Syntheses of Tungsten tert-Butylimido and Adamantylimido Alkylidene Complexes Employing Pyridinium Chloride As the Acid

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Supporting Information

ABSTRACT: Routes to new tungsten alkylidene complexes that contain tert-butylimido or adamantylimido ligands have been devised that begin with a reaction between WCl₆ and 4 equivalents of HNR(TMS) to give [W(NR)₂Cl(μ-Cl)(RNH₂)]₂ (R = t-Bu or 1-adamantyl). Alkylation leads to W-(NR)₂(CH₂R′)₂ (R′ = t-Bu or CMe₂Ph), which upon treatment with pyridinium chloride yields W(NR)(CHR′)Cl₂(py)₂ complexes, from which W(NR)(CHR′)(pyrrolide)₂ and two W(N-t-Bu)(CHR′)(pyrrolide)(OAr) complexes (OAr = hexamethyl- or hexaisopropylterphenoxide) have been prepared.

Olefins metathesis catalyzed by well-defined Mo, W, and Ru catalysts is the only way to prepare olefins from olefins catalytically and with a high degree of control.¹ Arylimido ligands usually have been employed in high oxidation state imido alkylidene complexes of molybdenum and tungsten, especially aryls that are mono- or disubstituted in the ortho position(s).² However, it has become clear that (i) adamantylimido alkylidene complexes of molybdenum are the catalysts of choice in some circumstances such as Z-selective ring-opening metathesis reactions³ and (ii) tungsten arylimido alkylidene complexes are often more successful than molybdenum complexes for Z-selective reactions.⁴ However, no tungsten-based alkylimido alkylidene complexes have been reported to our knowledge. Therefore, we were compelled to explore routes to tungsten tert-butylimido or adamantylimido alkylidene complexes.

A logical starting material for the synthesis of tert-butylimido alkylidene complexes of tungsten would be W(N-t-Bu)₂Cl₂(DME). However, attempts to prepare W(N-t-Bu)₂Cl₂(DME) through reactions between WO₂Cl₂(DME), tert-butylamine, Me₃SiCl, and NEt₃ under conditions analogous to those employed to prepare W(NAryl)₂Cl₂(DME) and Mo(NAryl)₂Cl₂(DME) complexes² have failed so far in our hands; similar reactions to synthesize the 1-adamantyl analogue, including conditions in which an N-sulfonimide is employed as the imido source,⁵ were also unsuccessful. As far as we are aware, W(N-t-Bu)₂Cl₂(DME) is still unknown, although adducts such as W(N-t-Bu)₂Cl₂(pyridine)₂ have been reported.⁶

In 1987 Nielson⁷ reported that addition of 4 equivalents of t-BuNH(TMS) to WCl₆ gave a compound with the formula W(N-t-Bu)₂(t-BuNH₂)Cl₂.⁸ This compound has also been prepared in 30% yield in a reaction between WO₂Cl₂(DME) and t-BuNH(TMS) in heptane or dimethoxyethane.⁹ By analogy with {W(N-t-Bu)(μ-NPh)(t-BuNH₂)Cl₂}₂ (1a, Figure 1) W(N-t-Bu)₂Cl₂(t-BuNH₂) was proposed to be a dimer that contains bridging tert-butylimido groups. We have confirmed that W(N-t-Bu)₂(t-BuNH₂)Cl₂ can be prepared conveniently on a 15 g scale as described by Nielson, but have found through XRD that it contains bridging chlorides, not bridging imido groups. The structure of [W(N-t-Bu)₂Cl(μ-Cl)(t-BuNH₂)]₂ (1a, Figure 1) can be viewed as essentially two square pyramids with slightly bent imido groups in the apical positions (those that contain {W(N-t-Bu)(μ-Ntolyl)(t-BuNH₂)Cl₂}₂).¹⁰ W(N-t-Bu)₂Cl₂(t-BuNH₂) was proposed to be a dimer that contains bridging tert-butylimido groups. We have confirmed that W(N-t-Bu)₂(t-BuNH₂)Cl₂ can be prepared conveniently on a 15 g scale as described by Nielson, but have found through XRD that it contains bridging chlorides, not bridging imido groups. The structure of [W(N-t-Bu)₂Cl(μ-Cl)(t-BuNH₂)]₂ (1a, Figure 1) can be viewed as essentially two square pyramids with slightly bent imido groups in the apical positions (those that contain

Figure 1. Thermal ellipsoid drawing (50%) of 1a. Selected bond distances (Å) and angles (deg): W1–Cl1 = 2.3942(6), W1–Cl3 = 2.6104(6), W1–Cl4 = 2.8063(6), W1–N1 = 2.210(2), W1–N2 = 1.754(2), W1–N3 = 1.743(2), W1–N1–C1 = 126.63(15), W1–N2–C5 = 159.36(18), W1–N3–C9 = 177.24(19), W1–Cl3–W2 = 106.72(2), W1–Cl4–W2 = 106.14(2).

