

Half-sandwich Chalcogenido Complexes of Niobium(v)

Ulrich Siemeling and Vernon C. Gibson*

Department of Chemistry, University Science Laboratories, South Road, Durham DH1 3LE, UK

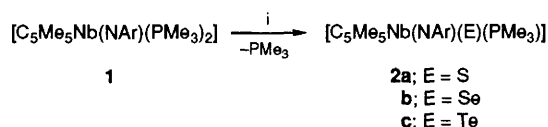
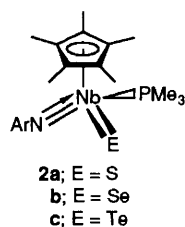
Treatment of $[\text{C}_5\text{Me}_5\text{Nb}(\text{NAr})(\text{PMe}_3)_2]$ **1** (Ar = 2,6- $\text{C}_6\text{H}_3\text{Pr}_2$) with elemental sulfur, selenium or tellurium, respectively, affords the terminal chalcogenido complexes $[\text{C}_5\text{Me}_5\text{Nb}(\text{NAr})(\text{E})(\text{PMe}_3)]$ (**2a**: E = S; **2b**: E = Se; **2c**: E = Te).

Transition metal oxo and sulfido chemistry is an area of major interest owing to the role of these species in industrial catalysis. The corresponding chemistry of selenium and tellurium, however, has remained virtually undeveloped.

Although a vast number of mononuclear terminal oxo and sulfido complexes is known, comparatively few examples of

analogous selenido compounds can be found in the literature,¹ and the first examples of terminal tellurido complexes were published only recently.² This reflects the tendency of the heavier group 16 elements to form bridged structure types and higher nuclearity clusters.

As part of our studies concerning early transition metal



Scheme 1 Reagents and conditions: i, a: sulfur (1.10 equiv.), room temp., 1 d, in toluene; b: selenium (1.05 equiv.), room temp., 2 d, in toluene; c: tellurium (1.05 equiv.), room temp., 2 d, in toluene

compounds that contain terminal multiply bonded main group units (such as 'oxo' or 'imido'), we have also investigated the possibility of preparing terminal sulfido, selenido and tellurido complexes utilising the metal-ligand fragment $[\text{C}_5\text{Me}_5\text{Nb}(\text{NAr})(\text{PMe}_3)]$. The latter may be readily generated *via* PMe_3 loss from the niobium(III) bis-phosphine derivative $[\text{C}_5\text{Me}_5\text{Nb}(\text{NAr})(\text{PMe}_3)_2]$ **1**.³

When a toluene solution of **1** is treated with a slight excess of elemental sulfur, selenium and tellurium, respectively, compounds of empirical formula $[\text{C}_5\text{Me}_5\text{Nb}(\text{NAr})(\text{E})(\text{PMe}_3)]$ (E = S, Se, Te) are obtained, and one equivalent of trimethylphosphine is liberated during the reaction (Scheme 1).

The sulfur compound **2a** forms dark-red microcrystals, the selenium complex **2b** is isolated as forest-green needles, and the tellurium complex **2c** as very dark-red plates; the respective yields after one recrystallisation from pentane are 58, 60 and 41%. Compounds **2a-c** are very soluble in benzene and toluene and are also quite soluble in pentane. To date, it has not proved possible to obtain single crystals suitable for a structure determination.

IR and NMR spectroscopic data for **2a-c** show that they are strictly isostructural and are in accord with a mononuclear structure containing a terminal chalcogenido unit.† Two resonances are observed for the isopropyl methyl groups of the Ar unit in both the ¹H and ¹³C NMR spectra of these compounds, which is to be expected for a mononuclear complex containing a four-coordinate chiral metal centre. Furthermore, the presence of a PMe_3 ligand that is directly coordinated to the niobium centre can be inferred from its unusually broad solution-state ³¹P NMR resonance ($\nu_1 =$

800 Hz), which arises owing to quadrupolar coupling to the ⁹³Nb nucleus. The coupling can be resolved in the solid state: a 121 MHz CPMAS ³¹P NMR spectrum of the selenium complex **2b** shows a decet with ¹J(⁹³Nb³¹P) being approximately 900 Hz. IR spectroscopic data do not show unambiguously the presence of terminal chalcogenido groups: the Nb-S stretch in **2a** can be assigned to a band at 465 cm⁻¹, which is on the borderline between a bridging and a terminal sulfido unit;‡ the same holds true for the selenium compound **2b**, whose Nb-Se stretch is observed at 335 cm⁻¹; no Nb-Te stretch can be observed for **2c** down to 250 cm⁻¹, which is consistent with simple isotopic substitution calculations.

