

**Direct Observation of an Equilibrium between
(Bu⁴CH₂)₂W(≡CBu⁴)(SiBu⁴Ph₂) and
(Bu⁴CH₂)W(=CHBu⁴)₂(SiBu⁴Ph₂) and an Unusual
Silyl Migration**

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The reactivity of α -hydrogen atoms in β -hydrogen free alkyl ligands (e.g., Bu⁴CH₂ and Me₃SiCH₂) has been of great interest primarily for the pivotal role of these atoms in the formation of high-oxidation-state alkylidene and alkylidyne complexes.^{1–3} The α -hydrogen atoms in d⁰ (Bu⁴CH₂)₃Ta=CDBu⁴ and (Bu⁴CH₂)₃W=CSiMe₃ are also known to undergo exchange among the α -carbon atoms.^{2b,4} In the latter case, deuterium labeling and kinetic studies are consistent with unimolecular and stepwise transfer of two hydrogen atoms in one alkyl ligand to the alkylidyne ligand in (Bu⁴CH₂)₃W=CSiMe₃. A bis(alkylidene) reactive intermediate “(Bu⁴CH₂)₂W(=CHSiMe₃)(=CHBu⁴)” was proposed in the transfer [(Bu⁴CH₂)₃W=CSiMe₃ ⇌ “(Bu⁴CH₂)₂W(=CHSiMe₃)(=CHBu⁴)” ⇌ (Bu⁴CH₂)₂W(CH₂SiMe₃)(=CBu⁴)].⁴ In a d² bis(alkylidene) complex Os(=CHBu⁴)₂(CD₂Bu⁴)₂, hydrogen/deuterium atoms were found to scramble among the α -carbon atoms at 0 °C.⁵ This exchange is believed to occur through an alkylidyne reactive intermediate “(Bu⁴CH₂)₃Os=CBu⁴”. Although the exchange of α -hydrogen atoms is a fundamental dynamic process in these archetypical alkylidene and alkylidyne complexes, there has been no report of a direct observation of such an exchange

between alkylidene and alkylidyne complexes. Herein, we describe, for the first time, the direct observation of such an exchange (Bu⁴CH₂)W(=CHBu⁴)₂(SiBu⁴Ph₂) (**2b**) ⇌ (Bu⁴CH₂)₂W(≡CBu⁴)(SiBu⁴Ph₂) (**2a**) and our studies of the process. **2b** is also one of the rare known d⁰ bis(neopentylidene) complexes; only tantalum and niobium d⁰ bis(neopentylidene) complexes have been reported.^{2e,5a,6} In addition, we were surprised to find that, in the reaction of **2** with O₂, the silyl ligand in **2a** formally underwent an unprecedented migration to the alkylidyne ligand to give a silyl-substituted alkylidene complex (Bu⁴CH₂)₂W(=O)[=C(Bu⁴)(SiBu⁴Ph₂)] (**3**).

Complex **2** was synthesized as part of our studies of cyclopentadienyl (Cp)-free silyl complexes of the early transition metals.^{6c,d,7,8} **2** was made by the reaction of Li(THF)₃SiBu⁴Ph₂⁹ in Et₂O with (Bu⁴CH₂)₂(Cl)W=CBu⁴ (**1**)^{8a} at -40 °C (Scheme 1).¹⁰ Warming the solution to -10 °C, followed by workup at this temperature and crystallization at -30 °C yielded crystalline **2** in 58% yield.¹⁰ Spectroscopic properties [¹H, ¹³C{¹H}], ¹H-gated-decoupled ¹³C, ¹H-¹³C heteronuclear correlation (HETCOR), and ²⁹Si{¹H} NMR] of **2a** and **2b** are consistent with the structure assignments and the existence of the two isomers in solution.¹⁰ The characteristic ¹³C NMR alkylidene resonance of **2b** at 272.30 ppm and alkylidyne resonance of **2a** at 318.38 ppm appear, respectively, as a doublet and a singlet in the ¹H-gated-decoupled ¹³C spectra. There is one ¹H NMR resonance at 6.03 ppm (=CH-Bu⁴) for the two alkylidene ligands in **2b** between 253 and 293 K. It is thus unlikely that these two ligands are involved in a fast rotation about the W=C bonds. If so, one would expect to observe three alkylidene α -hydrogen resonances for the *anti,anti*- and *syn,anti*-configurations¹⁰ in the ¹H NMR spectrum at low temperature. The presence of a single =CHBu⁴ ¹H NMR resonance thus suggests that the two alkylidene ligands adopt an *anti,anti*-configuration. Such configuration has been observed in *anti,anti*-Os(=CHBu⁴)₂(CH₂Bu⁴)₂.^{5a} The prochiral tungsten atom in **2a** gives rise to diastereotopic methylene (CH₂H_bBu⁴) protons with chemical shifts of 2.08 and -0.77 ppm (²J_{Ha-Hb} = 11.9 Hz). In the 2D-NOESY spectra of **2a** and **2b** at 296 K (t_{mix} = 3 s),¹⁰ strong *positive* cross-peaks were observed between the methylene (CH₂H_bBu⁴) protons in **2a** and the alkylidene (=CHBu⁴) and methylene (CH₂Bu⁴) protons in **2b**, consistent with a chemical exchange process between **2a** and **2b** at this temperature. The mixture of **2a** and **2b** is stable as solid, but slowly decomposes in solution at room temperature, forming HSiBu⁴Ph₂ and unknown species.

