



Department of Chemistry  
NMR Facilities  
Director: Dr. Carlos A. Steren

## NMR NEWS

February 2009

- \* To check on the [instrumental status](#) and the [reservation system](#), and find tutorials, links and more, visit our website [www.chem.utk.edu/nmr](http://www.chem.utk.edu/nmr)
- \* Bruker 400's BBI probe status: The problem is that the probe won't eject samples. Bruker does not have a magnet where to test the probe. This is because our magnet is wide bore and the standard magnets for liquid state NMR are narrow bore. So, now we have the probe back and I will run some tests to try to pinpoint the problem.
- \* The Varian 400's solid state probe has been repaired and now is back. The system will be back on service in one week.
- \* In this issue, we present recent NMR results from Dr. Xue's group. Dr. Xue and his group extensively use NMR in their research. Besides, standard  $^1\text{H}$  and  $^{13}\text{C}$  experiments, they also run  $^{31}\text{P}$ ,  $^{29}\text{Si}$ ,  $^2\text{H}$  and 2D NMR as well as variable temperature (VT) experiments.

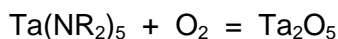
# NMR-Related Research in Xue Group

Ziling (Ben) Xue

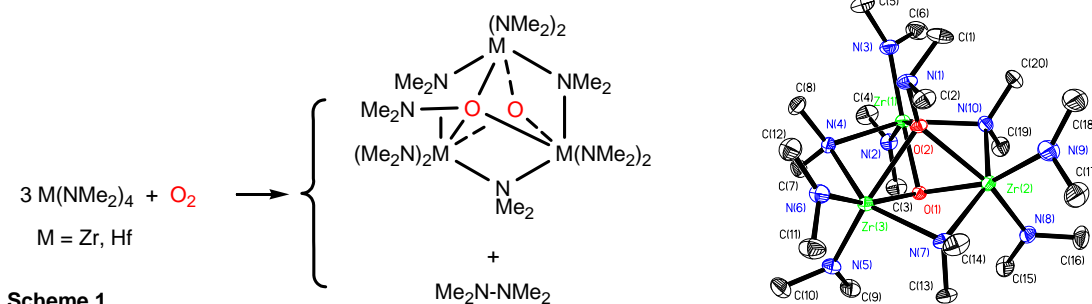
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Our group is interested in mechanistic pathways in reactions of inorganic-organometallic compounds. **NMR, especially variable-temperature NMR**, plays a critical role in the studies to characterize new complexes and to provide thermodynamic and kinetic parameters.

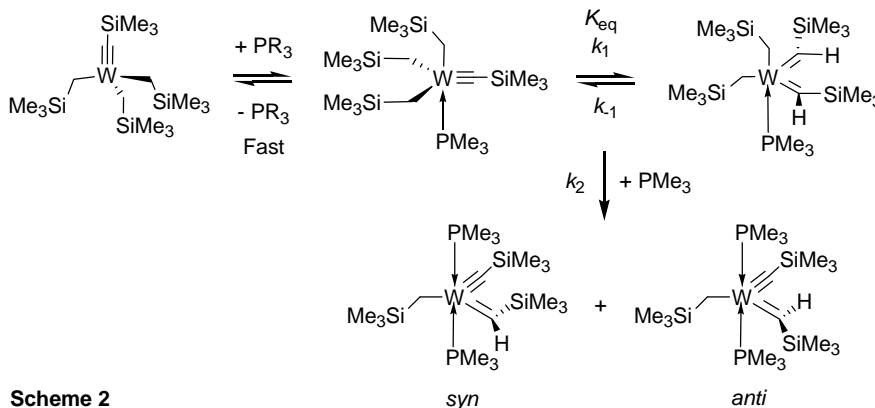
Reactions to make microelectronic materials are of particular interest to us. Recent developments to make metal oxide gate materials have been called "The most significant change...since Intel pioneered the modern...transistor in 1960s." <sup>1</sup>



We have investigated the mechanistic pathways in the formation of the metal oxide thin films and other microelectronic materials.<sup>2a-b</sup> Novel model compounds such as those in **Scheme 1** have been isolated and characterized by NMR spectroscopy.



