Communications

Activation and Cleavage of the C-S Bond in Nb-S^{t}Bu Complexes. Syntheses and Structural Characterizations of the Tetrahedral and Trigonal Bipyramidal $[Ph_4P][Nb^V(S)_2(^tBuS)_2]$ and $[Et_4N][Nb^V(S)(^tBuS)_4]$ Complexes

D. Coucouvanis,* Saleem Al-Ahmad, C. G. Kim, and Sang-Man Koo

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055

Received March 18, 1992

Early transition metal thiometalate complexes containing M=S units can be obtained by various methods that include (a) the synthesis of MS_4^{n-} anions by the action of H_2S on oxometalates in strongly alkaline solution[1] (M = V, n = 3; M = Mo, n = 2; M = W, n = 2; M = Re, n = 1), (b) the reaction of oxo[2] or alkoxido[3] complexes with $(Me_3Si)_2S$, (c) the high-temperature synthesis of K_nMS_4 "salts" from the elements,[4] and (d) the reaction of M=O groups with B_2S_3.[5] Another route to early transition metal sulfido groups (or derivatives of such groups) is available via C-S bond cleavage reactions of coordinated aliphatic thiolate ligands.[6b-d] Representative examples of these C-S bond cleavage reactions can be found in Nb-S[6] and Zr-S[7] chemistry. The C-S bond cleavage in Zr-SR compounds appears to proceed via two parallel pathways. With *tert*-butyl mercaptans both isobutane and isobutene are found as byproducts.[8] The former very likely is the end result of homolytic C-S bond cleavage, while the latter arises from heterolytic C-S bond cleavage that proceeds via a carbonium ion mechanism and β-proton elimination.[9] Not unexpectedly, this reaction does not readily occur with benzenethiolate ligands.[8] Among the known thiolate complexes or "mixed"-ligand complexes that contain thiolate ligands, and S^{2-} ligands generated by C-S bond cleavage reactions, are included the following: $[Nb(S)(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$,[6a] $[(Cp_2Nb)_2(\mu\text{-}S)_2]$,[6b] $[Re(S)(SCH_2CH_2S)_2]$,[6f] $[Nb(S)(Cl)_4]^-$,[6d] and $Li_4Nb_4S_2(SPh)_{12}$.[6c] The reductive cleavage of C-S bonds in the industrially important hydrodesulfurization reaction is catalyzed by various metal sulfides.[10] As a result, an understanding of the factors that influence the activation of C-S bonds in coordinated thiolate ligands remains an important goal of our studies in M-S coordination chemistry.

In a previous communication we reported on the synthesis and structural characterization of homoleptic, six-coordinate complexes of Nb(IV), Nb(V), and Ta(V) with monodentate, arenethiolate ligands.[11] The absence of sulfido ligands in these complexes attests to the difficulty in cleaving the Ph-S bond. In this communication we report on the synthesis and structural characterization of $[Ph_4P][Nb^V(S)_2(^tBuS)_2]$ (I) and $[Et_4N][Nb^V(S)(^tBuS)_4]$ (II), two mixed-ligand complexes of Nb(V) that contain sulfido ligands obtained as result of cleavage of the C-S bond in the $^tBuS^-$ ligands. The reaction of $NbCl_5$ with Na^{t}BuS in CH_3CN solution in ~1:6 molar ratio proceeds readily at ambient temperature, under an argon atmosphere, to give (as evidenced by ^1H NMR spectroscopy) a 1:9 mixture of the anions of I and II, $[Nb^V(S)_2(^tBuS)_2]^-$ and $[Nb^V(S)(^tBu\text{-}S)_4]^-$, which can be isolated in modest yield (ca. 50%) as red-orange, crystalline, Et_4N^+ salts.[12] The 1:6 molar ratio is the optimum ratio that gives the highest yield of II for a reaction-isolation time of ~1 h. Upon standing in CH_3CN solution, the relative concentrations of the anions slowly change in favor of I. The conversion of II to I occurs at a faster rate when solutions that contain both of these anions are treated with an excess of Na^{t}BuS. These observations are consistent with a $^tBuS^-$-assisted deprotonation of a $^tBu^+$ nascent carbonium ion that is obtained as a result of the polarization and activation of the C-S bond in the coordinated $^tBuS^-$ ligand. When not supplied externally, the $^tBuS^-$ base may become available as a result of ligand dissociation from II. Such a dissociation is likely to occur in view of the weakly bound axial $^tBuS^-$ ligand in II (vide infra). The isobutene, expected to be present in the aftermath of a $^tBuS^-$-assisted $^tBu^+$ deprotonation reaction, has been detected by a mass spectrometric study of the reaction byproducts. In this study, isobutane also was detected and, as in the Zr-S^{t}Bu system, it indicates that the C-S bond cleavage also may proceed homolytically. This contention is supported by the fact that the fragmentation pattern of deuterated isobutane was observed in the mass spectrum of the byproducts when the synthesis of I was carried out in CD_3CN solution. The presence of $(CD_2CN)_2$ in the products further suggests that $DC(CH_3)_3$ is obtained by deuterium abstraction from the solvent by a *tert*-butyl radical.

