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Facile Synthesis of a Tungsten Alkylidyne Catalyst for Alkyne Metathesis

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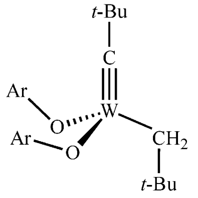
Summary: Reaction of $WCl_3(OAr)_3$ (Ar = 2,6-i-$Pr_2C_6H_3$) with 4 equiv of t-$BuCH_2MgCl$ in diethyl ether produces yellow crystalline W(C-t-Bu)(CH_2-t-Bu)$(OAr)_2$ in 40−50% isolated yield. W(C-t-Bu)(CH_2-t-Bu)$(OAr)_2$ is a versatile entry for preparing W(C-t-Bu)(CH_2-t-Bu)$(NPh_2)_2$ and subsequently other W(C-t-Bu)(CH_2-t-Bu)$(OR)_2$ species in situ, which are active alkyne metathesis catalysts.

Although metathesis of internal alkynes catalyzed by high-oxidation-state alkylidyne species[1−3] has not received the exposure enjoyed by alkene metathesis in the past decade,[4] alkyne metathesis is becoming useful for synthesizing certain organic molecules. Of note are compounds that contain a cis C═C bond in a ring[5] formed through selective cis hydrogenation of the triple bond with a Lindlar catalyst. This method circumvents the still-unsolved problem in alkene metathesis of selectively forming cis double bonds.

Tungsten alkylidyne trialkoxide alkyne metathesis catalysts were discovered in 1981.[2,6] The first synthesis consisted of the reaction of W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$[7] with HCl to yield W(C-*t*-Bu)Cl_3(dme), followed by displacement of the chlorides with alkoxides.[8] The key synthesis of volatile, yellow, crystalline W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$ in 50−60% yield consists of a reaction between $W(OMe)_3Cl_3$ and 6 equiv of *t*-$BuCH_2MgCl$, five of which ultimately are sacrificed. Other routes have been developed that consist of cleavage of a tungsten−tungsten triple bond upon reaction with an alkyne or nitrile.[9] Recent advances in alkyne metathesis have included syntheses of either homogeneous[10] or supported Mo-based catalysts.[11] In this paper we report a relatively "direct" route to new tungsten neopentylidyne species that contain a single neopentyl ligand.

The reaction between WCl_6 and 3 equiv of ArOH (Ar = 2,6-diisopropylphenyl) produces $W(OAr)_3Cl_3$ in high yield and on a large scale.[12] Addition of 4 equiv of *t*-$BuCH_2MgCl$ to $W(OAr)_3Cl_3$ in diethyl ether yields the neopentylidyne complex shown in eq 1. It can be isolated from the crude reaction mixture

$$W(OAr)_3Cl_3 + 4\ t\text{-}BuCH_2MgCl \longrightarrow$$



(1)

as a highly crystalline yellow complex in 40−50% yield. It seems likely that the metal remains in its highest oxidation state and that at least two diisopropylphenoxide ligands are bound to W at all times. We propose that the alkylidyne arises from sequential α-abstractions (alkyl to alkylidene followed by alkylidene to alkylidyne). Exactly when and how these abstractions take place is not known. Overall, the synthesis is related to that of W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$ from $WCl_3(OMe)_3$ but has the advantage of ready isolation of the product. It seems likely that the good yield of W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ is a consequence of its relatively crowded nature, which slows further attack by *t*-$BuCH_2MgCl$ on W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$, as can be demonstrated in separate experiments involving isolated W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ and *t*-$BuCH_2MgCl$. Similar reactions involving W(O-2,6-$Me_2C_6H_3)_3Cl_3$ do not produce an analogous product in a relatively large and/or easily isolated amount. The NMR spectroscopic parameters of W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ are not unusual for high-oxidation-state alkylidyne species of this general type[3] with $\delta(C_\alpha)$ 303.0 ppm and $J_{CW} = 271$ Hz in benzene-d_6.

The structure of W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ has been confirmed in an X-ray study (Figure 1). The W−C(1) bond length of 1.755(2) Å and W−C(6) bond length of 2.119(2) Å are typical of W−C triple and single bonds, respectively. The W−C(1)−C(2) bond angle of 175.62(17)° and W−C(6)−C(7) bond angle of 114.70(13)° are also not unusual. Both aryl groups of the phenoxide ligands reside above the $C_{alkyl}OO$ face, while the *tert*-butyl group of the neopentyl ligand resides below, presumably for steric reasons. Full details can be found in the Supporting Information. It should be noted that Chisholm has prepared a related alkyl alkylidyne species, $W(CCH_2CH_3)$(CH_2-*t*-Bu)(O-*i*-Pr)$_2$, through a reaction between W_2(O-*i*-Pr)$_4$(CH_2-*t*-Bu)$_2$ and 3-hexyne.[13] This compound was found to be dimeric in the solid state (through bridging isopropoxides), and no metathesis activity was reported.

