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Article

Formation of Sulfido Niobium Complexes Through C-S Bond Activation

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A reação entre $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbCl}_2$, $\eta^5\text{-C}_5\text{H}_5$ = Cp, e $(\text{Ph})_3\text{Sn(SPh)}$, em THF, originou os complexos $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(Cl)}(\mu\text{-S})\text{Sn(Ph)}_3\text{(Cl)}$, **1**, e $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(S)Cl}$, **2.** Os complexos **1** e **2** foram caracterizados por espectroscopias no IV, de RMN ^{1}H, RMN ^{13}C, RMN ^{119}Sn, Mössbauer, análise elementar e absorção atômica. Hidrólise de **1** originou a espécie μ-oxo $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(Cl)}(\mu\text{-O})\text{Sn(Ph)}_3\text{Cl}$, **3**, que foi caracterizada por espectroscopias no IV, RMN ^{1}H, RMN ^{13}C, Mössbauer, análise elementar, absorção atômica bem como por cristalografia de raios-X. O complexo **3** cristaliza no grupo de espaço $Pca2_1$ com a = 17.282(3), b = 18.122(4), c = 17.3269(2), V = 5426.2(16) Å^3 e Z = 8. Estudos adicionais indicaram que os complexos foram formados como resultado da substituição nucleofílica do cloro da ligação nióbio-cloro pelo ligante tiolato seguido da quebra da ligação C-S. A quebra ocorre com um excesso do composto tiolato igual ou maior que 2:1.

Upon reacting $(\eta^5\text{-C}_5\text{H}_5)_2\text{NbCl}_2$, $\eta^5\text{-C}_5\text{H}_5$ = Cp, and $(\text{Ph})_3\text{Sn(SPh)}$, in THF, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(Cl)}(\mu\text{-S})\text{Sn(Ph)}_3\text{(Cl)}$, **1**, and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(S)Cl}$, **2**, were obtained. Complexes **1** and **2** were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, Mössbauer spectroscopies, elemental analysis as well as by atomic absorption. Hydrolysis of **1** yielded the μ-oxo species, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb(Cl)}(\mu\text{-O})\text{Sn(Ph)}_3\text{Cl}$, **3**, which was characterized by IR, ^{1}H-NMR, ^{13}C-NMR and Mössbauer spectroscopies, elemental analysis, atomic absorption as well as by X-ray crystallography. It crystallizes in the space group $Pca2_1$ with a = 17.282(3), b = 18.122(4), c = 17.3269(2), V = 5426.2(16) Å^3, and Z = 8. Additional studies indicated that the complexes were formed as a result of the nucleophilic displacement of the niobium-chloride bond by the thiolate ligand followed by a C-S bond cleavage. The cleavage occurs with an excess of the thiolate compound equal to or greater than 2:1.

Keywords: *niobium, sulphido, tin thiolate, C-S bond activation*

Introduction

One of our research interests is to obtain niobium thiolato complexes, both mononuclear and heterobimetallic[1]. A useful strategy to metal thiolato complexes involves the exchange of a chloride ligand by a thiolate between two compounds where there exists a mismatching of the hardness and softness of the metal-thiolato and metal-halide bonds in the starting materials[2,3]. Once formed the thiolato complex can undergo further reactions; for example, sulfur can use the extra electron pairs to interact with other metal centers generating heterobimetallic complexes[1] or can undergo a C-S bond cleavage, yielding sulfido complexes[4]. Tin derivatives containing thiolate ligands have been used in this manner to obtain thiolate complexes of the transition metals under very mild conditions[3]. However, no such method has been reported in the literature for the production of niobium thiolato complexes. According to this we designed the reaction between Cp_2NbCl_2 and $(Ph)_3Sn(SPh)$[5]. As reported below, two new sulfido complexes could be obtained from this reaction, a heterobimetallic, $(\eta^5\text{-}C_5H_5)_2Nb(Cl)(\mu\text{-}S)Sn(Ph)_3Cl$, **1**, as the minor product of the reaction and the mononuclear $(\eta^5\text{-}C_5H_5)_2Nb(S)Cl$, **2**, as the major product of the reaction. Hydrolysis of **1** yielded $(\eta^5\text{-}C_5H_5)_2Nb(Cl)(\mu\text{-}O)Sn(Ph)_3Cl$, **3**, whose solid state structure could be determined. Here we report the synthesis and characterization of the complexes as well as studies that were done in order to understand their formation mechanism. Eletrochemical properties of complexes **1** and **2** are also reported.

