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Synthesis and characterization of cyclopentadienyl sulfur niobium complexes

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ABSTRACT

A trimetallic sulfide cluster $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (**2**) has been synthesized from the reaction of $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) with $(Me_3Si)_2S$ in a 4:3 ratio by the release of $SiClMe_3$. The trinuclear nature of complex **2** has been established by single crystal X-ray diffraction analysis. Thermal treatment of **2** with SiH_3Ph generated the dinuclear niobium(IV) complex $[Nb_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$ (**3**) in a quantitative way. Likewise, one-pot syntheses of **3** has been developed from reaction of **1**, $(Me_3Si)_2S$, and SiH_3Ph in toluene. A series of dinuclear sulfide niobium(IV) derivatives $[Nb_2(\eta^5\text{-}C_5Me_5)_2R_2(\mu\text{-}S)_2]$ (R = Me **4**, Et **5**, CH_2SiMe_3 **6**, C_3H_5 **7**, CH_2Ph **8**, *n*Bu **9**) can easily be obtained from the reaction of **3** with 2 equiv of the corresponding alkylating reagents. Single crystal X-ray diffraction analyses of **6** and **7** showed in all cases a *trans* disposition of the substituents.

1. Introduction

The chemistry of soluble transition-metal sulfides species [1] revealing well-defined and characterized structures are attractive candidates for a better understanding about action modes of most of the metalloproteins of biological significance [2] such as nitrogenase, hydrogenase … Therefore, in the last years there has been a growing interest not only in the crucial role of the metal centers but also in the careful selection/design of suitable auxiliary ligands.

The presence of the cyclopentadienyl ligand affords an accessible entry to di- and polynuclear soluble transition metal sulfide complexes [3], where the distinguishing chemical and electronic properties of the cyclopentadienyl ring make possible further studies. Moreover, the physical and chemical properties of this ligand can be significantly modified by little changes on the nature of the substituents on the ring [4]. Related to the latter, it is worth noting that the corresponding mononuclear compounds $[M(\eta^5\text{-}C_5H_5)Cl_4]$ (M = Nb, Ta), with non-substituted cyclopentadienyl ligands, reacts with $(Me_3Si)_2E$ (E = S, Se) to often form complex product mixtures [5].

In contrast, we have just reported [6] an efficient and selective synthetic method for a series of trinuclear, $[Ta_3(\eta^5\text{-}C_5Me_5)_{3\text{-}x}Cl_{3+x}(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (x = 0, 1), and dinuclear $[Ta_2(\eta^5\text{-}C_5Me_5)_2X_2(\mu\text{-}S)_2]$ (X = Cl, alkyl, aryl) sulfide tantalum complexes comprising the permethylated ligand (C_5Me_5), in a quantitative way (Fig. 1). In addition, the moderate-high yields of their synthesis along to the solubility exhibited by these species aims to the exploration on their further reactivity. According to these results, the present work extends this study to niobium, and examines the similarities found, both synthetically and structurally.

2. Results and discussion

In our recent work, the trinuclear sulfide tantalum species $[Ta_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ and $[Ta_3(\eta^5\text{-}C_5Me_5)_2Cl_4(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ were synthesized from the stoichiometric amounts of mononuclear complex $[Ta(\eta^5\text{-}C_5Me_5)Cl_4]$, as building block, and the hexamethyldisilathiane reagent, $(Me_3Si)_2S$, as sulfur source [6,7]. In this paper, the analogous niobium trimetallic cluster $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (**2**) was fruitfully prepared from the treatment of $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) with $(Me_3Si)_2S$ (3:4

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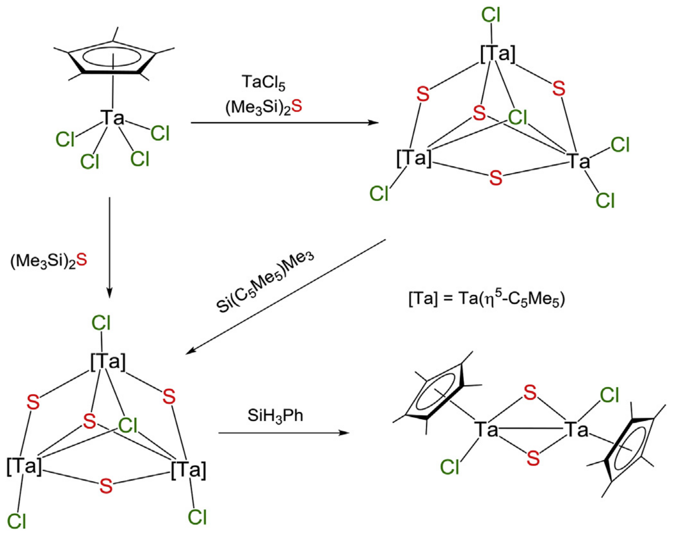


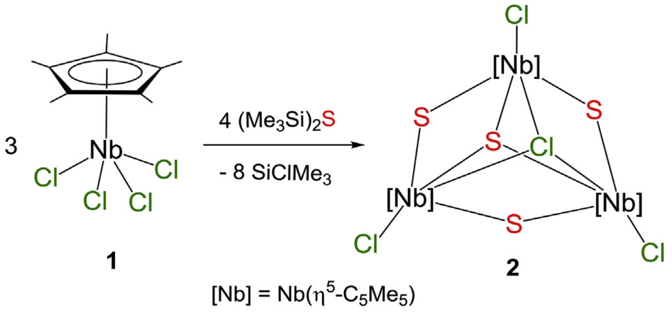
Fig. 1. Formation of discrete di- and trinuclear sulfide tantalum complexes.

ratio) in toluene heating at 100 °C for 72 h, as unique species, as outlined in Scheme 1. Complex **2** is isolated in 80% yield as a red microcrystalline solid along with $SiClMe_3$. However, all attempts to prepare the other analogous trinuclear species from compound **1**, $NbCl_5$, and $(Me_3Si)_2S$ in a 2:1:4 ratio resulted failed. Compound **2** is scarcely soluble in the usual solvents such as hexane, benzene, toluene, tetrahydrofurane or chloroform.

