

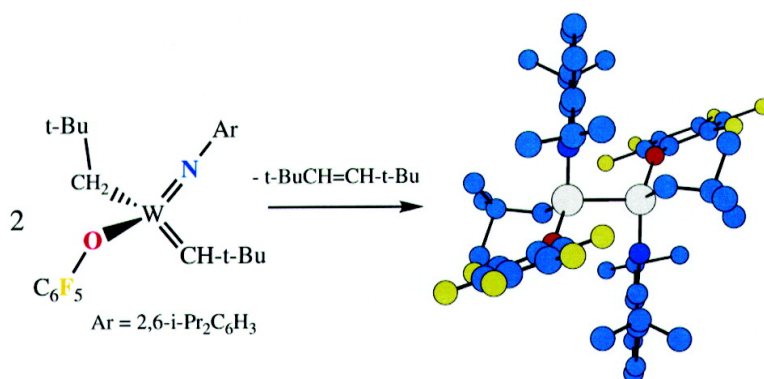
Communication

Formation of Dimers That Contain Unbridged W(IV)/W(IV) Double Bonds

Lourdes Pia H. Lopez, and Richard R. Schrock

J. Am. Chem. Soc., **2004**, 126 (31), 9526-9527 • DOI: 10.1021/ja0400988 • Publication Date (Web): 16 July 2004

Downloaded from <http://pubs.acs.org> on April 1, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Formation of Dimers That Contain Unbridged W(IV)/W(IV) Double Bonds

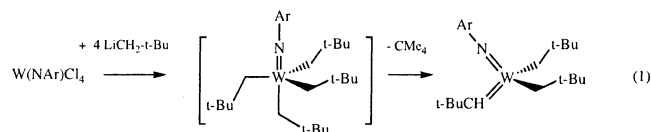
Lourdes Pia H. Lopez and Richard R. Schrock*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received April 5, 2004; E-mail: rrs@mit.edu

Certain molybdenum alkylidene complexes of the type $\text{Mo}(\text{NR})(\text{CHR})(\text{OR}')_2$ (or metallocyclobutane complexes derived from them) have been shown to decompose to yield dimeric species, e.g. $[\text{Mo}(\mu\text{-NAr})(\text{O}-t\text{-Bu})_2]_2$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$), which contains a symmetric, planar Mo_2N_2 core and a pseudotetrahedral arrangement about each Mo.¹ It has been assumed that tungsten complexes of the same general type also contain bridging imido groups.² In this communication we show that new tungsten imido alkylidene complexes of the type $\text{W}(\text{NR})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ decompose to yield dimeric species that contain *unbridged* $\text{W}=\text{W}$ double bonds. Such species are closely related to two compounds of the type $[\text{Re}(\text{C}-t\text{-Bu})(\text{OR})_2]_2$ ($\text{OR} = \text{O}-t\text{-Bu}$ or $\text{OCMe}(\text{CF}_3)_2$),³ which also contain “unsupported” $\text{M}=\text{M}$ bonds and are formed upon decomposition of alkylidene complexes of the type $\text{Re}(\text{C}-t\text{-Bu})(\text{CHR})(\text{OR})_2$ ($\text{R}' = \text{OEt}$ or OSiMe_3).³

Recently, we showed that active olefin metathesis catalysts of the type $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OR})$ ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) can be prepared by adding a variety of alcohols to $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$.⁴ Therefore we became interested in exploring analogous reactions involving $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$.² A three-step synthesis of $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ that is more convenient than the reported² six-step synthesis (from WCl_6) is shown in eq 1.⁵ Sterically crowded $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_4$, shown



arbitrarily as a trigonal bipyramidal species, is believed to be the intermediate that undergoes α hydrogen abstraction^{6,7} to produce $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ (cf. $\text{W}(\text{NPh})(\text{CHSiMe}_3)(\text{CH}_2\text{SiMe}_2)_2$). $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$, prepared as shown in eq 1, has been obtained only as a red-brown oil. However, addition of three equivalents of $t\text{-BuCH}_2\text{MgCl}$ to $\text{W}(\text{NAr})\text{Cl}_4$ yields $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3\text{Cl}$ cleanly (cf. $\text{W}(\text{NPh})(\text{CH}_2-t\text{-Bu})_3\text{Cl}$),⁸ which can be isolated and alkylated with $\text{LiCH}_2-t\text{-Bu}$ to yield $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ virtually quantitatively as an orange solid.