Experimental

General comments

All operations were carried out under pure dinitrogen, using Schlenk and vacuum techniques. Nitrogen was predried over an in line columm consisting of molecular sieves, calcium chloride and calcium sulfate. Hexane, tetrahydrofuran, toluene and heptane were distilled from sodium/benzophenone. Acetone was distilled over barium oxide. All solvents were used immediately following distillation or stored under nitrogen over the appropriate molecular sieves Cp_2NbCl_2, from Aldrich, was used as supplied. $(Ph)_3Sn(SPh)$ was prepared according to a literature procedure[5]. ^{119}Sn Mössbauer spectroscopy was performed in constant acceleration equipment moving a $CaSnO_3$ source kept at room temperature. The samples were cooled at liquid nitrogen temperature. All spectra were computer-fitted assuming Lorentzian lineshape. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer in the 4000-200 cm^{-1} range as a nujol mull, on CsI plates. ^1H- and ^{13}C-NMR spectra were recorded on a Brucker AC-400 spectrometer and referenced to internal $SiMe_4$. C and H analyses were performed using a Perkin-Elmer PE-2400 CHN microanalyser. Atomic absorption for tin was performed on a Hitachi Z-8200 Polarized Zeeman Atomic Absorption Spectrophotometer. A Bioanalytical Systems 100A voltammograph was used for cyclic voltammetry studies. The potencials were referred to a Ag/AgCl electrode with glassy carbon as the working electrode. The auxiliary electrode was Pt wire. Solutions were 2.5 mM in solute and 0.1 M in supporting electrolyte, $[Bu_4N][PF_6]$. The niobium samples and the supporting electrolyte were weighed inside the dry box. Purified solvents were syringed into the cell containing the supporting electrolyte under a flow of N_2.

Synthesis

In a Schlenk flask were loaded Cp_2NbCl_2 (100 mg, 0.340 mmol) and $(Ph)_3Sn(SPh)$ (310 mg, 0.680 mmol) in 20 mL of THF, and the violet solution was refluxed. As the reaction progressed the color of it turned to deep brown. After 2 h the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The brown residue that was left was extracted with toluene producing a violet solution. The solvent was evaporated under reduced pressure resulting in a violet residue that was washed with petroleum ether. The petroleum ether extract was evaporated under reduced pressure and the remaining off-white residue was submitted for a GC/MS analysis (vide-infra). The remaining violet solid was redissolved in toluene and upon addition of hexane complex **1** precipitated as a violet solid. Yield: 10%. The original brown residue was extracted with acetone and upon addition of hexane complex **2** precipitated as a dark violet solid. Yield 50%. **$(\eta^5\text{-}C_5H_5)_2Nb(Cl)(\mu\text{-}S)Sn(Ph)_3Cl$, complex 1.** Anal. Calcd. for $[C_{28}H_{25}NbSnCl_2S]$ (Found): C, 49.71 (50.49); H, 3.73 (3.76), S, 4.73 (3.10). Atomic absorption for tin calc. (found): 18.03 (18.62). ^1H-NMR (ppm, $(CD_3)_2CO$): 7.77 - 7.30 (m, $3C_6H_5$); 6.19 (s, $2C_5H_5$). ^{13}C-NMR (ppm, $CDCl_3$): 137.44 - 128.95 (m, C_6H_5); 115.73 (s, C_5H_5). ^{119}Sn-NMR (ppm, $(CD_3)_2CO$): -112.1. IR (cm^{-1}, CsI, nujol mulls): 3125m, 3060m, 1425s, 1370w, 1255w, 1070s, 1060s, 1015s, 990m, 810sh, 795s, 720s, 685s, 435m, 425m, 340m, 300w, 235w. Mössbauer spectra (mm/s): $\delta = 1.29 \pm 0.01$; $\Delta = 3.05 \pm 0.02$. **$(\eta^5\text{-}C_5H_5)_2Nb(S)Cl$, complex 2.** Anal. Calcd. for $[C_{10}H_{10}Nb(S)(Cl)]$ (Found): C, 41.33 (41.38), H, 3.46 (3.01). ^1H-NMR (ppm, $CDCl_3$): 6.15 (s, $2C_5H_5$). ^{13}C-NMR (ppm, $CDCl_3$): 113.59 (C_5H_5). (IR cm^{-1}), CsI, nujol mulls): 3090m, 1450s, 1370s, 1000m, 810s, 700w, 330w, 250m.