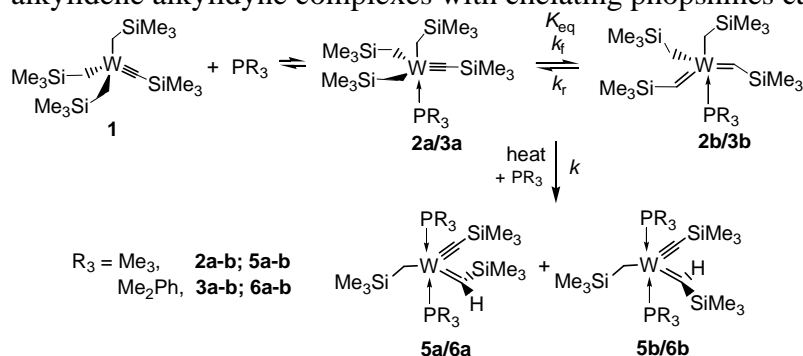
**Variable-temperature NMR** work and thermodynamic/kinetic parameters from the NMR studies led to the elucidation of the pathway to the rare complexes in Scheme 2 containing single, double and triply bonds to a single atom (W).



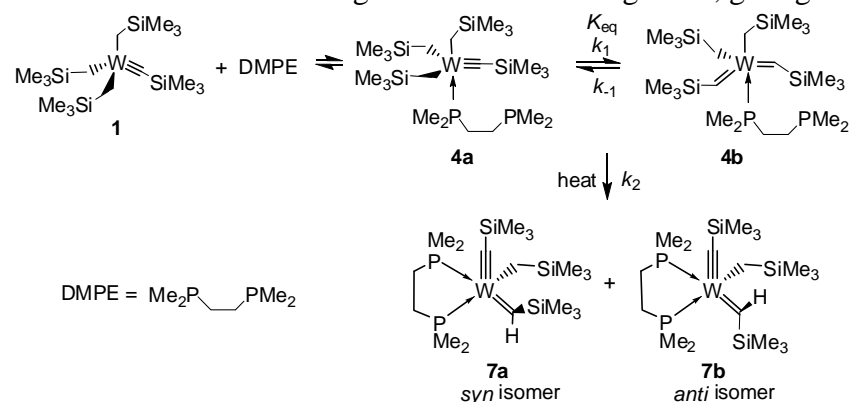
1. *New York Times*, *Associated Press*, *Los Angeles Times*, January 27, 2007.
2. (a) Chen, S.; Zhang, X.; Yu, X.; Qiu, H.; Yap, G.P.A.; Guzei, I.A.; Lin, Z.; Wu, Y.; Xue, Z. *J. Am. Chem. Soc.* **2007**, *129*, 14408. (b) Wang, R.; Zhang, X.; Chen, S.; Yu, X.; Wang, C.; Beach, D.B.; Wu, Y.; Xue, Z. *J. Am. Chem. Soc.* **2005**, *127*, 5204. (c) Morton, L.A.; Chen, S.; Qiu, H.; Xue, Z. *J. Am. Chem. Soc.* **2007**, *129*, 7277. (d) Morton, L.A.; Zhang, X.; Wang, R.; Lin, Z.; Wu, Y.; Xue, Z. *J. Am. Chem. Soc.* **2004**, *126*, 10208. (e) Yu, X.; Cai, H.; Guzei, I.A.; Xue, Z. *J. Am. Chem. Soc.* **2004**, *126*, 4472.

Dougan, B. A.; Xue, Z. *Organometallics*, 2009, 28, in press.

**Variable-temperature NMR** work and kinetic parameters from NMR studies led to the elucidation of the pathway to the rare complexes in Schemes 1 and 2 containing single, double and triply bonds to a single atom. The NMR characterization of such unique alkyl alkylidene alkylidyne complexes with a chelating diphosphine are presented here.<sup>1</sup> Further reading on our kinetic and thermodynamic studies on the tungsten alkylidyne, tungsten bis-alkylidene, and alkyl alkylidene alkylidyne complexes with chelating phosphines can be found in references 1 and 2.

