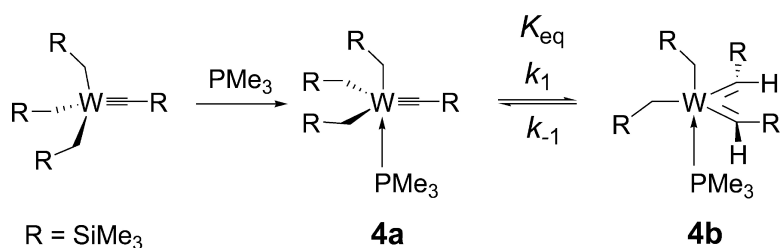


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## An Unusual Exchange between Alkylidyne Alkyl and Bis(alkylidene) Tungsten Complexes Promoted by Phosphine Coordination: Kinetic, Thermodynamic, and Theoretical Studies

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$d^0$ -Alkyl alkylidyne complexes  $(RCH_2)_3W\equiv CR'$  are known to undergo  $\alpha$ -H migration. Such  $\alpha$ -H exchanges lead to alkyl-alkylidyne scrambling in  $(Bu^tCH_2)_3W\equiv^{13}CBu^t$  (**1**- $^{13}C$ ),<sup>1a</sup> and  $(Bu^tCH_2)_3W\equiv CSiMe_3$  (**2a**).<sup>1b</sup> Detailed studies of **2a**  $\rightleftharpoons$   $(Bu^tCH_2)_2(Me_3SiCH_2)W\equiv CBu^t$  (**2b**) exchanges showed stepwise transfer of two H atoms from one alkyl to the alkylidyne in **2a** or **2b** with a proposed bis(alkylidene) " $(Bu^tCH_2)_2W(=CHSiMe_3)(=CHBu^t)$ " intermediate.<sup>1b</sup> In  $d^2$  Os bis(alkylidene)  $Os(=CHBu^t)_2(CD_2Bu^t)_2$ , H/D atoms were found to scramble.<sup>2</sup> This exchange is believed to occur through an alkylidyne intermediate " $(Bu^tCH_2)_3Os\equiv CBu^t$ ".

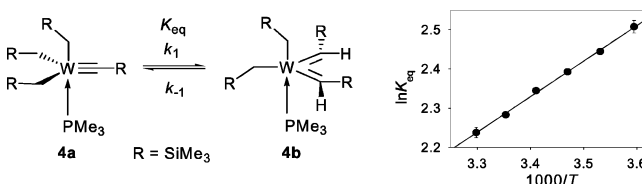
Although the  $\alpha$ -H exchange is a fundamental dynamic process in these  $d^0$  alkylidene and alkylidyne complexes, there is, to our knowledge, only one direct observation of such an exchange between bis(alkylidene) and alkylidyne tautomers:<sup>3,4</sup>  $(Bu^tCH_2)_2W(=CBu^t)(SiBu^tPh_2)$  (**3a**)  $\rightleftharpoons$   $(Bu^tCH_2)W(=CHBu^t)_2(SiBu^tPh_2)$  (**3b**).<sup>5</sup> Theoretical studies reveal that the silyl ligands here play a critical role in the relative stabilities of the  $d^0$  W bis(alkylidene) tautomer through  $\pi$  interaction between the silyl ligand and the electron density in the metal-alkylidyne/alkylidene bonds.<sup>5b</sup> We have observed that  $(Me_3SiCH_2)_3W\equiv CSiMe_3(PMe_3)$  (**4a**), an adduct between  $(Me_3SiCH_2)_3W\equiv CSiMe_3$  (**5a**) and  $PMe_3$ , undergoes an exchange with its bis(alkylidene) tautomer  $(Me_3SiCH_2)_2W(=CHSiMe_3)_2(PMe_3)$  (**4b**, Scheme 1). In the absence of phosphine, " $(Me_3SiCH_2)_2W(=CHSiMe_3)_2$ " (**5b**) was not observed. Unlike the exchange involving silyl complexes **3a** and **3b**, this is an unusual phosphine-promoted exchange. Assuming **5a** undergoes  $\alpha$ -H exchanges involving **5b** as an intermediate,<sup>1</sup> the current work suggests that  $PMe_3$  coordination significantly stabilizes **4b** so it is observable at room temperature. Our thermodynamic, kinetic, and theoretical studies of the **4a**  $\rightleftharpoons$  **4b** exchange are reported here.