A solution of complex **1**, in THF, under N_2, was treated with two drops of distilled water and it was converted quantitatively to **$(\eta^5\text{-}C_5H_5)_2Nb(Cl)(\mu\text{-}O)Sn(Ph)_3Cl$**, complex **3**. Anal. Calcd. for $[C_{28}H_{25}NbSnCl_2O]$ (Found): C, 50.96 (51.05) H, 3.82 (3.98), ^1H-NMR(ppm, $(CD_3)_2CO$): 7.77 - 7.30 (m, $3C_6H_5$), 6.38 (s, $2C_5H_5$); ^{13}C-NMR(ppm, $(CDCl_3)$: 136.33 - 131.14 (m, C_6H_5), 120.87 (C_5H_5). IR (cm^{-1},CsI, nujol mull): 3120m, 3065m, 3020m, 1425s, 1365w, 1250w, 1055s, 1010s, 990s, 805sh, 780vs, 710s, 675s, 450w, 300w, 250w. Mössbauer spectrum (mm/s): $\delta = 1.29 \pm 0.01$; $\Delta = 3.08 \pm 0.02$.

GC/MS analysis

MS (EI, 70eV): PhSPh, m/z = 186 (M^+); $(Ph)_3SnCl$, m/z = 385.5 (M^+); $[(Ph)_3Sn]_2$, m/z = 700 (M^+); the latter was identified by means of the fragmentation pattern of the monomer

X-ray crystal structure determination of (η^5-C_5H_5)$_2$Nb(Cl)(μ-O)Sn(Ph)$_3$Cl

Data collection was performed on a Siemens P4 diffractometer using graphite-monochromated Mo K_α (λ = 0.71073) radiation. Cell constants were obtained by a least-square fit of 38 accurately centered reflections with $\theta > 20°$. A total of 7334 reflections were collected at 298K in 2θ - θ scan mode with a variable scan rate (2.0 to 60.0), 3358 of which were considered as observed [$F \geq 4\sigma(F)$]. The structure was solved by a direct method employing a SHELXTL-PC program package[6]. The crystals have orthorhombic symmetry; according to the observed extinction rules both Pcam and $Pca2_1$ space groups could describe the crystal structure. Attempts to refine the structure in the centrosymmetric space group did not converge. The strucuture was refined to convergence in $Pca2_1$ space group by full matrix least-square methods; the function minimized was $\Sigma w(||F_o-F_c|^2/\Sigma w|F_0|^2$ with $w = 1/\sigma^2(F)$. The structure refinement using anisotropic displacement parameters for all atoms and without using any kind of constraints gave R = 0.076, Rw = 0.065. Nevertheless some of the carbon atoms had no acceptable values for the anisotropic displacement parameters. The final results were obtained imposing geometric constraints in the cyclopentadienyl rings; the carbon atoms were refined isotropically. Details of crystallographic data collection, structure refinement and crystal data are given in Table 1.

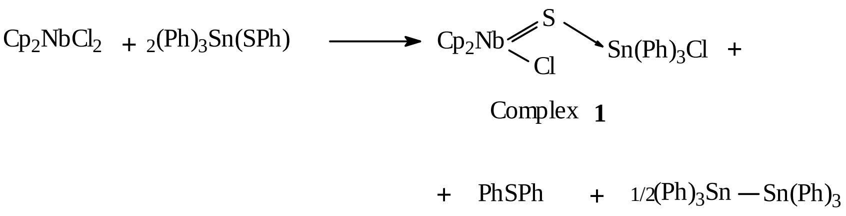
Results and Discussion

Reaction of (η^5-C_5H_5)$_2$NbCl$_2$ with 2 equiv. of (Ph)$_3$Sn(SPh), in THF, under reflux, afforded complexes **1** and **2**, as shown in Eqs. 1 and 2.

