PREPARATION AND REACTIONS OF NIOBIUM(V) SULPHIDE COMPLEXES

J. L. SEELA, J. C. HUFFMAN and G. CHRISTOU*

Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

Abstract—An improved synthetic procedure to \((\text{PPh}_4)[\text{NbScI}_4]\) (1) is described involving the reaction of NbCl_5 with two equivalents of NaSBu'. Complex 1 reacts with NaSPh to yield \((\text{PPh}_4)[\text{NbS(SPh)}_4]\) (2), the crystal structure of which confirms a square-pyramidal geometry at the metal with a multiply-bonded sulphur at the apex (Nb—S = 2.171(2) Å).

The sulphur-based chemistry of the group 6 metals, molybdenum and tungsten, has been the subject of intense investigation over many years. In contrast, the corresponding chemistry of the group 5 metals is still only poorly explored. We have a program directed towards the development of group 5 metal—sulphur chemistry and most of our efforts to date have been concentrated in vanadium. However, we herein describe some recent results with niobium involving the +5 oxidation level.

The anion \([\text{NbScI}_4]^-\) was considered an attractive starting point for the synthesis of \(\text{M—S—SR}\) complexes by metathesis. However, available procedures to this material are less than optimal with respect to yield, purity or convenience of preparation, and we have therefore sought a facile, one-step, high-yield procedure from readily-available starting materials. Given the tendency of Bu'S- to act as a sulphide (S_2-) source via C-S bond cleavage [eq. (1)]:

\[
\text{Bu'S}^- \rightarrow \text{Bu}^+ + \text{S}^2^- \quad (1)
\]

the reaction between NbCl_5 and equimolar amounts of NaSBu' in CH_2Cl_2 was investigated. Addition of PPh_4Cl to the reaction mixture led to isolation of approximately equal amounts of green \((\text{PPh}_4)[\text{NbScI}_4]\) (1) and yellow \((\text{PPh}_4)[\text{NbCl}_6]\). The formation of two products was rationalized according to eq. (2):

\[
2\text{NbCl}_5 + 2\text{Bu'S}^- \rightarrow \text{NbScI}_4 + \text{NbCl}_6 + \text{Bu}_2\text{S}^- \quad (2)
\]

thus, it was suspected that incomplete conversion of NbCl_5 to NbScI_4 was due to reaction of generated Bu'+ with remaining Bu'S- [eq. (3)]:

\[
\text{Bu}^+ + \text{Bu'S}^- \rightarrow \text{Bu'SBu}'. \quad (3)
\]

If this were really the case, then additional Bu'S- should result in clean formation of NbScI_4. Treatment of NbCl_5 with 2 equivalents of NaSBu' does indeed produce only NbScI_4 [eq. (4)], and isolated yields of pure crystalline \((\text{PPh}_4)[\text{NbScI}_4]\) are routinely ~ 60%. The NEt_4 salt can be prepared in a similar fashion.

\[
\text{NbCl}_5 + 2\text{Bu'S}^- \rightarrow \text{NbScI}_4 + \text{Bu}_2\text{S}^- + \text{Cl}^-. \quad (4)
\]

Treatment of complex 1 in MeCN with 4 equivalents of NaSPh leads to a rapid colour change from light green to intense red. Removal of solvent and recrystallization from THF–hexanes yields essentially black crystals of \((\text{PPh}_4)[\text{NbS(SPh)}_4]\) THF (2) [eq. (5)]:

\[
\text{NbScI}_4 + 4\text{NaSPh} \rightarrow \text{NbS(SPh)}_4 + 4\text{NaCl}. \quad (5)
\]

The structure of the anion is shown in Fig. 1; the niobium possesses square-pyramidal geometry with a multiply-bonded sulphur atom S(2) at the apex and four terminally-coordinated sulphur atoms from the PhS^- groups in the basal plane. The
important bond lengths and angles are collected in Table 1. It can readily be seen that the NbS₅ core possesses almost perfect C₄ᵥ symmetry, with the basal Nb—S bonds and S(2)—Nb(1)—S(3,10,17,24) angles lying in the very narrow ranges of 2.440–2.443 Å and 108.2–110.9°, respectively. Of interest is the apical Nb=S distance of 2.171(2) Å, which is at the longer end of the observed Nb=S values; inspection of Table 2 shows a range of 2.085–2.196 Å. We have noted elsewhere in our investigations of V=S chemistry that basal RS⁻ ligands result in noticeably longer apical V=O²⁻ and V=S²⁻ distances;⁶ we have rationalized this as due to the excellent electron-releasing properties of thiolate ligands. Note that the anionic nature of the PhS⁻ ligands cannot be the sole explanation, because NbSCl₅ has the shortest distance yet observed. Note also that the distance observed for complex 2 is even longer than those observed for some complexes possessing a sixth ligands trans to the sulphide.

The reactivity characteristics of complex 2 are under investigation. With excess PhCOCl, clean conversion back to complex 1 is observed [eq. (6)]:

\[ \text{NbS(SPh}_5 \rangle + 4\text{PhCOCl} \rightarrow \text{NbSCI}_5 + 4\text{PhCOSPh}. \]
The products from the reaction of 2 under a variety of other conditions (e.g. reduction, heating, treatment with MeI or I₂, etc.) are currently being investigated.

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REFERENCES