Polyhedron 58 (2013) 30–38

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Reactions of a tungsten alkylidyne complex with mono-dentate phosphines: Thermodynamic and theoretical studies

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ARTICLE INFO

*Article history:*
Available online 23 July 2012

Dedicated to the memory of Michelle Millar, a scientist and teacher who gave so much to the chemistry communities.

*Keywords:*
Alkylidyne
Alkylidene
Phosphine adduct
Equilibrium
DFT calculations
α-H abstraction

ABSTRACT

Addition of mono-dentate phosphines $PMe_3$ and $PMe_2Ph$ to the W(VI) alkyl alkylidyne complex $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**1**) is reversible, each reaching equilibrium. Thermodynamic studies of the equilibria have been conducted, giving $\Delta H° = -10.0(1.1)$ kcal/mol and $\Delta S° = -23(4)$ eu for the addition of $PMe_3$ and $\Delta H°' = -3.0\ (0.7)$ kcal mol$^{-1}$ and $\Delta S°' = -6(3)$ eu for the addition of $PMe_2Ph$, indicating that the addition is exothermic. The experimental measurement allows a benchmarking study to select a proper DFT method to describe the current system. Of the DFT methods tested, M06 has demonstrated superior performance in calculating binding energy of a bimolecular reaction. The calculated reaction pathways show that $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**1**) reacts with $PR_3$ to form $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PR_3)$ ($PR_3 = PMe_3$, **3a**; $PMe_2Ph$, **3b**), and the adduct then undergoes α-H migration to form $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PR_3)$ (**4a**, **4b**). **4a** and **4b** are found to be thermodynamically and kinetically stable intermediates. The calculations also suggest a pathway in the formation of the alkyl alkylidene alkylidyne complex $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PR_3)_2$ (**5a**).

## 1. Introduction

High-oxidation-state metal alkylidene and alkylidyne complexes containing M=C and M≡C bonds, respectively, often demonstrate unique chemistry and have been extensively studied [1–4]. The alkylidene and alkylidyne complexes usually contain ligands such as neopentyl ($-CH_2CMe_3$) and trimethylsilylmethyl ligands ($-CH_2SiMe_3$) that are free of β-H atoms [1–4]. Complexes containing a $-CH_2SiMe_3$ ligand with a β-Si atom often show properties different from those containing its neopentyl $-CH_2CMe_3$ analog. For example, Clark and Schrock reported that the reactions of $W(CH_2CMe_3)_3(\equiv CCMe_3)$ with phosphines $PMe_3$ and $Me_2PCH_2CH_2PMe_2$ (DMPE) give the bis-phosphine/chelating phosphine products $W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)(PMe_3)_2$ and $W(CH_2CMe_3)(=CHCMe_3)(\equiv CCMe_3)$(DMPE) through α-H abstraction [3b]. The structure of the latter was determined by Churchill and Youngs [5]. In comparison, we have found that $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$ (**1**) reacts with $PMe_3$, $PMe_2Ph$, and DMPE, forming phosphine adducts $W(CH_2SiMe_3)_3(\equiv CSiMe_3)(PR_3)$ ($PR_3 = PMe_3$, **3a**; $PMe_2Ph$, **3b**) (Scheme 1) and $W(CH_2SiMe_3)_3(\equiv CSiMe_3)$(DMPE-*P*) (**3e**) (Scheme 2) containing one free $PMe_2$ group [6]. These adducts undergo α-H migration to form their bis-alkylidene tautomers $W(CH_2SiMe_3)_2(=CHSiMe_3)_2(PR_3)$ (**4a**, **4b**) and $W(CH_2SiMe_3)_2(=CHSiMe_3)_2$(DMPE-*P*) (**4e**). The tautomeric mixtures are in equilibria, and undergo α-H abstraction to eliminate $SiMe_4$ to form, by reacting with free $PR_3$ and the free $PMe_2$ group in DMPE-*P* ligand, $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)(PR_3)_2$ (**5a-b, 6a-b**) (Scheme 1) and $W(CH_2SiMe_3)(=CHSiMe_3)(\equiv CSiMe_3)$(DMPE) (**5e**, **6e**) (Scheme 2), respectively [6].