Complexes **1** and **2** are violet and are very unstable in solution but stable in the solid state for several hours even in the presence of oxygen. Complex **1** is soluble in solvents like toluene, THF and dichloromethane; complex **2** in THF, dichloromethane and acetone. Signals due to the Cp rings in the ^{1}H-NMR spectrum were observed at $\delta = 6.19$ and $\delta = 6.15$ for complexes **1** and **2**, respectively, and are characteristic of Nb(V) complexes[7], in contrast to the niobum starting material that is a Nb(IV) complex. Besides the absorption bands assigned to the aromatic rings of complex **1** the IR spectrum contains bands at 425 cm^{-1}, 340 cm^{-1}, 300 cm^{-1}, and 235 cm^{-1} that were assigned to $\nu_{Nb=S}$, ν_{Sn-S}, ν_{Nb-Cl} and ν_{Sn-Cl}, respectively[8,9,10,11]. Also, for both complexes, the absorption band due to ν_{S-C6H5}, that is normally found at 1600 cm^{-1}, could not be observed[5]. The data obtained from the Mössbauer spectrum indicated that the tin atom was in a pentacordinate environment. The QS value of 3.05 mm/s is in agreement with other values reported in the literature for a tin compound having a trigonal bipyramidal geometry[12]. The presence of PhSPh, [(Ph)$_3$Sn]$_2$ and (Ph)$_3$SnCl was determined by the GC/MS analysis that was done on the petroleum ether extract (see Experimental).

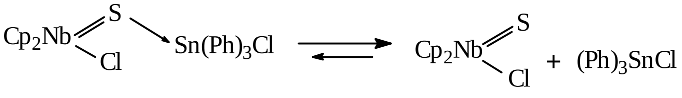
Complex **1** was allowed to react with water and complex **3** was obtained, Eq. 3.

Complex **3** is yellow and was also formed from solutions of complex **1** left standing in the NMR tube for one



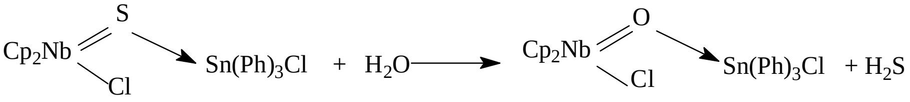
Complex **1**

(1)



Complex **1** Complex **2**

(2)



Complex **1** Complex **3**

(3)

hour. Complex **3** was stable both in the solid state and in solution in the presence of oxygen for prolonged periods of time. In the ^{1}H-NMR spectrum the signal for the Cp ring moved from $\delta = 6.19$ in complex **1** to $\delta = 6.38$ in complex 3, indicating the expected deshielding of the hydrogens in the oxo complex. In the ^{13}C-NMR the corresponding signals due to Cp were found at $\delta = 115.73$ and $\delta = 120.84$, respectively. In the IR spectrum the $\nu_{Nb=O}$ was observed as a broad band at 780 cm^{-1}[13] and the ν_{Sn-O} band was observed at 450 cm^{-1} as a medium intensity band[14]. The data obtained from the Mössbauer spectrum were similar to those of complex **1**.