The molecular structure of **2** was unambiguously determined by single-crystal X-ray diffraction analysis. ORTEP drawing is given in Fig. 2.

This structure allows a comparison with the previously reported tantalum analogous [6]. As shown in Fig. 2, the X-ray studies of complex **2** revealed a similar triangular arrangement for the three Nb atoms bridged by μ-S, μ_3-S and μ_3-Cl units. $Nb\cdots Nb$ distances are similar to those of the tantalum species (3.402(1)-3.545(1) Å), evidence for no M-M bonding in agreement with the oxidation-state [4]. Each niobium center can be rationalized as a distorted octahedral environment with μ-*S*-Nb-μ_3-Cl4/S4 angles in the range 74.0(1)-86.7(1)°, and Seq-Nb-Seq close to 150°. Niobium sulfur compounds often appear as part of complex product mixtures [8], therefore complex **2**, and the analogous tantalum compounds, $[Ta_3(\eta^5\text{-}C_5Me_5)_{3-x}Cl_{3+x}(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (x = 0, 1), represents the only examples of molecular triangular clusters with discrete sulfide cores $M_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ (M = Nb, Ta).

As can be seen in complex **2** (see Fig. 2), two of the chlorine atoms and one η^5-C_5Me_5 ligand are situated above the Nb_3S_3 plane, while the third chlorine atom and the other two η^5-C_5Me_5 groups lie below it, in agreement with a C_1 symmetry, in a similar manner to the analogous of tantalum. The niobium complex shows a dynamic behavior in solution, as it only exhibits one resonance at δ 1.75 for the pentamethylcyclopentadienyl rings in the ^1H NMR spectrum, at significantly higher field compared with the starting compound **1** (C_6D_6, δ = 1.89). The same trend is detected in the ^{13}C NMR spectrum. However, no change of the spectra took place upon lowering the temperature from room temperature to −80 °C.



Scheme 1. Synthesis of the trinuclear niobium complex **2**.

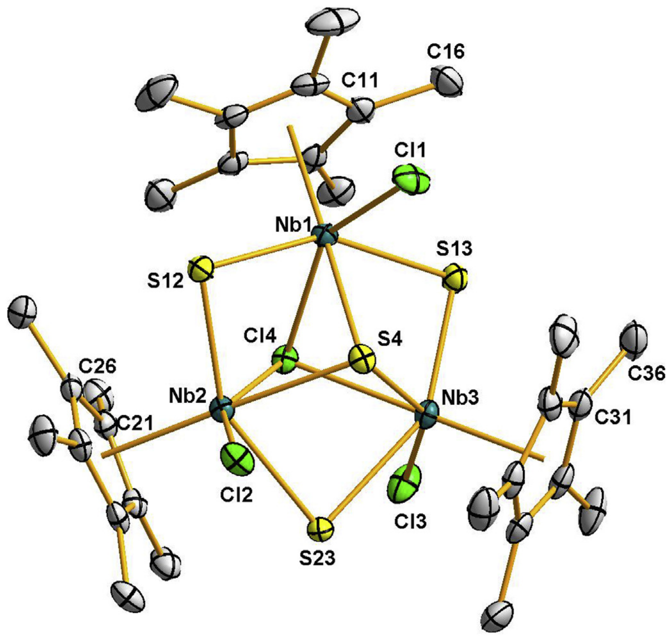
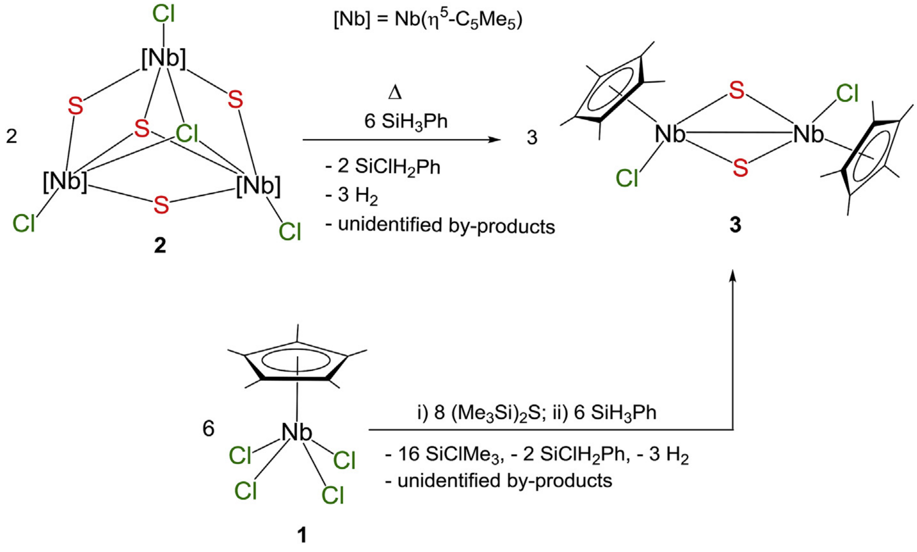


Fig. 2. Molecular structure of compound **2**. Thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity. Ranges or averaged values for selected lengths (Å) and angles (deg): $Nb\cdots Nb$ 3.378(3)-3.617(3), Nb–S 2.334(2)-2.694(3), Nb–Cl 2.456(2)-2.593(2), Nb–Cl4/S4–Nb 84.1(1)-93.3(1), Seq-Nb-Seq 149.6(1)-150.7(1), Seq-Nb-Cl4/S4 74.0(1)-86.7(1), Nb–*S*–Nb 84.1(1)-93.3(1), Cl4–Nb–S4 73.5(1)-74.7(1).