Addition of $\text{C}_6\text{F}_5\text{OH}$ to $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ (~ 0.1 M) in C_6D_6 at 25°C rapidly yields $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3(\text{OC}_6\text{F}_5)$ ($\delta_{\text{CH}_2} = 2.25$ ppm), which can be isolated as a yellow powder.⁹ A similar reaction between $(\text{CF}_3)_3\text{COH}$ and $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ in pentane at 25°C yields yellow crystalline $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3[\text{OC}(\text{CF}_3)_3]$ ($\delta_{\text{CH}_2} = 2.20$ ppm in C_6D_6). Species of this type are believed to have trigonal bipyramidal structures in which the alkoxide is in an apical position. They should be compared with known $\text{W}(\text{NPh})(\text{CH}_2-t\text{-Bu})_3(\text{O}-t\text{-Bu})$ ($\delta_{\text{CH}_2} = 1.94$ ppm).⁸

In contrast, addition of one equivalent of 1-adamantanol to $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ in pentane yields $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OAd})$ as a yellow powder (in C_6D_6 $\delta_{\text{CH}} = 8.86$ ppm, $J_{\text{HW}} = 14.5$ Hz; $\delta_{\text{CH}} = 253.1$ ppm, $J_{\text{CH}} = 110$ Hz). By analogy with similar reactions between $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})_2$ (and

related neophyl and neophylidene species) and adamantanol,⁴ $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OAd})$ is proposed to arise as a consequence of addition of adamantanol across a $\text{W}-\text{C}$ bond.

Upon heating solutions of $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3(\text{OC}_6\text{F}_5)$ or $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3[\text{OC}(\text{CF}_3)_3]$, neopentane is evolved, and $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ ($\delta_{\text{CH}} = 9.29$ ppm, $J_{\text{HW}} = 15$ Hz) and $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})[\text{OC}(\text{CF}_3)_3]$ ($\delta_{\text{CH}} = 9.39$ ppm, $J_{\text{HW}} = 15$ Hz) are formed. Plots of $\log[\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3(\text{OR})]$ versus time at 60°C are linear. When $\text{OR} = \text{OC}_6\text{F}_5$, $k = 7.0 \times 10^{-5} \text{ s}^{-1}$, while when $\text{OR} = \text{OC}(\text{CF}_3)_3$, $k = 1.7 \times 10^{-4} \text{ s}^{-1}$. Neither $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ nor $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})[\text{OC}(\text{CF}_3)_3]$ has been isolated in crystalline form, the latter because it has so far resisted all attempts to crystallize it, and the former because it, unlike $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$,⁴ is unstable with respect to bimolecular decomposition (see below). NMR studies suggest that all $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OR})$ compounds ($\text{OR} = \text{OC}_6\text{F}_5$, $\text{OC}(\text{CF}_3)_3$, or OAd) are *syn* species in which the neopentylidene's *tert*-butyl group points toward the imido ligand;^{6,7} no alkylidene H_α resonances for *anti* isomers have been observed.

Although $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})[\text{OC}(\text{CF}_3)_3]$ and $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OAd})$ are relatively stable in solution at 80°C , $\text{W}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ (formed by heating a 0.1 M solution of $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3(\text{OC}_6\text{F}_5)$ to 80°C in toluene- d_8) begins to decompose after $\sim 80\%$ of it has formed from $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})_3(\text{OC}_6\text{F}_5)$. The only observable products are $t\text{-BuCH}=\text{CH}-t\text{-Bu}$ (one isomer, presumably *trans*) and sparingly soluble “ $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$.” Two doublet resonances ($J_{\text{HH}} = 14.5$ Hz) are found for the neopentyl methylene protons at 2.47 and 3.09 ppm in the proton NMR spectrum of “ $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ ”, consistent with an absence of a plane that passes through the neopentyl methylene carbon atom.