Another example of the difference between $-CH_2SiMe_3$ and $-CH_2CMe_3$ ligands is the reactions shown in Scheme 3 [7]. $Ta(=CHR)_2(CH_2SiMe_3)(PMe_3)_2$ (R = $SiMe_3$, $CMe_3$) reacts with silanes to give metallocyclic products. In comparison, its neopentyl analog, $Ta(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$, forms unknown species with the silanes.

We have been interested in the tautomerizations between alkyl alkylidynes (**3a**, **3b**, **3e**) and bis-alkylidenes (**4a**, **4b**, **4e**) in Schemes 1 and 2 because these were among the few reported direct observation of exchanges through α-H migration [1j,m], although such exchanges had been implicated in several systems [8–12]. The tautomerization of silyl alkylidyne $(Me_3CCH_2)_2W(\equiv CCMe_3)(SiBu^tPh_2)$ with bis-alkylidene $(Me_3CCH_2)W(=CHCMe_3)_2(SiBu^tPh_2)$ was, to our knowledge, the first directly observed exchange [13].

In the current work, we studied the thermodynamics of the reversible addition of $PMe_3$ and $PMe_2Ph$ to **1** forming **3a** and **3b**, respectively, in order to probe the unusual chemistry of **1** in detail. Density functional theory (DFT) studies have been performed to: (1) understand the thermodynamics and kinetics of the transformation from **1** to **4**; (2) explain why **4** is a relatively stable intermediate along the pathway to **5**.

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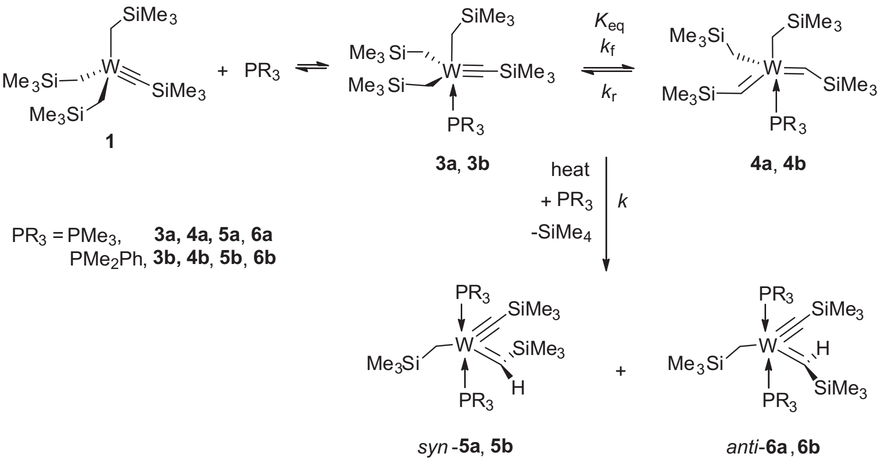
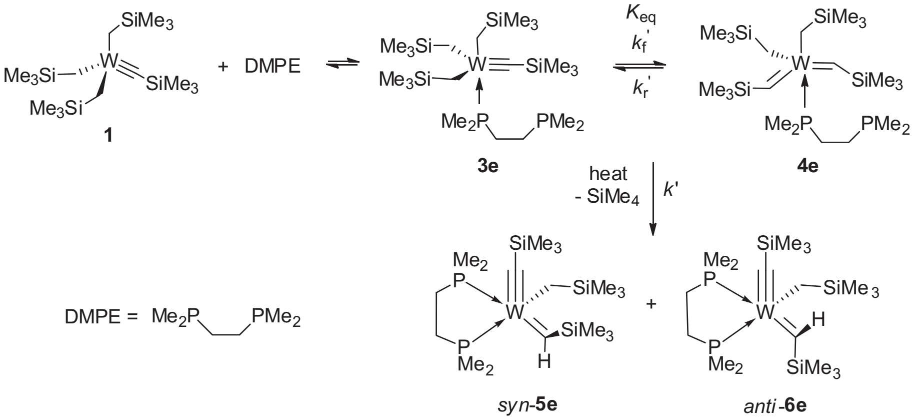
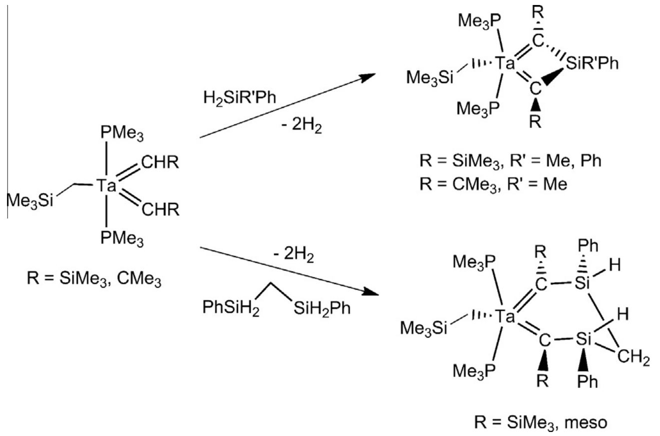
http://dx.doi.org/10.1016/j.poly.2012.07.042



