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Articles

Facile Reduction of Tungsten Halides with Nonconventional, Mild Reductants. 2. Four Convenient, High-Yield Solid-State Syntheses of the Hexatungsten Dodecachloride Cluster W_6Cl_{12} and Cluster Acid $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$, Including New Cation-Assisted Ternary Routes

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Tungsten hexachloride was reduced by Hg or Bi at moderately low temperatures (~350 °C) to afford good yields (Hg, 73%; Bi, 85%) of W_6Cl_{12} after conversion of the reduction product to the chloro acid $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$, recrystallization, and thermolysis in vacuo. Antimony was a less effective reductant because of the lower yield of chloro acid (31%) and the substantial quantities of insoluble byproducts found after HCl workup. The yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ from WCl_6 reduction by Sb improved dramatically to 79% with added KCl, while LiCl reduced the yield to only traces. In Bi reduction of WCl_6, the yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ decreased from 86 to 49% upon addition of NaCl, whereas added KCl had no effect on the yield. The Hg-, Bi-, Sb/KCl-, and Bi/KCl-based routes offer substantial experimental advantages over published methods for preparation of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ and W_6Cl_{12}.

Introduction

Tungsten dichloride, W_6Cl_{12}, one of two structural prototypes for mid-valent, early transition metal clusters with π-donor ligands,[1] is an important synthon for tungsten analogues of Chevrel phases,[2] tungsten thiochlorides,[3] organotungsten compounds,[4] alkene polymerization/metathesis catalysts,[5] and the discrete cluster $W_6(\mu_3\text{-}Cl)_8Cl_6^{2-}$ with interesting photophysical, photochemical, spectroscopic, and electrochemical properties.[6] W_6Cl_{12} has also been used in epitaxial growth of W on molybdenum.[7]

Tungsten dichloride has been prepared by reduction of WCl_6 with Na/Hg,[8] Al,[6f,9] Al in molten $NaAlCl_4$,[10] Mg,[9b] Zn,[9b] Pb,[9b] W,[2c,11] and WO_2 (reaction time, yield, and quality not described).[12] Tungsten tetrachloride can also serve as a precursor to W_6Cl_{12} by either thermal disproportionation[13] or reduction with Fe.[2b] Methods for the preparation of W_6Cl_{12} suffer from disadvantages, as noted elsewhere,[11b,10] which include slow reactions, high temperatures necessitating quartz ampules, low yields, contamination by reductant or intermediate reduction products, and violent explosions during the opening of sealed tubes.[6f] Many procedures require (1) small scales because of the reactants' physical nature, (2) careful control of ampule position over an extended reaction time, (3) careful control of thermal gradients, (4) the less convenient precursor WCl_4, (5) W prepurification in H_2 at 1000°, or (5) rocking furnaces for molten salt-based routes. Reported yields range from 35 to 60%. In most procedures, W_6Cl_{12} is purified by crystallization from con-

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centrated $HCl_{(aq)}$ to form the chloro acid salt $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ and thermolysis to brown to pale yellow W_6Cl_{12}.

We recently found several convenient, high-yield routes to crystalline and to highly reactive powdered $(WCl_4)_x$ based on reduction of WCl_6 with nonconventional reductants[14] and decided to test these new methodologies in the direct reduction of WCl_6 to W_6Cl_{12}. Herein, we report our observations on reduction of WCl_6 with Hg, Sb, Bi, or combinations of Sb or Bi with an alkali metal chloride. We also detail our procedures for four new, convenient, high-yield routes to $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ and W_6Cl_{12}.

Experimental Section

General Methods. Precursors and compounds were manipulated in a glovebox under a N_2/He atmosphere. A Thermolyne 21100 single-zone tube furnace (≤1200 °C) and positionable thermocouple were used in syntheses, with the furnace in a horizontal orientation unless otherwise noted. All syntheses employed dual-chamber borosilicate glass ampules of 25 mm o.d., 60−70 mL total chamber volume, and 14/20 outer joint at one end, with constrictions between the end reaction chamber and receiver chamber and between the receiver chamber and 14/20 joint. The ratio of lengths of furnace to sealed ampule was kept at ≥1.6 in order to ensure temperature uniformity over the reaction zone. Ampules were oven dried at 130 °C overnight. Reactants were introduced into the ampule's end reaction chamber with a long tapered funnel, the ground-jointed end closed with a gas inlet adapter, the ampule flame sealed under vacuum from a Schlenk line, and the reactants mixed thoroughly.

