, suggesting that the two alkylidene W═C bonds are in the equatorial positions. This observation is consistent with the NMR data of **1b** discussed earlier in this section. The W(1)−P(1) bond distance of 2.514(5) Å is similar to those [2.450(3) and 2.577(3) Å] in W(CH$_2$Bu^t)(═CHBu^t)(≡CBu^t)-[Me$_2$P(CH$_2$)$_2$PMe$_2$].[9]

Synthesis and Characterization of (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PMe$_2$Ph) (3a) and (Me$_3$SiCH$_2$)$_2$W(═CHSiMe$_3$)$_2$(PMe$_2$Ph) (3b). (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PMe$_2$Ph) (**3a**) and (Me$_3$SiCH$_2$)$_2$W(═CHSiMe$_3$)$_2$(PMe$_2$Ph) (**3b**) were prepared by a procedure similar to that used to prepare complexes **1a** and **1b**. Upon addition of PMe$_2$Ph to a solution of (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$) (**2a**) in toluene-d_8 at 23 °C, an immediate color change from yellow to orange-red was observed. NMR spec-

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troscopic data at −50 °C, vide infra, were consistent with the formation of the PMe$_2$Ph adduct (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PMe$_2$Ph) (**3a**). NMR spectroscopic characterization (^{1}H, ^{13}C, ^{31}P, ^{29}Si, and HMQC) of **3a** suggests that the PMe$_2$Ph ligand coordinates *cis* to the alkylidyne ligand as in **1a**. Upon warming the solution of **3a** in toluene-d_8 to 23 °C, **3a** was found to undergo alkyl-to-alkylidyne α-H migration to give bis-alkylidene (Me$_3$SiCH$_2$)$_2$W(=CHSiMe$_3$)$_2$(PMe$_2$Ph) (**3b**), which was characterized by ^{1}H, ^{13}C, ^{31}P, ^{29}Si, and HMQC NMR spectroscopy. As in **1a** $\rightleftharpoons$ **1b**, the two tautomers reach an equilibrium (**3a** $\rightleftharpoons$ **3b**) [K_{eq}(303 K) = 4.65(0.11)].

3a and **3b** also exhibit diastereotopic α-H atoms on the equatorial alkyl ligands, similar to those in **1a** and **1b** (Chart 1). The ^{1}H NMR resonances of the alkylidene H atoms in **1b** were observed as doublets at 8.217 ($^3J_{P-H}$ = 5.3 Hz) and 7.621 ($^3J_{P-H}$ = 3.6 Hz) ppm, respectively. Similarly, the ^{13}C NMR resonances of the alkylidene ligands in **3b** appeared as doublets at 257.8 and 256.0 ppm, respectively. These observations suggest that, as in **1b**, there are two inequivalent alkylidene ligands in **3b**. The coupling constants $^2J_{P-C-axial}$ and $^2J_{P-C-equatorial}$ of 32.2 and 0 Hz for the axial and equatorial −CH$_2$R ligands, respectively, and $^2J_{P-C}$ of 12.1 and 11.1 Hz for the two alkylidene ligands suggest that the two alkylidene and one alkyl ligands coordinate *cis* to the PMe$_2$Ph ligand. Two inequivalent alkylidene ligands suggest that **3b** adopts an *anti, syn* configuration similar to that of **1b**. The prochiral W atom in **3a** gives rise to diastereotopic α-H atoms (CH_aH_b-SiMe$_3$) for the equatorial alkyl ligands as a doublet of doublets at 0.750 ($^2J_{Ha-Hb}$ = $^3J_{P-H}$ = 14.8 Hz) and 0.530 ppm in the ^{1}H NMR spectrum at −50 °C.

The equilibrium mixture of **3a** and **3b** in solution was found thermally unstable. Repeated attempts to purify **3a**,**b** through crystallization gave oily liquids that decomposed.[10] Characterization of **3a**,**b** was thus based on their ^{1}H, ^{13}C, ^{31}P, ^{29}Si, ^{1}H-decoupled ^{13}C, and HMQC NMR spectra.

Attempted Reactions of (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (2a) with PCy$_3$ and PPh$_3$. Attempts were made to prepare compounds analogous to **1a**,**b** and **3a**,**b** using phosphines other than PMe$_3$ and PMe$_2$Ph. The addition of excess PCy$_3$ or PPh$_3$ to solutions of **2a** in toluene and heating the solutions for 2 days at 100 °C yielded no products. No complexation was observed between PPh$_3$ or PCy$_3$ and **2a**. It is not clear why these two phosphines do not form the adducts with **2a**.

Kinetic and Thermodynamic Studies of the 1a $\rightleftharpoons$ 1b Exchange. In the current work, (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PR$_3$) (**1a** and **3a**), adducts between phosphines PR$_3$ and alkyl alkylidyne (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (**2a**), were found to undergo exchanges with their bis-alkylidene tautomers (Me$_3$SiCH$_2$)$_2$W(=CHSiMe$_3$)$_2$(PR$_3$) (**1b** and **3b**). Given the unusual nature of the exchange processes of **1a**$\rightleftharpoons$**1b** and **3a**$\rightleftharpoons$**3b** in the presence of phosphines, further kinetic and thermodynamic studies were performed with the goal of elucidating the mechanism.

