

PREPARATION AND REACTIONS OF NIOBIUM(V) SULPHIDE COMPLEXES

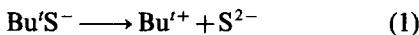
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Abstract—An improved synthetic procedure to $(\text{PPh}_4)[\text{NbS}\text{Cl}_4]$ (**1**) is described involving the reaction of NbCl_5 with two equivalents of NaSBu' . Complex **1** reacts with NaSPh to yield $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4]$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

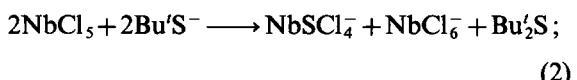
The sulphur-based chemistry of the group 6 metals, molybdenum and tungsten, has been the subject of intense investigation over many years. In contrast, the corresponding chemistry of the group 5 metals is still only poorly explored. We have a program directed towards the development of group 5 metal-sulphur 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 $[\text{NbS}\text{Cl}_4]^-$ was considered an attractive starting point for the synthesis of $\text{M}-\text{S}-\text{SR}$ complexes by metathesis. However, available procedures to this material are less than optimal with respect to yield, purity or convenience of preparation,¹ 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 (S^{2-}) source via C—S bond cleavage [eq. (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 $(\text{PPh}_4)[\text{NbS}\text{Cl}_4]$ (**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 NbCl_5 to NbSCl_4^- was due to reaction of generated 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 NbSCl_4^- . Treatment of NbCl_5 with 2 equivalents of NaSBu' does indeed produce only NbSCl_4^- [eq. (4)], and isolated yields of pure crystalline $(\text{PPh}_4)[\text{NbS}\text{Cl}_4]$ are routinely ~60%. The NEt_4^+ salt can be prepared in a similar fashion.



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 $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4] \cdot \text{THF}$ (**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 PhS^- groups in the basal plane. The

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† Crystal data for $(\text{PPh}_4)[\text{NbS}(\text{SPh})_4] \cdot \text{THF}$ at -155°C : triclinic, $P\bar{1}$, $a = 12.442(3)$, $b = 12.154(3)$, $c = 15.887(4)$ Å, $\alpha = 91.73(1)$, $\beta = 92.13(1)$, $\gamma = 102.67(1)^\circ$, $V = 2340.49$ Å³, $Z = 2$, $d_{\text{calc}} = 1.381$ g cm⁻³, $\mu = 5.297$ cm⁻¹, $\lambda = 0.71069$ Å, 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 (ν)

| Complex | Nb=S (Å) | ν (cm ⁻¹) | Reference |
|---|---------------------------------|---------------------------|--------------|
| NbS(SPh) ₄ ⁻ (2) | 2.171(2) ^a | 525 ^b | ^c |
| NbSCl ₄ ⁻ | 2.085(5) ^a | 552 | 1 |
| NbSCl ₃ (SPPH ₃) | 2.114(4) ^a | 536 | 2, 3 |
| NbSBr ₃ (THT) ₂ | 2.09(8) ^d | ^e | 4 |
| [NbSCl ₂ (SPPH ₃)(μ -Cl)] ₂ | 2.129(4) ^d | ^e | 2, 3 |
| Nb ₆ S ₁₇ ⁴⁻ | 2.196(4) ^d | 483 | 5, 6 |
| NbS(S ₃ CNEt ₂) ₃ | 2.122(1), 2.168(1) ^d | 493 | 7 |
| NbS(SC ₂ H ₄ S)(SC ₂ H ₄ SC ₂ H ₄ S) ⁻ | 2.192 ^d | 493 | 8 |

^a Site *trans* to Nb=S unoccupied.^b NEt₄⁺ salt; obscured in the PPh₄⁺ salt by cation bands.^c This work.^d Site *trans* to Nb=S occupied.^e Not reported.

important bond lengths and angles are collected in Table 1. It can readily be seen that the NbS₅ core possesses almost perfect C_{4v} 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;⁹ 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 NbSCl₄⁻ 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)]:

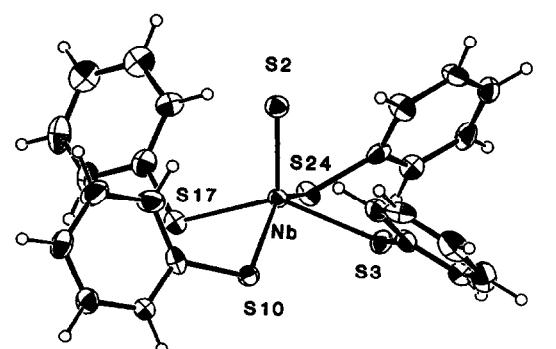
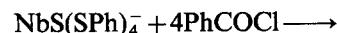


Fig. 1. ORTEP representation of complex 2 at the 50% probability level.

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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