WCl_6 (Cerac), Bi (325 mesh, Cerac), and Sb (100 mesh, Aldrich) were used as received. NaCl and KCl (Fisher) were dried at 180 °C overnight, and LiCl (Fisher) was dried in vacuo at 520 °C. Triply-distilled Hg was purified by filtration through a pinched paper filter into a cylinder containing ∼1 M HNO_3. The tungsten content was determined gravimetrically as WO_3 by HNO_3 oxidation followed by ignition.[13] Powder X-ray diffraction was performed on a Siemens D5000 diffractometer, with samples protected from hydrolysis by a thin film of poly(vinyl chloride).

The purification of W_6Cl_{12}, via dissolution in and crystallization from concentrated aqueous HCl (to form the chloro acid $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$) followed by decomposition in vacuo to W_6Cl_{12}, has been described.[2b,c,9c,10,11,15] These methods involve single recrystallization of the chloro acid, with the crystallinity and color (brown to pale yellow) of W_6Cl_{12} dependent on the rate and temperature[2a,4,15] of heating in vacuo. Here, we provide details for the quick purification of W_6Cl_{12} or its liberation from ternary mixtures. The key feature is triple recrystallization from HCl (starting with 12 M HCl increases the recovery of chloro acid, as the temperature gradient is high for solubility in 6−12 M HCl) to give canary yellow $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$, which consistently gave canary yellow W_6Cl_{12} upon thermolysis.

Isolation and Purification of W_6Cl_{12} via Recrystallization and Thermolysis of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$. Concentrated aqueous HCl (12 M, 25 mL per 3.5−4.0 g of impure chloro acid) was added to the impure product in a flask (attached to a water bubbler for trapping HCl vapor) and the mixture heated with intensive agitation to dissolve the material. After being cooled slowly, the solution was filtered with a medium-porosity fritted glass funnel and the greenish-yellow crystals mechanically separated easily from any fine insolubles (e.g., excess reductant) which adhered tightly to the fritted surface. The crystals were washed with 12 M HCl, redissolved in hot HCl, and recovered by filtration after slow cooling. After a third recrystallization, canary yellow crystalline $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained. Three recrystallizations were usually sufficient to obtain canary yellow product (for six samples analyzed, tungsten content ranged from 62.35 to 62.63%, with theory of 62.55% for $x = 7$). Approximately 1.7% loss of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was noted after each additional recrystallization.

A triply-recrystallized chloro acid sample (W, 62.41% found) was thermolyzed in vacuo to yellow W_6Cl_{12} by slowly (3−3.5 h) raising the temperature to 325 °C and heating for 1 h. The yield of W_6Cl_{12} from pure $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$ was virtually quantitative, as we obtained a 97.9% yield of canary yellow W_6Cl_{12} (Anal. Calcd for Cl_2W: W, 72.17. Found: W, 72.0).

Preparation of W_6Cl_{12} via Reduction of WCl_6 with Mercury. *Caution! This reaction should be performed in a hood with shielding of the furnace in order to prevent release of toxic Hg and mercury chlorides should the ampule shatter. Mercury has appreciable vapor pressure at elevated temperatures.* An ampule with WCl_6 (10.00 g, 25.2 mmol) and Hg (20.23 g, 100.9 mmol) in the reaction chamber was sealed under vacuum. A reaction was readily apparent after mixing, as the purple-gray WCl_6 changed to brown-gray, and Hg was consumed partially. No appreciable temperature rise was noted.

The ampule was placed at the center of the furnace and the temperature raised slowly (2 h) to 205 °C. After 2 days[16] the ampule was cooled and shaken. The ampule was returned to the furnace and the temperature raised slowly (2 h) to 350−360 °C. The estimated Hg_2Cl_2 pressure was ∼400 Torr.[17,18] After 1 day, the ampule was cooled, the contents mixed, and the ampule heated for 2 days at 350−360 °C. The ampule was repositioned with the receiver chamber in a cooler furnace zone and heated at 350−360 °C for 3 days[16] in order to trap Hg_2Cl_2 and trace amounts of Hg and/or $HgCl_2$. The ampule was cooled and opened in the glovebox. The gray nonvolatiles weighed 6.09 g (∼95% yield of impure W_6Cl_{12} based on WCl_6). The product was primarily W_6Cl_{12} as shown by X-ray diffraction. Triple recrystallization from hot aqueous HCl gave $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ (5.56 g, 75.0% yield for $x = 7$, based on WCl_6), which yielded yellow W_6Cl_{12} (4.67 g, 73% yield based on WCl_6) after thermolysis in vacuo.

