Facile Reduction of Tungsten Halides with Nonconventional, Mild Reductants. I. Tungsten Tetrachloride: Several Convenient Solid-State Syntheses, a Solution Synthesis of Highly Reactive (WCl4)x, and the Molecular Structure of Polymeric Tungsten Tetrachloride

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Received February 2, 1998

Polymeric $(WCl_4)_x$ has been prepared in crystalline form from WCl_6 by three new, safer solid-state approaches via mercury (in 83% yield), bismuth (82% yield), or antimony (97% yield) reduction. A modification of a published procedure for reduction of WCl_6 with red phosphorus, which improves $(WCl_4)_x$ purity, is also described. Highly reactive $(WCl_4)_x$ powder can be prepared in 99% yield via tin reduction of WCl_6 in 1,2-dichloroethane. $(WCl_4)_x$ powder was readily converted in high yields to the known $WCl_4(MeCN)_2$ and $W_2Cl_4(OMe)_4(HOMe)_2$. The molecular structure of $(WCl_4)_x$, as determined by single-crystal X-ray diffractometry, consists of a polymer of opposite-edge-sharing bioctahedra with alternating short $(W(1)-W(1A), 2.688(2)$ Å$)$ and long $(W(1)\cdots W(1B), 3.787(3)$ Å$)$ tungsten−tungsten distances. The acute $W(1)-Cl(2)-W(1A)$ angle $(69.4(2)°)$, obtuse $Cl(1)-W(1)-W(1A)$ angle $(94.99(12)°)$, short axial $Cl(1)\cdots Cl(1A)$ nonbonded distance $(3.085(10)$ Å, substantially less than twice the Cl van der Waals radius), and short $W(1)-W(1A)$ distance are consistent with a strong $W(1)-W(1A)$ interaction best described as a W≡W bond for this d^2-d^2 compound. Crystal data: Cl_4W, $a = 11.782(3)$ Å, $b = 6.475(1)$ Å, $c = 8.062(2)$ Å, $\beta = 131.14(1)°$, $V = 463.2(2)$ Å^3, monoclinic, $C2/m$, $Z = 4$.

Introduction

Tungsten tetrachloride is an important starting reagent in lower-valent tungsten and organotungsten chemistries. $(WCl_4)_x$ is a common synthon in tungstenocene,[1] multiply bonded ditungsten,[2] and hexatungsten(II) halide cluster[3] chemistries and has been used to prepare important compounds/materials, e.g., porphyrin complexes,[4] nanophase W_2C,[5] reactive $WCl_2(ligand)_4$ complexes,[6] ring-opening metathesis polymerization catalysts,[7] and alkyne complexes.[8] The earliest preparations of $(WCl_4)_x$ involved reduction of WCl_6 with H_2[9] or chlorination of WO_2

with CCl_4.[10] Newer synthetic routes are based on reduction of WCl_6 with red phosphorus (95% yield based on WCl_6),[11] Al (100% yield based on Al),[12] C_2Cl_4 (95% yield based on WCl_6, with brief preparative details;[13] 50% yield in an earlier detailed procedure[14]), $W(CO)_6$ in refluxing PhCl (96% yield based on $W(CO)_6$),[3d,15] and WO_2.[16] Most synthetic routes entail experimental complexities, including high pressures of reactants or byproduct, specialized equipment, slow reactions, high temperatures, careful temperature control, expensive reactant, difficulty in filtration of product, chlorohydrocarbon byproducts, a need for a two-zone furnace, or appreciable impurities if the reaction is not run under optimal conditions. Irreproducibility can be a problem; for example, in our hands the reaction of WCl_6 with C_2Cl_4 gave predominantly WCl_5. In the two most common routes (employing red P or $W(CO)_6$), care must be exercised in order to minimize residual levels of W phosphides, P, or PhCl, all of which can affect subsequent chemistry. The suitability of $(WCl_4)_x$ for a particular synthetic use can be critically dependent on the preparative route.[2a,11b,15a,c] Crystalline product has been reported only from reduction of WCl_6 with Al via chemical transport in a two-zone furnace (475, 225°) with careful temperature control because of the circulating $AlCl_3$.[12]

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A polymeric, octahedral chain structure[17] has been assigned[12] to solid $(WCl_4)_x$ on the basis of isomorphism of the powder X-ray diffraction data to that for $(NbCl_4)_x$. In the $(NbCl_4)_x$ structure, each octahedron shares a pair of opposite edges, with alternating short and long Nb···Nb separations.[18] An alternate[19] structural view is a close-packed array of chlorides with metal atoms in adjacent octahedral holes, filling half the octahedral holes in every second layer. To our knowledge, there has been no single-crystal X-ray diffractometry performed on $(WCl_4)_x$.