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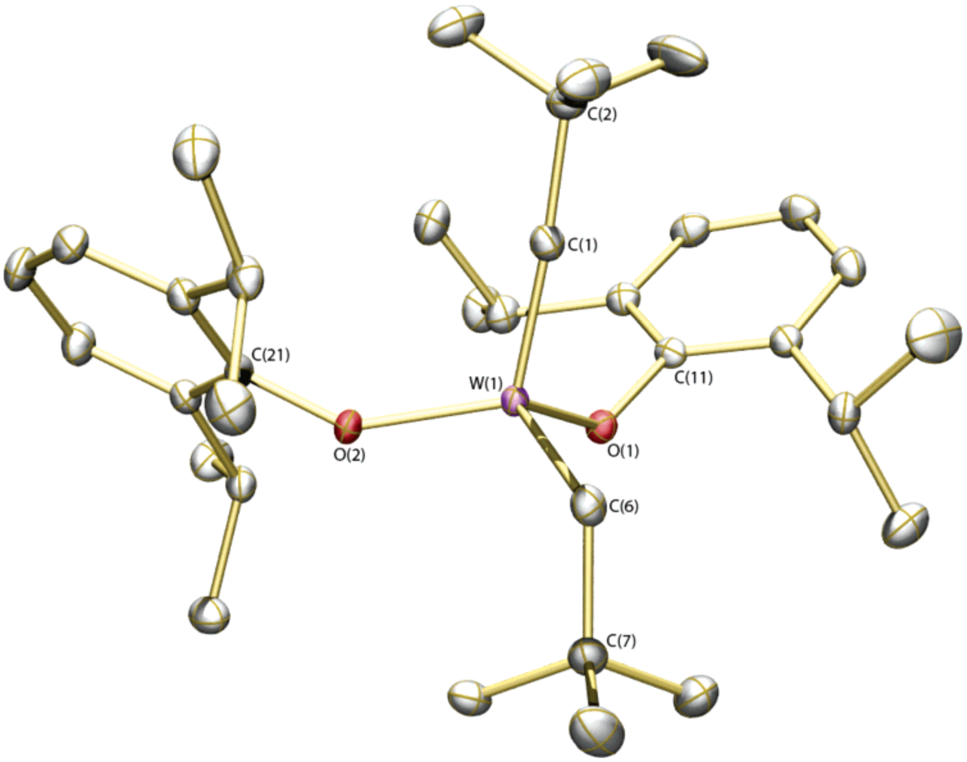
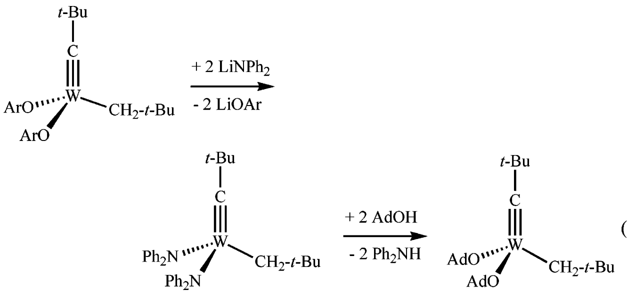


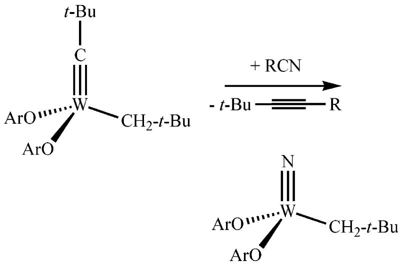
Figure 1. POV-ray drawing (ellipsoids at 50% probability) of W(C-*t*-Bu)(CH_2-*t*- Bu)($OAr)_2$. Selected bond distances and angles: W−C(1) = 1.755(2) Å, W−C(6) = 2.119(2) Å, W−O(1) = 1.8982(14) Å, W−O(2) = 1.8920(14) Å, W−C(1)−C(2) = 175.62(17)°, W−C(6)−C(7) = 114.70(13)°, W−O(1)−C(11) = 132.76(12)°, W−O(2)−C(21) = 145.95(13)°.