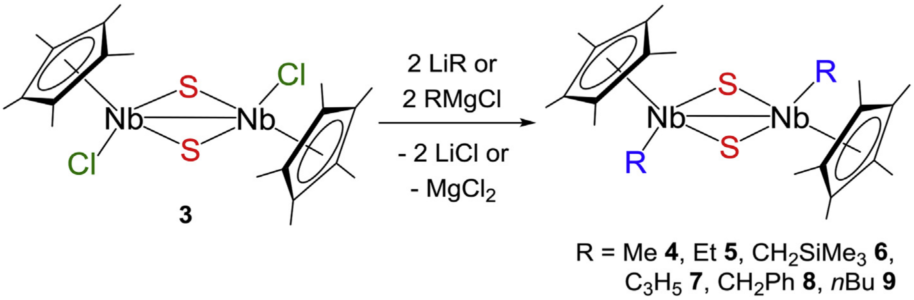
Following the same synthetic protocol found for tantalum to obtain group 5 species in low oxidation states, **2** was treated with several reducing agents, such as Na/Hg, Mg, 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene or SiH_3Ph. All reactions carried out with **2** afforded the diamagnetic dimetallic niobium(IV) sulfide derivative $[Nb_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$ (**3**). However, the best results were obtained by thermal treatment of compound **2** with SiH_3Ph (see Scheme 2 and Experimental Section). The reaction of **2** with SiH_3Ph was monitored by ^1H NMR spectroscopy in benzene-d_6 solution at room temperature revealing H_2 (*δ* 4.46) and $SiClH_2Ph$ (*δ* 5.06) formation along with other volatile unidentified products. Furthermore, one-pot syntheses of **3** has been achieved from reaction of **1**, $(Me_3Si)_2S$ and SiH_3Ph in toluene. Complex **3** has been characterized by elemental analysis and spectroscopic methods (IR, ^1H NMR, $^{13}C\{^1H\}$ NMR), as discussed below.

After similar salt metathesis strategies used for preparing dinuclear alkyl tantalum(IV) species, we accessed a series of dinuclear niobium(IV) alkyl/aryl complexes $[Nb_2(\eta^5\text{-}C_5Me_5)_2R_2(\mu\text{-}S)_2]$ (R = Me **4**, CH_2Me **5**, CH_2SiMe_3 **6**, C_3H_5 **7**, CH_2Ph **8**, *n*Bu **9**) in moderate-high yields. These reactions proceeded smoothly by treatment of **3** with the stoichiometric amounts of LiR (R = CH_2SiMe_3, *n*Bu), $[Mg(CH_2Ph)_2(thf)_2]$ or MgClR (R = Me, CH_2Me, C_3H_5) at room temperature in toluene or hexane, as outlined in Scheme 3. All the synthesized complexes were characterized by elemental analysis, spectroscopic methods (IR, NMR), and, in case of **6** and **7**, by X-ray diffraction analysis.

X-ray suitable crystals were obtained by cooling of a concentrated hexane or toluene solution of **6** and **7** to −20 °C respectively.



Scheme 2. Synthesis of sulfur-bridged niobium complex **3.**



Scheme 3. Preparation of dinuclear niobium alkyl complexes **4**–**9**.

The molecular structures are shown in Fig. 3, together with selected bond distances and angles. These complexes consist of dinuclear species comprising two Nb(η^5-C_5Me_5)R (R = CH_2SiMe_3, C_3H_5) units bridged by two sulfur ligands, where the geometry around both niobium atoms is close to a three-legged piano stool arrangement, with the two η^5-C_5Me_5 and alkyl ligands located in mutually *trans* orientation. The short Nb···Nb distances, 2.978(1) Å in **6** and 3.141(2) Å in **7** could be indicative of the presence of a bonding interaction between the two niobium centers, being the distance clearly influenced by the donor capability of the allyl ligand