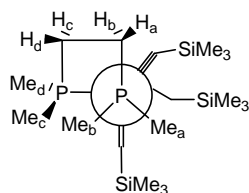


**Scheme 1** Prior to the formation of **5a-b/6a-b**, phosphine adducts **2a/3a** were observed as intermediates. **2a/3a** undergo reversible  $\alpha$ -H migration, giving bis-alkylidene tautomers **2b/3b**.<sup>2</sup>

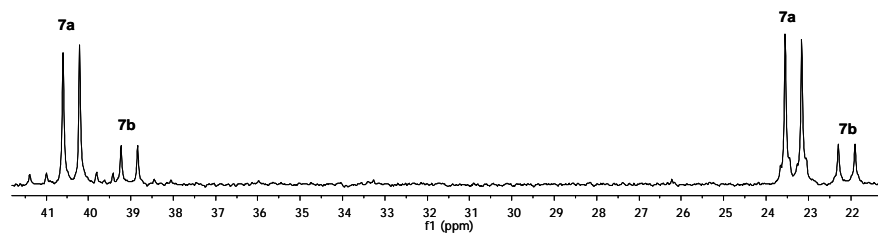


**Scheme 2** The tautomeric mixture **4a**  $\equiv$  **4b**, under heating, undergoes  $\alpha$ -H abstraction, yielding alkyl alkylidene alkylidyne complex  $\text{W}(\text{CH}_2\text{SiMe}_3)(=\text{CHSiMe}_3)(\equiv\text{CSiMe}_3)(\text{DMPE})$  (*syn*: **7a**; *anti*: **7b**). This conversion appears to start with the elimination of  $\text{SiMe}_4$  through  $\alpha$ -H abstraction, followed by the coordination of the dangling P atom.<sup>1</sup>

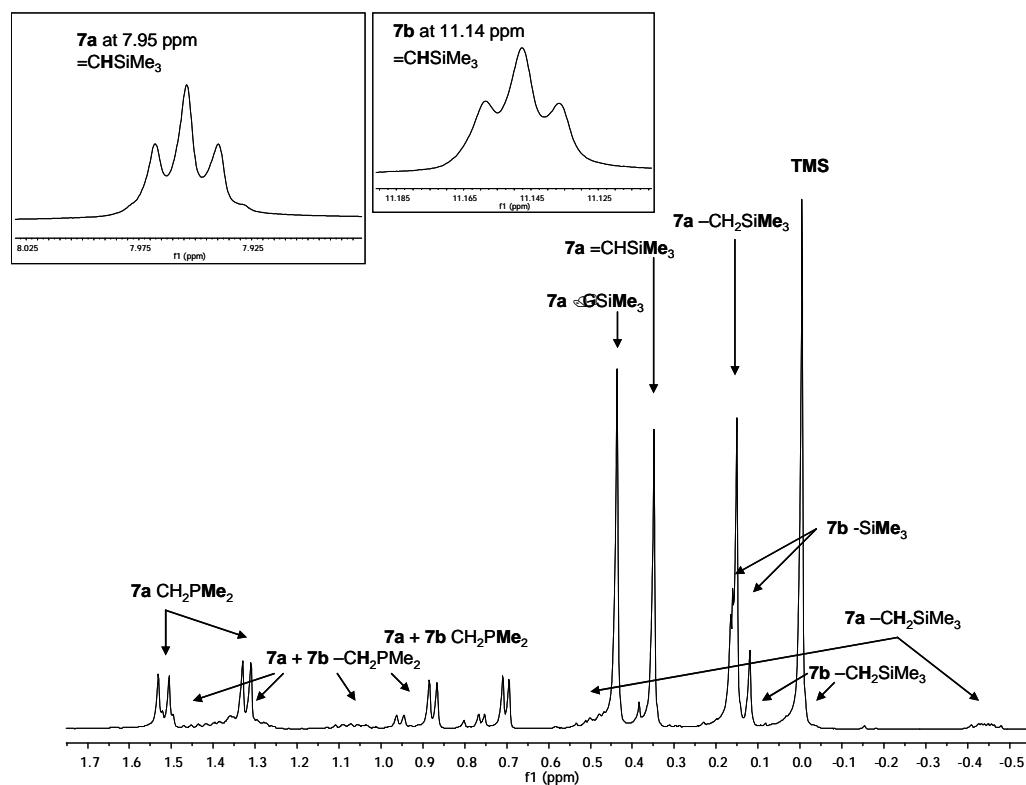
**NMR Characterization of  $\text{W}(\text{CH}_2\text{SiMe}_3)(=\text{CHSiMe}_3)(\equiv\text{CSiMe}_3)(\text{DMPE})$  (**7a-b**).<sup>1</sup>**