Variable-temperature NMR spectra of the tautomerization **1a** $\rightleftharpoons$ **1b** were studied, and the equilibrium constants, K_{eq} = [**1b**]/[**1a**], measured between 278 and 303 K are listed in Table 2. A plot of ln K_{eq} vs 1/T (Figure 2) gave ΔH° = −1.8(0.5) kcal/mol and ΔS° = −1.5(1.7) eu. The equilibrium constants (K_{eq}) range from 12.3(0.2) at 278 K to 9.37(0.12) at 303 K, indicating that the alkylidene isomer **1b** is favored. Decreasing the temperature shifts the equilibrium toward **1a**. The process **1a** $\rightleftharpoons$ **1b** is slightly exothermic, with ΔH° = −1.8(0.5) kcal/mol. It is interesting to note that the d^0 bis-alkylidene complex **1b** is thermodynamically close in energy to its alkylidyne isomer **1a** [Δ$G°_{298K}$ = −1.3(1.0) kcal/mol], although **1b** is slightly more stable. If there is an alkyl−alkylidyne scrambling process in (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (**2a**) as in (Bu^{t}CH$_2$)$_3$W≡CSiMe$_3$ $\rightleftharpoons$ (Bu^{t}CH$_2$)$_2$W(CH$_2$SiMe$_3$)(≡CBu^t), the proposed bis-alkylidene intermediate "(Me$_3$SiCH$_2$)$_2$W(=CHSiMe$_3$)$_2$" (**2b**) is much higher in energy than **2a**, and coordination with PMe$_3$ to give **1b** significantly lowers its energy so that **1a** $\rightleftharpoons$ **1b** equilibrium is observed.[2,5]

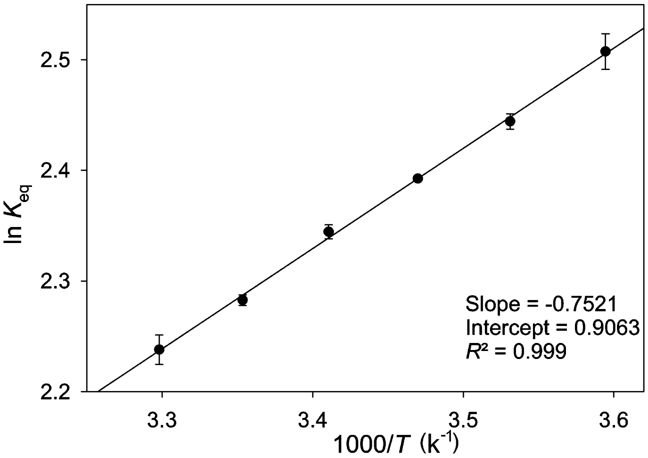

Figure 2. Plot of ln K_{eq} vs 1/T of the equilibrium **1a** $\rightleftharpoons$ **1b**.

In the previous study of the exchange of silyl complexes (Bu^{t}CH$_2$)$_2$W(≡CBu^t)(SiBu^{t}Ph$_2$) (**4a**) $\rightleftharpoons$ (Bu^{t}CH$_2$)W(=CHBu^t)$_2$(SiBu^{t}Ph$_2$) (**4b**), only the thermodynamic properties were reported. We have conducted kinetic studies of the unusual alkyl alkylidyne and bis-alkylidene exchange between **3a** and **3b**.

Variable-temperature ^{1}H NMR experiments for the **1a** $\rightleftharpoons$ **1b** exchange between 278 and 303 K show that the α-H migrations between **1a** and **1b** follow first-order reversible kinetics (eqs 3 and 4),[11]

$$\ln\left[\frac{(I_{1b-e} - I_{1b-t})}{(I_{1b-e} - I_{1b-0})}\right] = -(k_1 + k_{-1})t \qquad (3)$$

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[\mathbf{1b}]}{[\mathbf{1a}]} \qquad (4)$$

where I_{1b0}, I_{1bt}, and I_{1be} are the integrations of **1b** at time t = 0, t = t, and equilibrium, respectively; k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively. The kinetic plots for the exchange are shown in Figure 3, and the rate constants from eq 3 are given in Table 3. Eyring plots (Figure 4) lead to the activation parameters of the exchange: $\Delta H_1^\ddagger$ = 16.2(1.2) kcal/mol, $\Delta S_1^\ddagger$ = −22(4) eu for the forward reaction **1a** → **1b**, and $\Delta H_2^\ddagger$ = 18.0(1.3) kcal/mol, $\Delta S_2^\ddagger$ = −21(4) eu for the reverse **1b** → **1a** reaction. The **1a** $\rightleftharpoons$ **1b** exchange is significantly slower than the (Bu^{t}CH$_2$)$_2$W(≡CBu^t)(SiBu^{t}Ph$_2$) (**4a**) $\rightleftharpoons$ (Bu^{t}CH$_2$)W(=CHBu^t)$_2$(SiBu^{t}Ph$_2$) (**4b**) exchange. The latter was observed in the 2D-NOESY spectra (t_{mix} = 3 s) at 23 °C.[5a] The **1a** $\rightleftharpoons$ **1b** exchange is, however, much faster than the alkyl−alkylidene scrambling in (Bu^{t}CH$_2$)$_3$W≡CSiMe$_3$, which was observed at >70 °C.[2a] The

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(10) The liquid sample of **3a**,**b** was shipped overnight in an insulated container with dry ice for elemental analysis. The sample was analyzed immediately upon arrival. Repeated attempts to get elemental analysis of **3a**,**b** afforded the following data: Anal. Calcd: C 43.10; H 7.99; P 4.63. Found: C 48.47, 48.53; H 7.79, 7.80; P 4.22, 4.18.

(11) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanism*, 2nd ed.; McGraw-Hill: New York, 1995; pp 46−49.

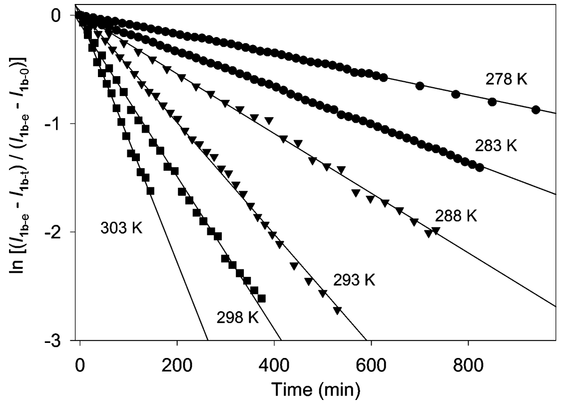


Figure 3. Kinetic plots of the reversible reactions **1a** $\rightleftharpoons$ **1b**.