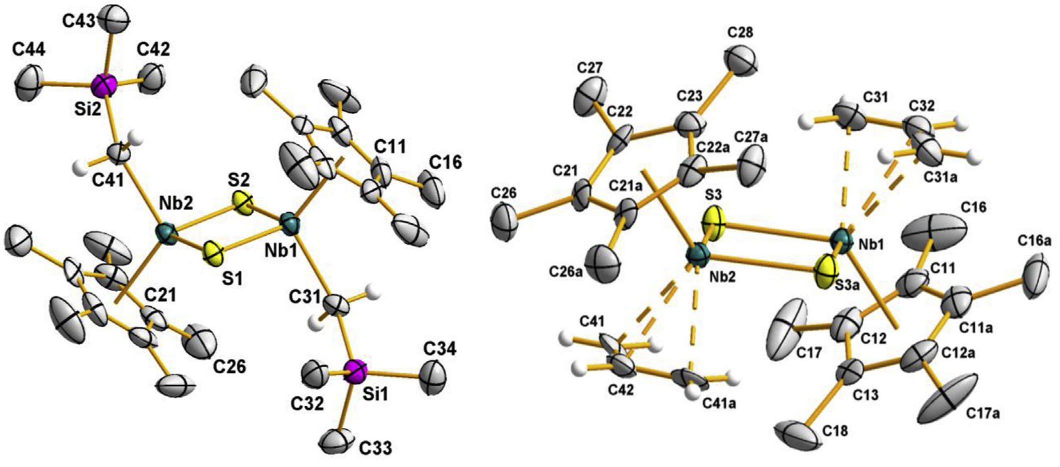


Fig. 3. Molecular structures of compounds **6** (left), and **7** (right). Thermal ellipsoids are at 50% probability. Hydrogen atoms are omitted for clarity. Selected averaged lengths (Å) and angles (°) for **6**: Nb–S 2.346(9), Nb–C31/41 2.177(1), Nb–Nb 2.978(1), Nb–*S*–Nb 78.8(1), *S*–Nb–S 101.2(1); **7**: Nb–S 2.384(1), Nb–C31/41 2.388(4), Nb–C32/42 2.40(1), Nb–Nb 3.141(2), Nb–*S*–Nb 82.4(1), *S*–Nb–S 97.6(1).

through the π-bonding system [9]. The Nb_2S_2 cores show a value of 360° for the sum of the S–Nb–S and Nb–S–Nb angles, in agreement with a planar geometry, but the different Nb···Nb distances with almost equal Nb–S lengths lead to a wider Nb–S–Nb angles in compound **7**.

The ^1H and ^{13}C NMR spectra of complexes **4**–**9** revealed a diamagnetic behavior in solution, and showed the equivalence of the η^5-C_5Me_5 ligands, with only one signal in the ^1H NMR spectra ($\delta = 1.51$–2.05) and two in the $^{13}C\{^1H\}$ NMR spectra ($\delta = 12.2$–13.3 C_5Me_5; 115.1–119.6 C_5Me_5), according to the spatial disposition found in the solid state for **6** and **7**. The alkyl groups [NbR; R = CH_2Me (**5**), CH_2SiMe_3 (**6**), CH_2Ph (**8**), $CH_2CH_2CH_2Me$ (**9**)] show signals for the α-hydrogens at −1.02 (**5**), −1.82 (**6**), −0.09 (**8**), −1.02 (**9**) ppm, slightly shifted downfield with respect to those reported for the dinuclear tantalum derivatives $[Ta_2(\eta^5\text{-}C_5Me_5)_2R_2(\mu\text{-}S)_2]$ (R = CH_2Me, CH_2SiMe_3) [6]. However, the $^{13}C\{^1H\}$ NMR resonances for the alkyl α-carbon, δ 57.0 (**5**), and 58.1 (**6**) (not observed for compounds **8** and **9**), have similar chemical shifts to those found for the mentioned tantalum(IV) alkyl complexes.

The complex $[Nb_2(\eta^5\text{-}C_5Me_5)_2Me_2(\mu\text{-}S)_2]$ (**4**) is formed as a mixture of isomers. NMR spectra for this compound and assignments can be found in the Supplementary data (Figs. S5 and S6) and the Experimental Section respectively. Attempts carried out to separate both isomers modifying the experimental conditions (time reaction, temperature or absence of light) did not lead to the desired result. In addition, a variable-temperature ^1H NMR analysis recorded in tolune-d_8 over the range of 25–90 °C does not show coalescence or broadening of the (η^5-C_5Me_5) ligand or niobium-Me signals, and a negligible change in the *cis-trans* isomers ratio was observed. This experimental feature was also observed in solution for the analogous dinuclear sulfide tantalum complex, $[Ta_2(\eta^5\text{-}C_5Me_5)_2Me_2(\mu\text{-}S)_2]$, and the existence of *cis*/*trans* isomerism was described with the aid of density functional theory calculations [6]. Thus, a possible explanation for the niobium species would involve the metal-metal bond breaking and subsequent exchange between the methyl and pentamethylcyclopentadienyl ligands through a square-planar geometry of one of the metal centers, as shown in Fig. 4.

Finally, an analysis of the NMR spectra of compound **7** display the well-known η^1-η^3 allyl isomerization on the NMR timescale at room temperature. Thus, in the ^1H NMR spectrum recorded in toluene-d_8 the equivalence of all four methylene protons is observed, giving rise to an A_4X coupling pattern, characteristic of a dynamic behavior. In addition, the ^{13}C NMR spectrum displays the resonances for the methyne and methylene carbon at δ 108.9 and 69.3 respectively. The low-temperature ^1H NMR spectra of **7** recorded over the temperature range of −70 to 25 °C (Fig. 5) do not show the split of the doublet; only a progressive broadening of the methylene protons signal that practically disappears into the base line (see also Fig. S15), whereas the methyne proton resonance remains sharp. This experimental feature was studied by density functional theory calculations for the analogous tantalum compound $[Ta_2(\eta^5\text{-}C_5Me_5)_2(C_3H_5)_2(\mu\text{-}S)_2]$. The results indicated that the η^3-allyl coordination mode was the most favored for both allyl groups, consistent with the crystal structure determined for compound **7**; although, with small differences between the η^3/η^1 and η^3/η^3 configurations. In addition, the low kinetic barrier determined for the η^1-η^3 allyl ligand rearrangement also explained the dynamic behavior observed in solution [6].