**Scheme 1.** Reactions of mono-dentate phosphines with **1** [6a,b,d].



**Scheme 2.** Reaction of the bidentate phosphine DMPE with **1** [6c].



**Scheme 3.** Reactions of PhR′SiH$_2$ (R′ = Me, Ph, CH$_2$SiH$_2$Ph) with phosphine alkylidene complexes.

## 2. Material, methods and computational details

All manipulations were performed under a dry nitrogen atmosphere with the use of either a dry box or standard Schlenk techniques. Solvents were purified by distillation from potassium/benzophenone ketyl. Toluene-$d_8$ was dried over activated molecular sieves and stored under N$_2$. WCl$_6$ was freshly sublimed under vacuum. W(CH$_2$SiMe$_3$)$_3$(≡CSiMe$_3$) (**1**) [3d] was prepared from (MeO)$_3$WCl$_3$ and six equivalents of Me$_3$SiCH$_2$MgCl by a procedure similar to that used in the preparation of W(CH$_2$CMe$_3$)$_3$(≡CCMe$_3$) [14]. $^1$H NMR spectra were recorded on a Bruker AMX-400 spectrometer.

For the thermodynamic studies, the equilibrium constants $K_{eq1}$ were obtained from at least five separate experiments at a given temperature, and their averages are listed in Table 1. The maximum random uncertainty in the equilibrium constants were combined with the estimated systematic uncertainty of ca. 5%. The total uncertainties in the equilibrium constants were used in the ln $K_{eq1}$ versus 1000/$T$ plot in Fig. 1 and the error propagation calculations. The estimated uncertainty in the temperature measurements for an NMR probe was 1 K. The enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) changes were calculated from an unweighted nonlinear least-squares procedure. The uncertainties in $\Delta H^\circ$ and $\Delta S^\circ$ were computed from the following error propagation formulas, which were derived from $-RT \ln K_{eq1} = \Delta H^\circ - T\Delta S^\circ$ [13].

$$(\sigma\Delta H^\circ)^2 = \frac{R^2\left(T_{\max}^2T_{\min}^4 + T_{\min}^2T_{\max}^4\right)}{(T_{\max}-T_{\min})^4}\left[\ln\left(\frac{K_{eq1(\max)}}{K_{eq1(\min)}}\right)\right]^2\left(\frac{\sigma T}{T}\right)^2 + \frac{2R^2T_{\max}^2T_{\min}^2}{(T_{\max}-T_{\min})^2}\left(\frac{\sigma K_{eq1}}{K_{eq1}}\right)^2 \qquad (1)$$