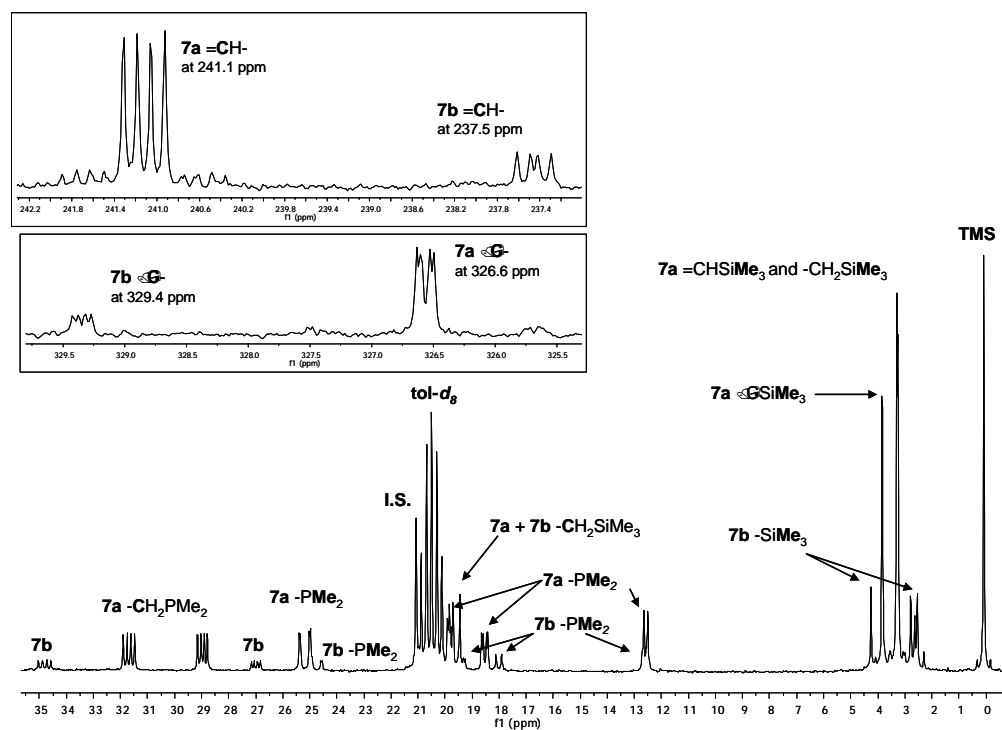
**Chart 1** Newman projections of **7a** showing the diastereotopic H atoms in  $\text{CH}_a\text{H}_b\text{SiMe}_3$  and H and P atoms in the DMPE ligand.