3. Conclusions

In summary, the trinuclear complex of composition $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ can be prepared in a direct fashion from the mononuclear niobium complex $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$, as building block, and $(Me_3Si)_2S$, as sulfur source. Furthermore, the reduction of the trimetallic complex with SiH_3Ph rendered the dinuclear species $[Nb_2(\eta^5\text{-}C_5Me_5)_2Cl_2(\mu\text{-}S)_2]$ in a nearly quantitative way. Likewise, using the latter as real starting material, a series of dinuclear cyclopentadienyl sulfide metal complexes have been synthesized, in which the introduction of the pentacyclopentadienyl ligand significantly improves the synthesis and characterization of the complexes formed. By applying the synthetic protocol followed here, further studies are now in progress.

4. Experimental Section

4.1. General procedures

All manipulations were carried out under a dry argon atmosphere using Schlenk-tube and cannula techniques or in a conventional argon-filled glovebox. Solvents were carefully refluxed over the appropriate drying agents and distilled prior to use: C_6D_6 and hexane (Na/K alloy), $CDCl_3$ (CaH_2), tetrahydrofurane (Na/benzophenone) and toluene (Na). Starting material $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$ was prepared following reported procedure for titanium [10], $LiCH_2SiMe_3$, [11] and $[Mg(CH_2Ph)_2(thf)_2]$ [12] were synthesized according to published procedures. Grignard reagents MgClR (R = Me, 3 M in thf; CH_2Me, C_3H_5, 2 M in thf), Li*n*Bu (1.6 M in hexane), $NbCl_5$, $(Me_3Si)_2S$ and SiH_3Ph were purchased from Aldrich and were used without further purification. Microanalyses (C, H, N, S) were performed in a LECO CHNS-932 microanalyzer. Samples for IR spectroscopy were prepared as KBr pellets and recorded on the PerkinElmer IR-FT Frontier spectrophotometer (4000-400 cm^{-1}). ^1H and ^{13}C NMR spectra were obtained by using Varian NMR System spectrometers: Unity-300 Plus, Mercury-VX, Unity-500 and Bruker 400 Ultrashield, and reported with reference to solvent resonances.

4.1.1. Preparation of $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (2)

A toluene (5 mL) solution of $(Me_3Si)_2S$ (0.96 g, 5.40 mmol) was added to $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) (1.50 g, 4.05 mmol) in toluene (30–40 mL) placed into a Carius tube (100 mL) with a Young's valve. The argon pressure was reduced, and the reaction mixture was heated to 100 °C for 72 h. The resulting solution was filtered, and the solvent removed under vacuum to afford **2** as a red solid

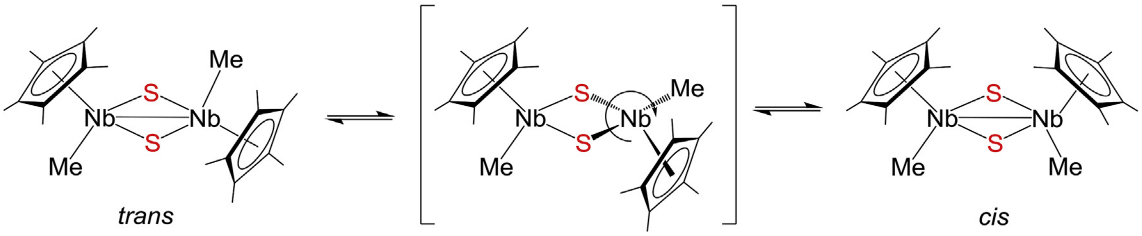


Fig. 4. Proposal mechanism for the isomerization of complex **4**.

