

Salt-Free Reducing Reagent of Bis(trimethylsilyl)cyclohexadiene Mediates Multielectron Reduction of Chloride Complexes of W(VI) and W(IV)

Hayato Tsurugi,[†] Hiromasa Tanahashi,[†] Haruka Nishiyama,[†] Waldemar Fegler,[‡] Teruhiko Saito,[†] Andreas Sauer,[‡] Jun Okuda,[‡] and Kazushi Mashima^{†,*}

[†]Department of Chemistry, Graduate School of Engineering Science, Osaka University, and CREST, JST, Toyonaka, Osaka 560-8531, Japan

[‡]Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52056 Aachen, Germany

S Supporting Information

ABSTRACT: We developed a salt-free reduction of WCl_6 using 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (MBTCD) in toluene to give a low-valent trinuclear tungsten complex involving W(II) and W(III) centers, while in the presence of redox active ligands such as α -diketone and α -diimine the same reduction produced W(IV) complexes with the corresponding redox-active ligands, (α -diketone) WCl_4 and (α -diimine) WCl_4 . A W(VI) complex with two α -diketone ligands, (α -diketone) $_2\text{WCl}_2$, was found to be synthetically equivalent to low-valent W(IV) species that trapped azopyridine to give (α -diketone) WCl_2 (azopyridine).

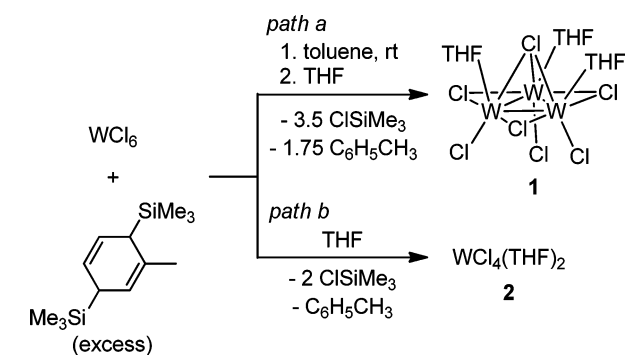
Low-valent early transition metal species have attracted special attention due to their important role in the activation of small molecules such as dinitrogen and carbon monoxide, leading to ammonia, tris(trimethylsilyl)amine, and CO-coupling products.¹ Reduction of high-valent early transition metal complexes is the general strategy for preparing highly reactive low-valent early transition metal species, and strong reductants such as amalgams of alkaline and alkaline-earth metals, zinc dust, and alkylmetal reagents are conventionally used as the reductants.² The generation of low-valent metal species using the conventional reductants, however, is always accompanied by reductant-derived metal salts as well as side-products through over-reduction. Thus, such a reducing method sometimes not only hampers isolation of the desired low-valent metal complexes but also retards their reactivity or catalytic performance due to coordination of the metal salt to the catalytically active metal center.³

Among the low-valent early transition metal complexes, low-valent tungsten complexes are highly powerful chemical species that activate not only single covalent bonds but also various $\text{C}=\text{X}$ double bonds and $\text{C}\equiv\text{C}$ and $\text{N}\equiv\text{N}$ triple bonds. Therefore, extensive studies have focused on the preparation of low-valent tungsten species.^{4,5} Although the versatility of such low-valent tungsten species is well demonstrated, the reduction of high-valent tungsten species, including W(VI), W(V), and W(IV) complexes, requires rather strong reductants, which generate reductant-derived metal salts, resulting in a low yield of the low-valent tungsten species in many cases.⁶ To improve the reducing