Addition of 2 equiv of $LiNPh_2 \cdot Et_2O$ to an ether solution of W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ yields W(C-*t*-Bu)(CH_2-*t*-Bu)-$(NPh_2)_2$ as a pale yellow crystalline species in 70% isolated yield (eq 2). Treatment of W(C-*t*-Bu)(CH_2-*t*-Bu)$(NPh_2)_2$ with 2 equiv of 1-adamantanol then produces W(C-*t*-Bu)(CH_2-*t*-Bu)-$(OAd)_2$ and 2 equiv of Ph_2NH within minutes at 22 °C, as judged through NMR studies. W(C-*t*-Bu)(CH_2-*t*-Bu)$(NPh_2)_2$ is related to the recently reported Mo(NAr)(CH-*t*-Bu)$(NPh_2)_2$,[14] which has been shown to serve as a precursor to olefin metathesis catalysts of the type Mo(NAr)(CH-*t*-Bu)$(OR)_2$ prepared in situ upon addition of alcohols. Conversion of W(C-*t*-Bu)(CH_2-*t*-Bu)$(NPh_2)_2$ into W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAd)_2$ is not surprising, in view of similar transformations involving molybdenum alkylidyne species that have been published in the last several years.[10,11] Such alcoholysis reactions bode well for the facile synthesis of a variety of mono- or dialkoxide species in solution or on a silica surface.[15,16]



(2)

W(C-*t*-Bu)(CH_2-*t*-Bu)$(OAr)_2$ reacts over a period of 2.5 h in pentane (40 mM) with 10 equiv of RC≡N (R = Ph, Me) to produce deep red, crystalline W(N)(CH_2-*t*-Bu)$(OAr)_2$ in 80% isolated yield (eq 3). W(N)(CH_2-*t*-Bu)$(OAr)_2$ is readily soluble and therefore unlikely to be a polymer containing W−N−W chains, which is typical of several W(N)$(OR)_3$ species such as $[W(N)(O\text{-}t\text{-}Bu)_3]_x$[17] and $[W(N)(OAr)_3]_x$.[18] Reactions analogous to that in eq 3 have been observed for several trialkoxide tungsten alkylidyne species.[3,18,19] The reverse reaction between a trialkoxide molybdenum nitride and an internal alkyne has also been reported recently, though we do not know at this time if eq 3 is reversible.[20] We were somewhat surprised by the intense color of the nitride species, which is the consequence of a broad absorption centered at 468 nm in the visible spectrum



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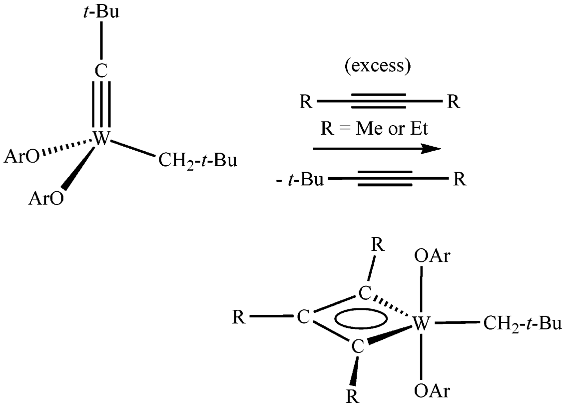
with $\epsilon = 8070$ M^{-1} cm^{-1}. The precise nature of this transition is not known at this stage.

The reaction of W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAr)$_2$ with excess 2-butyne or 3-hexyne results in formation of the red (R = Me) to orange (R = Et), pentane-soluble, symmetric metallacyclobutadiene species (eq 4). The W[C(*t*-Bu)CRCR](CH$_2$-*t*-Bu)(OAr)$_2$ species can be observed by NMR and even cocrystallizes with the W[C$_3$R$_3$](CH$_2$-*t*-Bu)(OAr)$_2$ species. However, W[C(*t*-Bu)-CRCR](CH$_2$-*t*-Bu)(OAr)$_2$ appears to decompose slowly through loss of the *t*-Bu-substituted alkyne. The W[C$_3$R$_3$](CH$_2$-*t*-Bu)-(OAr)$_2$ species are analogous to related trialkoxide species that contain OAr[21] or OCH(CF$_3$)$_2$[22] groups. NMR spectra at 20 °C show time-averaged C_{2v} symmetry, consistent with the structure depicted in eq 4, where both diisopropylphenyl and neopentyl groups are rotating rapidly on the NMR time scale. The carbon resonances are found at chemical shifts that are typical for high-oxidation-state metallacyclobutadiene species: e.g., in W(C$_3$Et$_3$)(CH$_2$-*t*-Bu)(OAr)$_2$ δ(C$_\alpha$) 242.7 ppm (J_{CW} = 122 Hz) and δ(C$_\beta$) 146.8 ppm (J_{CW} = 21 Hz). Some poly(alkyne) is formed during the synthesis of each W[C$_3$R$_3$](CH$_2$-*t*-Bu)(OAr)$_2$ species, although the insoluble polymers are easily removed from the solution and W[C$_3$R$_3$](CH$_2$-*t*-Bu)(OAr)$_2$ can thereby be isolated cleanly.



