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COMMUNICATION

CONVENIENT, HIGH YIELD SYNTHESES OF $[Nb(O)Cl_3]$, $[Nb(O)Cl_3(CH_3CN)_2]$ AND $[Nb(O)Cl_3(THF)_2]$. FORMATION AND DECOMPOSITION OF INTERMEDIATE ALKOXO (AND SILOXO) DERIVATIVES OF GENERAL FORMULA $[NbCl_4(OR)]_2$ (R = Me, Et, $SiMe_3$)

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Abstract—Trimethylsilylaklylethers, Me_3SiOR (R = Me, Et) and hexamethyldisiloxane react with $NbCl_5$ in dichloromethane under ambient conditions to give readily isolable mono-alkoxides, $[NbCl_4(OR)]_2$ (R = Me, **1**; Et, **2**) and the thermally sensitive siloxide $[NbCl_4(OSiMe_3)]_2$ (**3**), respectively. At 80°C in 1,2-dichloroethane, **1–3** undergo efficient conversion to $[Nb(O)Cl_3]$ with elimination of RCl. In acetonitrile solution, the reaction of $NbCl_5$ with $(Me_3Si)_2O$ proceeds smoothly to give $[Nb(O)Cl_3(CH_3CN)_2]$ which is readily converted to $[Nb(O)Cl_3(THF)_2]$ upon dissolution in tetrahydrofuran (THF).

Oxychlorides of general formula $M(O)Cl_3$ are known for all three members of the group 5 triad.[1] While volatile $V(O)Cl_3$ is readily prepared by treatment of V_2O_5 with $SOCl_2$,[2] the heavier congeners have not proved accessible via this method or a similarly mild synthetic procedure. For example, established routes to niobium oxychloride include *inter alia* treatment of the pentahalide with Sb_2O_3 in a stream of gaseous chlorine,[3] the action of molecular oxygen on heated pentahalide,[4] or pyrolysis of the pentachloride diethyl ether adduct.[4]

Recently, we have reported a convenient, mild procedure for the controlled introduction of oxygen atoms into the coordination sphere of the heavier group 6 transition metals.[5] Here, we describe the extension of this methodology to the synthesis of $Nb(O)Cl_3$ via isolable mono-alkoxide intermediates, and the preparation of the solvent-stabilized monomers $[Nb(O)Cl_3(CH_3CN)_2]$ and $[Nb(O)Cl_3(THF)_2]$.

EXPERIMENTAL

Solvents and reagents were dried and distilled prior to use, and all manipulations were carried out on a conventional inert gas/vacuum line, or in a dry box under an atmosphere of nitrogen. $(Me_3Si)_2O$ (Aldrich), Me_3SiOMe (Fluka) and Me_3SiOEt (Fluka) were distilled from P_2O_5 or dried over molecular sieves (4 Å) before use. $NbCl_5$ (Aldrich) was used as received. Elemental analyses were provided by the microanalytical service of this department. ^1H NMR spectra were recorded at 250 MHz on a Bruker AM 250 spectrometer. IR spectra (Nujol mulls between KBr or CsI plates) were recorded using Perkin–Elmer 577 and 457 spectrophotometers. Mass spectra were recorded on a VG 7070E mass spectrometer.

Synthesis of $[NbCl_4(OMe)]_2$ (**1**)

A dichloromethane solution of Me_3SiOMe (1.15 g, 11.1 mmol in 15 cm^3 of CH_2Cl_2) was added dropwise to a suspension of $NbCl_5$ (3 g, 11.1 mmol) in dichloromethane (20 cm^3) at room temperature.

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The mixture was stirred for 2 h during which the $NbCl_5$ suspension reacted to give a colourless solution. Filtration, followed by concentration to half volume and cooling to −30°C afforded colourless crystals of $[NbCl_4(OMe)]_2$ (2.60 g, 88%). Found: Nb, 34.8; Cl, 53.2; C, 4.4; H, 0.99. Calc. for CH_3Cl_4NbO: Nb, 35.0; Cl, 53.4; C, 4.5; H, 1.14%. IR data (Nujol mull, cm^{-1}): 1140(w), 1060(s,br), 910(w), 865(w), 775(w), 735(w), 720(w), 595(m), 570(m), 390(m), 350(m). The CI^+ mass spectrum (isobutane carrier gas) gave molecular ions at *m/z* 532 and 215 corresponding to protonated $[NbCl_4(OMe)]_2$ and $Nb(O)Cl_3$, respectively. ^1H NMR (250 MHz, $CDCl_3$): δ 5.17 [singlet, CH_3].