During the course of our studies on tungsten halide cluster chemistry, we found an improved approach (in terms of purity) to the synthesis of $(WCl_4)_x$ via reduction of WCl_6 with red phosphorus. Because of the high pressures of PCl_3 which can be generated during this reaction, we examined other reductants. We found that mercury, antimony, and bismuth were convenient reductants in safer sealed-tube furnace reactions for preparation of crystalline $(WCl_4)_x$ in good to excellent yields, and that Sn is an effective reductant for solution preparation of highly reactive $(WCl_4)_x$ in high yield. We report here preparative details for these improved and new synthetic routes, preparation of known derivatives to test the suitability of the highly reactive $(WCl_4)_x$, and the results of a single-crystal X-ray diffraction study on $(WCl_4)_x$.

Experimental Section

General. Compounds were manipulated in a Vacuum Atmospheres glovebox under prepurified N_2/He (He to assist cooling of the recirculation blower). A Thermolyne 21100 single-zone tube furnace (≤ 1200 °C) with positionable thermocouple was used in syntheses. Borosilicate glass ampules of 25 mm OD with a standard taper 14/20 outer joint were sealed at one end, constricted at two or three locations (depending on the synthetic approach), and then oven-dried overnight at 130 °C. To ensure temperature uniformity throughout the reaction zone and to preclude lower temperature zones (where intermediate reduction products such as WCl_5 could form), the ratio of lengths of tube furnace to glass ampule was kept at ≥ 1.6. Precursors were introduced into the ampule in the glovebox, the ground jointed end closed off with a stopcock-equipped adapter, and the tube flame sealed under dynamic vacuum from a Schlenk line. Reductions in 1,2-dichloroethane were performed in Schlenk glassware.

WCl_6 (Cerac), red P (Aldrich), Bi (325 mesh, Cerac), Sb (100 mesh powder, Aldrich), and Sn (325 mesh powder, Aldrich) were used as received. 1,2-Dichloroethane (Aldrich) and CH_2Cl_2 (Fisher) were thoroughly degassed with argon and distilled from granular P_2O_5. MeCN (Aldrich, anhydrous) was used as received. MeOH (Aldrich, anhydrous) was stored over 4 Å molecular sieves. Triply distilled Hg was purified by filtration through a pinched paper filter into a glass cylinder containing ~ 1 M aqueous HNO_3.

Tungsten content was determined gravimetrically as WO_3 by treating samples with HNO_3 followed by ignition.[12] Qualitative microanalyses for Hg, Bi, Sb, and Sn were performed according to published procedures.[20] Chlorine analysis was performed by gravimetric methods after removal of tungsten content according to the following procedure: An accurately weighed sample of $(WCl_4)_x$ (0.17−0.19 g) was decomposed in 5 mL of 1 M KOH at room temperature. The resulting suspension was oxidized by adding 2 drops of 30% H_2O_2. After approximately 1 h, the solution was diluted to ~ 50 mL volume and heated at 100 °C for ~ 20 min in order to complete oxidation of tungsten and decompose traces of peroxides. A 0.1 M solution of $Ba(NO_3)_2$ (7 mL) was added dropwise with stirring to the hot sample solution. The
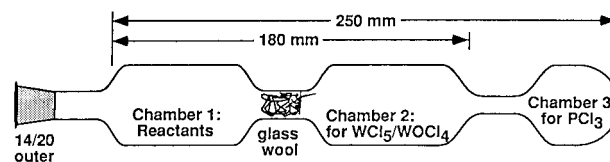
Figure 1. Ampule design for preparation of $(WCl_4)_x$ via reduction of WCl_6 with P (not to scale).

solution and precipitated $BaWO_4$ were heated at 100 °C for ~ 20 min and allowed to sit at room-temperature overnight. The precipitate was removed with a glass fritted funnel and washed with distilled water. The mother liquor volume was adjusted to 75−80 mL and neutralized by adding 12 drops of concentrated ($\sim 70\%$) HNO_3. A 0.5 M solution of $AgNO_3$ (5.5 mL) was then added dropwise with stirring. The resulting solution and precipitated AgCl were heated at 100 °C for ~ 20 min and allowed to sit overnight at room temperature while protected from light. The AgCl precipitate was filtered with a glass fritted funnel, washed with distilled water, oven-dried for 1−2 h at 150 °C, and weighed. Chlorine analyses are the average of two determinations.

Far IR spectra were recorded on a Perkin-Elmer 983G dispersive IR spectrometer on samples in KBr pellets. Powder X-ray diffraction was performed on a Siemens D5000 automated diffractometer, with samples protected from hydrolysis by a thin sheet of poly(vinyl chloride).

Preparation of $(WCl_4)_x$ via Reduction of WCl_6 with Red Phosphorus. *Note: Dangerous pressures of PCl_3 develop during this reaction, and glass vessels are unreliable at pressures in excess of 1 atm, particularly those which have not been thoroughly annealed during construction and seal-off or which have been scratched. Individuals who repeat this procedure are urged to calculate the PCl_3 vapor pressure under their conditions (ampule volume, quantities of reactants, temperature) before proceeding, and to adjust these experimental conditions to lower the PCl_3 pressure which could be generated. Appropriate and conservative safety precautions, including shielding of the tube furnace, enclosure of the apparatus within a fume hood, and use of face shield and protective gloves, must be followed.*

A straight borosilicate glass ampule of 25 mm OD with total inner volume of ~ 70 mL was constructed with three adjacent chambers: the first, in which the reactants were loaded and which had a standard taper 14/20 outer joint on its end, the second (similar size), in which sublimed impurities were collected at the end of the reaction, and the third (smaller than first and second), in which PCl_3 was to be collected (Figure 1). The first and second chambers were separated by a wide constriction which was plugged with borosilicate glass wool. The third chamber was separated from the second chamber by a narrower constriction (ID 1.5−2 mm).