Variable-temperature NMR spectra of the isomerization **2b** ⇌ **2a** were studied, and the equilibrium constants, K_{eq} = [**2a**]/[**2b**], measured between 237 and 287 K are listed in Table 1. A plot of ln K_{eq} vs 1/T¹² gave a linear fit and yielded $\Delta H^\circ = -0.9(0.2)$

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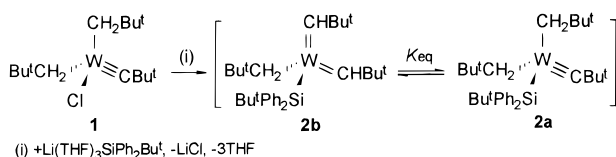
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Scheme 1

**Table 1.** Equilibrium Constants (K_{eq}) for $2b \rightleftharpoons 2a^a$

T (K)	$K_{eq} \pm \sigma K_{eq(ran)}$	T (K)	$K_{eq} \pm \sigma K_{eq(ran)}$	T (K)	$K_{eq} \pm \sigma K_{eq(ran)}$
287 ± 1	3.34 ± 0.05	267 ± 1	3.760 ± 0.004	247 ± 1	4.260 ± 0.004
282 ± 1	3.45 ± 0.04	262 ± 1	3.860 ± 0.001	242 ± 1	4.450 ± 0.002
277 ± 1	3.520 ± 0.005	257 ± 1	3.990 ± 0.016	237 ± 1	4.590 ± 0.006
272 ± 1	3.620 ± 0.015	252 ± 1	4.130 ± 0.011		

^a The largest random uncertainty is $\sigma K_{eq(ran)}/K_{eq} = 0.05/3/34 = 1.5\%$. The total uncertainty $\sigma K_{eq}/K_{eq}$ of 5.2% was calculated from $\sigma K_{eq(ran)}/K_{eq} = 1.5\%$ and the estimated systematic uncertainty $\sigma K_{eq(sys)}/K_{eq} = 5\%$ by $\sigma K_{eq}/K_{eq} = [(\sigma K_{eq(ran)}/K_{eq})^2 + (\sigma K_{eq(sys)}/K_{eq})^2]^{1/2}$.¹¹

kcal/mol and $\Delta S^\circ = -0.6(0.8)$ eu.^{10,13} The equilibrium constants K_{eq} range from 4.590(0.006) at 237 K to 3.34(0.05) at 287 K, indicating that the alkyldiene isomer **2a** is favored, and increasing the temperature shifts the equilibrium toward **2b**. The process **2b** → **2a** is slightly exothermic with $\Delta H^\circ = -0.9(0.2)$ kcal/mol. This enthalpy change outweighs the entropy change [$\Delta S^\circ = -0.6(0.8)$ eu] in the isomerization **2b** → **2a** to give $\Delta G^\circ = -0.7(0.4)$ kcal/mol at 287(1) K in favor of **2a**. It is interesting to note that the d⁰ alkyldiene complex **2a** is thermodynamically close in energy to its bis(alkylidene) isomer **2b**, although **2a** is slightly more stable. In the α -hydrogen exchange in (Bu^tCH₂)₃W≡CSiMe₃ ⇌ (Bu^tCH₂)₂W(CH₂SiMe₃)≡CBu^t, the proposed bis(alkylidene) intermediate “(Bu^tCH₂)₂W(=CHSiMe₃)≡CHBu^t” is so much higher in energy than the ground-state alkyldiene structures that this intermediate is not observed.⁴ It is not clear why the energy difference between **2a** and **2b** is small, and why **2b** can be directly observed in the current studies.