Synthesis of $[NbCl_4(OEt)]_2$ (**2**)

A similar procedure to that described for $[NbCl_4(OMe)]_2$ may be used for the preparation of $[NbCl_4(OEt)]_2$ (yield 90%). Characterizing data: Found: Nb, 33.1; Cl, 50.2; C, 8.7; H, 1.9. Calc. for $C_2H_5Cl_4NbO$: Nb, 33.2; Cl, 50.7; C, 8.6; H, 1.8%. IR data (Nujol mull, cm^{-1}): 1350(m), 1265(m), 1135(sh), 1090(s), 1035(s,br), 945(s), 900(m,br), 835(m,br), 815(m,br), 580(m), 540(w), 490(w), 390(br). ^1H NMR (250 MHz, $CDCl_3$): δ 5.46 [q, $^3J_{HH} = 7.0$ Hz, CH_2]; δ 1.76 [t, $^3J_{HH} = 7.0$ Hz, CH_3].

Synthesis of $[Nb(O)Cl_3]$ (**4**)

A 1,2-dichloroethane solution of $(Me_3Si)_2O$ (1.8 g, 11.1 mmol in 15 cm^3 of $C_2H_4Cl_2$) was added to a suspension of $NbCl_5$ (3 g, 11.1 mmol) in dichloroethane (20 cm^3) at room temperature. The mixture was swiftly warmed to 80°C with stirring, and maintained at this temperature for 4.5 h. Dissolution of yellow $NbCl_5$ was accompanied by formation of a white granular precipitate. After cooling to room temperature, the supernatant solution was decanted from the white solid, which was collected, washed with light petroleum ether (b.p. 40–60°C, 2 × 20 cm^3) and dried *in vacuo* to yield 2.03 g (75%) of $Nb(O)Cl_3$. Found: Cl, 49.6; Nb, 43.3. Calc. for Cl_3NbO: Cl, 49.4; Nb, 43.2% (small amounts of residual Me_3SiO may lead to variable microanalytical data). IR data (Nujol mull, cm^{-1}): 780(s,br), ν(Nb—O—Nb).

Synthesis of $[Nb(O)Cl_3(CH_3CN)_2]$ (**5**)

An acetonitrile solution of $(Me_3Si)_2O$ (1.8 g, 11.1 mmol in 15 cm^3 of CH_3CN) was added dropwise at room temperature to a suspension of $NbCl_5$ (3 g, 11.1 mmol) in acetonitrile (20 cm^3). The mixture was stirred at room temperature for 2 h to give a colourless solution which was filtered, concentrated to half volume under reduced pressure and cooled to −30°C. The resultant colourless crystalline product was collected and dried *in vacuo* to yield $[Nb(O)Cl_3(CH_3CN)_2]$ (3.1 g, 95%). Found: C, 15.9; H, 2.1; N, 9.4. Calc. for $C_4H_6Cl_3N_2NbO$: C, 16.1; H, 2.0; N, 9.4%. IR data (Nujol mull, cm^{-1}): 960(s,br), ν(Nb═O).

Synthesis of $[Nb(O)Cl_3(THF)_2]$ (**6**)

Tetrahydrofuran (30 cm^3) was added to $[Nb(O)Cl_3(CH_3CN)_2]$ (0.53 g, 1.78 mmol) at −30°C. The mixture was warmed to room temperature with stirring to afford a colourless solution. After 15 min the mixture was filtered, concentrated to *ca* 5 cm^3 and cooled to −10°C. Addition of cold pentane (10 cm^3, −20°C) gave white crystals of $[Nb(O)Cl_3(THF)_2]$ (0.57 g, 90%). Found: C, 26.1; H, 4.4. Calc. for $C_8H_{16}Cl_3NbO_3$: C, 26.7; H, 4.4%. IR data (Nujol mull, cm^{-1}): 1348(m), 1300(w), 1250(m), 1180(m), 1037(w), 1046(m), 1015(s), 995(s), 960(s), 930(m), 920(m), 860(s,br), 833(s,br), 675(m), 578(w), 365(s,br), 326(s), 250(m).