(4)

In contrast, addition of excess 3-hexyne to W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAd)$_2$, generated in situ from W(C-*t*-Bu)(CH$_2$-*t*-Bu)-(NPh$_2$)$_2$ and 2 equiv of 1-adamantanol, yields only the propylidyne species W(CEt)(CH$_2$-*t*-Bu)(OAd)$_2$, according to NMR studies after several minutes at 22 °C. There is no evidence for formation of tungstacyclobutadiene species or poly(3-hexyne).

Finally, W(C-*t*-Bu)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$ itself reacts slowly, but cleanly, with 3-hexyne (in a 1:1 mixture of alkyne to pentane) over a period of 4 days at 22 °C to yield pale orange-yellow W(CEt)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$. So far samples of W(CEt)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$ have contained small quantities of W(C-*t*-Bu)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$, but there is little doubt of its formulation on the basis of NMR parameters. (It has been noted that W(C-*t*-Bu)-(NR$_2$)$_3$ species do not react readily with internal aliphatic alkynes, although the conditions were not stated.[23]) No poly-(3-hexyne) was formed in these reactions, as one might expect on the basis of an absence of any observable metallacycles.

The alkyne metathesis activities of W(C-*t*-Bu)(CH$_2$-*t*-Bu)-(OAr)$_2$ and W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAd)$_2$ were explored through metathesis of 3-heptyne. Exposure of a pentane or ether solution of W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAr)$_2$ to ~50 equiv of 3-heptyne leads to formation of the expected 3-hexyne and 4-octyne metathesis products, but relatively slowly. The reaction requires more than 24 h to reach equilibrium at 22 °C. Also, significant amounts of poly(alkyne) are formed during the reaction, which hinders rigorous kinetic analyses. The results are consistent with sluggish breakup of the metallacyclobutadiene intermediate. Similar results have been observed with W(C-*t*-Bu)(OAr)$_3$.[21] In contrast, W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAd)$_2$ (generated in situ) was found to equilibrate 50 equiv of 3-heptyne within 3 h in pentane at 23 °C and no poly(alkyne) was formed during this metathesis reaction. These results, along with the observation of the propylidyne species by NMR, are consistent with the resting state for alkyne metathesis in the adamantoxide derivative being the alkylidyne. They also suggest that diphenylamine does not prevent metathesis by W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAd)$_2$. Not surprisingly, W(C-*t*-Bu)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$ metathesizes 3-heptyne only exceedingly slowly at room temperature and only at high concentrations of alkyne.

The results reported here are noteworthy for several reasons. First, they provide additional evidence[3] that stable tungstacyclobutadiene species not only hinder metathesis turnover but also create the possibility of further reaction with alkyne to yield poly(alkyne), perhaps through an irreversible "expanding ring" mechanism at a single tungsten center. The opposite extreme is W(C-*t*-Bu)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$, in which the metal is too electron rich and sterically hindered to react readily with internal alkynes. Evidently W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAd)$_2$ provides close to the correct balance between a relatively electron rich and a relatively electron poor metal. Second, these results suggest that a neopentyl ligand does not become involved in side reactions to any significant degree in any of the reactions reported here. For example, no bis(alkylidene) intermediate is formed through α-proton migration from neopentyl to alkylidyne. α-Proton migration has been observed for several tungsten alkylidyne species.[24] Third, W(C-*t*-Bu)(CH$_2$-*t*-Bu)(NPh$_2$)$_2$ can be obtained relatively easily and is likely to serve as a precursor for a wide variety of homogeneous and heterogeneous catalysts generated through addition of ROH.

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Supporting Information Available: Text giving complete experimental procedures for all compounds and a CIF file, a fully labeled thermal ellipsoid diagram, a table giving crystallographic data and refinement parameters for W(C-*t*-Bu)(CH$_2$-*t*-Bu)(OAr)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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