In an attempt to obtain crystals of complex **1** suitable for X-ray crystallographic analysis, a toluene/heptane solution was left in the refrigerator for some days. Light violet crystals not of complex **1**, but rather of complex **3** were obtained. This is rationalized by the great sensitivity of complex **1** to moisture, most probably on the walls of the flask, thus converting complex **1** into complex **3** upon standing in the refrigerator for several days. The color of the crystals was much more characteristic of complex **1**, that is a violet complex, but as complex **3** is yellow and gives light yellow crystals, we could not determine which complex we had by the colour of the solid Further attempts to obtain crystals of pure complex **1** were unsuccessful. The crystal structure of **3**, Fig. 1, was determined to have two independent conformers in the unit cell, conformers A and B, differing mainly in the orientation of the Cp rings. In conformer A the Cp rings are staggered and in conformer B they are eclipsed. The angle defined by the vectors connecting the centroids of the Cp rings to Nb were 130.7 and 130.3 in conformers A and B, respectively. The Nb-O-Sn bond angle in conformer A is 168.4 and in conformer B, 173.5. The coordination geometry around the Sn atom is a relatively regular trigonal bipyramidal in agreement with the data obtained from the Mössbauer spectrum. The axial positions are occupied by the more eletronegative atoms, chlorine and oxygen[12,15,16]. The equatorial plane is defined by the carbon atoms of the phenyl rings. The average equatorial angle is 119.35 in both conformers and the ClSnC average axial-equatorial angle is 94.5 and the average OSnC angle is 85.3, Table 1. The Cl-Sn-O angles were the same in both conformers, 174.4. The Sn-O bond distance of 2.366 Å (mean value) is longer than related bonds in other complexes, *e.g.*, $(R_f)_2(Cl)Sn(\mu_2\text{-}O)Sn(Cl)(R_f)_2$, 2.315(1) Å[15] and $Sn_2(C_2Cl_3O_2)_2(C_6H_5)_4(OH_2)$, 2.162 (5) Å[16], indicating that the interaction between tin and oxygen in complex **3** is a weak interaction. A dative bond fits this description because it is a weak interaction and also because the formation of this type of bond is favorable by the use of the extra electron pairs of oxygen, to interact with more than one metal center. The Sn-Cl bond distance is also a little longer than in related complexes[15,16,17]. The Nb-O bond lenght of 1.777 Å (mean value) is appropriate for a double bond. It is smaller than the related bond in the complex $\{Cp_2Nb(SnMe_3)\}_2(\mu\text{-}O)$, 1.943 Å[17] and has a value between the bond distance in the complexes $Cp_2Nb(O)Cl$[18] and $[(Nb(\eta^5\text{-}C_5H_5)_2Cl\}_2(\mu\text{-}O)]^{2+}$ [19], 1.737 Å and 1.880 Å respectively. For these two compounds the niobium - oxygen bond is described as having double bond character. The Nb-Cl bond distance of 2.373 Å (mean value) is also smaller than the related bond in the complex $Cp_2Nb(O)Cl$, 2.439(2) Å[18].

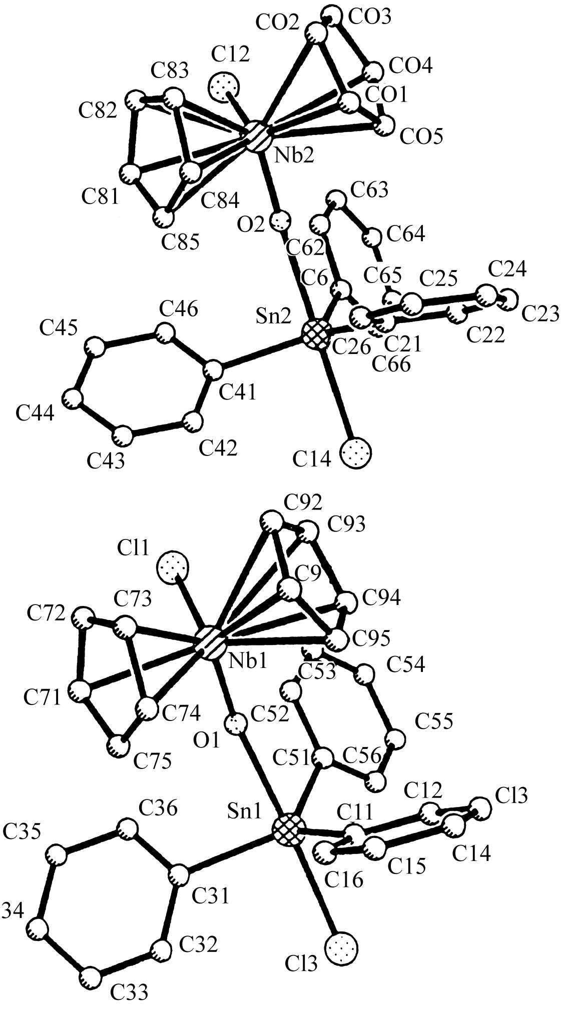


Figure 1. Molecular structure of complex 3 drawn at the 30% probability level; conformer A (bottom), conformer B (top).

