

## PREPARATION AND REACTIONS OF NIOBIUM(V) SULPHIDE COMPLEXES

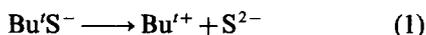
J. L. SEELA, J. C. HUFFMAN and G. CHRISTOU\*

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

**Abstract**—An improved synthetic procedure to  $(\text{PPh}_4)[\text{NbSCl}_4]$  (1) is described involving the reaction of  $\text{NbCl}_5$  with two equivalents of  $\text{NaSBu}'$ . Complex 1 reacts with  $\text{NaSPh}$  to yield  $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4]$  (2), the crystal structure of which confirms a square-pyramidal geometry at the metal with a multiply-bonded sulphur at the apex ( $\text{Nb—S} = 2.171(2) \text{ \AA}$ ).

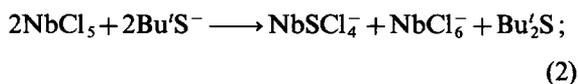
The sulphur-based chemistry of the group 6 metals, molybdenum and tungsten, has been the subject of intense investigation over many years. In contrast, the corresponding chemistry of the group 5 metals is still only poorly explored. We have a program directed towards the development of group 5 metal-sulphur 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  $[\text{NbSCl}_4]^-$  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,<sup>1</sup> and we have therefore sought a facile, one-step, high-yield procedure from readily-available starting materials. Given the tendency of  $\text{Bu}'\text{S}^-$  to act as a sulphide ( $\text{S}^{2-}$ ) source via  $\text{C—S}$  bond cleavage [eq. (1)]:



the reaction between  $\text{NbCl}_5$  and equimolar amounts of  $\text{NaSBu}'$  in  $\text{CH}_2\text{Cl}_2$  was investigated.

Addition of  $\text{PPh}_4\text{Cl}$  to the reaction mixture led to isolation of approximately equal amounts of green  $(\text{PPh}_4)[\text{NbSCl}_4]$  (1) and yellow  $(\text{PPh}_4)[\text{NbCl}_6]$ . The formation of two products was rationalized according to eq. (2):



thus, it was suspected that incomplete conversion of  $\text{NbCl}_5$  to  $\text{NbSCl}_4^-$  was due to reaction of generated  $\text{Bu}'^+$  with remaining  $\text{Bu}'\text{S}^-$  [eq. (3)]:



If this were really the case, then additional  $\text{Bu}'\text{S}^-$  should result in clean formation of  $\text{NbSCl}_4^-$ . Treatment of  $\text{NbCl}_5$  with 2 equivalents of  $\text{NaSBu}'$  does indeed produce only  $\text{NbSCl}_4^-$  [eq. (4)], and isolated yields of pure crystalline  $(\text{PPh}_4)[\text{NbSCl}_4]$  are routinely ~ 60%. The  $\text{NEt}_4^+$  salt can be prepared in a similar fashion.



Treatment of complex 1 in MeCN with 4 equivalents of  $\text{NaSPh}$  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  $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4] \cdot \text{THF}$  (2) [eq. (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  $\text{PhS}^-$  groups in the basal plane. The

\* Author to whom correspondence should be addressed.

† Crystal data for  $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4] \cdot \text{THF}$  at  $-155^\circ\text{C}$ : triclinic,  $P\bar{1}$ ,  $a = 12.442(3)$ ,  $b = 12.154(3)$ ,  $c = 15.887(4) \text{ \AA}$ ,  $\alpha = 91.73(1)$ ,  $\beta = 92.13(1)$ ,  $\gamma = 102.67(1)^\circ$ ,  $V = 2340.49 \text{ \AA}^3$ ,  $Z = 2$ ,  $d_{\text{calc}} = 1.381 \text{ g cm}^{-3}$ ,  $\mu = 5.297 \text{ cm}^{-1}$ ,  $\lambda = 0.71069 \text{ \AA}$ , 6142 unique reflections ( $6 \leq 2\theta \leq 45^\circ$ ) collected at  $6.0^\circ \text{ min}^{-1}$ . The structure was solved by direct methods (MULTAN) and Fourier techniques, and refined by full-matrix least-squares to  $R = 5.93$  and  $R_w = 5.81\%$  for 4916 reflections with  $F > 2.33\sigma(F)$ .

Table 1. Selected structural parameters for complex 2

| (a) Bonds        |          |                   |          |
|------------------|----------|-------------------|----------|
| Nb(1)—S(2)       | 2.171(2) | Nb(1)—S(17)       | 2.440(2) |
| Nb(1)—S(3)       | 2.443(2) | Nb(1)—S(24)       | 2.441(2) |
| Nb(1)—S(10)      | 2.441(2) |                   |          |
| (b) Angles       |          |                   |          |
| S(2)—Nb(1)—S(3)  | 108.2(1) | S(10)—Nb(1)—S(17) | 82.0(1)  |
| S(2)—Nb(1)—S(10) | 110.9(1) | S(10)—Nb(1)—S(24) | 138.4(1) |
| S(2)—Nb(1)—S(17) | 109.5(1) | S(17)—Nb(1)—S(24) | 84.4(1)  |
| S(2)—Nb(1)—S(24) | 110.7(1) | Nb(1)—S(3)—C(4)   | 112.9(2) |
| S(3)—Nb(1)—S(10) | 83.7(1)  | Nb(1)—S(10)—C(11) | 113.6(2) |
| S(3)—Nb(1)—S(17) | 142.3(1) | Nb(1)—S(17)—C(18) | 113.8(3) |
| S(3)—Nb(1)—S(24) | 83.5(1)  | Nb(1)—S(24)—C(25) | 113.8(2) |