The first chamber was loaded with 24.12 g (60.8 mmol) of WCl_6 and 1.256 g (40.5 mmol) of red P through the ground-joint end. A vacuum adapter was attached and the entire tube evacuated. The ampule was then flame sealed at the constriction between the ground joint and first chamber and the reagents mixed by shaking. The entire ampule was placed in the center of the tube furnace such that WCl_5 could not leave the reaction zone. The temperature was raised to 200 °C during 12 h, and then to 300 °C during 12 h. Assuming ideal gas behavior for PCl_3 at 300 °C (above its critical temperature), the estimated PCl_3 pressure was 27 atm based on the ampule volume. After the furnace was shut off and cooled to 100 °C, the ampule was removed from the furnace and its smaller third chamber immersed in liquid nitrogen for trapping PCl_3. After 5 min, the frozen chamber was sealed-off by torch, and the first chamber returned to the furnace in order to sublime $WOCl_4$ and WCl_5 into the cool second chamber. A temperature of 230−240 °C was maintained for 1 day, then, after cooling, the ampule was removed from the furnace and opened in the glovebox. The yield of black, nonvolatile crystalline product was 18.69 g (94% based on phosphorus).

Powder X-ray diffraction data was consistent with $(WCl_4)_x$; no WCl_6 or WCl_5 were detected. Anal. Calcd for WCl_4: W, 56.45. Found: W, 56.6.

Preparation of $(WCl_4)_x$ via Reduction of WCl_6 with Mercury. *Note: This reaction should be performed in a fume hood with shielding*

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of the furnace in order to prevent release of toxic, volatile Hg and HgCl$_2$ should the ampule seal fail or the ampule shatter. Mercury has appreciable vapor pressure at elevated temperatures. A dual chamber borosilicate glass ampule, with standard taper 14/20 outer joint on one end, constrictions in the middle and between the joint and the first chamber, and total volume of ∼80 mL was loaded with WCl$_6$ (10.00 g, 25.22 mmol) and Hg (5.00 g, 24.93 mmol) in the first chamber. After evacuation, the ampule was flame-sealed between the first chamber and joint and the reagents mixed by shaking. A reaction was readily apparent after mixing, as the crystalline WCl$_6$ changed from purple-gray to brownish-gray, and Hg was consumed. No appreciable temperature rise was noted.

The ampule was placed in the center of the furnace and the temperature raised slowly (∼2 h) to 205 °C. After 1 day, the temperature was raised slowly (∼2 h) to 360 °C. The estimated pressure in the ampule at 360 °C was 3.4 atm.[21] After ∼10 h, the temperature was lowered slowly (2−2.5 h) to 205 °C. The ampule was partially slid out of the furnace in order to sublime HgCl$_2$ as well as any WOCl$_4$ and WCl$_5$ into the cool second chamber. After heating for ∼8 h, the ampule was removed, cooled, and opened in the glovebox.

The nonvolatile, black microcrystalline product weighed 6.82 g (83% yield based on WCl$_6$). A small quantity (∼0.2 g) of large (WCl$_4$)$_x$ crystals was isolated from an ampule zone at intermediate temperature. Colorless crystals of HgCl$_2$ in the cold ampule end were mixed with a small quantity of black needles of transported (WCl$_4$)$_x$; this (WCl$_4$)$_x$ was not isolated, but differential sublimation to remove HgCl$_2$ is possible and would improve the final yield.

Anal. Calcd for WCl$_4$: W, 56.45; Cl, 43.55. Found: W, 56.5; Cl, 43.52. According to powder X-ray diffraction, both the black microcrystals and transported black crystals were (WCl$_4$)$_x$, and no WCl$_6$ or WCl$_5$ was detected. No Hg was detected in either by qualitative microanalysis.

In another experiment using the same quantities of starting materials, all steps of the above synthesis were conducted at 200−210 °C. Weight of (WCl$_4$)$_x$ = 6.16 g (75% yield based on WCl$_6$).

Preparation of (WCl$_4$)$_x$ via Reduction of WCl$_6$ with Bismuth. A borosilicate glass ampule (similar to that used for the synthesis with Hg) was loaded with WCl$_6$ (10.00 g, 25.2 mmol) and Bi (3.51 g, 16.8 mmol). After evacuation, the ampule was sealed and the reagents mixed by shaking. The ampule was placed in the center of the furnace and the mixture heated for 1 day at 210−220 °C. The temperature was raised to 290 °C and the ampule repositioned so that the empty chamber was in a cooler zone (if the empty chamber is removed from the furnace, then BiCl$_3$ will plug the ampule constriction). After 3 days the receiver chamber was repositioned partially outside of the furnace and heating continued for 17 h. After cooling, the ampule was withdrawn, but a small quantity of white crystals (BiCl$_3$) was noted in the product. To reduce the level of BiCl$_3$ contamination, the ampule was returned to the furnace and heated for 6 days at 290−295 °C, with a portion of the receiver chamber outside of the furnace. After cooling, the ampule was removed and opened in the glovebox. The yield of black, nonvolatile, crystalline (WCl$_4$)$_x$ in the first chamber was 6.74 g (82% based on WCl$_6$).