The solution of the structure of complex **3** together with the proposed structure for related Ta sulfido complex described in the literature[20] permitted us to propose the structures shown in Fig. 2 for complexes **1** and **2**. In the proposed structures the Nb atom shares a double bond with sulfur and the Sn atom shares a dative bond with sulfur in complex **1**.

The important step in the reactions here described for the formation of the sulphido complexes is the cleavage of the $S\text{-}C_6H_5$ bond. Several mechanisms have been proposed for the desulphurization of organic groups that involve the participation of metal centers[21]. In the present study, performing the reaction in a 1:1 molar ratio did not yield the

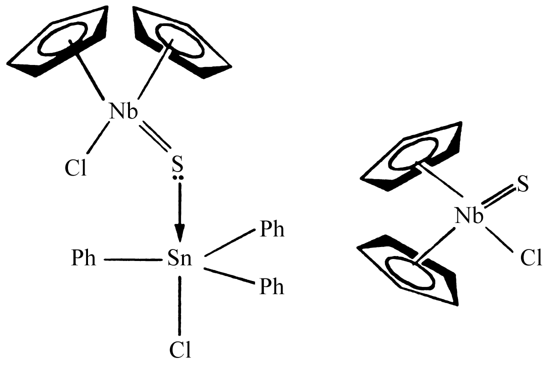
Table 1. Summary of crystallographic data for (η^5-$C_5H_5)_2Nb(Cl)(\mu$-$O)Sn(Ph)_3Cl$.

Molecular formula	$C_{28}H_{25}NbCl_2OSn$
formula weight	660.0
space group	$Pca2_1$
a, Å	17.282(3)
b, Å	18.122(4)
c, Å	17.326(2)
V, Å^{-3}	5426(2)
temp, °C	25
Z	8
D(calcd), Mg m^{-3}	1.616
radiation	MoKα (λ = 0.71073)
μ, mm^{-1}	1.5588
R	0.076
wR*	0.065
GOF*	1.48
no. of reflns collected	7334
no. of reflns obsd	3358
no. of params	196

* $wR = [\Sigma w(F_o-F_c)^2/\Sigma(F_o)^2]$; $w = [\sigma^2(F)+gF^2]^{-1}$; $GOF = [\Sigma w(F_o-F_c)^2/N_{data} - N_{par}]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (deg) for complex 3 with e.s.d's in parenthesis.

Bond Lengths	
Conformer A	Conformer B
Nb(1)-O(1)= 1.771(15)	Nb(2)-O(2)= 1.784(17)
Nb(1)-Cl(1)= 2.370(9)	Nb(2)-Cl(2)= 2.376(9)
Sn(1)-O(1)= 2.356(15)	Sn(2)-O(2)= 2.376(17)
Sn(1)-Cl(3)= 2.500(8)	Sn(2)-Cl(4)= 2.502(9)
Bond Angles	
Cl(1)-Nb(1)-O(1)= 98.0(5)	Cl(2)-Nb(2)-O(2)= 97.5(6)
Nb(1)-O(1)-Sn(1)= 168.4(9)	Nb(2)-O(2)-Sn(2)= 173.5(9)
C(11)-Sn(1)-C(31)= 118.4(6)	C(21)-Sn(2)-C(41)= 119.6(7)
C(11)-Sn(1)-C(51)= 119.7((7)	C(21)-Sn(2)-C(61)=120.8(7)
C(11)-Sn(1)-Cl(3)= 94.0(5)	C(21)-Sn(2)-Cl(4)= 95.4(5)
Cl(3)-Sn(1)-C(51)= 98.2(5)	Cl(4)-Sn(2)-C(61)= 97.6(6)
Cl(3)-Sn(1)-O(1)= 174.4(4)	Cl(4)-Sn(2)-O(2)= 174.3(5)



Complex **1** Complex **2**

Figure 2. Proposed molecular structures for complexes **1** and **2**.