Table 3. Equilibrium (K_{eq}) and Rate Constants (k_1 and k_{-1}) of the 1a $\rightleftharpoons$ 1b Exchange[a]

T (K)[b]	K_{eq}[c]	$k_1 \times 10^5$ (s^{-1})[d]	$k_{-1} \times 10^6$ (s^{-1})[d]
278(1)	12.3(0.2)	1.42(0.02)	1.160(0.018)
283(1)	11.52(0.08)	2.47(0.13)	2.14(0.11)
288(1)	10.941(0.012)	4.16(0.04)	3.80(0.04)
293(1)	10.43(0.07)	7.6(0.3)	7.3(0.3)
298(1)	9.80(0.05)	10.55(0.10)	10.71(0.10)
303(1)	9.37(0.12)	17.5(0.5)	18.6(0.6)

[a] Solvent: toluene-d_8. [b] The relatively small temperature range of 25 K in the current thermodynamic and kinetic studies leads to relatively large uncertainties in thermodynamic ($\Delta H°$ and $\Delta S°$) and kinetic ($\Delta H^‡$ and $\Delta S^‡$) parameters, as the error calculations in the Experimental Section show. [c] The largest random uncertainty is $\sigma K_{eq(ran)}/K_{eq} = 0.2/12.3 = 1.6\%$. The total uncertainty $\sigma K_{eq}/K_{eq}$ of 5.2% was calculated from $\sigma K_{eq(ran)}/K_{eq} = 1.6\%$ and the estimated systematic uncertainty $\sigma K_{eq(sys)}/K_{eq} = 5\%$ by $\sigma K_{eq}/K_{eq} = [(\sigma K_{eq(ran)}/K_{eq})^2 + (\sigma K_{eq(sys)}/K_{eq})^2]^{1/2}$. [d] The largest random uncertainties are $\delta k_{1(ran)}/k_1 = 0.13/2.47 = 5.3\%$ and $\delta k_{-1(ran)}/k_{-1} = 0.11/2.14 = 5.1\%$. The total uncertainties $\delta k_1/k_1 = 0.0726$ and $\delta k_{-1}/k_{-1} = 0.0717$ were calculated from $\delta k_{(ran)}/k$ and the estimated systematic uncertainty $\delta k_{(sys)}/k = 5\%$ by $\delta k/k = [(\delta k_{(ran)}/k)^2 + (\delta k_{(sys)}/k)^2]^{1/2}$.

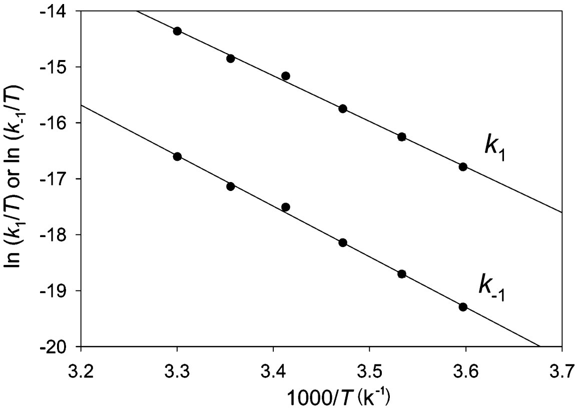
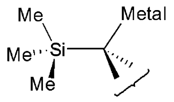


Figure 4. Eyring plots for the reversible reactions **1a** $\rightleftharpoons$ **1b**.

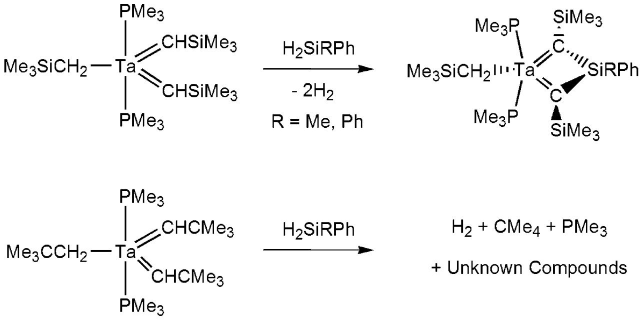
activation free energy $\Delta G_1{}^‡{}_{298K}$ of 23(2) kcal/mol for the forward reaction **1a** → **1b** is 28.1(1.1) kcal/mol lower than that for the alkyl−alkylidene scrambling in $(Bu^tCH_2)_3W{\equiv}CSiMe_3$.[2a]

Under heating to over 60 °C, the alkyl alkylidynes $\rightleftharpoons$ bis-alkylidenes equilibrium mixtures of **1a**,**b** and **3a**,**b** were found to slowly eliminate $SiMe_4$ and convert to alkyl alkylidene alkylidyne complexes $W(CH_2SiMe_3)({=}CHSiMe_3)({\equiv}CSiMe_3)(PR_3)_2$.[12]

Chart 2. Stabilization of the M−C Bond by an Adjacent Si Atom[13]



Scheme 2. Comparison of Reactions of $(R'CH_2)Ta({=}CHR')_2(PMe_3)_2$ ($R' = Me_3Si, Me_3C$) with H_2SiRPh



It is interesting to note that $(Bu^tCH_2)_3W{\equiv}CBu^t$ reacts with neat PMe_3 in a sealed tube at 100 °C, giving $(Bu^tCH_2)W({\equiv}CBu^t)({=}CHBu^t)(PMe_3)_2$ through α-H abstraction and CMe_4 elimination, as Schrock and Clark have reported.[1k] When ca. 1 equiv of PMe_3 was added to *a solution* of $(Bu^tCH_2)_3W{\equiv}CBu^t$ in benzene-d_6 *at room temperature*, a similar reaction giving $W(CH_2Bu^t)({=}CHBu^t)({\equiv}CBu^t)(PMe_3)_2$ and CMe_4 occurred. *No adduct between* $(Bu^tCH_2)_3W{\equiv}CBu^t$ *and* PMe_3 *was observed* prior to the formation of $W(CH_2Bu^t)({=}CHBu^t)({\equiv}CBu^t)(PMe_3)_2$.