RESULTS AND DISCUSSION

When niobium pentachloride is treated with equimolar amounts of Me_3SiOR (R = Me, Et, $SiMe_3$) in dichloromethane at room temperature, an immediate reaction ensues leading to dissolution of the starting halide. The resulting colourless or pale yellow solutions give rise to white, crystalline, thermally sensitive compounds of general formula $[NbCl_4(OR)]_2$ (R = Me, **1**; Et, **2**; $SiMe_3$, **3**) [eq. (1)], which are readily isolable for R = Me and Et. It has not proved possible to isolate **3** under ambient conditions without partial decomposition, due to its thermal sensitivity. However, the tantalum analogue of **3** is stable at room temperature and has been fully characterized.[6]

$$2NbCl_5 + 2Me_2SiOR \longrightarrow [NbCl_4(OR)]_2 + 2Me_2SiCl \quad (R = Me, \mathbf{1};\ Et, \mathbf{2};\ SiMe_3, \mathbf{3}). \tag{1}$$

Compounds **1** and **2** have been characterized by microanalysis, IR and NMR spectroscopies (see Experimental), and are formulated as dimeric species on the basis of low resolution CI^+ mass spectrometry (the solution instability of compounds **1**–**3** precluding accurate molecular weight determinations) and by analogy with the known edge-shared bi-octahedral geometry of $NbCl_5$.[7]

However, the available data do not allow us to distinguish unequivocally between alkoxo or halide bridges. Although it has been suggested that phenoxy bridges prevail in $[NbCl_4(OPh)]_2$,[8] this does not appear to be the case for **1** and **2**: IR spectra reveal bands assignable to ν(Nb—O) at 595 and 580 cm^{-1}, respectively, which are consistent with terminal alkoxo groups.[9] The chloro ligands are then presumed to occupy bridging sites. X-ray structural analyses are presently in progress to resolve these details.

The thermal instability of compounds **1–3** arises due to their facile decomposition to $Nb(O)Cl_3$ (**4**) with liberation of RCl [eq. (2)].

$$[NbCl_4(OR)]_2 \xrightarrow{80°C, C_2H_4Cl_2} 2Nb(O)Cl_3 + 2RCl$$
$$(R = Me, \mathbf{1}; Et, \mathbf{2}; SiMe_3, \mathbf{3}). \quad (2)$$

Of compounds **1–3**, **3** is the least stable, slowly releasing Me_3SiCl in solution at room temperature to give a white deposit of $Nb(O)Cl_3$. Similar, albeit slower, decomposition occurs in the solid state. The process proceeds swiftly in dichloroethane solution at 80°C affording a good yield of $Nb(O)Cl_3$ with only minor organic contamination due to residual trimethylsiloxy groups (these have not proved troublesome in subsequent transformations). Indeed, the treatment of $NbCl_5$ with $(Me_3Si)_2O$ at an elevated temperature allows the preparation of $[Nb(O)Cl_3]$ directly according to eq. (3). In addition, when $NbCl_5$ is reacted with $(Me_3Si)_2O$ at room temperature in CH_3CN, the previously reported acetonitrile adduct, $[Nb(O)Cl_3(CH_3CN)_2]$[10] (**5**) is obtained in 95% yield [eq. (4)]. This "one-pot", room temperature procedure offers a considerable improvement over the previously available method.[10]

$$NbCl_5 + (Me_3Si)_2O \xrightarrow{80°C, C_2H_4Cl_2} [Nb(O)Cl_3] + 2Me_3SiCl \quad (3)$$

$$NbCl_5 + (Me_3Si)_2O \xrightarrow{CH_3CN(s), RT, 2h} [Nb(O)Cl_3(CH_3CN)_2] + 2Me_3SiCl. \quad (4)$$

However, analogous treatment of $NbCl_5$ with $(Me_3Si)_2O$ in THF does not afford $[Nb(O)Cl_3(THF)_2]$ (**6**) cleanly. Instead, **6** is readily isolated in 90% yield by dissolution of **5** in THF [eq. (5)].

$$[Nb(O)Cl_3(CH_3CN)_2] \xrightarrow{THF(s), 15\,min} [Nb(O)Cl_3(THF)_2] + 2CH_3CN. \quad (5)$$

In summary, the treatment of $NbCl_5$ with silylated ethers offers convenient, high yield syntheses of mono-alkoxide niobium derivatives, and either base-free or solvent-stabilized $[Nb(O)Cl_3]$. We are particularly interested in utilizing the oxyhalide derivatives as precursors to oxo complexes of niobium. In preliminary investigations, a number of tertiary phosphine and alkoxide niobium oxo derivatives have been prepared which will be reported separately.

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