method without metal salt formation, several organic-based reductants have been used for the reduction of WCl_6 :⁷ allyltrimethylsilane and alkenes are effective for generating W(V) and W(IV) species with the formation of easily removable organic products or chlorotrimethylsilane. Access to the more reactive W(II) and W(III) species without any salt contact, however, is in high demand. Recently, we developed an organosilicon-based reductant, 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (abbr. MBTCD), for reducing tantalum and niobium pentachlorides.⁸ Although allyltrimethylsilane did not reduce TaCl_5 and NbCl_5 , low-valent tantalum and niobium species were generated by the addition of MBTCD to toluene solutions of TaCl_5 and NbCl_5 . The high reducing ability of MBTCD led us to prepare highly valuable low-valent tungsten species in a salt-free manner by reducing WCl_6 using MBTCD with easy removal of the byproducts, toluene and chlorotrimethylsilane. Herein, we report the multielectron reduction of WCl_6 by simple treatment with MBTCD to produce a salt-free W(II)–W(III) species, which, to the best of our knowledge, is the first example of a trinuclear cluster of tungsten which is free of additional salts. In situ generated low-valent tungsten species were immediately trapped by 4,4'-dimethylbenzil (abbr. α -diketone), N,N' -bis(aryl)-1,4-diaza-1,3-butadiene (abbr. α -diimine), or 1,2-bis(arylimino)acenaphthene (abbr. BIAN) ligands to form (L) WCl_4 complexes. Moreover, the isolated bis(α -diketone) WCl_2 served as a low-valent tungsten source: electron-accepting molecules such as azopyridine reacted with bis(α -diketone) WCl_2 with the release of one α -diketone ligand to produce (α -diketone) WCl_2 (azopyridine).

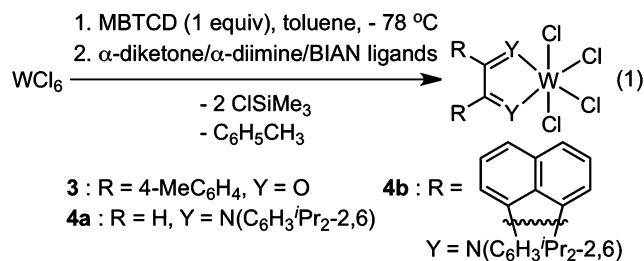
We first examined the reduction of WCl_6 using excess MBTCD in toluene at room temperature, which resulted in the immediate precipitation of black powders from the reaction mixture. ¹H NMR observation of the reaction in C_6D_6 revealed the generation of 3.5 equiv of ClSiMe_3 and 1.75 equiv of $\text{C}_6\text{H}_5\text{CH}_3$, equal to the consumption of 1.75 equiv of MBTCD, suggesting that the powders contained divalent and trivalent tungsten atoms (Scheme 1, path a). Although the black powder could not be dissolved in any nonpolar solvents, it was soluble in polar coordinating solvents such as THF. In fact, extraction of the black precipitates with THF afforded greenish black micro-

Received: February 13, 2013

Scheme 1. Reduction of WCl_6 Using 1-Methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene


crystals of $\text{W}_3\text{Cl}_7(\text{THF})_3$ (**1**) in 91% yield. The X-ray diffraction studies revealed the trinuclear structure of the tungsten complex **1**, in which three tungsten atoms are arranged in an equilateral triangle and formal oxidation states are W(II), W(II), and W(III). One μ^3 -Cl ligand is located above the plane of the triangle, and three μ -Cl ligands are in the W_3 plane. Each tungsten atom is further coordinated by one terminal chloride and one THF ligand. The averaged oxidation state of the tungsten atoms is +2.33, and to the best of our knowledge, this is the lowest oxidation state for the triangular group 6 metal clusters.⁹ These results indicated that WCl_6 was reduced to $[\text{WCl}_{2.33}]_n$ aggregates in toluene in the first stage, and the addition of THF led to the formation of the trinuclear paramagnetic species **1**. In contrast, reduction of WCl_6 in THF using excess MBTCD resulted in the formation of $\text{WCl}_4(\text{THF})_2$ (**2**) in quantitative yield;^{7d} its further reduction by MBTCD did not proceed, however, probably due to the coordination of THF to the in situ generated low-valent tungsten species accordingly preventing further reduction (Scheme 1, path b).