The studies here reveal the differences in the reactivities of trimethylsilylmethylidyne complex $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ (**2a**) and its *tert*-butyl analogue $(Bu^tCH_2)_3W{\equiv}CBu^t$ toward PMe_3. The former forms an adduct (**1a**) with PMe_3, which subsequently converts to its bis-alkylidene tautomer **1b** through unusual α-H migration. The **1a** $\rightleftharpoons$ **1b** mixture under heating then undergoes α-H abstraction reaction.[12] The latter, $(Bu^tCH_2)_3W{\equiv}CBu^t$, readily undergoes α-H abstraction reaction in the presence of PMe_3. It is not clear what leads to the differences, and we are conducting studies in order to gain insight into the differences. It is however well known that silicon stabilizes an adjacent carbon−metal bond (Chart 2).[13] Complexes with $-CH_2SiMe_3$ and/or $=CHSiMe_3$ ligands have shown unique chemistry.[6d,e] For example, $(Me_3SiCH_2)Ta({=}CHSiMe_3)_2(PMe_3)_2$ reacts with H_2SiRPh (R = Me, Ph) to yield novel metallasilacyclobutadiene complexes (Scheme 2). In comparison, its neopentyl analogue $(Bu^tCH_2)Ta({=}CHBu^t)_2(PMe_3)_2$ was found to decompose to unknown species when exposed to H_2SiRPh.[6d,e]

Thermodynamic and Kinetic Studies of the 3a $\rightleftharpoons$ 3b Exchange. A Comparison of PMe$_3$ and PMe$_2$Ph. PMe_2Ph is bulkier than PMe_3, and the phenyl group often acts as an electron-withdrawing group. Both yielded alkylidyne adducts in their reactions with **2a**: $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_3)$ (**1a**) and $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_2Ph)$ (**3a**). The thermodynamic and kinetic studies were conducted for the $(Me_3SiCH_2)_3W({\equiv}CSiMe_3)(PMe_2Ph)$ (**3a**) $\rightleftharpoons$ $(Me_3SiCH_2)_2W({=}CHSiMe_3)_2(PMe_2Ph)$ (**3b**) exchange at 303 K. The **3a** $\rightleftharpoons$ **3b** equilibrium [$K_{eq}' = 4.65(0.11)$ at 303 K] is shifted more to the left (**3a**) than the **1a** $\rightleftharpoons$ **1b** equilibrium [$K_{eq} = 9.37(0.12)$ at 303 K]. Perhaps the bulkier PMe_2Ph ligands with an electron-withdrawing phenyl group donate less electron density to the metal centers in **3a** and **3b**, shifting the equilibrium to alkyl alkylidyne **3a**.

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(12) Morton, L. A. Ph. D. Dissertation, The University of Tennessee, Knoxville, 2005.

(13) Fleming, I. In *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*; Barton, D., Ollis, W. D., Eds.; Vol. 3 (Volume editor: Jones, D. N.), Pergamon: New York, 1979; pp 545−547.

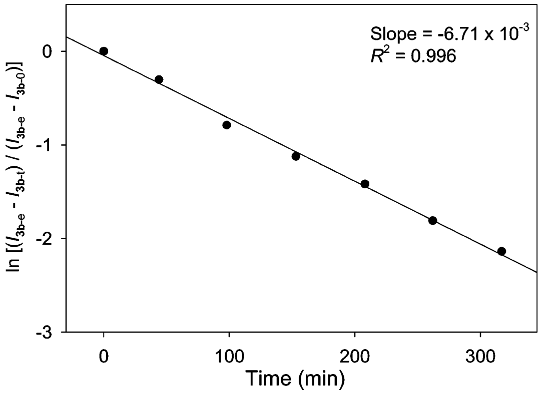

Figure 5. Kinetic plot of the formation of **3b** from **3a** at 303 K. $I_{\mathbf{3b}-0}$, $I_{\mathbf{3b}-t}$, and $I_{\mathbf{3b}-e}$ are the integrations of **3b** at $t = 0$, $t = t$, and equilibrium, respectively.

Kinetic studies using a kinetic equation similar to eq 3 give $k_1' = 1.0(0.1) \times 10^{-4}\ \mathrm{s}^{-1}$ and $k_{-1}' = 2.2(0.2) \times 10^{-5}\ \mathrm{s}^{-1}$ for the **3a** → **3b** and the reverse **3b** → **3a** conversions at 303 K, respectively (Figure 5). In comparison, the rates for the **1a** ⇌ **1b** exchanges in the PMe$_3$ complexes are $k_1 = 1.75(0.05) \times 10^{-4}\ \mathrm{s}^{-1}$ and $k_{-1} = 1.86(0.06) \times 10^{-5}\ \mathrm{s}^{-1}$. The forward **3a** → **3b** conversion in the PMe$_2$Ph complexes is slower than the **1a** → **1b** conversion, whereas the reverse **3b** → **3a** conversion is slightly faster than the **1b** → **1a** conversion. The **1a** ⇌ **1b** equilibrium is more shifted to **1b** [$K_{eq} = 9.37(0.12)$] than in the **3a** ⇌ **3b** equilibrium [$K_{eq}' = 4.65(0.11)$], resulting in a higher kinetic barrier for the reverse **1b** → **1a** conversion. It is not clear what leads to the higher kinetic barrier.

Conclusions

It is interesting to note that phosphine coordination to alkyl alkylidyne (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (**2a**) to yield (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PMe$_3$) (**1a**) plays an important role in the rare reversible transformation of **1a** to its bis-alkylidene tautomer (Me$_3$SiCH$_2$)$_2$W(=CHSiMe$_3$)$_2$(PMe$_3$) (**1b**). In the absence of phosphine, "(Me$_3$SiCH$_2$)$_2$W(=CHSiMe$_3$)$_2$" (**2b**), bis-alkylidene tautomer of (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (**2a**), might be too high in energy than **2a** to be directly observed. The **1a** ⇌ **1b** and **3a** ⇌ **3b** exchanges are only the second reported alkyl alkylidyne ⇌ bis-alkylidene tautomerizations, and **1b** and **3b** are rare d^0 bis-alkylidene complexes. In the first reported case of alkyl alkylidyne ⇌ bis-alkylidene exchange [between (Bu^{t}CH$_2$)$_2$W(≡CBu^t)(SiBu^{t}Ph$_2$) (**4a**) and (Me$_3$CCH$_2$)W(=CHCMe$_3$)$_2$(SiBu^{t}Ph$_2$) (**4b**) (eq 1)],[5] silyl ligands are believed to be critical to the direct observation of the bis-alkylidene complex **4b**.[5b] Studies of the current **1a** ⇌ **1b** exchange give the thermodynamic parameters for the equilibrium and kinetic activation parameters of the forward and reverse reactions.