Anal. Calcd for WCl$_4$: W, 56.45. Found: W, 57.2. Trace levels of bismuth-containing species were detected in the product by qualitative microanalysis.

Preparation of (WCl$_4$)$_x$ via Reduction of WCl$_6$ with Antimony. A borosilicate glass ampule was loaded with 10.00 g (25.2 mmol) of WCl$_6$ and 2.04 g (16.7 mmol) of Sb. After evacuation, the ampule was sealed, the reagents mixed, and the ampule placed in the center of the furnace. After heating at 75−80 °C for 12 h, 105 °C for 12 h, and 130 °C for 12 h (calculated vapor pressure of SbCl$_3$, 46 Torr), the empty chamber of the ampule was removed from the tube furnace in order to distill SbCl$_3$ and sublime WOCl$_4$ and WCl$_5$. A temperature of 125−130 °C was maintained for 1 day to distill SbCl$_3$, then the temperature was raised to 160 °C (for 1 day) and 215 °C (for 1 day) in order to remove any WOCl$_4$ and WCl$_5$. After cooling, the ampule was removed

and opened in the glovebox. The yield of black, nonvolatile, crystalline product was 7.99 g (97% yield based on WCl$_6$).

Anal. Calcd for WCl$_4$: W, 56.45; Cl, 43.55. Found: W, 56.5; Cl, 43.39. No Sb was detected by qualitative microanalysis.

Preparation of (WCl$_4$)$_x$ via Reduction of WCl$_6$ with Sn in 1,2-Dichloroethane. A 100 mL Schlenk flask was loaded with WCl$_6$ (12.00 g, 30.26 mmol), Sn powder (1.796 g, 15.13 mmol), and 60 mL of 1,2-dichloroethane. The mixture was stirred at room temperature for 17 h, yielding a gray suspension. A reflux condenser was attached and the mixture heated and stirred at 80−90 °C for 2 days. The graphitic suspension did not change appearance during heating. After cooling, the flask was transferred to the glovebox and the suspension centrifuged in a compact centrifuge. The supernatant was removed, the solid resuspended in CH$_2$Cl$_2$, and the mixture centrifuged. The supernatant was removed and the resuspension in CH$_2$Cl$_2$/centrifugation process repeated four times. The solid was washed into a 125 mL flask with fresh CH$_2$Cl$_2$, the supernatant decanted, and the precipitate dried under dynamic vacuum at room temperature. The yield was 9.812 g (99.6% based on WCl$_6$). The product was a graphitic fine powder with poor crystallinity (by X-ray diffractometry) and high reactivity.

Anal. Calcd for WCl$_4$: W, 56.45; Cl, 43.55. Found: W, 56.6; Cl, 43.27. No Sn was detected by qualitative microanalysis.

In a smaller scale reaction, 3.00 g WCl$_6$ (7.57 mmol) and 0.449 g Sn (3.78 mmol) in 15 mL C$_2$H$_4$Cl$_2$ gave 2.405 g powdered (WCl$_4$)$_x$ (98% yield based on WCl$_6$). SnCl$_4$ was recovered from the supernatant as the insoluble bis-pyridine adduct. Yield = 1.511 g (95% based on Sn).

Reaction of (WCl$_4$)$_x$ (Prepared in Solution via Sn Reduction) with Acetonitrile. Preparation of WCl$_4$(MeCN)$_2$. A suspension of (WCl$_4$)$_x$ (0.200 g, 0.61 mmol) in 7 mL of acetonitrile was stirred at room temperature. The suspension turned gray-purple after 1 day of stirring and red-brown after an additional day. The supernatant was decanted and the precipitate washed with MeCN, in which it was insoluble, and dried in vacuo. The yield of red-brown WCl$_4$(MeCN)$_2$ powder was 0.202 g (81% based on WCl$_4$).

Anal. Calcd for C$_4$H$_6$Cl$_4$N$_2$W: W, 45.09. Found: W, 45.15. The IR spectrum (4000−250 cm^{-1}) matched literature values.[15a,22]

Reaction of (WCl$_4$)$_x$ (Prepared in Solution via Sn Reduction) with Methanol. Preparation of W$_2$Cl$_4$(OMe)$_4$(HOMe)$_2$. An exothermic reaction was noted upon mixing 0.300 g (0.92 mmol) of (WCl$_4$)$_x$ with 4 mL of MeOH at room temperature. The (WCl$_4$)$_x$ dissolved completely in less than 1 min, forming a transparent green solution. After 4−5 min, the solution became cloudy and a greenish-yellow precipitate was noted. After sitting overnight, green crystalline precipitate formed. The precipitate was resuspended, heated at 65 °C for one minute, and cooled to 20°. The supernatant was decanted, the solid washed with MeOH, and the solid dried in vacuo. The yield of crystalline W$_2$Cl$_4$(OMe)$_4$(HOMe)$_2$ was 0.234 g (73% based on WCl$_4$).

