COMMUNICATION

THE USE OF HEXAMETHYLDISILTHIANE IN THE SYNTHESIS OF TRANSITION METAL THIOHALIDES

VERNON C. GIBSON,* ALAN SHAW and DAVID N. WILLIAMS

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, U.K.

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Abstract—The thiohalide compounds $W(S)Cl_4$, $W(S)_2Cl_2$, $Mo(S)Cl_3$, $Nb(S)Cl_3$, $Ta(S)Cl_3$, $Nb(S)Cl_3(CH_3CN)_2$, $Ta(S)Cl_3(CH_3CN)_2$, $Mo(O)(S)Cl_2$ and $W(O)(S)Cl_2$ may be obtained in high yield by low temperature treatment of the appropriate metal halide with hexamethyldisilthiane.

Transition metal thiohalides have proved accessible by a variety of methods.¹⁻⁶ However, most routes involve high temperature sealed tube/furnace procedures. The only report of a generally applicable room temperature procedure concerns the reaction of transition metal halides with Sb_2S_3 in CS_2 solvent over 1–3 days.⁷

In recent studies, we have shown that hexamethyldisiloxane is a particularly useful reagent for the mild synthesis of oxyhalide materials^{8,9} according to eq. (1).

$$MCl_{x} + (Me_{3}Si)_{2}O \longrightarrow M(O)Cl_{x-2} + 2Me_{3}SiCl.$$
(1)

Therefore, we envisaged that the analogous sulphur reagent, $(Me_3Si)_2S$, would be suitable for the controlled, mild synthesis of related thiohalide compounds [eq. (2)] which are not conveniently accessible by other methods.

$$MCl_{x} + (Me_{3}Si)_{2}S \longrightarrow M(S)Cl_{x-2} + 2Me_{3}SiCl.$$
(2)

Indeed, we have found that reactions of transition metal halides with $(Me_3Si)_2S$ proceed with such exothermicity that cooling is generally required. Thus, dropwise addition of a cooled $(-30^{\circ}C)$ dichloromethane solution of $(Me_3Si)_2S$ to a suspension of the appropriate metal halide in dichloromethane at $-78^{\circ}C$, followed by warming of the mixture to

room temperature with stirring allows the high yield preparation of the known thiohalide compounds $Mo(S)Cl_3$, $W(S)Cl_4$, $W(S)_2Cl_2$, $Nb(S)Cl_3$ and $Ta(S)Cl_3$. This procedure also allows the synthesis of the mixed oxythiohalide derivatives $W(O)(S)Cl_2$ and $Mo(O)(S)Cl_2$. The tungsten compound may be obtained from WCl_6 by sequential treatment with equimolar amounts of $(Me_3Si)_2O$ and $(Me_3Si)_2S$ in either order of addition. $Mo(O)(S)Cl_2$ is obtained from the reaction of $Mo(O)Cl_4$ with $(Me_3Si)_2S$ and, to our knowledge, has not been reported previously.

If the reaction is carried out in a coordinating solvent such as acetonitrile, then solvent adducts such as Nb(S)Cl₃(CH₃CN)₂ and Ta(S)Cl₃ (CH₃CN)₂ may be obtained in excellent yield [eq. (3)].

$$MCl_{5} + (Me_{3}Si)_{2}S \xrightarrow{CH_{3}CN(5)} M(S)Cl_{3}(CH_{3}CN)_{2}$$
$$M = Nb, Ta. \quad (3)$$

Here, we give details of the preparations of base-free $W(S)Cl_4$ and the solvent adduct Nb(S)Cl₃(CH₃CN)₂. Commercially available reagents can be tolerated since the solubility of the products allows their ready purification. The other less soluble thiohalide materials may be prepared by essentially analogous procedures, but it is advisable to use pure reagents e.g. locally prepared (Me₃Si)₂S¹⁰ rather than commercially available material [commonly contaminated with (Me₃Si)₂O] since subsequent separation of oxide contaminants is less easy.

^{*}Author to whom correspondence should be addressed.

EXPERIMENTAL

All reactions and product manipulations were performed on a conventional vacuum line using standard Schlenk techniques, or in a dry-box under an atmosphere of argon. Solvents were dried, distilled and degassed prior to use. Metal, sulphur and halide analyses were provided by the microanalytical service at Durham. IR spectra (Nujol mulls between KBr and/or CsI plates) were recorded using Perkin-Elmer 577 and 457 spectrophotometers. MoCl₅, WCl₆, NbCl₅, TaCl₅ (Aldrich) and Mo(O)Cl₄ (Alfa) were either used as received or purified, where necessary, by sublimation. $W(O)Cl_4$ was prepared by a literature procedure.⁸ (Me₃Si)₂S is commercially available (Fluka) or may be prepared by a literature procedure.10

Synthesis of W(S)Cl₄

A dichloromethane solution of $(Me_3Si)_2S$ (2.25) g, 12.6 mmol in 15 cm³ CH₂Cl₂) was added dropwise with stirring to a suspension of WCl_6 (5.0 g, 12.6 mmol) in dichloromethane (20 cm^3) at -78°C , over a period of 15 min. An immediate reaction ensued leading to a red solution and precipitation of a brown, amorphous solid. The mixture was allowed to warm to room temperature and stirred for a further 30 min. Filtration of the supernatant solution, followed by concentration and cooling to -78°C afforded red moisture sensitive crystals of $W(S)Cl_4$ (2.95 g, 65%). A second extraction of the residue with CH_2Cl_2 (20 cm³) followed by crystallization resulted in a combined yield of 75% of analytically pure W(S)Cl₄. Found: W, 51.5; Cl, 39.5; S, 9.0. Calc. for Cl₄SW: W, 51.4; Cl, 39.6; S, 9.0%. IR : v(W = S) 560 cm⁻¹ (sharp, strong).

Synthesis of [Nb(S)Cl₃(CH₃CN)₂]

An acetonitrile solution of $(Me_3Si)_2S(1.97 \text{ g}, 11.1 \text{ mmol in } 10 \text{ cm}^3 \text{ CH}_3\text{CN})$ was added dropwise

to a suspension of NbCl₅ (3.0 g, 11.1 mmol) in acetonitrile (20 cm³) at -30° C. The mixture was warmed to room temperature with stirring to give a green solution which gradually turned yellow with stirring overnight. The volatile components were then removed under reduced pressure and the residue was dried in vacuo to give a 95% yield of crude Nb(S)Cl₃(CH₃CN)₂. An analytically pure sample was obtained by re-extraction with CH₃CN (30 cm³), followed by filtration, concentration to half volume and cooling to -30° C to afford yellow crystals. Yield 2.26 g (65%). Found: Nb, 29.9; Cl, 32.9; S, 10.1; C, 15.1; H, 2.0; N, 8.1. Calc. for C₄H₆N₂Cl₃NbS: Nb, 29.7; Cl, 33.9; S, 10.2; C, 15.3; H, 1.9; N, 8.9%. IR: $v(C \equiv N)$ 2310(s), 2280(s); v(Nb=S) 532(s) cm⁻¹.

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