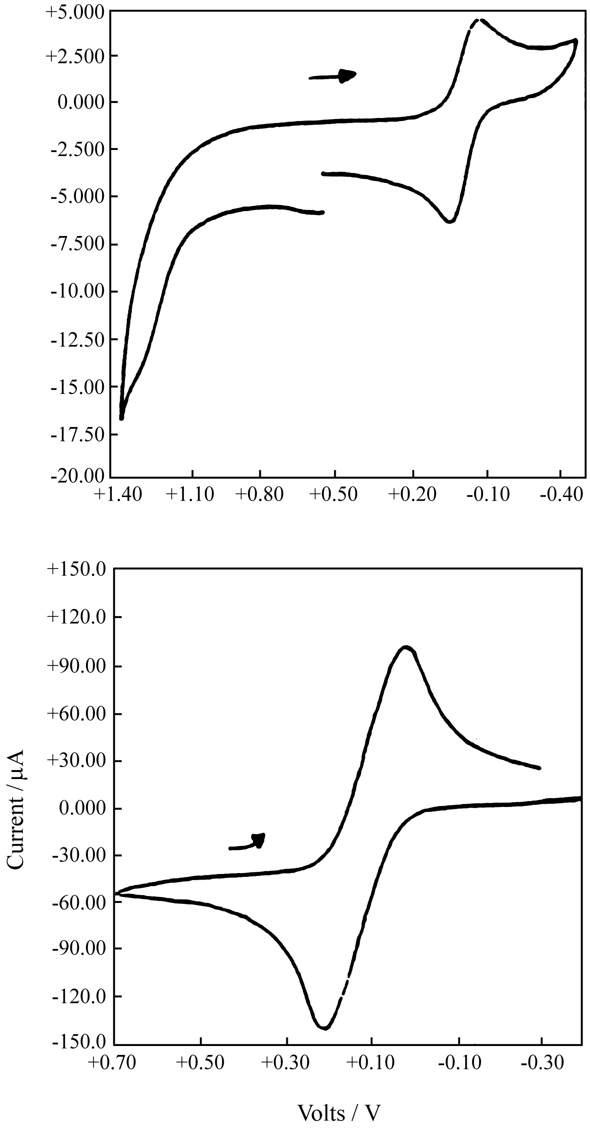
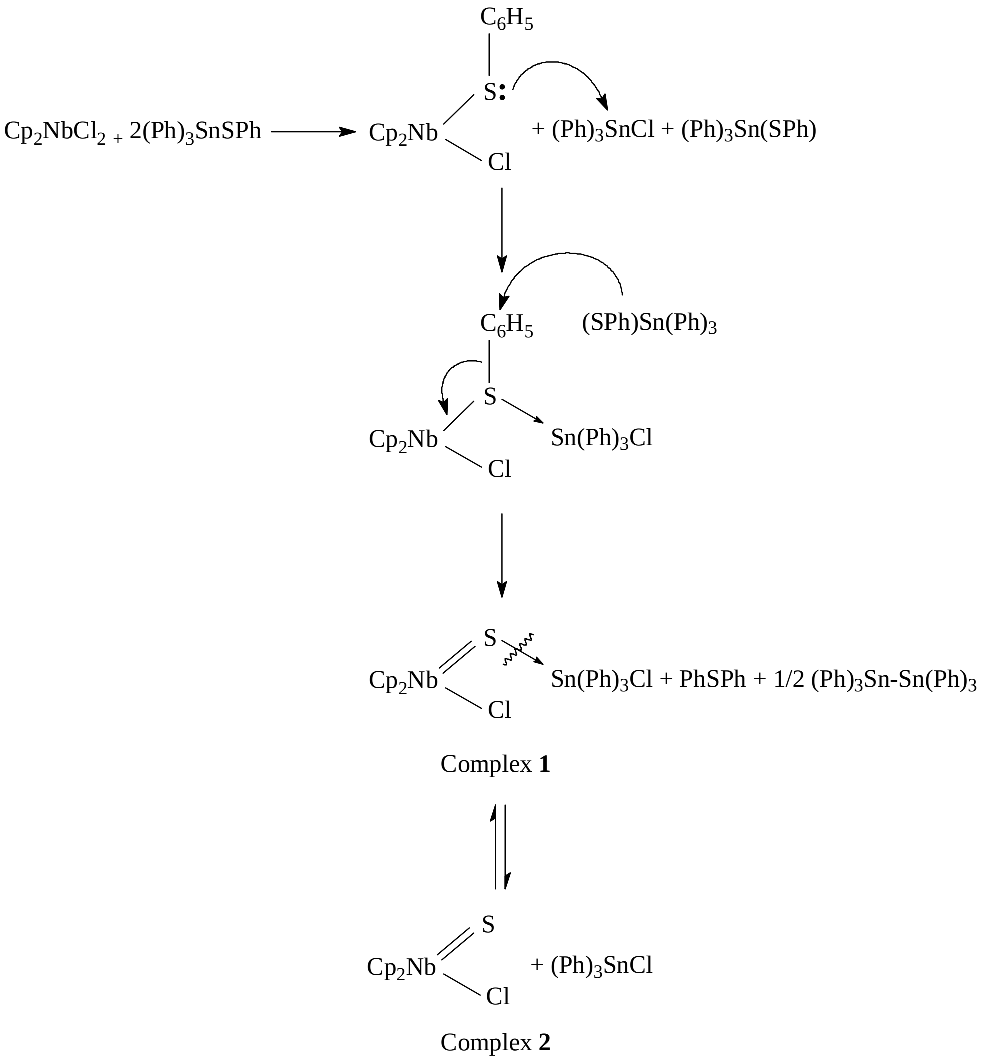