In the solid-state CPMAS (cross-polarization magic angle spinning) ¹³C{¹H} NMR of crystalline **2**, both **2a** and **2b** were observed, indicating that both isomers are present in the crystalline solids. Crystals of **2** were found to be severely disordered, and attempts to refine the structure of **2a(2b)** were unsuccessful.

When a yellow-orange solution of **2** in benzene-*d*₆ was exposed to 1 equiv of gaseous O₂ at room temperature, a rapid reaction occurred and the color of the solution turned red. We were surprised to find the formation of an oxo-alkylidene complex (Bu^tCH₂)₂W(=O)[=C(Bu^t)(SiBu^tPh₂)] (**3**) in this reaction in 32% yield by NMR (Scheme 2).¹⁰ Formally the silyl ligand in (Bu^tCH₂)₂W(=CBu^t)(SiBu^tPh₂) (**2a**) migrates to the alkyldiene ligand in this reaction to give an alkylidene ligand [=C(Bu^t)(SiBu^tPh₂)] in **3**. To our knowledge, this is the first observation of such a migration of a silyl ligand. It is likely that this is an oxygen-induced silyl migration, although we cannot at present rule out other possible pathways. Ahn and Mayr have reported a formal insertion of an alkyldiene group into a W–N bond and the elimination of HBr in the reaction of TpW(=CHPh)(=X)Br [Tp = tris(pyrazolyl)borate; X = NR, O] with Br₂.¹⁴

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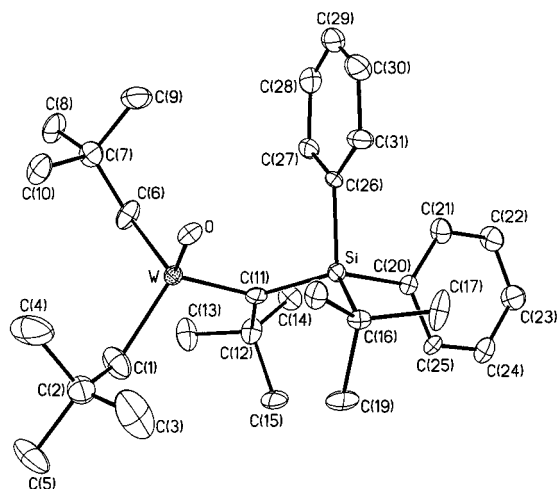
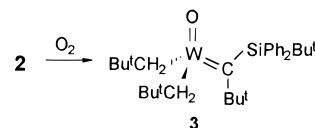


Figure 1. ORTEP of **3** showing 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): W–O 1.686(5), W–C(1) 2.112(9), W–C(6) 2.118(9), W–C(11) 1.920(7), O–W–C(1) 111.8(3), O–W–C(6) 109.5(3), O–W–C(11) 104.1(3).

Scheme 2



Spectroscopic properties of **3** are consistent with the structure assignment.¹⁰ The ¹³C NMR alkylidene resonance of **3** at 269.65 ppm appears as a singlet in the ¹H-gated-decoupled ¹³C spectrum. The molecular structure of **3** has been determined by X-ray crystallography, and is shown in Figure 1.¹⁵ Complex **3** exhibits distorted tetrahedral geometry around the tungsten center. The W=C bond distance of 1.920(7) Å is similar to those observed for other d⁰ alkyldiene complexes of tungsten.^{3a,16} The W=O bond distance of 1.686(5) Å is also similar to those observed for tungsten–oxo complexes.^{3a} Complex **3**, which is thermally stable at room temperature, reacts further with excess O₂ to give unknown species. Studies are currently underway to probe the mechanism of the reaction of **2** with O₂.

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Supporting Information Available: Experimental details, the computation of errors in ΔH° and ΔS° , a chart of *anti,anti*- and *syn,anti*-**2b**, a plot of $\ln K_{eq}$ vs $1/T$, a partial phase-sensitive 2D-NOESY spectrum of **2** and a complete list of the crystallographic data for **3** (13 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(15) Crystal data for **3** at 223 K:¹⁰ orthorhombic, *Pna*2₁, *a* = 21.8650(5) Å, *b* = 17.2786(2) Å, *c* = 8.31220(10) Å, *V* = 3140.32(9) Å³, *Z* = 4, *R*(*R*_w) = 2.91(5.29)% for 3931 unique reflections with *F* > 4σ(*F*), GOF = 1.035.

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