Experimental Section

General Comments. All manipulations were performed under a dry nitrogen atmosphere with the use of either a drybox or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. Benzene-d_6 and toluene-d_8 were dried over activated molecular sieves and stored under N$_2$. WCl$_6$ was freshly sublimed under vacuum. (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ (**2a**)[1m] was prepared from W(OMe)$_3$Cl$_3$ and 6 equiv of Me$_3$SiCH$_2$MgCl by a procedure similar to that used in the preparation of (Me$_3$CCH$_2$)$_3$W≡CCMe$_3$.[14] ^{1}H and ^{13}C 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 NMR, ^{29}Si NMR, HMQC (heteronuclear multiple quantum coherence), and ^{1}H-gated-decoupled-^{13}C spectra were recorded on a Bruker AMX-400 spectrometer. Elemental analysis was performed by Complete Analysis Laboratories Inc., Parsippany, NJ.

For the thermodynamic studies, the equilibrium constants K_{eq} were obtained from at least two separate experiments at a given temperature, and their averages are listed in Table 3. The *maximum* random uncertainty in the equilibrium constants was combined with the estimated systematic uncertainty of ca. 5%. The total uncertainties in the equilibrium constants were used in the ln K_{eq} vs 1/T plot in Figure 2 and error propagation calculations. The estimated uncertainty in the temperature measurements for an NMR probe was 1 K. The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes were calculated from an unweighted nonlinear least-squares procedure contained in the SigmaPlot Scientific Graph System. The uncertainties in $\Delta H°$ and $\Delta S°$ were computed from the following error propagation formulas, which were derived from $-RT \ln K_{eq} = \Delta H° - T\Delta S°$.

$$(\sigma\Delta H°)^2 = \frac{\mathrm{R}^2({T_{max}}^2{T_{min}}^4 + {T_{min}}^2{T_{max}}^4)}{(T_{max} - T_{min})^4}\left[\ln\left(\frac{K_{eq(max)}}{K_{eq(min)}}\right)\right]^2\left(\frac{\sigma T}{T}\right)^2 + \frac{2\mathrm{R}^2{T_{max}}^2{T_{min}}^2}{(T_{max} - T_{min})^2}\left(\frac{\sigma K_{eq}}{K_{eq}}\right)^2 \quad (5)$$

$$(\sigma\Delta S°)^2 = \frac{2\mathrm{R}^2{T_{min}}^2{T_{max}}^2}{(T_{max} - T_{min})^4}\left[\ln\left(\frac{K_{eq(max)}}{K_{eq(min)}}\right)\right]^2\left(\frac{\sigma T}{T}\right)^2 + \frac{\mathrm{R}^2({T_{max}}^2{T_{min}}^2)}{(T_{max} - T_{min})^2}\left(\frac{\sigma K_{eq}}{K_{eq}}\right)^2 \quad (6)$$

T_{min} and T_{max} are the minimum and maximum temperatures in the current studies; T is the mean temperature in the current studies. $K_{eq(min)}$ and $K_{eq(max)}$ are the minimum and maximum equilibrium constants, respectively. $\sigma K_{eq}/K_{eq}$ is given in Table 3. For the kinetic studies, the rate constants k_1 and k_{-1} were obtained from at least two separate experiments at a given temperature, and their averages are listed. The estimated uncertainty (σT) in the temperature measurements for an NMR probe was 1 K. The enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) were calculated from an unweighted nonlinear least-squares procedure contained in the SigmaPlot Scientific Graph System. The uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were computed from the error propagation formulas[15] derived by Girolami and coworkers from the Eyring equation. The values of $\sigma k/k$ are given in Table 3. These error propagation calculations show that the smaller the temperature range ($T_{max} - T_{min}$) of studies is, the larger the uncertainties in both thermodynamic ($\Delta H°$ and $\Delta S°$) and kinetic ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) parameters are.

NMR Experiments. Complete and unambiguous assignments of all proton and carbons resonances were achieved on the basis of chemical shift considerations, as well as NMR experiments, namely, HMQC and ^{1}H-gated-decoupled-^{13}C experiments. HMQC was used to assign diastereotopic protons in complexes **1a**,**b** and **3a**,**b**. ^{1}H-gated-decoupled-^{13}C experiments were utilized to determine the number of H atoms that are bonded to an α-C atom and to calculate the $^1J_{C-H}$ coupling constants.

Preparation of (Me$_3$SiCH$_2$)$_3$W(≡CSiMe$_3$)(PMe$_3$) (1a). 1a was prepared by the vacuum transfer of PMe$_3$ (0.104 mmol) to a J. R. Youngs NMR tube containing **2a** (48 mg, 0.0904 mmol) in toluene-d_8. The reaction mixture is kept frozen in liquid nitrogen until placed in the precooled NMR probe at −50 °C. **1a**: ^{1}H NMR (toluene-d_8, 400.11 MHz, −50 °C, J in Hz) δ 0.904 (d, 9H, PMe_3,