Since no interpretable mass spectra could be obtained for **2a-c**, a molecular weight determination (cryoscopy in benzene) was performed for **2b**. The result of the M_w determination establishes that **2b** (and hence also **2a** and **c**) is monomeric in solution (M_w found: 558; M_w calc.: 554.6).

We, therefore, conclude that compounds **2a-c** are terminal chalcogenido complexes of niobium(V):

Compounds **2a-c** represent the first complete series of metal complexes incorporating the heavier group 16 elements as terminal chalcogenido ligands.

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† All new compounds gave satisfactory microanalytical and spectroscopic data. Selected NMR spectroscopic data for **2a-c** in C_6D_6 solution (¹H NMR: 400.0 MHz, external SiMe_4 ; ¹³C NMR: 100.6 MHz, external SiMe_4).

2a: ¹H NMR δ 1.00 (d, *J* 8.8 Hz, 9 H, PMe_3), 1.26 (d, *J* 6.8 Hz, 6 H, CHMe_2), 1.52 (d, *J* 5.8 Hz, 6 H, CHMe_2), 1.97 (s, 15 H, C_5Me_5), 4.05 (br s, 2 H, CHMe_2), 6.98 (t, *J* 7.6 Hz, 1 H, *p*-ArH), 7.19 (d, *J* 7.6 Hz, 2 H, *m*-ArH); ¹³C NMR δ 12.1 (C_5Me_5), 18.5 (d, *J* 27.5 Hz, PMe_3), 24.4 and 25.8 (CHMe_2), 27.5 (CHMe_2), 117.0 (C_5Me_5), 121.9 and 122.7 (*o*- and *m*-ArC), 141.7 (*ipso*-ArC) 152.3 (*p*-ArC).

2b: ¹H NMR δ 1.01 (d, *J* 8.8 Hz, 9 H, PMe_3), 1.23 (d, *J* 6.8 Hz, 6 H, CHMe_2), 1.51 (d, *J* 5.8 Hz, 6 H, CHMe_2), 1.94 (s, 15 H, C_5Me_5), 4.03 (br s, 2 H, CHMe_2), 6.97 (t, *J* 7.6 Hz, 1 H, *p*-ArH), 7.19 (d, *J* 7.6 Hz, 2 H, *m*-ArH); ¹³C NMR δ 12.4 (C_5Me_5), 19.1 (d, *J* 27.8 Hz, PMe_3), 24.4 and 26.1 (CHMe_2), 27.4 (CHMe_2), 117.1 (C_5Me_5), 122.0 and 122.9 (*o*- and *m*-ArC), 141.9 (*ipso*-ArC) 151.8 (*p*-ArC).

2c: ¹H NMR δ 1.00 (d, *J* 8.8 Hz, 9 H, PMe_3), 1.20 (d, *J* 6.8 Hz, 6 H, CHMe_2), 1.48 (d, *J* 5.8 Hz, 6 H, CHMe_2), 1.89 (s, 15 H, C_5Me_5), 4.03 (br s, 2 H, CHMe_2), 6.93 (t, *J* 7.6 Hz, 1 H, *p*-ArH), 7.23 (d, *J* 7.6 Hz, 2 H, *m*-ArH); ¹³C NMR δ 13.0 (C_5Me_5), 19.4 (d, *J* 28.0 Hz, PMe_3), 24.1 and 26.3 (CHMe_2), 26.8 (CHMe_2), 117.2 (C_5Me_5), 122.1 and 122.6 (*o*- and *m*-ArC), 142.5 (*ipso*-ArC) 150.3 (*p*-ArC).

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‡ Compare for example the values for the terminal sulfido compound $\text{SNbCl}_3(\text{PMe}_3)_3$ ($\nu_{\text{Nbs}} = 455 \text{ cm}^{-1}$; ref. 4) and the bridging sulfido compound $[\text{cis}-(\text{C}_5\text{H}_5)_2\text{Mo}_2\text{O}_3\text{S}]$ ($\nu_{\text{MoS}} = 450 \text{ cm}^{-1}$; ref. 5).