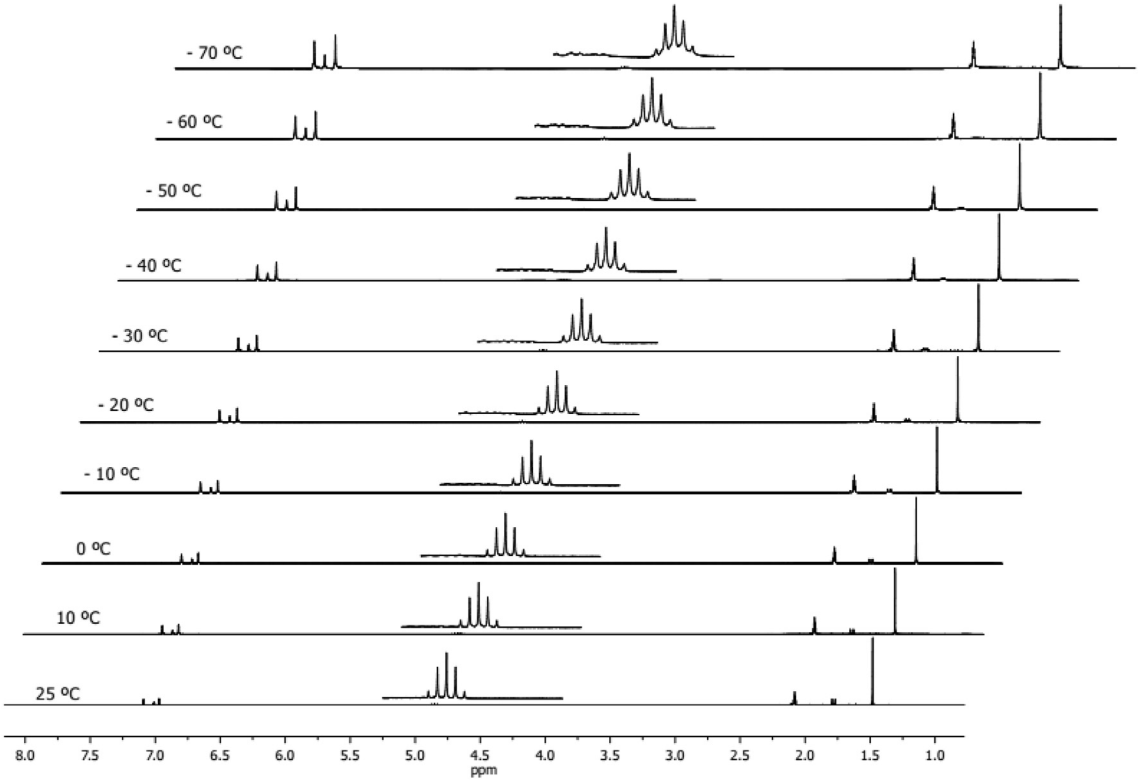


Fig. 5. Variable-temperature ^{1}H NMR spectra for compound **7** (C_7D_8, 500 MHz).

(Yield: 1.03 g, 80%). A crystallographic analysis was carried out with crystals of **2** obtained from a C_6D_6 solution in an NMR tube. IR (KBr, cm^{-1}): $\bar{\upsilon} = 2998$, 2964 (w, CH aliph.), 2911 (m, CH aliph.), 1494 (s, CC), 1435 (s, CC), 1377 (vs, CC), 1019 (m, CC). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.75$ (s, 45H, C_5Me_5). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = not detected (C_5Me_5), 13.1 (C_5Me_5). Elemental analysis (%) calcd. for $C_{30}H_{45}Cl_4Nb_3S_4$ (954.47): C, 37.75; H, 4.75; found: C, 37.22; H, 4.84. Repeated attempts to obtain good sulfur analyses for complex **2** were unsuccessful.

4.1.2. *Synthesis of [Nb$_2$(η^5-C$_5$Me$_5$)$_2$Cl$_2$(μ-S)$_2$] (**3**)*

METHOD A: SiH_3Ph (0.34 g, 3.14 mmol) was added to a toluene solution (40–45 mL) of $[Nb_3(\eta^5\text{-}C_5Me_5)_3Cl_3(\mu_3\text{-}Cl)(\mu\text{-}S)_3(\mu_3\text{-}S)]$ (**2**) (1.00 g, 1.05 mmol) placed into a Carius tube (100 mL) with a Young's valve. The argon pressure was reduced, and the reaction mixture was heated to 100 °C for 72 h, and then filtered. The resulting dark green solid **3** (0.84 g, 90%) was obtained after drying under vacuum. **METHOD B:** To a suspension of $[Nb(\eta^5\text{-}C_5Me_5)Cl_4]$ (**1**) (1.50 g, 4.05 mmol) in toluene (30–40 mL) placed in a Carious-tube (100 mL) with a Young's valve was added $(Me_3Si)_2S$ (0.96 g, 5.39 mmol) dissolved in a few milliliters of toluene. The argon pressure was reduced, and the reaction mixture was heated to 90 °C for 72 h. After cooling the reaction mixture was added SiH_3Ph (0.44 g, 4.05 mmol) and the reaction was heated once more to 90 °C for 72 h. The resulting solution was filtered, and the solvent removed under vacuum to afford **3** as a dark green solid (Yield: 1.13 g, 94%). IR (KBr, cm^{-1}): $\bar{\upsilon} = 2980$, 2953 (w, CH aliph.), 2906 (m, CH aliph.), 1480, 1424 (m, CC), 1377, 1023 (s, CC). ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.89$ (s, 30H, C_5Me_5). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 120.3$ (C_5Me_5), 12.9 (C_5Me_5). Elemental analysis (%) calcd. for $C_{20}H_{30}Cl_2Nb_2S_2$ (591.30): C, 40.62; H, 5.11; S 10.84; found: C, 40.82; H, 4.99; S 10.61.

4.1.3. *Synthesis of [Nb$_2$(η^5-C$_5$Me$_5$)$_2$Me$_2$(μ-S)$_2$] (**4**)*

To a solution of **3** (0.50 g, 0.85 mmol) in toluene (40 mL) placed in a 100 mL Schlenk vessel was added a thf solution of MgClMe (0.56 mL, 1.70 mmol) at 0 °C. After stirring for 4 h at room temperature, the reaction mixture was filtered through Celite. After that, the filtrate was concentrated to a few milliliters under vacuum. The solution was then cooled to −20 °C to give a a green solid crystalline (Yield: 0.45 g, 97%). The ^{1}H NMR spectra of both filtrate and crystalline solid display an identical mixture of *cis*- and *trans*-isomers in a ≈70:30 ratio. IR (KBr, cm^{-1}): $\bar{\upsilon} = 2978$ (m, CH aliph.), 2899 (s, CH aliph.), 1481 (w, CC), 1427 (m, CC), 1376 (s, CC), 1025 (s, CC). ^{1}H NMR (300 MHz, C_6D_6): **4**-*cis/trans* $\delta = 2.01$, 1.95 (s, 30H, C_5Me_5), −0.41, −1.58 (s, 6H, Nb–*Me*). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 115.1$, 117.6 (C_5Me_5), 32.1, 23.2 (Nb–*Me*), 12.4, 12.7, (C_5Me_5). Elemental analysis (%) calcd. for $C_{22}H_{36}Nb_2S_2$ (550.46): C, 48.00; H, 6.59; S 11.65; found: C, 47.13; H, 6.12; S 11.74.