Addition of  $PMe_3$  to a solution of **5a** in toluene- $d_8$  leads to immediate color change and the formation of **4a**. NMR spectra of **4a** at  $-50$  °C suggest that  $PMe_3$  coordinates cis to the alkylidyne ligand.<sup>6</sup> Two sets of resonances in a 1:2 ratio were observed for the  $Me_3SiCH_2$  ligands in the  $^1H$ ,  $^{13}C$ , and  $^{29}Si$  NMR spectra of **4a** at  $-50$  °C. The coupling constant  $^2J_{P-C-ax}$  of 36.5 Hz is, as expected, larger than  $^2J_{P-C-eq}$  of 7.2 Hz. The resonance of the alkylidyne C atom in **4a** at 358.81 ppm was observed as a doublet ( $^2J_{P-C} = 14.5$  Hz) in the  $^1H$ -gated-decoupled  $^{13}C$  NMR spectrum. Upon warming, **4a** converted to **4b**. The two tautomers reach an equilibrium: **4a**  $\rightleftharpoons$  **4b**. The two alkylidene ligands in **4b** are inequivalent. The alkylidene C resonances were observed as doublet of doublets at 256.43 ( $^1J_{C-H} = 123.5$  Hz;  $^2J_{P-C} = 11.8$  Hz) and 254.71 ppm ( $^1J_{C-H} = 102.6$  Hz;  $^2J_{P-C} = 12.6$  Hz) in the  $^1H$ -gated-decoupled  $^{13}C$  NMR spectrum at  $-50$  °C.  $^2J_{P-C-ax}$  and  $^2J_{P-C-eq}$  of 32.3 and 0 Hz for the  $-CH_2SiMe_3$  ligands are consistent with these two alkyls coordinated trans and cis, respectively, to  $PMe_3$  to give the structure of **4b** in Scheme 1.

**Table 1.**  $K_{eq}$ ,  $k_1$ , and  $k_{-1}$  of the **4a**  $\rightleftharpoons$  **4b** Exchange (toluene- $d_8$ )<sup>6</sup>

T (K)	$K_{eq}$	$k_1 \times 10^5$ (s <sup>-1</sup> )	$k_{-1} \times 10^6$ (s <sup>-1</sup> )
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)

**Scheme 1.** **4a**  $\rightleftharpoons$  **4b** Exchange and Thermodynamic  $\ln K_{eq}$  vs  $1/T$  Plot



The resonances of the alkylidene H atoms in **4b** were observed as doublets at 7.985 and 7.192 ppm, respectively. These observations suggest that **4b** adopts an anti,syn configuration (Scheme 1), and it is unlikely that the two ligands are involved in a fast rotation about the W=C bonds.  $(RCH_2)(R'CH=)_2Ta(PMe_3)_2$ , bis(phosphine) Ta analogues of **4b**, have been reported.<sup>7</sup> The prochiral W atom in **4a** gives rise to diastereotopic  $\alpha$ -H atoms ( $CH_aH_b-SiMe_3$ ) for the equatorial alkyl ligands observed as doublet of doublets at 0.751 and 0.213 ppm in its  $^1H$  NMR spectrum at  $-50$  °C. The diastereotopic  $\alpha$ -H atoms ( $CH_aH_b-SiMe_3$ ) in chiral **4b** for the equatorial alkyl ligand were observed as doublet of doublets at 0.917 and 0.876 ppm in the  $^1H$  NMR spectrum at  $-50$  °C.