Anal. Calcd for C$_3$H$_{11}$O$_3$Cl$_2$W: W, 52.72. Found: W, 52.05. The far-IR spectrum matched literature values.[23]

Single-Crystal Diffractometry on (WCl$_4$)$_x$. A black needle-shaped crystal with 0.24 × 0.04 × 0.04 mm dimensions, from reduction of WCl$_6$ with Hg, was used in data collection. Crystals with larger cross-sections appeared fibrous at the ends, consistent with multiple crystallites and/or twinning. The crystal was examined while immersed in oil with low oxygen solubility, mounted via grease onto a glass fiber (epoxied to a brass pin) under inert gas purge, and cooled with a stream of gaseous dinitrogen. The crystal was placed in the diffractometer cold stream with the long dimension (*b* axis) approximately parallel to the diffractometer ϕ axis.

The data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo Kα radiation and a graphite monochromator, at 210 K using ω scans. Intensity standards were measured at 2 h intervals; no changes in the standards were detected. Net intensities were obtained by profile analysis of the 661 data. Data reduction was performed with computer programs from the MolEN (Enraf-Nonius) package. Lorentz and polarization corrections were applied, as was an empirical absorption correction based on three ψ scans measured at 10° intervals. The

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transmittance range was 0.313−0.985, with an average value of 0.561. Equivalent data were averaged, yielding 438 unique data (R_{int} = 0.094, 368 data > $4\sigma(F)$). Two reflections were excluded from the final refinement cycles after inspection of their profiles revealed small extraneous peaks of unknown origin. On the basis of preliminary examination of the crystal, the space group $C2/m$ was assigned.

Structure solution and refinement was performed with software programs from the SHELXTL v. 5.0 software package (XS, direct methods; XL, refinement; XP, for thermal ellipsoid illustrations; XCIF, preparation of tables). The preliminary structure model was obtained by direct methods. Refinement was performed using a rigid bond restraint for the anisotropic thermal parameters. A $I > 2\sigma(I)$ cutoff was used in selecting data to calculate $R1$ for comparison purposes.

The molecule consists of a linear one-dimensional polymer with the W(1) atom situated on a crystallographic 2-fold axis and the bridging chlorine atoms (Cl(2), Cl(3)) positioned on crystallographic mirror planes (y = 0.0, y = 0.5, respectively).

Results and Discussion

Modification of the Procedure Employing Red Phosphorus as Reductant. The reduction of WCl_6 with red phosphorus is an economical synthetic route but suffers from the need for careful stoichiometric control in order to avoid contamination of $(WCl_4)_x$ with residual phosphorus or tungsten phosphides. We find that the risk of this increases with the use of the apparatus and approach described[11a] by Novikov, et al., i.e., a multichamber L-shaped glass tube with a receiver end outside of the furnace for collection of PCl_3 (along with $POCl_3$ from reduction of residual $WOCl_4$). With a portion of the tube outside of the furnace, some of the WCl_6 (and WCl_5) can sublime from the reaction zone. This would result in an increase of the P:WCl_6 ratio at the reaction zone and thus greater contamination with phosphorus.

We find that use of a triple-chamber *straight* ampule, with the third chamber for removal of PCl_3, improves the $(WCl_4)_x$ quality. By heating the entire ampule during the reduction, the nonstoichiometry from sublimation of WCl_6 and WCl_5 is eliminated. After reduction, the ampule is withdrawn from the furnace, the PCl_3 collected by distillation into a liquid-nitrogen-cooled collection chamber, and the collection chamber sealed off. Then the ampule is partially returned to the furnace and residual WCl_6 and WCl_5 is sublimed away from the $(WCl_4)_x$.

A significant safety drawback of this modified red P route is the substantial PCl_3 pressure (calculated at 27 atm at 300 °C for the tube diameter and quantity of reactants employed; critical T = 290 °C) developed within the sealed tube prior to collection of the PCl_3. Therefore, we sought a safer, lower pressure synthetic route involving a main group reductant which was easily removable by distillation/sublimation. To achieve a convenient vapor pressure of 10 Torr for sublimation/distillation, the following main group chlorides require temperatures[24] of 3.4 °C for $SnCl_4$, 95 °C for $SbCl_3$, 180 °C for $HgCl_2$, 247 °C for Hg_2Cl_2, and 257 °C for $BiCl_3$. By comparison, WCl_5 exerts 10 Torr of vapor pressure at 169 °C, WCl_6 requires 198 °C, and PCl_3 requires only −21 °C. Therefore, we examined the use of mercury and antimony in solid-state reductions, and also the less toxic bismuth (despite the high temperature needed to remove $BiCl_3$).