4.1.4. *Synthesis of [Nb$_2$(η^5-C$_5$Me$_5$)$_2$Et$_2$(μ-S)$_2$] (**5**)*

To a solution of **3** (0.50 g, 0.85 mmol) in toluene (40 mL) placed in a 100 mL Schlenk vessel was added a thf solution of MgClEt (0.84 mL, 1.70 mmol) at 0 °C. After stirring for 4 h at room temperature, the reaction mixture was filtered through Celite, and the solvent was then removed in vacuum to yield **5** as a brown-orange solid (Yield: 0.45 g, 92%). IR (KBr, cm^{-1}): $\bar{\upsilon} = 2976$ (m, CH aliph.), 2901 (s, CH aliph.), 1486, 1427 (w, CC), 1375 (s, CC), 1027 (s, CC). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 2.01$ (s, 30H, C_5Me_5), 0.67 (t, 6H, $J = 9$ Hz, CH_3CH_2), −1.02 (c, 4H, $J = 9$ Hz, CH_3CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): $\delta = 117.5$ (C_5Me_5), 57.0 (CH_3CH_2), 15.8 (CH_3CH_2), 12.5 (C_5Me_5). Elemental analysis (%) calcd. for $C_{24}H_{40}Nb_2S_2$ (578.52): C, 49.83; H, 6.97; S 11.08; found: C, 49.30; H, 6.86; S 10.89.

4.1.5. *Synthesis of [Nb$_2$(η^5-C$_5$Me$_5$)$_2$(CH$_2$SiMe$_3$)$_2$(μ-S)$_2$] (**6**)*

A 100 mL Schlenk vessel was charged in the glovebox with **3**

(0.50 g, 0.85 mmol), $LiCH_2SiMe_3$ (0.16 g, 1.70 mmol), and toluene (50–60 mL). After stirring for 24 h at room temperature, the reaction mixture was filtered through a medium porosity glass frit, and the solvent was then removed in vacuum to yield **6** as a green solid (Yield: 0.45 g, 77%). IR (KBr, cm^{-1}): $\bar{\upsilon} = 2957$ (w, CH aliph.), 2905 (m, CH aliph.), 1485 (w, CC), 1426 (m, CC), 1377 (s, CC), 1024 (s, CC). ^1H NMR (300 MHz, C_6D_6): δ = 2.01 (s, 30H, $C_5\mathit{Me}_5$), 0.02 (s, 18H, Me_3SiCH_2), –1.82 (s, 4H, $Me_3SiC\mathit{H}_2$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 117.1 (C_5Me_5), 58.1 (Me_3SiCH_2), 13.3 ($C_5\mathit{Me}_5$), 4.1 (Me_3SiCH_2). Elemental analysis (%) calcd. for $C_{28}H_{52}Nb_2S_2Si_2$ (694.83): C, 48.40; H, 7.54; S 9.23; found: C, 48.17; H, 6.90; S 8.38.

4.1.6. Synthesis of $[Nb_2(\eta^5\text{-}C_5Me_5)_2(C_3H_5)_2(\mu\text{-}S)_2]$ (7)

To a solution of **3** (0.50 g, 0.85 mmol) in toluene (50–60 mL) placed in a 150 mL Schlenk vessel was added a thf solution of $MgCl(C_3H_5)$ (0.85 mL, 1.70 mmol) at 0 °C. The reaction mixture was filtered through Celite after stirring at room temperature for 4 h, and the solvent was then removed in vacuum to yield **7** as a red solid (Yield: 0.41 g, 81%). A crystallographic analysis was carried out with a single crystal of **7** obtained from a hexane solution. IR (KBr, cm^{-1}): $\bar{\upsilon} = 2973$ (m, CH aliph.), 2898 (s, CH aliph.), 1428 (m, CC), 1374 (s, CC), 1026 (s, CC). ^1H NMR (300 MHz, C_6D_6): δ = 4.91 (A_4X, 2H, $^3J = 12$ Hz, $CH_2C\mathit{H}CH_2$), 1.90 (A_4X, 8H, $^3J = 12$ Hz, $C\mathit{H}_2CHC\mathit{H}_2$), 1.51 (s, 30H, $C_5\mathit{Me}_5$). ^1H NMR (500 MHz, C_7D_8): δ = 4.85 (A_4X, 2H, $^3J = 10$ Hz, $CH_2C\mathit{H}CH_2$), 1.78 (A_4X, 8H, $^3J = 10$ Hz, $C\mathit{H}_2CHC\mathit{H}_2$), 1.48 (s, 30H, $C_5\mathit{Me}_5$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 119.6 (C_5Me_5), 108.8 ($CH_2\mathit{C}HCH_2$), 69.2 ($\mathit{C}H_2CH\mathit{C}H_2$), 12.3 ($C_5\mathit{Me}_5$). $^{13}C\{^1H\}$ NMR (125 MHz, C_7D_8): δ = 119.8 (C_5Me_5), 108.9 ($CH_2\mathit{C}HCH_2$), 69.3 ($\mathit{C}H_2CH\mathit{C}H_2$), 12.3 ($C_5\mathit{Me}_5$). MS (EI, 70 eV), *m*/*z* (%): 602 (3) $[M]^+$, 561 (12) $[M - C_3H_5]^+$, 520 (2) $[M\text{-}2C_3H_5]^+$. The compound was repeatedly submitted to elemental analysis, but we failed to obtain satisfactory results.