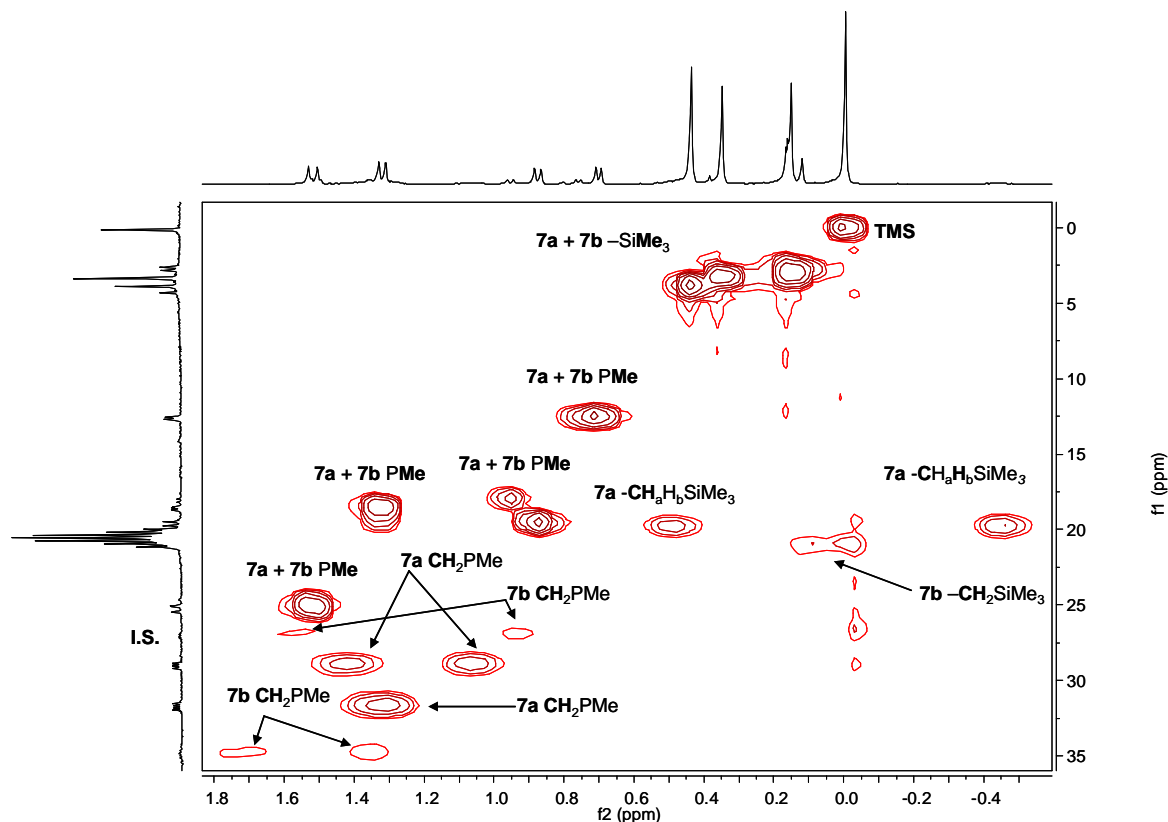
**Figure 1.**  $^{31}\text{P}$  NMR spectrum of **7a** and **7b** at room temperature. The  $^{31}\text{P}$  NMR spectrum of **7a** shows doublets at 40.21 and 23.16 ppm suggesting that the P atoms are inequivalent. Likewise, two doublets at 38.84 and 22.41 ppm of **7b** were found.



**Figure 2.**  $^1\text{H}$  NMR spectrum of **7a** and **7b** at room temperature. The alkyldiene H atoms in **7a** and **7b** were observed as two overlapping doublet of doublets at 7.95 and 11.14 ppm, due to the coupling to  $^{31}\text{P}$  ( $S = \frac{1}{2}$ ). The four  $\alpha$ -methyl groups in the DMPE ligand for **7a** are inequivalent (Chart 1) and observed as four doublets at 1.52, 1.32, 0.88, and 0.71 ppm. Likewise, four doublets for **7b** appear at 1.51, 1.32, 0.96, and 0.76 ppm for its four  $\alpha$ -methyl groups. The diastereotopic ethylene protons in the DMPE ligand (Chart 1) in **7a** and **7b** were observed as complex multiplets.



**Figure 3.**  $^{13}\text{C}$  NMR spectrum of **7a** and **7b** at room temperature. (I.S. = 4,4'-dimethylbiphenyl). Due to the coupling to  $^{31}\text{P}$  ( $S = 1/2$ ), the alkydylidene C resonance of **7a** and **7b** were observed as a dd at 241.14 and 237.46 ppm. Likewise the alkydylidene  $^{13}\text{C}$  resonance of **7a** and **7b** appear as overlapping dd at 326.56 and 329.35 ppm. The P-CH<sub>2</sub>-CH<sub>2</sub>-P resonances in **7a** were observed as two dd at 31.76 and 29.05 ppm. Two dd in **7b** appear at 34.92 and 27.05 ppm. (dd = doublet of doublets)



**Figure 4.** HSQC of **7a** and **7b** at room temperature. (I.S. = 4,4'-dimethylbiphenyl).

## References

1. Dougan, B. A.; Xue, Z. "Reaction of a tungsten alkylidyne complex with a chelating diphosphine.  $\alpha$ -hydrogen migration in the intermediates and formation of an alkyl alkylidene alkylidyne complex." *Organometallics* **2009**, *28*, in press.
2. (a) Morton, L. A.; Wang, R.; Yu, X.; Campana, C. F.; Guzei, I. A.; Yap, G. P. A.; Xue, Z. *Organometallics* **2006**, *25*, 427. (b) Morton, L. A.; Chen, S.; Qiu, H.; Xue, Z.-L. *J. Am. Chem. Soc.* **2007**, *129*, 7277. (c) Morton, L. A.; Zhang, X.; Wang, R.; Lin, Z.; Wu, Y.; Xue, Z. *J. Am. Chem. Soc.* **2004**, *126*, 10208.

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