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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

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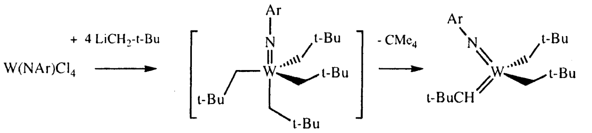
Certain molybdenum alkylidene complexes of the type $Mo(NR)(CHR')(OR'')_2$ (or metalacyclobutane complexes derived from them) have been shown to decompose to yield dimeric species, e.g. $[Mo(\mu-NAr)(O-t-Bu)_2]_2$ ($Ar = 2,6-i-Pr_2C_6H_3$), which contains a symmetric, planar Mo_2N_2 core and a pseudotetrahedral 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 $W(NR)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ decompose to yield dimeric species that contain *unbridged* W═W double bonds. Such species are closely related to two compounds of the type $[Re(C-t-Bu)(OR)_2]_2$ ($OR = O-t-Bu$ or $OCMe(CF_3)_2$),[3] which also contain "unsupported" M═M bonds and are formed upon decomposition of alkylidene complexes of the type $Re(C-t-Bu)(CHR')(OR)_2$ ($R' = OEt$ or $OSiMe_3$).[3]

Recently, we showed that active olefin metathesis catalysts of the type $Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)$ ($Ar = 2,6-i-Pr_2C_6H_3$) can be prepared by adding a variety of alcohols to $Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$.[4] Therefore we became interested in exploring analogous reactions involving $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$.[2] A three-step synthesis of $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ that is more convenient than the reported[2] six-step synthesis (from WCl_6) is shown in eq 1.[5] Sterically crowded $W(NAr)(CH_2-t-Bu)_4$, shown arbitrarily as a trigonal bipyramidal species, is believed to be the intermediate that undergoes α hydrogen abstraction[6,7] to produce $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ (cf. $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$[8]). $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$, prepared as shown in eq 1, has been obtained only as a red-brown oil. However, addition of three equivalents of $t-BuCH_2MgCl$ to $W(NAr)Cl_4$ yields $W(NAr)(CH_2-t-Bu)_3Cl$ cleanly (cf. $W(NPh)(CH_2-t-Bu)_3Cl$[8]), which can be isolated and alkylated with $LiCH_2-t-Bu$ to yield $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ virtually quantitatively as an orange solid.



(1)

Addition of C_6F_5OH to $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ (∼0.1 M) in C_6D_6 at 25 °C rapidly yields $W(NAr)(CH_2-t-Bu)_3(OC_6F_5)$ ($\delta_{CH_2} = 2.25$ ppm), which can be isolated as a yellow powder.[9] A similar reaction between $(CF_3)_3COH$ and $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ in pentane at 25 °C yields yellow crystalline $W(NAr)(CH_2-t-Bu)_3[OC(CF_3)_3]$ ($\delta_{CH_2} = 2.20$ 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 $W(NPh)(CH_2-t-Bu)_3(O-t-Bu)$ ($\delta_{CH_2} = 1.94$ ppm).[8]

In contrast, addition of one equivalent of 1-adamantanol to $W(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ in pentane yields $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd)$ as a yellow powder (in C_6D_6 $\delta_{CH} = 8.86$ ppm, $J_{HW} = 14.5$ Hz; $\delta_{CH} = 253.1$ ppm, $J_{CH} = 110$ Hz). By analogy with similar reactions between $Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)_2$ (and related neophyl and neophylidene species) and adamantanol,[4] $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd)$ is proposed to arise as a consequence of addition of adamantanol across a W−C bond.

Upon heating solutions of $W(NAr)(CH_2-t-Bu)_3(OC_6F_5)$ or $W(NAr)(CH_2-t-Bu)_3[OC(CF_3)_3]$, neopentane is evolved, and $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ ($\delta_{CH} = 9.29$ ppm, $J_{HW} = 15$ Hz) and $W(NAr)(CH-t-Bu)(CH_2-t-Bu)[OC(CF_3)_3]$ ($\delta_{CH} = 9.39$ ppm, $J_{HW} = 15$ Hz) are formed. Plots of $\log[W(NAr)(CH_2-t-Bu)_3(OR)]$ versus time at 60 °C are linear. When $OR = OC_6F_5$, $k = 7.0 \times 10^{-5}\ s^{-1}$, while when $OR = OC(CF_3)_3$ $k = 1.7 \times 10^{-4}\ s^{-1}$. Neither $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ nor $W(NAr)(CH-t-Bu)(CH_2-t-Bu)[OC(CF_3)_3]$ 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 $Mo(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$,[4] is unstable with respect to bimolecular decomposition (see below). NMR studies suggest that all $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OR)$ compounds ($OR = OC_6F_5$, $OC(CF_3)_3$, 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 $W(NAr)(CH-t-Bu)(CH_2-t-Bu)[OC(CF_3)_3]$ and $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OAd)$ are relatively stable in solution at 80 °C, $W(NAr)(CH-t-Bu)(CH_2-t-Bu)(OC_6F_5)$ (formed by heating a 0.1 M solution of $W(NAr)(CH_2-t-Bu)_3(OC_6F_5)$ to 80 °C in toluene-d_8) begins to decompose after ∼80% of it has formed from $W(NAr)(CH_2-t-Bu)_3(OC_6F_5)$. The only observable products are $t-BuCH{=}CH-t-Bu$ (one isomer, presumably trans) and sparingly soluble "$W(NAr)(CH_2-t-Bu)(OC_6F_5)$." Two doublet resonances ($J_{HH} = 14.5$ Hz) are found for the neopentyl methylene protons at 2.47 and 3.09 ppm in the proton NMR spectrum of "$W(NAr)(CH_2-t-Bu)(OC_6F_5)$", consistent with an absence of a plane that passes through the neopentyl methylene carbon atom.