Table 2. Comparison of Nb=S distances and stretching frequencies ( $\nu$ )

| Complex   | Nb=S (Å)                        | $\nu$ (cm <sup>-1</sup> ) | Reference |
|---|---------------------------------|---------------------------|-----------|
| NbS(SPh) <sub>4</sub> <sup>-</sup> (2)  | 2.171(2) <sup>a</sup>           | 525 <sup>b</sup>          | c         |
| NbSCl <sub>4</sub> <sup>-</sup>   | 2.085(5) <sup>a</sup>           | 552                       | 1         |
| NbSCl <sub>3</sub> (SPPPh <sub>3</sub> )  | 2.114(4) <sup>a</sup>           | 536                       | 2, 3      |
| NbSBr <sub>3</sub> (THT) <sub>2</sub>   | 2.09(8) <sup>d</sup>            | e                         | 4         |
| [NbSCl <sub>2</sub> (SPPPh <sub>3</sub> )( $\mu$ -Cl)] <sub>2</sub>   | 2.129(4) <sup>d</sup>           | e                         | 2, 3      |
| Nb <sub>6</sub> S <sub>17</sub> <sup>+</sup>  | 2.196(4) <sup>d</sup>           | 483                       | 5, 6      |
| NbS(S <sub>3</sub> CNEt <sub>2</sub> ) <sub>3</sub>   | 2.122(1), 2.168(1) <sup>d</sup> | 493                       | 7         |
| NbS(SC <sub>2</sub> H <sub>4</sub> S)(SC <sub>2</sub> H <sub>4</sub> SC <sub>2</sub> H <sub>4</sub> S) <sup>-</sup> | 2.192 <sup>d</sup>              | 493                       | 8         |

<sup>a</sup> Site *trans* to Nb=S unoccupied.

<sup>b</sup> NEt<sub>4</sub><sup>+</sup> salt; obscured in the PPh<sub>4</sub><sup>+</sup> salt by cation bands.

<sup>c</sup> This work.

<sup>d</sup> Site *trans* to Nb=S occupied.

<sup>e</sup> Not reported.

important bond lengths and angles are collected in Table 1. It can readily be seen that the NbS<sub>5</sub> core possesses almost perfect C<sub>4v</sub> 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°, respec-

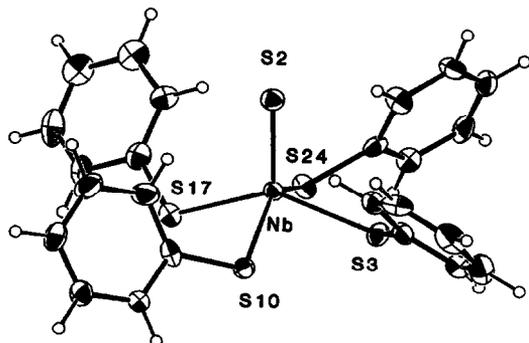
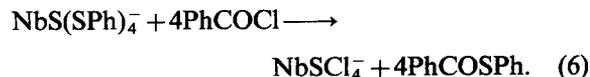


Fig. 1. ORTEP representation of complex 2 at the 50% probability level.

tively. 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<sup>-</sup> ligands result in noticeably longer apical V=O<sup>2+</sup> and V=S<sup>2+</sup> distances;<sup>9</sup> we have rationalized this as due to the excellent electron-releasing properties of thiolate ligands. Note that the anionic nature of the PhS<sup>-</sup> ligands cannot be the sole explanation, because NbSCl<sub>4</sub><sup>-</sup> 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)]:



The products from the reaction of **2** under a variety of other conditions (e.g. reduction, heating, treatment with MeI or I<sub>2</sub>, etc.) are currently being investigated.

*Acknowledgement*—This work was supported by NSF Grant CHE 8808019.

### REFERENCES

1. U. Muller and P. Klingelhofer, *Z. Anorg. Allg. Chem.* 1984, **510**, 109.
2. M. G. B. Drew, G. W. A. Fowles, R. J. Hobson and D. A. Rice, *Inorg. Chim. Acta* 1976, **20**, L35.
3. M. G. B. Drew and R. J. Hobson, *Inorg. Chim. Acta* 1983, **72**, 233.
4. M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.* 1983, 2251.
5. J. Sola, Y. Do, J. M. Berg and R. H. Holm, *J. Am. Chem. Soc.* 1983, **105**, 7794.
6. J. Sola, Y. Do, J. M. Berg and R. H. Holm, *Inorg. Chem.* 1985, **24**, 1706.
7. Y. Do and R. H. Holm, *Inorg. Chim. Acta* 1985, **104**, 33.
8. K. Tatsumi, Y. Sekiguchi, A. Nakamura, R. E. Cramer and J. J. Rupp, *J. Am. Chem. Soc.* 1986, **108**, 1358.
9. J. K. Money, J. C. Huffman and G. Christou, *Inorg. Chem.* 1985, **24**, 3297.