Reduction of WCl_6 with Mercury. Despite its toxicity, elemental mercury offers several important advantages as a reductant for WCl_6. First, the mild reductant mercury lessens the chance for overreduction of WCl_6 to tungsten metal. The volatility of Hg at reduced pressure ensures diffusion of the reductant throughout the reaction tube and easy removal at the end of the reaction. The potential reduction byproducts, $HgCl_2$ and Hg_2Cl_2, are volatile and thus separable from $(WCl_4)_x$ but exert lower vapor pressures (~3.4 atm at 360 °C). Finally, the formation of W/Hg intermetallics is unlikely, and mercuric chlorotungstates such as $HgWCl_6$ did not form under our reaction conditions. We obtained >83% yield of crystalline $(WCl_4)_x$ by the Hg reduction route.

Because of the toxicities of mercury and mercuric chloride and the effect of residual amounts of Hg or $HgCl_x$ (neither detected qualitatively) on some applications of $(WCl_4)_x$ derived from Hg reduction, we decided to examine alternate low-cost reductants which would form volatile byproducts.

Reduction of WCl_6 with Bismuth. We obtained a good yield (82%) of crystalline $(WCl_4)_x$ from reduction with bismuth, though the $(WCl_4)_x$ contained detectable levels of bismuth by qualitative microanalysis. The W analysis of this material was also slightly high (57.2% found, 56.46% theory); as the W analysis procedure does not remove involatile Bi-containing impurities, contamination with bismuth-containing species may account for the higher W analysis. We conclude that bismuth is a less desirable reductant under our reaction conditions because of the Bi contamination and the lengthy time (>6.5 days at ~290 °C) needed to sublime $BiCl_3$.

Reduction of WCl_6 with Antimony. Antimony proved to be the best reductant of those examined by solid-state approaches, because (1) the yield was virtually quantitative, (2) the $SbCl_3$ pressure at 130 °C was considerably less than 1 atm, (3) $SbCl_3$ distillation required only 1 day, and (4) no Sb-containing species could be detected in the $(WCl_4)_x$ by qualitative microanalysis.

Reduction of WCl_6 with Tin in 1,2-Dichloroethane. We expected that the reaction of Sn with WCl_6 in the solid-state would be too exothermic, which would exacerbate the high vapor pressure (bp 112 °C) from $SnCl_4$; thus, reduction of WCl_6 in the solid-state with tin would have little safety advantage over that of red phosphorus. In a trial experiment, we verified that tin powder was too active a reductant for a sealed ampule reduction in the solid state.

Solution reduction methods often lead to products with smaller particle size and thus higher reactivity, while facilitating temperature control during an exothermic reaction. There have been several reports of in situ reduction of WCl_6, in the presence of ligands (L), to WCl_4L_2 compounds. For example, WCl_4-$(PPh_3)_2$ was prepared by zinc reduction of WCl_6 in CH_2Cl_2,[25] and WCl_4(dme) (dme = 1,2-dimethoxyethane) was prepared by cyclopentene reduction[1] of WCl_6. In these and other studies,[26] there was no attempt to characterize the reduced tungsten product(s) prior to addition of ligand. We therefore examined the use of tin as a reductant in solution, and chose a solvent with appropriate boiling point and in which the $SnCl_4$ byproduct would be soluble.

The reduction of WCl_6 with tin powder in 1,2-dichloroethane solution is facile; in fact, a graphitic suspension is evident within 1−2 h at room temperature after mixing. The graphitic suspension after heating was isolated by centrifugation (without centrifugation, 1 day is needed to allow settling) and washing multiple times with CH_2Cl_2. $(WCl_4)_x$ can be isolated in virtually quantitative yield and is free of tin contamination as shown by qualitative microanalysis. Powder X-ray diffractometry showed

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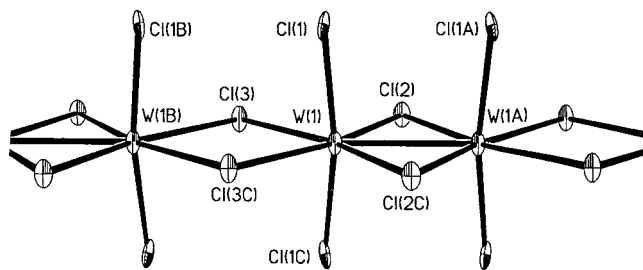
Figure 2. Thermal ellipsoid plot (50% probability ellipsoids) of a portion of the polymeric molecular structure of $(WCl_4)_x$.

that the $(WCl_4)_x$ was poorly crystalline. $SnCl_4$ can be recovered quantitatively from the supernatant by precipitation as the bis-(pyridine) adduct.