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$^2J_{\mathrm{P-H}} = 7.2$), 0.751 (dd, 2H, *eq*-$\mathrm{C}H_a\mathrm{H_b}$-$\mathrm{SiMe_3}$, $^2J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 14.4$), 0.503 (s, 9H, $\equiv$CSi*Me*$_3$), 0.487 (d, 2H, *ax*-CH_2SiMe$_3$, $^3J_{\mathrm{P-H}} = 10.7$), 0.329 (s, 9H, *ax*-CH$_2$Si*Me*$_3$), 0.316 (s, 18H, *eq*-CH$_2$Si*Me*$_3$), 0.213 (dd, 2H, *eq*-$\mathrm{CH_a}H_b$-SiMe$_3$, $^3J_{\mathrm{P-H}} = 28.2$, $^2J_{\mathrm{H-H}} = 14.1$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.63 MHz, −50 °C, *J* in Hz) δ 358.81 (d, $\equiv$*C*SiMe$_3$, $^2J_{\mathrm{P-C}} = 14.5$, $^1J_{\mathrm{W-C}} = 159.1$), 81.69 (d, *ax*-*C*H$_2$SiMe$_3$, $^2J_{\mathrm{P-C}} = 36.5$, $^1J_{\mathrm{W-C}} = 117.9$), 49.45 (d, *eq*-*C*H$_2$SiMe$_3$, $^1J_{\mathrm{H-C}} = 111.6$, $^2J_{\mathrm{P-C}} = 7.2$, $^1J_{\mathrm{W-C}} = 59.9$), 17.84 (d, P*Me*$_3$, $^1J_{\mathrm{H-C}} = 128.2$, $^1J_{\mathrm{P-C}} = 22.8$), 4.23 (s, $\equiv$CSi*Me*$_3$, $^1J_{\mathrm{H-C}} = 117.8$, $^3J_{\mathrm{W-C}} = 50.1$), 3.55 (s, *ax*-CH$_2$Si*Me*$_3$, $^1J_{\mathrm{H-C}} = 117.1$, $^3J_{\mathrm{W-C}} = 33.2$), 3.48 (s, *eq*-CH$_2$Si*Me*$_3$, $^1J_{\mathrm{H-C}} = 117.1$, $^3J_{\mathrm{W-C}} = 25.0$); ^{31}P{^{1}H} (toluene-d_8, 161.97 MHz, −50 °C, *J* in Hz) δ −5.64 (s, $^1J_{\mathrm{W-P}} = 28.9$); ^{29}Si{^{1}H} (toluene-d_8, 79.49 MHz, −50 °C, *J* in Hz) δ −0.269 (d, *ax*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 2.0$), −2.482 (d, *eq*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 4.9$, $^2J_{\mathrm{W-Si}} = 50.2$), −21.129 (d, $\equiv$C*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 2.3$, $^2J_{\mathrm{W-Si}} = 52.3$). The assignments of the ^{1}H and ^{13}C NMR were confirmed by low-temperature HMQC experiments.

Preparation of $(\mathrm{Me_3SiCH_2})_2\mathrm{W}(=\mathrm{CHSiMe_3})_2(\mathrm{PMe_3})$ (2b). A solution of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**, 95 mg, 0.179 mmol) in pentane was frozen by liquid nitrogen in a 125 mL Schlenk flask. The flask headspace was evacuated. PMe$_3$ (0.358 mmol) was then vacuum transferred to the flask submerged in liquid nitrogen. The PMe$_3$ was then condensed in the flask, and the flask was warmed to room temperature. To the flask was then added nitrogen, and the contents were stirred overnight at room temperature. Cooling the solution at −30 °C overnight gave crystals of **2b** (87 mg, 0.143 mmol, 80% yield): ^{1}H NMR (toluene-d_8, 400.11 MHz, −20 °C, *J* in Hz) δ 7.985 (d, 1H, =C*H*SiMe$_3$, $^3J_{\mathrm{P-H}} = 5.6$), 7.192 (d, 1H, =C*H*SiMe$_3$, $^3J_{\mathrm{P-H}} = 4.0$), 1.024 (d, 9H, P*Me*$_3$, $^2J_{\mathrm{P-H}} = 7.8$), 0.917 (dd, 1H, *eq*-$\mathrm{C}H_a\mathrm{H_b}$-SiMe$_3$, $^3J_{\mathrm{P-H}} = 17.7$, $^2J_{\mathrm{H-H}} = 11.3$), 0.876 (dd, 1H, *eq*-$\mathrm{CH_a}H_b$-SiMe$_3$, $^3J_{\mathrm{P-H}} = 32.2$, $^2J_{\mathrm{H-H}} = 11.3$; overlapped with *eq*-$\mathrm{C}H_a\mathrm{H_b}$-SiMe$_3$ peak), 0.388 (s, 9H, *ax*-CH$_2$Si*Me*$_3$, $^2J_{\mathrm{Si-H}} = 6.0$), 0.388 (d, 2H, *ax*-C$H_2$SiMe$_3$, $^3J_{\mathrm{P-H}} = 11.4$; overlapped with *ax*-CH$_2$Si*Me*$_3$ peak), 0.342 (s, 9H, *eq*-CH$_2$Si*Me*$_3$), 0.280 (s, 9H, =CHSi*Me*$_3$), 0.128 (s, 9H, =CHSi*Me*$_3$); ^{13}C{^{1}H} (toluene-d_8, 100.63 MHz, −40 °C, *J* in Hz) δ 256.43 (d, =*C*HSiMe$_3$, $^1J_{\mathrm{H-C}} = 123.5$, $^2J_{\mathrm{P-C}} = 11.8$), 254.71 (d, =*C*HSiMe$_3$, $^1J_{\mathrm{H-C}} = 102.6$, $^2J_{\mathrm{P-C}} = 12.6$), 50.71 (s, *eq*-*C*H$_2$SiMe$_3$, $^1J_{\mathrm{H-C}} = 105.3$, $^1J_{\mathrm{W-C}} = 43.0$), 38.01 (d, *ax*-*C*H$_2$SiMe$_3$, $^1J_{\mathrm{H-C}} = 111.0$, $^2J_{\mathrm{P-C}} = 32.3$), 18.80 (d, P*Me*$_3$, $^1J_{\mathrm{H-C}} = 126.4$, $^1J_{\mathrm{P-C}} = 26.4$), 4.82 (s, *ax*-CH$_2$Si*Me*$_3$, $^1J_{\mathrm{H-C}} = 118.1$), 3.08 (s, *eq*-CH$_2$Si*Me*$_3$, $^1J_{\mathrm{H-C}} = 118.8$), 1.76 (s, =CHSi*Me*$_3$, $^1J_{\mathrm{H-C}} = 117.3$), 1.64 (s, =CHSi*Me*$_3$, $^1J_{\mathrm{H-C}} = 117.3$); ^{31}P{^{1}H} (toluene-d_8, 161.97 MHz, −50 °C, *J* in Hz) δ 0.61 (s, $^1J_{\mathrm{W-P}} = 115.5$); ^{29}Si{^{1}H} (toluene-d_8, 79.49 MHz, −50 °C, *J* in Hz) δ −0.73 (d, *ax*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 19.2$), −1.96 (d, *eq*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 4.1$), −8.63 (d, =CH*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 2.9$), −9.89 (d, =CH*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 4.8$). ^{1}H and ^{13}C assignments were confirmed by low-temperature HMQC experiments. Anal. Calcd: C, 37.61, H, 8.47. Found: C, 37.43, H, 8.66.