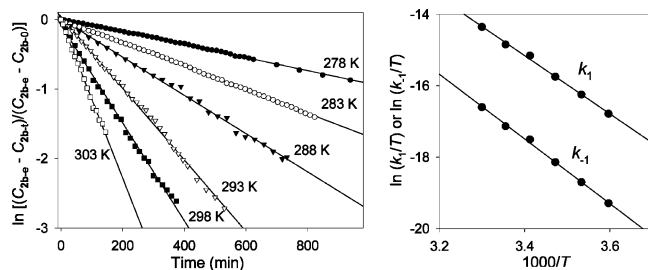
Cooling the solution of **4a** and **4b** to  $-30$  °C gave crystals, which were found to be those of **4b**, indicating that **4b** preferentially crystallized from the mixture. Elemental analysis of the crystals is consistent with the composition of **4b**.

It is interesting to note that **1**, a neopentyl analogue of **5a**, reacts with neat  $PMe_3$  in a sealed tube at 100 °C, giving  $(Bu^tCH_2)W(=C^tBu)(=CH^tBu)(PMe_3)_2$  (**6**) through  $\alpha$ -H abstraction and  $CMe_4$  elimination, as Schrock and Clark have reported.<sup>3j</sup> When a solution of **1** in benzene- $d_6$  was added ca. 1 equiv of  $PMe_3$  at room temperature, a similar reaction giving **6** and  $CMe_4$  occurred.<sup>6</sup> No adduct between **1** and  $PMe_3$  was observed. The difference in the reactivities of **5a** and its neopentyl analogue **1** toward  $PMe_3$  is interesting, although it is not clear what lead(s) to the difference. Complexes with  $CH_2SiMe_3$  and/or  $=CHSiMe_3$  ligands have shown unique chemistry.<sup>7e</sup>

Variable-temperature NMR spectra of the tautomerization **4a**  $\rightleftharpoons$  **4b** were studied to give the equilibrium constants  $K_{eq} = [4b]/[4a]$  (Table 1).<sup>6</sup> A plot of  $\ln K_{eq}$  vs  $1/T$  (Scheme 1) gave  $\Delta H^\circ = -1.8(0.5)$  kcal/mol,  $\Delta S^\circ = -1.5(1.7)$  eu, and  $\Delta G^\circ_{298K} = -1.3(1.0)$  kcal/mol.  $K_{eq}$  ranges from 12.3(0.2) at 278 K to 9.37(0.12) at 303

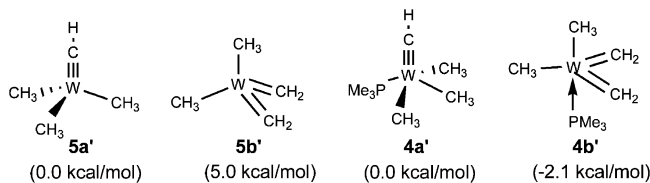
<sup>†</sup> The University of Tennessee.

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**Figure 1.** Kinetic and Eyring plots of the reversible reactions  $4a \rightleftharpoons 4b$ .

**Chart 1.** Calculated Relative Energies for  $5a'$ ,  $5b'$ ,  $4a'$ , and  $4b'$

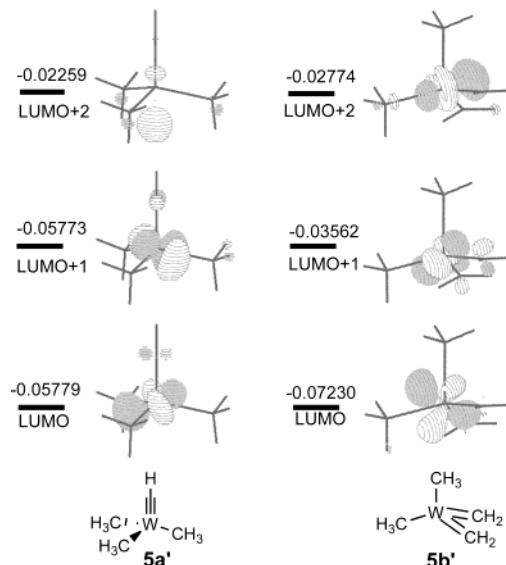


K, indicating that the alkylidene tautomer  $4b$  is slightly favored. Decreasing the temperature shifts the equilibrium toward  $4b$ . The process  $4a \rightleftharpoons 4b$  is slightly exothermic. If there is an alkyl-alkylidene scrambling process in  $5a$  as in  $2a \rightleftharpoons 2b$ , the proposed bis(alkylidene) intermediate  $5b$  is much higher in energy than  $5a$ , and coordination with  $PMe_3$  to give  $4b$  significantly lowers its energy so that the equilibrium  $4a \rightleftharpoons 4b$  is observed.