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N(2) and N(5) in Figure 1) “joined” to create an octahedral geometry about tungsten through relatively long W−Cl bridges (e.g., W(1)−Cl(4) = 2.8063(6) Å). Interestingly, the N(1)−Cl(2) and N(4)−Cl(1) distances (3.34 Å) are in the range observed when a hydrogen bond is present between an NH proton and chloride (N···Cl = 3.30 Å).11 Also, one of the two protons on each amine nitrogen points toward the terminal chloride on the neighboring tungsten (e.g., H···Cl(1) = 2.448 Å). Therefore, we propose that two hydrogen bonds stabilize the structure of 1a. The fact that 1a can be prepared in dimethoxyethane,9 as noted earlier, attests to the integrity of the dimeric structure of 1a, at least toward dimethoxyethane, although addition of nitrogen donors to 1a, e.g., pyridine6 or di-tert-butyl-1,4-diaza-1,3-butadiene,9 leads to formation of monomeric complexes of the type W(N(t-Bu))2Cl2. The 1-adamantylimido analogue of 1a (1b) was prepared similarly and has a structure that is closely analogous to that of 1a (see SI). Heating a solution of 1b in DME at 120 °C for 24 h in a high-pressure vessel results in neither replacement of the amines by dimethoxyethane nor decomposition of 1b.

In spite of the presence of tert-butylamine in 1a, we find that 1a reacts cleanly with 2 equivalents of t-BuCH2MgCl (per W) to give W(N(t-Bu))2(CH2-t-Bu)2 (2a) in 87% yield. W(N-t-Bu)2(CH2-t-Bu)2, so far has been obtained only as a light brown oil that becomes solid at ca. −20 °C. However, the analogous reaction between 1b and Me3PCH2CH2MgCl yielded crystalline W(NAd)2(CH2CMe2Ph)2 (2b), XRD of which revealed the expected pseudotetrahedral structure shown in Figure 2. The neopentyl analogue of 2b (2c) has also been synthesized and can be isolated as a crystalline solid in 53% yield.

Addition of 3 equivalents of triflic acid to 2a, 2b, or 2c in a mixture of 1,2-dimethoxyethane and ether, which is the method employed to form M(NR)(CHR')(OTf)2(DME) complexes of Mo and W2b in our hands has not yet led to W(NR)(CHR')(OTf)2(DME) complexes (R = t-Bu or Ad). We also found that triflic acid could not be employed in order to remove the tert-butylimido group selectively from Mo(NAr*)(N-t-Bu)-(CH2CMe2Ph)2 (Ar* = 2,6-dimethylphenyl) to give Mo(NAr*)2(CHCMe2Ph)(OTf)2(DME).12 Instead, 3 equivalents of 3,5-lutidinium chloride was found to give Mo(NAr*)2(CHCMe2Ph)Cl3(3,5-lutidine) in good yield. Therefore we turned to reactions employing pyridinium chloride. Addition of 3 equivalents of pyridinium chloride to 2a or 2c led to formation of W(NR)(CH-t-Bu)Cl2(py)2 (R = t-Bu (3a) or 1-Ad (3b)) in good yield (eq 1).

An XRD of crystals obtained through recrystallization of 3a from a mixture of methylene chloride and pentane showed the crystal to be [W(NR)(CHR')(μ-Cl)(py)]2, formed through loss of one pyridine from 3a (Figure 3). The W≡N and W≡C bond lengths and W−N−C and W−C−C angles are normal, as are the terminal, approximately equal, and longer bridging W−Cl bond lengths. The W−N bond length (2.207(5) Å) is within the expected range. In contrast, there is no evidence for formation of a dimer analogous to 3a through loss of pyridine from 3b.

The reaction between 3a and 2 equivalents of lithium 2,5-dimethylpyrroli dine led to formation of W(N(t-Bu))(CHCMe2Ph)-(2,5-Me2pyr)2 (4a) in 58% isolated yield. We propose that the one pyrroli de is bound to the metal in 4a in an η1 fashion, while the other is bound in an η1 fashion, as found in bispyrroli dine complexes of Mo or W of this general type that do not contain donor ligands,13 unless the pyrroli de cannot bind readily in an η1 fashion, as in the case of 2-mesitylpyrroli dine.5 Compound 4a was treated with 1 equivalent of HMTOH (2,6-(2,4,6-Me3C6H2)3C6H4OH) in benzene to generate the MAP complex W(N(t-Bu))(CHCMe2Ph)(2,5-Me2pyr)(OHMT) (MAP = monoaroyloxide pyrroli de; 5a).