4.1.7. Synthesis of $[Nb_2(\eta^5\text{-}C_5Me_5)_2(CH_2Ph)_2(\mu\text{-}S)_2]$ (8)

A 100 mL Schlenk vessel was charged in the glovebox with **3** (0.40 g, 0.68 mmol), $[Mg(CH_2Ph)_2(thf)_2]$ (0.24 g, 0.68 mmol), and toluene (50–60 mL). After stirring for 24 h at room temperature, the reaction mixture was filtered through a medium porosity glass frit, and the solvent was then removed in vacuum to yield **8** as a green solid (Yield: 0.22 g, 46%). IR (KBr, cm^{-1}): $\bar{\upsilon} = 3051$, 3013 (w, CH arom.), 2976, 2954 (w, CH aliph.), 2904 (m, CH aliph.), 2851 (w, CH aliph.), 1593 (m, CC), 1487 (m, CC), 1426 (w, CC), 1377 (m, CC), 1026 (s, CC). ^1H NMR (500 MHz, C_6D_6): $\delta = 7.03$ (t, 4H, $J = 8$ Hz, H_m, $CH_2\mathit{Ph}$), 6.81 (t, 2H, $J = 8$ Hz, H_p, $CH_2\mathit{Ph}$), 6.68 (d, 4H, $J = 8$ Hz H_o, $CH_2\mathit{Ph}$), 1.85 (s, 30H, $C_5\mathit{Me}_5$), –0.09 (s, 4H, $C\mathit{H}_2Ph$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): $\delta = 144.7$ (C_{ipso}, $CH_2\mathit{Ph}$), 129.2 (C_p, $CH_2\mathit{Ph}$), 127.9 (C_m, $CH_2\mathit{Ph}$), 122.9 (C_o, $CH_2\mathit{Ph}$), 118.6 (C_5Me_5), not detected ($\mathit{C}H_2Ph$), 12.2 ($C_5\mathit{Me}_5$). Elemental analysis (%) calcd. for $C_{34}H_{44}Nb_2S_2$ (702.66): C, 58.12; H, 6.31; S 9.13; found: C, 57.54; H, 6.03; S 8.84.

4.1.8. Synthesis of $[Nb_2(\eta^5\text{-}C_5Me_5)_2(CH_2CH_2CH_2Me)_2(\mu\text{-}S)_2]$ (9)

To a solution of **3** (0.26 g, 0.44 mmol) in toluene (50–60 mL) placed in a 150 mL Schlenk vessel was added a hexane solution of Li*n*Bu (0.55 mL, 0.88 mmol) at 0 °C. The reaction mixture was filtered through Celite after stirring at room temperature for 4 h, and the solvent was then removed in vacuum to yield **9** as a green solid (Yield: 0.06 g, 21%). IR (KBr, cm^{-1}): $\bar{\upsilon} = 2957$, 2907 (m, CH aliph.), 2848 (w, CH aliph.), 1486 (w, CC), 1456 (w, CC), 1427 (w, CC), 1374 (s, CC), 1025 (m, CC). ^1H NMR (300 MHz, C_6D_6): δ = 2.05 (s, 30H, $C_5\mathit{Me}_5$), 0.95–0.60 (m, 14H, $CH_2C\mathit{H}_2C\mathit{H}_2\mathit{Me}$), –1.02 (m, 4H, $C\mathit{H}_2CH_2CH_2Me$). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 117.4 (C_5Me_5), not detected ($\mathit{C}H_2CH_2CH_2Me$), 33.7 ($CH_2\mathit{C}H_2CH_2Me$), 29.0 ($CH_2CH_2\mathit{C}H_2Me$), 13.7 ($CH_2CH_2CH_2\mathit{Me}$), 12.3 ($C_5\mathit{Me}_5$). Elemental analysis (%) calcd. for $C_{28}H_{48}Nb_2S_2$ (634.62): C, 53.00; H, 7.62; S 10.10; found: C, 52.31; H, 6.97; S 9.40.

4.2. X-ray structure determinations

Crystals of **2** were obtained from a C_6D_6 solution in an NMR tube at room temperature, while complexes **6**, and **7** were obtained by slow cooling at –20 °C of the corresponding toluene or hexane solutions respectively. Single crystals were coated with mineral oil, mounted on Mitegen MicroMounts with the aid of a microscope, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 150 K (**2**) or 200 K (**6**, **7**) on a Bruker-Nonius KappaCCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and an Oxford Cryostream 700 unit. Crystallographic data for all complexes is presented in Table S1 in the Suplemantary data.

The structures were solved, by using the WINGX package [13], by direct methods (SHELXS-2013 for complexes **2**, and **7**) [14] or intrinsic phasing (SHELXT-2014 for **6**) [15] and refined by least-squares against F^2 (SHELXL-2014) [16]. Crystals of **2** crystallized with three benzene solvent molecules. Additionally, it was not possible to determine unequivocally the identity of the μ_3-bridging atoms, thus S4 and Cl4 bridging atoms were refined with the aid of the EXYZ and EADP Shelx's commands to obtain occupancies of 46% and 54%, respectively. All the hydrogen atoms for the three structures were positioned geometrically and refined by using a riding model while all the non-hydrogen atoms were refined anisotropically.

Compound **7** crystallizes with a variable amount of magnesium chloride, which has complicated the obtaining of good single crystals, the structural determination and a good elemental analysis. Once the chemical model was obtained, a few peaks remained in the map of densities that could not be refined conveniently by assigning them to some type of specific atom (with different occupancies), nor trying to execute the squeeze protocol (PLATON). Probably those peaks correspond to disordered magnesium halide, unfortunately, all the attempts we have made to obtain better crystals have been unsuccessful, but we sincerely believe that this crystalline structure does not offer any doubt about the anti-disposition of the allyl ligands or the π-type bonding system. Finally, a twin law could not be found for hkl data using programs such as TwinRotMat or Rotax.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.022.

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