The addition of 1 equiv of MBTCD to a toluene solution of WCl_6 at low temperature resulted in the formation of a WCl_4 species as a dark-gray suspension when the reaction mixture was warmed to room temperature. Subsequently, redox-active ligands, such as 4,4'-dimethylbenzil, N,N' -bis(aryl)-1,4-diaza-1,3-butadiene, and 1,2-bis(arylimino)acenaphthene ligands, were added to trap the low-valent tungsten species to give the corresponding tetrachlorotungsten complexes **3**, **4a**, and **4b** in good yield (eq 1).



In their ^{13}C NMR spectra, the resonances for the carbonyl carbons of the α -diketone ligand or the imine carbons of the α -diimine ligand were observed at δ_{C} 192.6 for **3**, δ_{C} 150.8 for **4a** (a resonance of the corresponding imine carbons for **4b** was not observed), indicating that the ligands coordinated to the metal center in a neutral mode to form W(IV) species in solution.^{8b,10} In the solid state, the neutral coordination modes of α -diimine and BIAN ligands for **4a** and **4b** bearing W(IV) were further confirmed by X-ray diffraction analyses (C1–N1, 1.37(3) Å,

C1–C1*, 1.49(3) Å for **4a**), whereas the solid-state structure of **3** revealed that **3** adopts a dianionic ene-diolate ligand coordinating to W(VI) species, based on the elongated C–O bonds (1.317(7) and 1.322(7) Å) and the shortened C–C bond (1.416(8) Å) of the ligand motif (Figure 1).^{10a,b} The different coordination mode

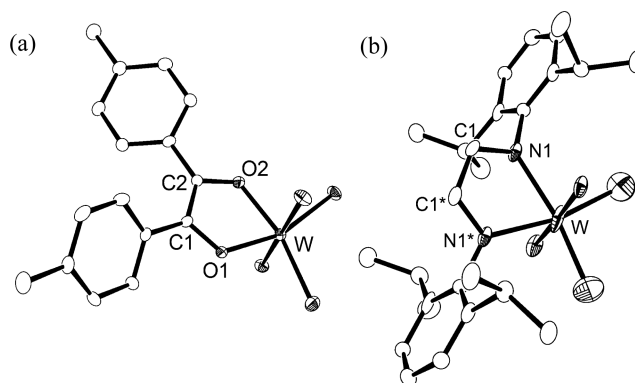
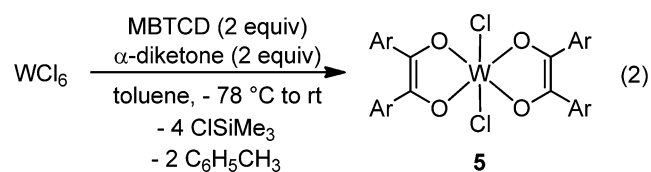


Figure 1. Molecular structures of tungsten complexes **3** and **4a**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): (a) for **3**: W–O1, 1.948(4); W–O2, 1.976(4); C1–C2, 1.416(8); C1–O1, 1.322(7); C2–O2, 1.317(7). (b) for **4a**: W–N1, 2.174(17); C1–N1, 1.37(3); C1–C1*, 1.49(3).

for **3** in the solid state compared with that of **4a** and **4b** might be due to the small dihedral angle between the metallacycle, W–O1–C1–C2–O2, and 4-methylphenyl rings (26.1°) that accelerates the reduction of the α -diketone ligand in dianionic form due to the extended π -conjugation from the metallacycle to one aromatic ring.¹¹

Although isolation of highly reduced W(II) species without any supporting ligands and solvents was difficult in pure form due to facial aggregation in the reaction mixture as described in Scheme 1, the addition of 2 equiv of the α -diketone ligand to the reaction mixture of 2 equiv of MBTCD and WCl_6 in toluene led to the isolation of bis(α -diketone) WCl_2 (**5**) as a purple powder in 93% yield (eq 2).