The synthesis of pure I also is accomplished by the oxidation of II with a stoichiometric amount of elemental sulfur in CH_3CN solution (eq 1), and the $[Ph_4P]^+$ "salt" I is isolated as yellow-brown crystals in 30% yield. In this reaction elemental sulfur

(1) Muller, A.; Diemann, E.; Jostes, R.; Bogger, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934 and references therein.
(2) (a) Money, J. K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297-3302. (b) Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809.
(3) (a) Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 7784. (b) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9654.
(4) Latroche, M.; Ibers, J. A. *Inorg. Chem.* **1990**, *29*, 1503.
(5) Callahan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211.
(6) (a) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 1358-1359. (b) Skripkin, Yu. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285-292. (c) Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1258. (d) Seela, J. L.; Huffman, J. C.; Christou, G. *Polyhedron* **1989**, 1797. (e) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 86-87. (f) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L225-L226.
(7) (a) Coucouvanis, D.; Lester, R. K.; Kanatzidis, M. G.; Kessissoglou, D. P. *J. Am. Chem. Soc.* **1985**, *107*, 8279. (b) Coucouvanis, D.; Hadjikyriacou, A. I.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1224.
(8) Hadjikyriacou, A. Ph.D. Thesis, University of Michigan, 1988.
(9) (a) Boorman, P. M.; O'Dell, B. D. *J. Chem. Soc., Dalton Trans.* **1967**, 932. (b) Boorman, P. M.; Chiveri, T.; Mahadev, K. N. *Inorg. Chim. Acta* **1976**, *19*, L35.
(10) (a) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (b) Topsoe, J.; Clausen, B. S. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 395. (c) Weisser, O.; Landa, S. *Sulfide Catalysts: Their Properties and Applications*; Pergamon Press: London, 1973.
(11) Koo, S.-M.; Bergero, R.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1990**, *29*, 4844.
(12) Analytical data for I are as follows. Calcd for $NbPS_4C_{32}H_{38}$ (MW 674.8): C, 57.0; H, 5.69. Found: C, 57.1; H, 5.52. The ^1H-NMR spectrum in CD_3CN solution shows a single resonance for the S^{t}Bu ligands at 1.38 ppm and a multiplet between 7.9 and 7.6 ppm due to the Ph_4P^+ cation. The ^1H-NMR spectrum of II in CD_3CN solution shows two resonances for the S^{t}Bu ligands at 1.38 and 1.58 ppm in a ~1:9 ratio and the Et_4N^+ resonances at 3.7 ppm (q) and 1.2 ppm (t). In view of the difficulties encountered in obtaining II without an admixture of I, not analytical data were obtained for II.