Preparation of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}(\equiv\mathrm{CSiMe_3})(\mathrm{PMe_2Ph})$ (3a). To a solution of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**, 50 mg, 0.094 mmol) in toluene-d_8 was added ca. 10-fold excess PMe$_2$Ph via cannula transfer to a J. R. Youngs NMR tube. An immediate color change from yellow to orange-red was observed, signifying the formation of **3a**. At −50 °C the solution of **3a** was stable. **3a**: ^{1}H NMR (toluene-d_8, 399.97 MHz, −50 °C, *J* in Hz) δ 7.4−7.0 (m, 5H, PMe$_2$*Ph*), 1.30 (d, 6H, P*Me*$_2$Ph, $^2J_{\mathrm{P-H}} = 6.0$), 0.750 (dd, 2H, *eq*-$\mathrm{C}H_a\mathrm{H_b}$-SiMe$_3$, $^2J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 14.8$), 0.506 (s, 9H, $\equiv$CSi*Me*$_3$), 0.599 (broad singlet, 2H, *ax*-CH_2SiMe$_3$), 0.363 (s, 9H, *ax*-CH$_2$Si*Me*$_3$), 0.243 (s, 18H, *eq*-CH$_2$Si*Me*$_3$), 0.530 (broad, 2H, *eq*-$\mathrm{CH_a}H_b$-SiMe$_3$); ^{13}C{^{1}H} NMR (toluene-d_8, 100.59 MHz, −60 °C, *J* in Hz) δ 358.91 (d, $\equiv$*C*SiMe$_3$, $^2J_{\mathrm{P-C}} = 14.1$), 83.86 (d, *ax*-*C*H$_2$SiMe$_3$, $^2J_{\mathrm{P-C}} = 34.2$), 50.38 (d, *eq*-*C*H$_2$SiMe$_3$, $^2J_{\mathrm{P-C}} = 7.0$, 16.74 (d, P*Me*$_2$Ph, $^1J_{\mathrm{P-C}} = 22.1$), 3.59 (s, $\equiv$CSi*Me*$_3$, $^3J_{\mathrm{W-C}} = 51.3$), 2.97(s, *ax*-CH$_2$Si*Me*$_3$), 2.82 (s, *eq*-CH$_2$Si*Me*$_3$); ^{31}P{^{1}H} (toluene-d_8, 161.92 MHz, −60 °C, *J* in Hz) δ 6.57 (s); ^{29}Si{^{1}H} (toluene-d_8, 79.46 MHz, −60 °C, *J* in Hz) δ 0.677 (d, *ax*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 1.0$), −1.22 (d, *eq*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 4.8$), −19.28 (d, $\equiv$C*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 1.9$, $^2J_{\mathrm{W-Si}} = 51.0$).

Preparation of $(\mathrm{Me_3SiCH_2})_2\mathrm{W}(=\mathrm{CHSiMe_3})_2(\mathrm{PMe_2Ph})$ (3b). Upon warming a solution of **3a** to room temperature, it was converted to **3b**. **3b** was stable for several days in solution at room temperature. Attempts to obtain pure crystals of **3a**,**b** yielded a dark brown oil, which was thermally unstable.[10] **3b**: ^{1}H NMR (toluene-d_8, 399.97 MHz, −20 °C, *J* in Hz) δ 8.22 (d, 1H, =C*H*SiMe$_3$, $^3J_{\mathrm{P-H}} = 5.3$), 7.62 (d, 1H, =C*H*SiMe$_3$, $^3J_{\mathrm{P-H}} = 3.6$), 7.5−7.0 (m, PMe$_2$*Ph*), 1.38 (d, 6H, P*Me*$_2$Ph, $^2J_{\mathrm{P-H}} = 7.6$), 0.728 (dd, 1H, *eq*-$\mathrm{C}H_a\mathrm{H_b}$-SiMe$_3$, $^3J_{\mathrm{P-H}} = 18.6$, $^2J_{\mathrm{H-H}} = 11.2$), 1.01 (dd, 1H, *eq*-$\mathrm{CH_a}H_b$-SiMe$_3$, $^3J_{\mathrm{P-H}} = 33.0$, $^2J_{\mathrm{H-H}} = 11.2$), 0.331 (s, 9H, *ax*-CH$_2$Si*Me*$_3$), 0.372 (d, 2H, *ax*-C$H_2$SiMe$_3$, $^3J_{\mathrm{P-H}} = 9.2$), 0.326 (s, 9H, *eq*-CH$_2$Si*Me*$_3$), 0.137 (s, 9H, =CHSi*Me*$_3$), 0.056 (s, 9H, =CHSi*Me*$_3$); ^{13}C{^{1}H} (toluene-d_8, 100.59 MHz, −20 °C, *J* in Hz) δ 257.8 (d, =*C*HSiMe$_3$, $^2J_{\mathrm{P-C}} = 12.1$), 256.0 (d, =*C*HSiMe$_3$, $^2J_{\mathrm{P-C}} = 11.1$), 53.5 (s, *eq*-*C*H$_2$SiMe$_3$), 37.4 (d, *ax*-*C*H$_2$SiMe$_3$, $^2J_{\mathrm{P-C}} = 32.2$), 15.5 (d, P*Me*$_2$Ph, $^1J_{\mathrm{P-C}} = 26.2$), 4.25 (s, *ax*-CH$_2$Si*Me*$_3$), 2.90 (s, *eq*-CH$_2$Si*Me*$_3$), 1.86 (s, =CHSi*Me*$_3$), 1.67 (s, =CHSi*Me*$_3$); ^{31}P{^{1}H} (toluene-d_8, 161.92 MHz, −60 °C, *J* in Hz) δ 13.9 (s, $^1J_{\mathrm{W-P}} = 97.1$); ^{29}Si{^{1}H} (toluene-d_8, 79.46 MHz, −20 °C, *J* in Hz) δ 1.09 (s, *ax*-CH$_2$*Si*Me$_3$), −1.75 (d, *eq*-CH$_2$*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 5.6$), −7.85 (d, =CH*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 2.9$), −9.16 (d, =CH*Si*Me$_3$, $^3J_{\mathrm{P-Si}} = 4.0$).