Complex **5** was alternatively prepared by treating complex **3** with the α -diketone ligand in the presence of MBTCD (1 equiv), suggesting that the formation of **5** from WCl_6 proceeded in a stepwise manner through the formation of complex **3**. The complex **5** was characterized by the ^{13}C NMR spectrum, which displayed a singlet signal at δ_{C} 162.2 assignable to the dianionic ene-diolate moiety.^{10a,b} Such a coordination mode of the α -diketone ligand indicated that four electrons were totally stored in the two α -diketone ligands to form two dianionic ene-diolate ligands, giving formal W(VI) species **5**. Electrons stored in the redox-active ligands of metal complexes are utilized for the activation of small molecules by transferring the electrons from the ligands to substrates,¹² and the bis(α -diketone) WCl_2 complex **5** was thus expected to serve as a synthetic equivalent to low-valent W species.

In contrast to the difficulty of the reduction of the THF adduct **2**, W(IV) species having redox-active ligands could be reduced,

probably due to the relatively electron-deficient character of the W(IV) metal center. In fact, the reduction of complex **4a** using MBTCD in the presence of the α -diketone ligand afforded tungsten complex **6** bearing α -diketone and α -diimine ligands (Scheme 2). Complex **6** was a ^1H NMR silent species, and the molecular structure was clarified by X-ray diffraction study (Figure 2).

Scheme 2. Reduction of (α -Diimine)WCl₄ (4a**) Using MBTCD**

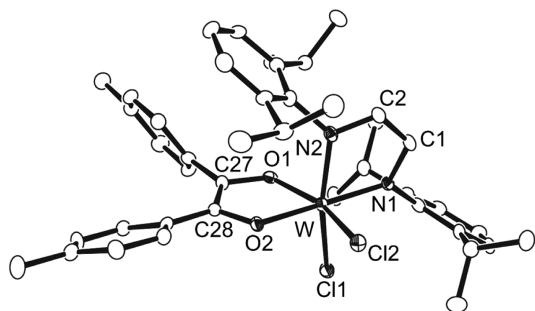
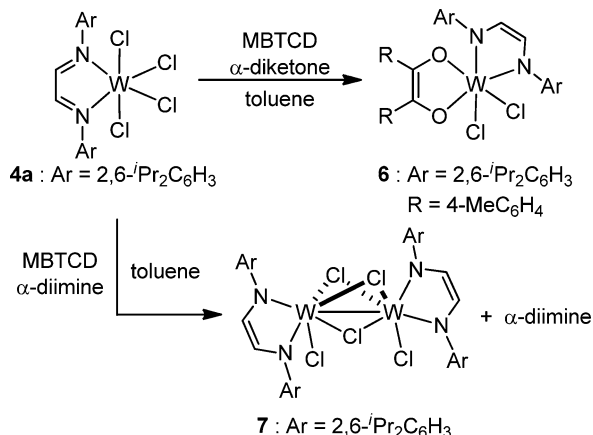


Figure 2. Molecular structure of tungsten complex **6**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): W–O1, 1.956(5); W–O2, 2.014(5); W–N1, 2.016(6); W–N2, 2.037(6); C1–C2, 1.355(10); C1–N1, 1.371(8); C2–N2, 1.390(8); C27–C28, 1.384(10); C27–O1, 1.362(8); C28–O2, 1.330(8).