An X-ray study reveals that sparingly soluble “ $\text{W}(\text{NAr})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)$ ” is a centrosymmetric (heterochiral) dimer (Figure 1) in which there are no bridging ligands and a double bond (2.4445(3) Å) between the two tungstens. Among the striking features of the structure is a $\text{N}-\text{W}-\text{W}$ angle close to 90° ($90.38(10)^\circ$). The $\text{W}-\text{N}$ bond length (1.749(3) Å) and $\text{W}-\text{N}-\text{C}$ angle ($165.5(3)^\circ$) are not unusual. The $\text{W}-\text{C}(19)-\text{C}(20)$ angle ($119.3(3)^\circ$) is typical of a relatively “undistorted” neopentyl group, while the $\text{W}-\text{O}(1)-\text{C}(13)$ angle ($146.7(3)^\circ$) suggests that a significant degree of π bonding is present, which opens the $\text{W}-\text{O}-\text{C}$ angle significantly. This structure is similar to the structures of two related d^2/d^2 $[\text{Re}(\text{C}-t\text{-Bu})(\text{OR})_2]_2$ ($\text{OR} = \text{O}-t\text{-Bu}$ or $\text{OCMe}(\text{CF}_3)_2$) species³ in which the $\text{Re}=\text{Re}$ bond lengths are 2.3836(8) and 2.396(1) Å (respectively), the $\text{C}=\text{Re}=\text{Re}$ angles are $90.0(2)^\circ$ and $89.5(1)^\circ$ (respectively), and the alkylidene ligands are *trans* to one another. The shapes of the W (and Re) compounds suggest that three mutually perpendicular π bonds are formed from the d_{xz} , d_{yz} , and d_{xy} orbitals, with the four σ bonds being formed from the three p orbitals and some combination of s and d_{z^2} orbitals.¹⁰ The transoid arrangement of the multiply bound alkylidene ligands in the Re complexes was

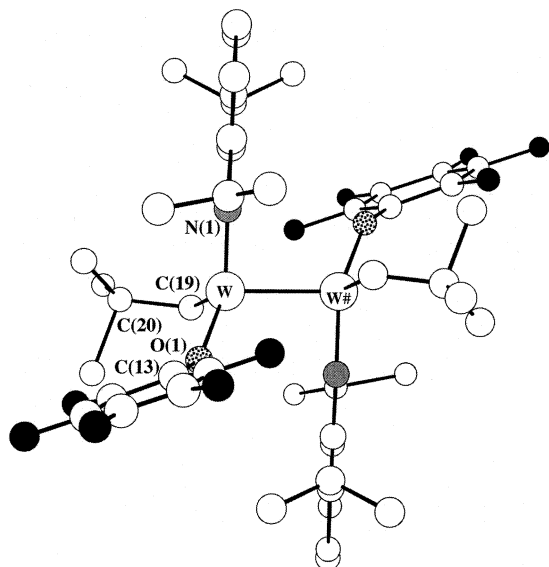


Figure 1. Chem3D drawing of the structure of centrosymmetric $[W(NAr')(CH_2-t-Bu)(OC_6F_5)]_2$. $W-N = 1.749(3)$ Å, $W-O = 1.933(2)$ Å, $W-C = 2.139(3)$ Å, $W-W\# = 2.4445(3)$ Å, $W-N(1)-C(1) = 165.5(3)^\circ$, $W-O(1)-C(13) = 146.7(3)^\circ$, $W-C(19)-C(20) = 119.3(3)^\circ$, $N(1)-W-W\# = 90.38(10)^\circ$, $O(1)-W-W\# = 113.17(9)^\circ$, $C(19)-W-W\# = 98.08(10)^\circ$, $N(1)-W-O(1) = 132.30(13)^\circ$, $N(1)-W-C(19) = 106.23(15)^\circ$, $O(1)-W-C(19) = 110.31(14)^\circ$.

found to be energetically preferred in theoretical studies of model compounds.¹⁰

The reaction between $W(NAr')(CH-t-Bu)(dme)(triflate)_2$ ($Ar' = 2,6-Me_2C_6H_3$)¹¹ and two equivalents of $t-BuCH_2MgCl$ yields $W(NAr')(CH-t-Bu)(CH_2-t-Bu)_2$ as an orange powder, which upon treatment with pentafluorophenol yields $W(NAr')(CH_2-t-Bu)_3(OC_6F_5)$ quantitatively. Upon heating a toluene- d_8 solution (0.10 M) of $W(NAr')(CH_2-t-Bu)_3(OC_6F_5)$ to 60 °C, $W(NAr')(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ forms and decomposes to yield $t-BuCH=CH-t-Bu$ and sparingly soluble $[W(NAr')(CH_2-t-Bu)(OC_6F_5)]_2$. On the basis of the inequivalent neopentyl methylene protons in the proton NMR spectrum of $[W(NAr')(CH_2-t-Bu)(OC_6F_5)]_2$ in toluene- d_8 we propose that this compound also contains an unsupported $W=W$ bond. $W(NAr')(CH_2-t-Bu)_3(OC_6F_5)$ evolves neopentane intramolecularly more slowly than $W(NAr')(CH_2-t-Bu)_3(OC_6F_5)$, while intermediate $W(NAr')(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ decomposes bimolecularly more quickly than intermediate $W(NAr')(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ at the concentrations employed. Both can be ascribed to subtle steric differences between the NAr and NAr' groups.