An X-ray study reveals that sparingly soluble "$W(NAr)(CH_2-t-Bu)(OC_6F_5)$" 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 N−W−W angle close to 90° (90.38(10)°). The W−N bond length (1.749(3) Å) and W−N−C angle (165.5(3)°) are not unusual. The W−C(19)−C(20) angle (119.3(3)°) is typical of a relatively "undistorted" neopentyl group, while the W−O(1)−C(13) angle (146.7(3)°) suggests that a significant degree of π bonding is present, which opens the W−O−C angle significantly. This structure is similar to the structures of two related d^2/d^2 $[Re(C-t-Bu)(OR)_2]_2$ ($OR = O-t-Bu$ or $OCMe(CF_3)_2$) species[3] in which the Re═Re bond lengths are 2.3836(8) and 2.396(1) Å (respectively), the C≡Re═Re angles are 90.0(2)° and 89.5(1)° (respectively), and the alkylidyne 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 alkylidyne ligands in the Re complexes was

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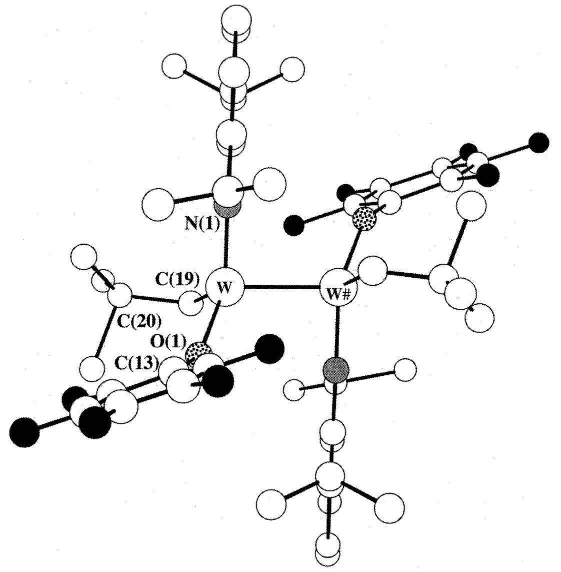

Figure 1. Chem3D drawing of the structure of centrosymmetric $[W(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$. (W−N = 1.749(3) Å, W−O = 1.933(2) Å, W−C = 2.139(3) Å, W−W# = 2.4445(3) Å, W−N(1)−C(1) = 165.5(3)°, W−O(1)−C(13) = 146.7(3)°, W−C(19)−C(20) = 119.3(3)°, N(1)−W−W# = 90.38(10)°, O(1)−W−W# = 113.17(9)°, C(19)−W−W# = 98.08(10)°, N(1)−W−O(1) = 132.30(13)°, N(1)−W−C(19) = 106.23(15)°, O(1)−W−C(19) = 110.31(14)°).

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

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

It has been reported that unstable $W(CHEt)(NAr')[OCMe(CF_3)_2]_2$, which is prepared by treating $W(CH\text{-}t\text{-}Bu)(NAr')[OCMe(CF_3)_2]_2$ with *cis*-3-hexene, decomposes to yield $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$.[2] It was proposed that $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$ contains bridging imido ligands, although the presence of two inequivalent trifluoromethyl groups in the carbon NMR spectrum of $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$ is inconsistent with a structure analogous to that of $[Mo(\mu\text{-}NAr)(O\text{-}t\text{-}Bu)_2]_2$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$).[1] We have shown that $W(CH\text{-}t\text{-}Bu)(NAr')[OCMe_2(CF_3)]_2$ also reacts with *cis*-2-pentene to yield $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ 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 $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$ and $\{W(NAr')[OCMe_2(CF_3)]_2\}_2$ also contain unsupported W═W bonds. (No X-ray study of either species has yet been successful.)[15]

Finally, we recently found that $Mo(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$,[4] which is much more stable than $W(NAr)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)$, will react with 10 equiv of *trans*-3-hexene at 25 °C to yield $[Mo(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$, which was shown in an X-ray study to be a *homochiral* molecule related to $[W(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$ (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 $[W(OCH_2\text{-}t\text{-}Bu)_4]_x$, 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.

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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 $[W(NAr)(CH_2\text{-}t\text{-}Bu)(OC_6F_5)]_2$. X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) 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.

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