Preparation of W_6Cl_{12} via Reduction of WCl_6 with Antimony in the Presence of KCl. WCl_6 (10.00 g, 25.2 mmol), Sb (4.094 g, 33.6 mmol), and KCl (0.627 g, 8.4 mmol) were heated in a sealed 60 mL ampule from room temperature

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to 240 °C over 2 h. The ampule was repositioned with its receiver chamber partially outside of the furnace. After 1 h at 235−245 °C, the ampule was removed from the furnace and tilted to allow the liquid $SbCl_3$ to solidify in the end of the receiver chamber. The dark nonvolatiles were pulverized by shaking and positioned at the end of the reaction chamber. The ampule was returned to the furnace, which was reoriented in a tilted position (∼45°). After heating at 350 °C for 24 h, the temperature was lowered to 200 °C, the furnace returned to the horizontal position, and the ampule relocated with its receiver chamber partially outside of the furnace. After 1 h at 235−245 °C, the ampule was removed from the furnace and tilted to allow the liquid $SbCl_3$ to solidify in the end of the receiver chamber. The yellow-brown nonvolatiles were pulverized by shaking and positioned in the end of the reaction chamber. The ampule was positioned in the furnace with the receiver chamber located almost completely outside (to keep $SbCl_3$ solidified). After 24 h at 350 °C, the ampule was cooled and opened in the glovebox. The weight of yellow-brown powder was 7.146 g.

A 2.00 g portion gave greenish-yellow needles when crystallized from 15 mL of boiling HCl. After two recrystallizations, 1.645 g of canary yellow $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained (79.4% yield based on WCl_6). Anal. Calcd for $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$: W, 62.55. Found: W, 62.63.

Preparation of W_6Cl_{12} via Reduction of WCl_6 with Bismuth. An ampule was sealed with WCl_6 (10.00 g, 25.2 mmol) and Bi (7.027 g, 33.6 mmol) in the reaction chamber. The mixture was heated at the furnace center for 1 day at 230 °C. After cooling, the solids were homogenized by shaking and then heated for 2 days at 335 °C. The receiver chamber was withdrawn partially from the furnace and $BiCl_3$ removed by sublimation at 315−335 °C for 3 days. After cooling, the ampule was opened in the glovebox. The red-brown, crystalline nonvolatiles weighed 7.670 g (theory for W_6Cl_{12}, 6.424 g) which, according to X-ray diffraction, were an unknown phase. The $BiCl_3$ weighed 9.292 g (88% based on Bi), consistent with residual Bi content in the nonvolatiles.

A portion of the involatile solid (5.28 g) was mixed with concentrated HCl (15 mL), resulting in a slight exotherm and a yellow-brown solid. The solid was filtered and recrystallized five times from concentrated HCl to give 4.24 g of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ (83.0% yield, for $x = 7$, based on WCl_6). Thermolysis yielded 3.56 g of yellow W_6Cl_{12} (81% yield based on WCl_6).

In a substantially shorter procedure, WCl_6 (10.00 g, 25.2 mmol) and Bi (7.027 g, 33.6 mmol) were sealed in the end chamber of a ∼60 mL ampule. The ampule was placed in the center of the furnace and the temperature raised slowly to 230 °C during 2 h and then to 355 °C during 2 h. The ampule was then repositioned with the receiver chamber in a cooler furnace zone. Heating was continued at 350 °C for 24 h. After cooling, the ampule was opened in the glovebox. The chocolate-brown crystalline nonvolatiles weighed 7.828 g, consistent with appreciable bismuth content since the theoretical yield of W_6Cl_{12} was 6.424 g.

A portion of the product (3.00 g) was treated with ∼3 mL of concentrated aqueous HCl while agitating for ∼10 min at room temperature, leading to a slight exotherm and a yellow-brown fine precipitate. The precipitate was separated, washed with HCl (in which it was insoluble), and dissolved in 15 mL of boiling concentrated HCl. Upon cooling, greenish-yellow needles formed. After two recrystallizations, 2.458 g of canary yellow $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained (86.3% yield based on WCl_6). Anal. Calcd for $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$: W, 62.55. Found: W, 62.41.