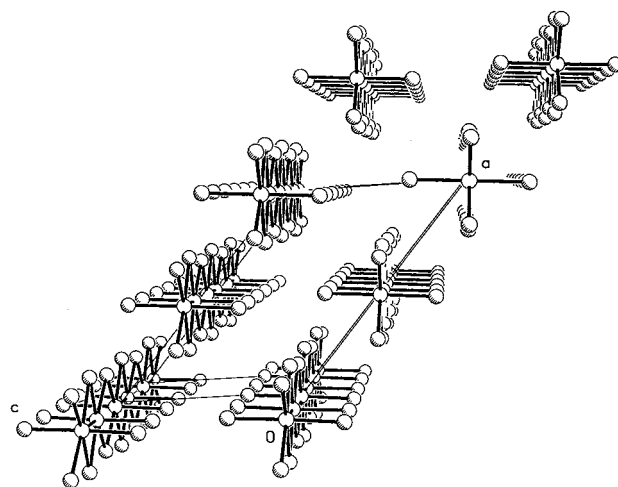**Comparative Reactivities of Various Forms of $(WCl_4)_x$.** We found that crystalline $(WCl_4)_x$ obtained from the solid-state methods is substantially less reactive than the powder formed by solution-phase Sn reduction. In general, the lowest reactivity was observed for crystalline $(WCl_4)_x$ obtained at the highest temperature, though microcrystalline $(WCl_4)_x$ synthesized by reduction with red phosphorus at 300 °C or with Hg at 350 °C demonstrated similar reactivity.

To characterize the $(WCl_4)_x$ powder obtained in this work by solution-phase reduction of WCl_6 with Sn, we performed syntheses similar to those described in the literature with conventionally prepared $(WCl_4)_x$. $(WCl_4)_x$ powder reacted readily with methanol, acetonitrile, and tetrahydrofuran (thf) to yield known compounds, which supports its chemical composition. $(WCl_4)_x$ powder also reacted with diethyl ether to yield a presently uncharacterized substance; $WCl_4(OEt_2)_2$ is reported to be either unisolable[26] or stable only at low temperature.[2f,27] Interestingly, thf and diethyl ether are often used as "inert" solvents in reactions of conventionally prepared $(WCl_4)_x$, so the ready reaction of the powdered $(WCl_4)_x$ with these solvents suggests that the tin-derived powder is a far more reactive form of $(WCl_4)_x$.

The reaction of powdered $(WCl_4)_x$ with neat methanol rapidly gave, in 73% isolated yield, the known[23,28] ditungsten compound $W_2Cl_4(OMe)_4(HOMe)_2$, with identical color, solubility properties, and far IR spectrum. The acetonitrile adduct $WCl_4(MeCN)_2$ was obtained in 81% yield, and matched solubility, appearance, and IR characteristics of the reported compound.[15a,22]

The reactivity of $(WCl_4)_x$ may be related to the value of x, with reactivity decreasing for crystalline samples with larger values of x. The powdered $(WCl_4)_x$ may also be a different structural form, since $MoCl_4$ exists in two forms, a linear oligomeric α-form[14,29] with the same structure as that of $(NbCl_4)_x$, and a cyclic hexameric β-form.[30]

Molecular Structure of $(WCl_4)_x$. Figure 2 shows a thermal ellipsoid plot of a portion of the polymeric chain of $(WCl_4)_x$, and Figure 3 shows a unit cell packing diagram. Tables 1−3 list crystallographic data, fractional coordinates and isotropic thermal parameters, and selected bond and nonbonded distances and angles. The structure consists of a polymeric chain of edge-shared, distorted bioctahedra with alternating short (W(1)−W(1A), 2.688(2) Å) and long (W(1)···W(1B), 3.787(3) Å)

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Figure 3. Unit cell plot (spheres of arbitrary dimensions) of $(WCl_4)_x$ down the polymer chain axis (*b* axis).

Table 1. Crystallographic Data for $(WCl_4)_x$

empirical formula = Cl_4W	fw = 325.65
a = 11.782(3) Å	space group = $C2/m$ (No. 12)
b = 6.475(1) Å	T = 210°K
c = 8.062(2) Å	λ = 0.71073 Å (Mo Kα)
β = 131.14(1)°	ρ_{calcd} = 4.670 g cm^{-3}
V = 463.2(2) Å^3	μ = 2.704 cm^{-1}
Z = 4	R1^a (F_o) = 0.0523
wR2 (F_o^2) = 0.1301	

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for $(WCl_4)_x$

	x	y	z	U(eq)^a
W(1)	0	2076(2)	0	11(1)
Cl(1)	227(5)	2382(7)	3025(8)	15(1)
Cl(2)	2179(6)	0	1906(10)	14(1)
Cl(3)	1832(6)	5000	1581(10)	13(1)

^{a} (U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor).

Table 3. Selected Bond Distances (Å), Intramolecular Contacts (Å), and Bond Angles (deg) for $(WCl_4)_x{}^a$

W(1)−W(1A)	2.688(2)	Cl(1)−W(1)−Cl(1C)	170.0(2)
W(1)−Cl(1)	2.280(5)	Cl(1)−W(1)−Cl(2)	92.4(2)
W(1)−Cl(2)	2.359(5)	Cl(1)−W(1)−Cl(2C)	93.3(2)
W(1)−Cl(3)	2.500(4)	Cl(1)−W(1)−Cl(3)	86.2(2)
		Cl(2)−W(1)−Cl(3)	83.97(13)
W(1)···W(1B)	3.787(3)	Cl(2)−W(1)−Cl(2C)	110.6(2)
Cl(1)···Cl(1A)	3.085(10)	Cl(3)−W(1)−Cl(2C)	165.48(13)
Cl(1)···Cl(1B)	3.390(10)	Cl(3)−W(1)−Cl(3C)	81.5(2)
		Cl(1)−W(1)−W(1A)	94.99(12)
		W(1)−Cl(2)−W(1A)	69.4(2)
		W(1)−Cl(3)−W(1B)	98.5(2)

