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COMMUNICATION

NEW, IMPROVED SYNTHESES OF THE GROUP 6 OXYHALIDES, $W(O)Cl_4$, $W(O)_2Cl_2$ AND $Mo(O)_2Cl_2$

VERNON C. GIBSON,* TERENCE P. KEE and ALAN SHAW
Department of Chemistry, University Science Laboratories, South Road,
Durham DH1 3LE, U.K.

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Abstract—Hexamethyldisiloxane is a useful reagent for the convenient, high yield preparation of oxyhalide derivatives of molybdenum and tungsten.

Oxo complexes of the group 6 elements play a central role in a variety of industrial and biological oxidation processes.[1] Progress towards understanding the reactivity of the metal–oxo moiety in these systems is largely dependent upon the availability of convenient and generally applicable routes to complexes through which the properties of the oxo ligand can be addressed. However, useful starting materials such as oxyhalides have not generally been available via mild synthetic procedures. For example, $W(O)Cl_4$ is most commonly accessed by prolonged reflux of the hydrated metal oxide with $SOCl_2$,[2,3]† while $Mo(O)_2Cl_2$ and $W(O)_2Cl_2$ are prepared by a pyrolysis of $Mo(O)Cl_3$ resulting in a mixture of $Mo(O)_2Cl_2$ and $Mo(O)Cl_4$,[4] and by heating a 2 : 1 mixture of WO_3 and WCl_6 in a sealed tube,[5] respectively.

As part of a programme of research directed towards the study of metal-bound oxygen atoms, we have searched for a method of introducing oxygen atoms into the metal coordination sphere under controlled, mild conditions. Here, we wish to describe the use of hexamethyldisiloxane, $(Me_3Si)_2O$ for the convenient preparation of oxyhalide compounds of the group 6 metals.

EXPERIMENTAL

All manipulations of air and/or moisture sensitive materials were carried out on a conventional vacuum line using standard Schlenk or cannula techniques, or in a dry-box under an atmosphere of nitrogen. Solvents were dried, distilled and degassed prior to use. Metal and halide analyses were provided by the microanalytical service at Durham. IR spectra (Nujol mulls between KBr plates) were recorded using Perkin–Elmer 577 and 457 spectrophotometers. WCl_6, $Mo(O)Cl_4$ (Alfa) and $(Me_3Si)_2O$ (Aldrich) were used as received.

All oxyhalide products were obtained in analytically pure form.

Synthesis of $W(O)Cl_4$

A dichloromethane solution of $(Me_3Si)_2O$ (2.05 g, 12.6 mmol in 15 cm^3 CH_2Cl_2) was added dropwise to a suspension of WCl_6 (5.0 g, 12.6 mmol) in dichloromethane (20 cm^3) at room temperature over a period of 15 min. An immediate reaction ensued leading to deposition of $W(O)Cl_4$ in the form of red crystals. The mixture was stirred for a further 60 min. The supernatant liquor was then removed by filtration and the solid was collected, washed with petroleum ether (b.p. 40–60°C, 2×20 cm^3) and dried *in vacuo*. Yield 4.28 g, 99%. Found: W, 53.9; Cl, 41.2. Calc. for Cl_4OW: W, 53.8; Cl, 41.5%. IR: ν(W—O—W), 880–900 cm^{-1} (broad, strong). For synthesis purposes, further purification by sublimation is unnecessary.

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* Author to whom correspondence should be addressed.

† $W(O)Cl_4$ may also be prepared by the treatment of WCl_6 with Me_3SiOMe at room temperature in dichloromethane (R. R. Schrock, personal communication).

Synthesis of $W(O)_2Cl_2$

A petroleum ether (b.p. 100–120°C) solution of $(Me_3Si)_2O$ (2.38 g, 14.7 mmol in 15 cm^3 petroleum ether) was added to a suspension of $W(O)Cl_4$ (5.0 g, 14.6 mmol) in high boiling petroleum ether (b.p. 100–120°C, 40 cm^3). The mixture was heated overnight at 100°C to give a yellow solid and a colourless solution. After cooling to room temperature, the supernatant solution was decanted from the solid, which was collected, washed with light petroleum ether (b.p. 40–60°C, 2×20 cm^3) and dried *in vacuo*. Yield 3.99 g, 95%. Found: W, 63.7; Cl, 24.4. Calc. for Cl_2O_2W: W, 64.1; Cl, 24.7% IR: ν(W—O—W), 800–830 cm^{-1} (broad, strong).

Synthesis of $Mo(O)_2Cl_2$

A dichloromethane solution of $(Me_3Si)_2O$ (3.2 g, 19.7 mmol in 15 cm^3 CH_2Cl_2) was added to a suspension of $Mo(O)Cl_4$ (5.0 g, 19.7 mmol) in dichloromethane (20 cm^3). The mixture was stirred at room temperature overnight to give a yellow solid and a colourless solution. The supernatant solution was decanted from the solid, which was collected, washed with light petroleum ether (b.p. 40–60°C, 2×20 cm^3) and dried *in vacuo*. Yield 3.78 g, 97%. Found: Cl, 35.7. Calc. for Cl_2O_2Mo: Cl, 35.7%. IR: ν(Mo—O—Mo), 800–830 cm^{-1} (broad, strong).

CONCLUSION

Treatment of the halides (or oxyhalides) of the group 6 metals with commercially available hexamethyldisiloxane facilitates the introduction of oxygen atoms into the metal coordination sphere in a controlled, mild fashion, with minimal risk of product contamination as the sole by-product, Me_3SiCl, is volatile and hence readily removed. The pertinent features of this transformation are shown in eq. (1).

$$[M]Cl_2 + (Me_3Si)_2O \rightarrow [M]{=}O + 2Me_3SiCl. \quad (1)$$

Thus, the preparations described here offer improved, high yield routes to excellent purity oxyhalide products, which should have general use in the synthesis of new oxo complexes of these metals. The use of $(TMS)_2O$ for the introduction of oxygen atoms into the coordination sphere of other metals and well-defined organotransition metal environments will form subjects of future reports.

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