In our earlier communication of the exchange of silyl complexes  $3a \rightleftharpoons 3b$ , only the thermodynamic properties were reported. In the current work, we conducted kinetic studies of the unusual alkyl-alkylidene and bis(alkylidene) exchange. First-order reversible kinetics<sup>8</sup> was observed in variable-temperature  $^1H$  NMR experiments for the  $4a \rightleftharpoons 4b$  exchange between 278 and 303 K (Figure 1).<sup>6</sup> Eyring plot (Figure 1) leads to the kinetic parameters of the exchange:  $\Delta H_1^\ddagger = 16.2(1.2)$  kcal/mol,  $\Delta S_1^\ddagger = -22.3(4.0)$  eu for  $4a \rightarrow 4b$ , and  $\Delta H_2^\ddagger = 18.0(1.3)$  kcal/mol,  $\Delta S_2^\ddagger = -20.9(4.3)$  eu for  $4b \rightarrow 4a$ . The  $4a \rightleftharpoons 4b$  exchange is significantly slower than that of  $3a \rightleftharpoons 3b$ ; the latter was observed in 2D-NOESY spectra ( $t_{mix} = 3$  s) at 23 °C. The  $4a \rightleftharpoons 4b$  exchange is, however, much faster than the alkyl-alkylidene scrambling in  $(Bu^iCH_2)_3W=CSiMe_3$  ( $2a$ ) observed at  $>70$  °C.<sup>1b</sup>  $\Delta G_1^\ddagger_{298K}$  of 23(2) kcal/mol for the forward reaction  $4a \rightarrow 4b$  is lower than that ( $\Delta G^\ddagger_{298K} = 28.1(1.1)$  kcal/mol) for  $2a \rightarrow 2b$ .

The experiments show that  $4a$ , the  $PMe_3$  adduct of  $5a$ , undergoes tautomerization and is in equilibrium with its bis(alkylidene) tautomer  $4b$ . To understand the effect of the phosphine ligand here, B3LYP calculations were carried out.<sup>6</sup> The results of the calculations of the model complexes (Chart 1) show that  $PMe_3$  promotes the conversion of the alkylidene complex to the bis(alkylidene) tautomer.  $4b'$  is calculated to be more stable than  $4a'$  by 2.1 kcal/mol, consistent with the experimentally measured  $\Delta H^\circ (-1.8(0.5)$  kcal/mol) for  $4a \rightarrow 4b$ .

The relative energies suggest that  $PMe_3$  binds with the bis(alkylidene) tautomer relatively more strongly than with the alkylidene tautomer, reversing the relative stability. To understand how  $5a'$  and  $5b'$  interact with  $PMe_3$ , we examine their lowest unoccupied orbitals (LUMOs, Figure 2), which are responsible for interaction with  $PMe_3$ . The structures of  $5a'$  and  $5b'$  together with the relative binding ability of  $5a'$  and  $5b'$  are closely related to the orbital feature and orbital energies of the LUMOs. The maximum amplitudes of the LUMOs determine the  $PMe_3$  coordination sites. The structures of  $4a'$  and  $4b'$  indicate that  $PMe_3$  prefers the coordination sites trans to  $W-CH_3$  instead of  $W=CH_2$  or  $W\equiv CH$ , reflecting the stronger trans influence properties of  $W=CH_2$  and  $W\equiv CH$ . The LUMO of  $5b'$  is much lower in energy than that of  $5a'$ , giving greater ligand binding energy. Clearly, the  $PMe_3$  coordination affects the thermal stabil-



**Figure 2.** Spatial plots of three LUMOs for alkylidene and bis(alkylidene) tautomers with orbital energies (au).

ities of the tautomers significantly. Studies are now in progress to understand the effects on the kinetics of the  $4a \rightleftharpoons 4b$  exchange and how different alkyl ligands affect the alkylidene and bis(alkylidene) exchange.

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**Supporting Information Available:** Experimental and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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