Attempted Preparation of the Adducts between PCy$_3$ or PPh$_3$ and $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (2a). Two separate experiments were conducted with 50 mg of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**), 4,4′-dimethylbiphenyl (an internal standard), and toluene-d_8 in J. R. Youngs 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 in ^{1}H NMR spectroscopy.

Kinetic Study of the Conversion of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}(\equiv\mathrm{CSiMe_3})(\mathrm{PMe_3})$ (1a) to 1b. At least two experiments for each temperature were conducted. To a mixture of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**), 4,4′-dimethylbiphenyl (an internal standard), and toluene-d_8 in J. R. Youngs NMR tubes in liquid nitrogen was added ca. 2−21 equiv of PMe$_3$ through vacuum transfer. The samples were kept below −78 °C before insertion into the NMR probe. The NMR probe was precooled or preheated to the set temperature. After the NMR tubes were inserted into the probe, the ^{1}H NMR spectra were taken after the temperature was stabilized, and the integrations of **1b**, relative to those of the internal standard, were used as $I_{\mathbf{1b}-0}$ at $t = 0$. Once the equilibrium between **1a** and **1b** was reached, the integration of **1b** was used as $I_{\mathbf{1b}-\mathrm{e}}$.

Thermodynamic Study of the Equilibrium between 1a and 1b. Three samples of **1a**,**b** were prepared with at least 10 equiv of PMe$_3$ and kept at room temperature for over 24 h to ensure equilibrium was established. The samples were then placed in a circulation bath at 278.0(0.1), 283.0(0.1), 288.0(0.1), 293.0(0.1), 298.0(0.1), or 303.0(0.1) K for at least 6 h. ^{31}P NMR spectra were taken at −50 °C with a relaxation delay of 10 s. $K_{\mathrm{eq}} = [\mathbf{1b}]/[\mathbf{1a}] = I_{\mathbf{1b}}/I_{\mathbf{1a}}$ were calculated from the integrations of the two tautomers.

Kinetic and Thermodynamic Studies of the Conversion of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}(\equiv\mathrm{CSiMe_3})(\mathrm{PMe_2Ph})$ (3a) to 3b at 303 K. To a mixture of $(\mathrm{Me_3SiCH_2})_3\mathrm{W}\equiv\mathrm{CSiMe_3}$ (**2a**, 35 mg, 0.066 mmol), 4,4′-dimethylbiphenyl (an internal standard), and toluene-d_8 in J. R. Youngs NMR tubes was added ca. 10-fold excess PMe$_2$Ph via cannula transfer. Kinetic measurements were taken in duplicate on a Bruker 400 MHz NMR at 303 K. Integration of the ^{1}H P*Me*$_2$− peak of **3b** was used in the kinetic plot. For thermodynamic measurements, two samples of **3a**,**b** were prepared with at least 10 equiv of PMe$_2$Ph and kept at room temperature for over 24 h to ensure that equilibrium was established. The samples were placed in a circulation bath at 303.0(0.1) K for at least 6 h. ^{31}P NMR spectra were taken at −50 °C with a relaxation delay of 10 s. $K_{\mathrm{eq}} = [\mathbf{3b}]/[\mathbf{3a}] = I_{\mathbf{3b}}/I_{\mathbf{3a}}$ were calculated from the integrations of the two tautomers.

Reaction of $(Bu^tCH_2)_3W{\equiv}CBu^t$ with PMe_3 at Room Temperature in Benzene-*d*$_6$. To $(Bu^tCH_2)_3W{\equiv}CBu^t$ (100 mg, 0.214 mmol) in benzene-d_6 in a J. R. Youngs NMR tube in liquid nitrogen was added ca. 1 equiv of PMe_3 through vacuum transfer. A slow reaction at room temperature occurred to give $(Bu^tCH_2)W({\equiv}CBu^t)({=}CHBu^t)(PMe_3)_2$. After 3 days at 23 °C, a mixture of unreacted $(Bu^tCH_2)_3W{\equiv}CBu^t$ (and PMe_3) and $(Bu^tCH_2)W({\equiv}CBu^t)({=}CHBu^t)(PMe_3)_2$ in ca. 1:2 ratio was observed. No adduct between $(Bu^tCH_2)_3W{\equiv}CBu^t$ and PMe_3 in the mixture was observed.

Determination of the X-ray Crystal Structure of 1b. The crystal structure was determined on a Bruker AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector and fitted with an upgraded Nicolet LT-2 low-temperature device. Suitable crystals were coated with Paratone oil and mounted under a stream of nitrogen at −100 °C. Intensity data were measured with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Background counts were measured at the beginning and the end of each scan with the crystal and counter kept stationary. The structure was solved by direct methods, and then a 2-fold twinning law (TWIN 0 1 0 1 0 0 0 0 −1, and BASF 0.45126) was used to solve the twinning by merohedry. All non-H atoms and four C's in both axial ligands were refined with anisotropic displacement coefficients. All H atoms were placed in calculated positions and introduced into the refinement as fixed contributors with an isotropic *U* value of 0.008 Å^2.

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Supporting Information Available: NMR spectra of **1a** and **1b** and crystallographic data for **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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