^{a} Symmetry transformations used to generate equivalent atoms: A, x, −y, z; B, x, −y + 1, z; C, −x, y, −z.

tungsten−tungsten distances. The W−Cl distances increase from 2.280(5) Å (W(1)−Cl(1)) for the axial chlorine to 2.359(5) Å for the bridge chlorine (W(1)−Cl(2)) within the bonded bioctahedron portion to a long 2.500(4) Å for the bridge chlorine (W(1)−Cl(3)) between tungsten atoms which are not interacting significantly. The acute W(1)−Cl(2)−W(1A) angle of 69.4(2)° and obtuse Cl(2)−W(1)−Cl(2C) angle of 110.6(2)° are typical of edge-shared bioctahedra in discrete dinuclear compounds of the early transition metals with significant metal−metal bonding interaction.[31] By contrast, the bridge chlorine angle (W(1)−

Cl(3)−W(1B)) for the long tungsten−tungsten separation (W(1)···W(1B)) is an obtuse 98.5(2)°. The axial chlorine atoms (Cl(1), Cl(1A)) on the bioctahedron with the short W(1)−W(1A) distance are bent away from each other (Cl(1)−W(1)−W(1A), 94.99(12) Å), and these chlorine atoms are appreciably closer (3.085(10) Å) than twice the Cl van der Waals radius, 1.70−1.90 Å.[32]

The molecular structures of related molecules can provide insight into the structure of (WCl$_4$)$_x$. The higher-valent halide (WCl$_5$)$_2$ (i.e., W$_2$Cl$_8$(μ-Cl)$_2$) has a discrete, more ideal biocta-hedral structure as a solid with a long, nonbonded W···W separation of 3.814(2) Å, a W−Cl(axial) distance of 2.254(4) Å, a W−Cl(terminal, equatorial) distance of 2.243(3) Å, a W−Cl(bridge) distance of 2.519(3) Å, and a (μ-Cl)−W−(μ-Cl) angle of 81.5(1)°.[33] The tungsten atoms are displaced from each other, consistent with the lack of a W−W bond, and the axial chlorines in each "hemisphere" of the bioctahedron are thus bent toward each other. The W−Cl(axial) distance for (WCl$_5$)$_2$ is marginally smaller than that for (WCl$_4$)$_x$ as would be expected for the increase in formal valence.

Crystalline (WCl$_4$)$_x$ is remarkably isostructural with (NbCl$_4$)$_x$, as was postulated by McCarley and Brown.[12] In the (NbCl$_4$)$_x$ structure, the edge-sharing bioctahedra have significant distor-tions from ideal bioctahedral geometry, and there are alternating short (3.029(2) Å) and long (3.794(2) Å) Nb···Nb separations.[18] There is a small but significant bending of the axial chlorine atoms away from the bonded niobium atoms (possibly because of van der Waals repulsions).

Taken together with comparative structural data for (WCl$_5$)$_2$ and (NbCl$_4$)$_x$, the (1) bending away of the axial chlorine atoms bonded to W(1) and W(1A), (2) short contact between the axial chlorine atoms, (3) short W(1)−W(1A) distance in the double-bond range[34] for d^2−d^2 W(IV)−W(IV), particularly with chloride bridges, and (4) acute angle at the chlorine atoms Cl(2) and Cl(2C) which bridge W(1) and W(1A) are all consistent with a W=W double bond description for the W(1)−W(1A) interaction.

Conclusion

The most convenient, highest yield methods for preparation of polymeric WCl$_4$ were found to be solid-state reduction of WCl$_6$ with antimony and reduction of WCl$_6$ with tin in dichloroethane. Mercury reduction of WCl$_6$ is also a useful method for preparation, despite toxicity concerns, in that the yield is high and unreacted mercury and HgCl$_2$ can be removed easily. Reduction with bismuth gives a lower yield of product with bismuth contamination, and requires substantially greater time to sublime BiCl$_3$. The solution-phase reduction with tin affords highly reactive (WCl$_4$)$_x$ powder, which can be used to make the known compounds WCl$_4$(MeCN)$_2$ and W$_2$Cl$_4$(OMe)$_4$-(HOMe)$_2$. Crystalline (WCl$_4$)$_x$, as obtained from the reduction of WCl$_6$ with Hg, possesses a polymeric chain structure of opposite edge-linked octahedra with alternating short (W=W) and long W···W distances, an acute W−Cl−W angle for the chlorine atoms bridging the short W=W distance, and ap-preciable repulsive interaction between adjacent axial chlorines on each side of the short W=W bond.

Supporting Information Available: Alternate thermal ellipsoid plots of molecular structure, tables listing detailed crystallographic data, anisotropic displacement parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

IC9801286

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