0020-1669/92/1331-2996$03.00/0

Table I. Summary of Interatomic Distances (Å) and Angles (deg) in $(Ph_4P)[Nb(S)_2(S^tBu)_2]$ (I), $(Et_4N)[Nb(S)(S^tBu)_4]$ (II), $(Ph_4P)[Nb(S)(SPh)_4]$ (III), and $Na(THF)_3Nb(SPh\text{-}pMe)_6$ (IV)

	I	II	III[a]	IV[b]
		Distances[c]		
M–S_t[d]	2.187	2.194 (2)	2.171 (2)	
range	2.184 (3), 2.191 (4)			
M–S_L	2.377	2.38 (1)[e]	2.441 (2)	2.488 (9),[f] 2.405 (3)[g]
range	3.374 (5), 2.380 (4)	2.364 (6)–2.407 (2)	2.440 (2)–2.442 (2)	2.392 (7)–2.506 (7)
M–$S_{L,ax}$		2.567 (2)[h]		
C–S_L	1.87	1.86 (3)		1.76 (2)
range	1.85 (1), 1.89 (1)	1.84 (2)–1.91 (2)		1.71 (2)–1.79 (2)
		Angles[c]		
S_t–M–S_t[b]	111.8 (1)			
S_L–M–S_L[b]	111.5 (1)	117.8 (2.8)[e]		
range		115.3 (2)–122.3 (1)		
S–M–S	109.5 (4.9)[i]	81.2 (2.3)[j]		78.4 (3),[f] 86.1 (3)[g]
range	103.0 (2)–115.0 (2)	77.6 (1)–84.0 (2)		77.2 (2)–92.1 (2)
S–M–S		98.7 (5)[k]	109.8 (7)[k]	
range		97.9 (1)–99.3 (3)	108.2 (1)–110.9 (1)	
M–S_L–C_L	114.2	120.6 (2.4)	113.5 (4)	115.3 (6)
range	113.7 (6), 114.6 (6)	115.2 (5)–124.1 (3)	112.9 (2)–113.8 (3)	114.2 (8)–116.3 (9)

[a] From ref 6d. [b] From ref 11. [c] Mean values of crystallogrpahically independent, chemically equivalently, structural parameters. The number in parentheses represents the larger of the individual standard deviations or the standard deviation from the mean, $\sigma = [\sum_{i=1}^{N}(x_i - \bar{x})^2/N(N-1)]^{1/2}$. [d] S_t = terminal sulfido ligands. [e] Equatorial Nb–S^{t}Bu distances or angles. [f] Distances affected by counterion (Na^+) PhS^- interactions. [g] Unperturbed Nb–SPh distances. [h] Nb–S distance with the axial S^{t}Bu ligand. [i] All S–M–S angles. [j] $S_{L,ax}$–Nb–$S_{L,eq}$ angles. [k] S_t–Nb–$S_{L,eq}$ angles.

oxidizes two of the coordinated $^-S^tBu$ ligands with a concomitant generation of the S^{2-} ligand. The reaction of $NbCl_5$ with equimolar amounts of NaS^tBu has been reported previously to give $[Nb^V(S)(Cl)_4]^-$, which was used subsequently in the synthesis of the $[Nb^V(S)(SPh)_4]^-$ anion of III.[6d] The latter has a square pyramidal structure with the terminal sulfido ligand located in the axial position.

$$[Nb^V(S)(S^tBu)_4]^- + {}^1/_8S_8 \rightarrow [Nb^V(S)_2(S^tBu)_2]^- + {}^tBuSS^tBu \quad (1)$$