It has been reported that unstable $W(CH_2Et)(NAr')[OCMe_2(CF_3)_2]_2$, which is prepared by treating $W(CH-t-Bu)(NAr')[OCMe_2(CF_3)_2]_2$ with *cis*-3-hexene, decomposes to yield $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$.² It was proposed that $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ contains bridging imido ligands, although the presence of two inequivalent trifluoromethyl groups in the carbon NMR spectrum of $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ is inconsistent with a structure analogous to that of $[Mo(\mu-NAr)(O-t-Bu)_2]_2$ ($Ar = 2,6-i-Pr_2C_6H_3$).¹ We have shown that $W(CH-t-Bu)(NAr')[OCMe_2(CF_3)_2]_2$ also reacts with *cis*-2-pentene to yield $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ in which the two

methyl groups in the trifluoro-*tert*-butoxide are inequivalent (with resonances at 1.27 and 1.92 ppm in toluene- d_8). Therefore, we suspect that $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ and $\{W(NAr')[OCMe_2(CF_3)_2]_2\}_2$ also contain unsupported $W=W$ bonds. (No X-ray study of either species has yet been successful.)¹⁵

Finally, we recently found that $Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)_4$, which is much more stable than $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)_4$, will react with 10 equiv of *trans*-3-hexene at 25 °C to yield $[Mo(NAr)(CH_2-t-Bu)(OC_6F_5)]_2$, which was shown in an X-ray study to be a *homochiral* molecule related to $[W(NAr)(CH_2-t-Bu)(OC_6F_5)]_2$ (Figure 1).¹⁴ Therefore unsupported $M=M$ bonds are not restricted to W and Re.

To the best of our knowledge, no Mo or W dimers are known that contain “unsupported” $M=M$ bonds in the presence of potentially bridging ligands. (See also discussion in refs 3 and 10.) These species are strikingly different from a compound such as $[W(OCH_2-t-Bu)_4]_x$, a polymeric species that contains bridging neopentoxides.¹³ We are now in the process of expanding the library of synthetically accessible $M=M$ species and exploring their fundamental reactions.

Acknowledgment. We thank the National Science Foundation (CHE-0138495) for supporting this research and D. Yandulov for assistance in refining the crystal structure.

Supporting Information Available: Experimental details, labeled thermal ellipsoid drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[W(NAr)(CH_2-t-Bu)(OC_6F_5)]_2$. X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902–2907.
- Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evtitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262–2275.
- Toreki, R.; Schrock, R. R.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 3610–3611.
- Sinha, A.; Schrock, R. R. *Organometallics* **2004**, *23*, 1643–1645.
- The feasibility of this approach was first demonstrated by A. Sinha with $t-BuCH_2MgCl$; this reaction mixture tends to contain a significant quantity of $W(NAr)(CH_2-t-Bu)_3Cl$.
- Schrock, R. R., Ed. *Reactions of Coordinated Ligands*; Plenum: New York, 1986.
- Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1–73.
- Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 7483–7491.
- Preparative scale reactions were carried out in pentane.
- Barckholtz, T. A.; Bursten, B. E.; Nicolai, G. P.; Casey, C. P. *J. Organomet. Chem.* **1994**, *478*, 153–160.
- This species was prepared by a method analogous to that employed to prepare $W(NAr)(CH-t-Bu)(dme)(triflate)_2$; see Supporting Information for details.
- Tsang, W. C. P.; Hultzsich, K. C.; Alexander, J. B.; Bonitatebus, P. J. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652–2666.
- Chisholm, M. H.; Streib, W. E.; Tiedtke, D. B.; Wu, D. D. *Chem. Eur. J.* **1998**, *4*, 1470–1479.
- A. Sinha; unpublished results to be reported in due course.
- Note added in proof: An X-ray structure of the latter has confirmed a structure that is, overall, similar to that shown in Figure 1 and that contains an unbridged $W=W$ bond 2.4905(3) Å long.

JA0400988