Figure 3. Cyclic voltammograms of 2.5 mM solutions of complex 1 (top) and complex 2 (bottom) in 10^{-1} M $[Et_4N]PF_6$ with a glassy carbon electrode at a scan rate of 200 mV/s.



Scheme 1.

sulphido complexes, even for prolonged periods of time under reflux. Reaction using a 1:2 Nb/Sn molar ratio yielded the same amount of products both at room temperature or under reflux and upon increasing the molar ratio of the tin thiolate the yield of formation of complex **2** increased much more than the yield of complex **1**. According to these results we could conclude that, in the reactions described here, first there must be a nucleophilic displacement of the niobium - chloride bond by the thiolate ligand followed by a C-S bond cleavage, yielding the sulphido complexes. The key factor in promoting the cleavage is the excess of tin thiolate. The other tin compounds found in the reaction medium, shown in Eq. 1, together with PhSPh, is further evidence for the participation of the excess of the tin thiolate in the cleavage; these compounds can only be formed in the presence of $(Ph)_3Sn(SPh)$. In Scheme 1 a mechanism is suggested that accounts for all of the experiments that were done.

According to Curtis *et al.*[21a], complex **1** is likely to be formed first because coordination of the thiolate to more than one metal centers can activate the C-S bond to homolytic scission by lowering the bond dissociation energy. The Sn-S bond, as a weak bond, breaks very easily originating complex **2**.

Eletrochemical studies

Cyclic voltammograms in the cathodic potencial region for complexes **1** and **2** are shown in Fig. 3. Both complexes showed quasi-reversible waves. The heterobimetallic complex, Fig. 3 (top), showed a potencial for the reduction of Nb(V) to Nb(IV) at $E_{1/2}$ = +54 mV. No redox wave associated with Sn was observed. For the mononuclear complex, Fig. 3 (bottom), the reduction potencial for Nb(V) to Nb(IV) was observed at $E_{1/2}$ = +113 mV. The reduction potential for Nb(V) to Nb(IV) occurs at a less positive value for the heterobimetallic than for the mononuclear complex and can be attributed to a electron delocalization over the two metals in complex **1**.

Conclusions

Due to the stability of the C-S bond in aromatic thiolate ligands the clevage of this bond is not common but it is a very important step in the desulphurization of organic fuels[22]. In the reactions described here they occur very easily. The use of just a two fold excess of the tin thiolate is sufficient to promote it. This study permitted us to find an easy route to cleave a C-S aromatic bond and to obtain organometallic niobium sulfido complexes, and reinforces, once more, the importance of the interactive cooperation of two different metals in effecting transformations. The reduction potential for Nb(V) to Nb(IV) for the complexes described here occurs at a less negative potencial than literature values reported for other niobium-sulfur complexes [1] indicating that niobium sulfido complexes are more resistent to oxidation than related thiolate complexes both mononuclear and heterobimetallic.

Acnowledgments

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Supporting information available. Listings of X-ray data, positional and thermal parameters, bond distances and angles and packing diagram.

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