In the solid state structure of complex **6**, both C–O and C–N bonds are elongated compared to the original neutral ligands, and the long–short–long sequences of the ligand backbones indicate two electron reductions at both α -diketone and α -diimine ligands to form W(VI) species in the solid state.^{8b} In contrast, when complex **4a** was further reduced by MBTCD in the presence of the α -diimine ligand as a trial to prepare bis(α -diimine)WCl₂, approximately 0.8 equiv of MBTCD was consumed to give a triply chloride-bridged dimeric and paramagnetic tungsten complex **7**, in which the additional α -diimine ligand was not incorporated.¹³ Geometries of the α -diimine ligand backbone in **7** indicate the dianionic coordination of the both α -diimine ligand to the tungsten metal center.¹⁴ The distance of W1–W2 is 2.8948(8) Å, consistent with the tungsten–tungsten single bond.¹⁵

Because of the redox reactivity of α -diketone and α -diimine ligands from neutral to dianion, we used complex **5** as a low-valent equivalent for catching small molecules. The reactions of **5** with azopyridine yielded (α -diketone)WCl₂(azopyridine) with

the release of 1 equiv of α -diketone.¹⁴ During the reaction, the transient W(IV) species was immediately trapped by azopyridine to give tungsten complex **8** (eq 3). The overall molecular structure was clarified by X-ray diffraction study, which revealed the coordination of dianionic α -diketone and neutral azopyridine ligands to the tungsten metal center (Figure 3).¹⁶

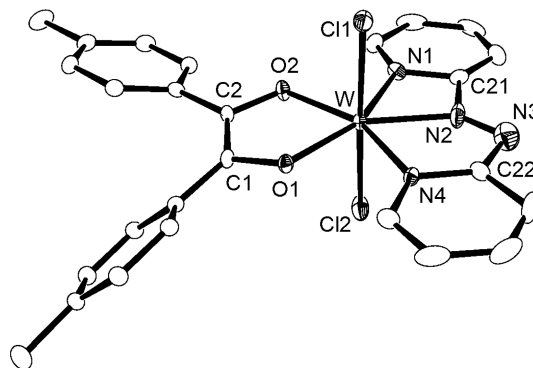
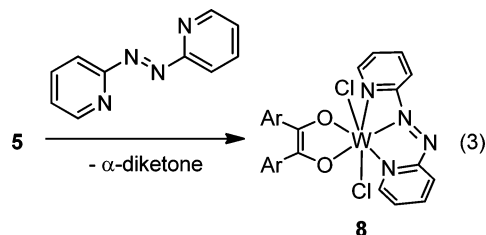


Figure 3. Molecular structure of tungsten complex **8**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å): W–O1, 1.969(3); W–O2, 2.005(3); C1–C2, 1.382(6); C1–O1, 1.329(5); C2–O2, 1.332(5); W–N1, 2.120(4); W–N2, 2.063(5); W–N4, 2.126(4); C21–N2, 1.536(7); N2–N3, 1.213(7); C22–N3, 1.326(7).



In summary, we developed a mild reduction method for tungsten species using a well-designed organosilicon-based reagent, MBTCD. Low-valent W(II) species were accessible without conventional metal- or alkylmetal-based reductants, and low-valent tungsten cluster **1** was isolated as a W(II,II,III) triangular trinuclear cluster. In contrast, in the presence of α -diketone and α -diimine ligands, in situ generated W(IV) or W(II) species were immediately trapped by the redox-active ligands to afford (α -diketone)WCl₄, (α -diimine)WCl₄, and (α -diketone)₂WCl₂, where electrons stored in the redox-active ligand backbone were effectively transferred to the tungsten metal center by adding electron-accepting molecules. Further extension of the reduction of group 6 metal complexes using MBTCD and related compounds is ongoing in our laboratory.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details, molecular structures of tungsten complexes **1**, **4b**, and **7**, and intermolecular π – π stacking of **3** in the solid state (PDF) and a CIF file for complexes **1**, **3**, **4a**, **4b**, **6**, **7**, and **8**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

mashima@chem.es.osaka-u.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.S. thanks the Japan Society for the Promotion of Science for a fellowship and JSPS Japanese-German Graduate Externship. W.F. and A.S. thank the Deutsche Forschungsgemeinschaft through the International Research Training Group SeleCa (GRK 1628) for financial support. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST), Japan, and Grant-in-Aid for Scientific Research on Innovative Areas, "Molecular Activation Directed toward Straightforward Synthesis", MEXT, Japan.

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