In an attempt at improving the yield of the above procedure, 10% excess Bi was utilized at 1.5 times the scale (15 g of WCl_6; 11.6 g of Bi) in the same size ampule. The ampule was heated to 355 °C in 2 h and at 355 °C for 3 h before being repositioned with the receiver chamber in a cooler zone for distillation of $BiCl_3$ (1.5 days at 355 °C). An 83.4% yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained after HCl workup of the involatiles. Anal. Calcd for $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$: W, 62.55. Found: W, 62.35.

Preparation of W_6Cl_{12} via Reduction of WCl_6 with Bismuth in the Presence of KCl. WCl_6 (15.00 g, 37.8 mmol), Bi (10.541 g, 50.4 mmol), and KCl (0.941 g, 12.6 mmol) in a 60 mL ampule were heated slowly at the furnace center to 230 °C during 2 h, to 355 °C during 2 h, and at 355 °C for 2 days. The ampule was repositioned, with its receiver chamber in a cooler furnace zone, and heated at 400 °C for 24 h and 440 °C for 18 h. After cooling, the ampule was opened in the glovebox. The brown solidified melt weighed 12.776 g, consistent with considerable Bi-containing species (theoretical yield of $K_2W_6(\mu_3\text{-}Cl)_8Cl_6$, 10.576 g).

A 4.547 g portion was treated with ∼3 mL of concentrated aqueous HCl while being agitated for ∼10 min at room temperature, giving a slight exotherm and a fine tan precipitate. The precipitate was separated, washed with HCl, and dissolved in 25 mL of boiling concentrated aqueous HCl. Upon cooling, greenish-yellow crystals formed. After two recrystallizations, 3.440 g of canary yellow $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained (87.0% yield based on WCl_6). Anal. Calcd for $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$: W, 62.55. Found: W, 62.59.

In a separate experiment, a 60 mL ampule with WCl_6 (10.00 g, 25.2 mmol), Bi (7.027 g, 33.6 mmol), and KCl (0.627 g, 8.4 mmol) in the reaction chamber was heated in the center of the tilted (∼45°) furnace; the temperature was raised slowly to 230 °C during 2 h and then to 355 °C during 2 h. Heating was continued at 355−365 °C for 2 days. The furnace was reoriented to horizontal and the ampule repositioned with the receiver chamber in a cooler furnace zone. Heating was continued at 355−365 °C for 2 days. The ampule was repositioned with the receiver chamber partially outside of the furnace. After 3 h at 355−365 °C, the ampule was cooled and opened in the glovebox. The brown solidified melt weighed 10.313 g (theoretical yield of $K_2W_6(\mu_3\text{-}Cl)_8Cl_6$, 7.051 g).

A 3.00 g portion was worked up with HCl as above. After three recrystallizations, 1.875 g of canary yellow $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ was obtained (86.9% yield based on WCl_6). Anal. Calcd for $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_7$: W, 62.55. Found: W, 62.50.

Results and Discussion

Reduction of WCl_6 with Mercury. For the preparation of W_6Cl_{12} from inexpensive WCl_6, mercury offers several advantages as a reductant (eq 1). First, as a mild reductant the chance

$$6WCl_6 + 24Hg \rightarrow W_6Cl_{12} + 12Hg_2Cl_2 \qquad (1)$$

for overreduction of WCl_6 to tungsten is eliminated. The volatility of Hg at reduced pressure ensures diffusion throughout the mixture and easy removal at completion. The byproduct Hg_2Cl_2 is volatile and thus separable from W_6Cl_{12} but exerts low vapor pressures (∼400 Torr at 360 °C). Finally, chlorotungstates such as $HgWCl_6$ did not form under our conditions. We obtained a 73% yield of canary yellow W_6Cl_{12} based on

WCl_6 after thermal decomposition of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$, a yield 13% higher than the best literature route.[2b] The overall procedure takes slightly over 8 days (unoptimized), which is one disadvantage; we obtained a lower yield (47% of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ for $x = 7$) when this reaction time was reduced to 2 days. Despite the 8 day reaction time (we believe that 4 days would be sufficient), the Hg-based reduction approach is not hampered by the need for careful temperature control or ampule positioning and is thus more convenient than most other literature methods.

While ternary routes involving added KCl were shown to improve procedures involving Sb or Bi as reductant (vide infra), addition of KCl to the Hg-based reduction of WCl_6 led to a novel tungsten cluster which is presently undergoing further characterization.

Some applications of W_6Cl_{12} derived from Hg reduction (e.g., photochemistry) may be affected by trace amounts of Hg or Hg-containing species (neither detected qualitatively), though this is minimized via the chloro acid purification route. Therefore, we examined other low-cost and lower toxicity reductants which would form volatile byproducts.