An attempted synthesis of W(N(t-Bu))(CHCMe2Ph)(pyr)2 (where pyr is the parent pyrroli de) in a manner similar to
that described for 4a was not successful. Isolation and storage of bis(parent)pyrrolide complexes of Mo has also been problematic, but a solution to their synthesis and use was provided through formation of 2,2'-bipyridine adducts as intermediates.\(^{15}\) As in Mo chemistry, we find that W(N-t-Bu)(CHCMe\(_3\))(pyr)(HOHMT) (6a) can be prepared in 83% yield. The \(^1\)H NMR spectrum of 6a obtained in CD\(_2\)Cl\(_2\) showed four alkyldene resonances at room temperature. However, after the sample was heated to 100 °C overnight in CD\(_2\)Cl\(_2\) in a sealed tube the \(^1\)H NMR spectrum at room temperature showed just one isomer to be present. Limited solubility of 6a prevents the determination of whether the alkyldene is the syn or anti isomer.

Compound 6a was treated with 1 equivalent of ZnCl\(_2\) (dioxane) (in order to remove 2,2'-bipyridine) and 0.84 equivalent of HIPTOH (2,6-(2,4,6-i-Pr\(_2\)C\(_6\)H\(_4\))C\(_6\)H\(_4\)OH) in toluene, and the mixture was placed in an ultrasonic sonicator for 15 h. The yellow-brown mixture was filtered through a pad of Celite, and W(N-t-Bu)(CHCMe\(_3\))(pyr)-(OHIPT) (7a) isolated in good yield from the filtrate (eq 2).

Exchange of the pyrrolide ligand with chloride is minimal during formation of 7a. W(N-t-Bu)(CHCMe\(_3\))(pyr)(OHMT) (8a) can be synthesized in an analogous manner.

The solid-state structure of 8a was determined in an X-ray study (Figure 4). It is interesting to note that the distance between tungsten and the imido nitrogen is relatively short compared with W=N distances in MAP complexes of arylimido tungsten species. Compound 8a has a W=N distance 1.670 Å, whereas several 2,6-dissopropylimido and 3,5-dimethylphenyl-

![Figure 4. Thermal ellipsoid drawing (50%) of 8a. Selected bond distances (Å) and angles (deg): W(1)–N(1) = 1.670(3), W(1)–N(2) = 2.021(4), W(1)–C(1) = 1.916(3), W(1)–O(1) = 1.8691(12), W(1)–N(1)–C(6) = 169.5(5), W(1)–C(1)–C(2) = 141.9(3), W(1)–O(1)–C(21) = 173.81(13), N(1)–W(1)–C(1) = 105.63(14), O(1)–W(1)–C(1) = 108.10(10), N(2)–W(1)–N(1) = 105.42(10), O(1)–W(1)–N(2) = 109.29(6), C(1)–W(1)–N(2) = 100.62(10), N(1)–W(1)–O(1) = 125.10(12).](image)

Compounds 9a–12a are essentially insoluble and therefore isolated readily in good yields and high purity simply through filtration. The aniline (ArNH\(_2\)) and alkane (R’CH\(_2\)) were the only byproducts observed (in high yields versus an internal standard) in \(^1\)H NMR spectra of the filtrates of the reaction mixtures from which ether had been removed in vacuo. Proton NMR spectra of 9a–12a (in CD\(_2\)Cl\(_2\)) are consistent with the presence of two isomers, one that contains trans chlorides and another (out of two possible) that contains cis chlorides. A spectrum of W(N(2,6-Me\(_2\)C\(_6\)H\(_4\))(CHCMe\(_3\)Ph)Cl\(_2\))(bipy), for example, has alkyldene \(\alpha\)-proton resonances at 11.29 and 10.48 ppm for cis and trans isomers, respectively, the ratio of which varies with reaction conditions. Limited solubility of 9a–12a in CD\(_2\)Cl\(_2\) prevented confirmation (by either \(^1\)H or \(^13\)C NMR studies) of the proposal that the alkyldene in each case is the syn isomer.

We conclude that tert-butylimido and adamantylidino alkyldene complexes of tungsten are now readily accessible from tungsten hexachloride, that pyridinium chloride can be employed to initiate an \(\alpha\)-abstraction reaction that generates the alkyldene, and that HCl can be employed in the presence of 2,2'-bipyridine to make several tungsten arylimido alkyldene complexes. Therefore, the use of WCl\(_6\) and HCl in some form is recommended.

**ASSOCIATED CONTENT**

**Supporting Information**

Experimental details for the synthesis of all compounds and details of the X-ray structural studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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■ REFERENCES