Reduction of WCl_6 with Antimony. We had shown earlier[14] that Sb was the best reductant of the three (Sb, Hg, Bi) for the preparation of $(WCl_4)_x$ in high yield, but Sb proved to be less effective as a reductant for the direct preparation of W_6Cl_{12}. Only a 31% yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ (for $x = 7$) was obtained, under conditions which facilitated $SbCl_3$ reflux. While it is possible that reduction at higher temperature could improve the yield, the marginal increase in yield compared to that obtained with Bi or Hg would not compensate for the increased hazard from the elevated $SbCl_3$ pressure in the ampule. The yield decreased to a very low level when the reduction time was shortened and the ampule positioned so that $SbCl_3$ would sublime to a cooler zone rather than reflux over the reaction mixture. We postulate that $SbCl_3$ reflux (which entails higher internal pressures, 10−11 atm[19] under our experimental conditions) is critical in reductions by Sb of WCl_6 to oxidation states below W(IV).

The yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ from Sb reduction of WCl_6 was decreased to traces when LiCl was added but increased substantially (to 79%) with KCl. Once again, a shorter reaction time for reduction accompanied by KCl, under conditions which precluded $SbCl_3$ reflux, led to a drastic lowering of yield (to 21%) of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$.

Reduction of WCl_6 with Bismuth. Bismuth is the most effective reductant for the preparation of W_6Cl_{12} from WCl_6 (eq 2), as we obtained a high yield of the chloro acid $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$. The effective yield of W_6Cl_{12}

$$6WCl_6 + 8Bi \rightarrow W_6Cl_{12} + 8BiCl_3 \qquad (2)$$

from WCl_6 through the chloro acid is 86%, considerably higher than reported yields of W_6Cl_{12}. The high solubility of Bi in the initially formed $BiCl_3$ ensures diffusion of Bi throughout the reaction mixture. Another advantage of Bi as a reductant is the low $BiCl_3$ vapor pressure, 125 Torr at 350 °C,[18] which improves the safety and allows facile separation by distillation at completion. The red-brown, crystalline, Bi-containing nonvolatiles are an unknown phase not corresponding to W_6Cl_{12} which is currently under study by single-crystal X-ray diffraction. This solid is readily converted by aqueous HCl to a high yield of the chloro acid $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$.

We examined the effect of reduction times, temperatures, and the Bi stoichiometry on product yield. Long reduction times (6 days) are not necessary for high yield, as we obtained an 86% yield of $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ after 28 h total time for reduction (at a slightly higher temperature) and $BiCl_3$ distillation. As in the case with Hg-based reduction, reduction with Bi does not require careful temperature control or ampule positioning. The yield was not improved with 10% excess Bi. While ternary-based routes with NaCl gave drastically lower yield (49% of chloro acid), the use of KCl gave essentially the same yield (87%) as in its absence. The reason(s) for the yield dependence on cation is presently unknown.

Conclusion

Bismuth and mercury are effective reductants for the convenient direct preparation of W_6Cl_{12} from inexpensive WCl_6 in high overall yields (Bi, 85%; Hg, 73%) at comparatively low temperatures (~350 °C). The Bi reduction and $BiCl_3$ distillation, which are complete in 28 h, affords a Bi-containing material which yields the chloro acid salt $(H_3O)_2[W_6(\mu_3\text{-}Cl)_8Cl_6](OH_2)_x$ upon washing with and recrystallization from hydrochloric acid. Antimony is a less effective reductant, giving only a moderate yield (31%) of chloro acid upon workup, but the yield can be improved dramatically (to 79%) by going to a ternary mixture of KCl, WCl_6, and Sb and performing the reduction under conditions of $SbCl_3$ reflux. All reductions can be performed in borosilicate glass ampules and do not require particular care in temperature control and gradients or use of highly purified WCl_6.

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Supporting Information Available: Text describing procedures for alternate, lower yield preparations of W_6Cl_{12} via reduction of WCl_6 with Hg (shorter reaction time), Sb, Sb/LiCl, Sb/KCl (shorter reaction time), and Bi/NaCl (3 pages). Ordering information is given on any current masthead page.

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[19] *Gmelin's Handbuch der Anorganischen Chemie (Gmelin's Handbook of Inorganic Chemistry)*; Verlag Chemie, GmbH: Weinheim/Bergstrasse, Germany, 1950; antimony, Vol. 18, Part B, p 416.