The structures of I and II were determined.[13] In the structure of the latter, the $[Nb^V(S)(S^tBu)_4]^-$ and $[Nb^V(S)_2(S^tBu)_2]^-$ anions occupy the same crystallographic site in a 9:1 ratio and "share" two of the S^{t}Bu ligands. The structures of the anion in I and the major anion component of II are shown in Figure 1. Selected structural data are shown in Table I and are compared to corresponding data in the structures of III and $Na(THF)_3Nb^V(SPh\text{-}pMe)_6$ (IV).[13] The five-coordinate Nb^V ion in $[Nb^V(S)(S^tBu)_4]^-$ shows a distorted trigonal bipyramidal structure (S(4)–Nb–S(5) = 175.2°) in contrast to the square pyramidal structure adopted by the $[Nb^V(S)(SPh)_4]^-$ anion.[6d] The structural difference between II and III undoubtedly is due to the considerable steric demands of the S^{t}Bu ligands. The Nb atom in II is located 0.36 Å above the equatorial S(1)S(2)S(3) plane and toward the terminal sulfide ligand (S(5)). A strong trans influence is apparent in the very long (2.567 (2) Å) Nb–S(4) bond and, as suggested above, probably is reponsible for the instability of II and its facile conversion to I. The anion in I is tetrahedrally coordinated by two sulfido and two S^{t}Bu ligands. In both I and II, the Nb–S^{t}Bu bonds at 2.377 and 2.38 (1) Å, respectively, are shorter than the Nb^V–SPh bonds in III and IV, respectively, at 2.441 (2) and 2.43 Å and reflect the better donor properties of the S^{t}Bu ligands. The $[(Cp)_2Nb(SR)_2]^+$ complexes are structurally and electronically related to I with the isolobal η^5-Cp^- ligands in place of the terminal sulfido ligands. In these complexes[14] the Nb–SR bond lengths (R = Ph, 2.417 (1) Å; R = *p*-ClPh, 2.406 (3) and 2.420 (3) Å) also are longer than those in I. The Nb=S bond lengths in I and II at 2.187 and 2.194 (2) Å, respectively, are longer than Nb=S in III (2.171 (2) Å) and are found in the long side of a rather wide range that covers the

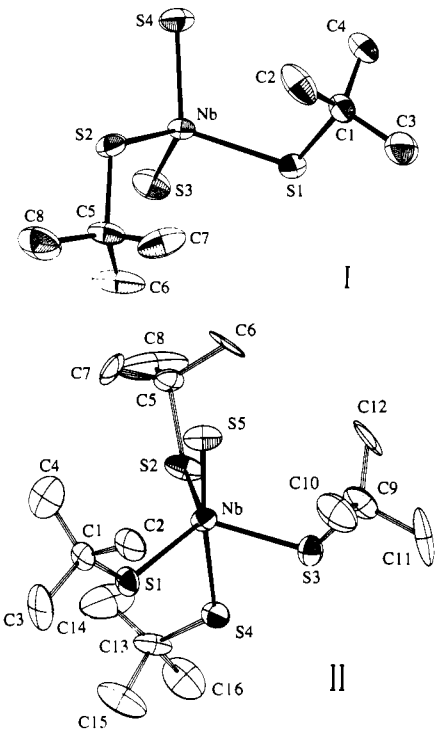

Figure 1.

(13) Crystal and refinement data: Yellow-brown crystals of $[Ph_4P][Nb^V(S)_2(S^tBu)_2]$ (I) are monoclinic, space group $P2_1/c$ with $a = 18.379$ (3) Å, $b = 11.247$ (4) Å, $c = 18.450$ (4) Å, $\beta = 117.46$ (1)°, and $Z = 4$. Brown crystals of $(Et_4N)[Nb^V(S)(S^tBu)_4]_{0.9}[Nb^V(S)_2(S^tBu)_2]_{0.1}$ (II) are monoclinic, space group $P2_1$ with $a = 10.218$ (3) Å, $b = 17.129$ (4) Å, $c = 10.229$ (4) Å, $\beta = 104.19$ (3)°, and $Z = 2$. Single-crystal X-ray diffraction data for both crystals were collected on a Nicolet R3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The site of the anion in II was found to be occupied by both $[Nb^V(S)(S^tBu)_4]^-$ (90%) and $[Nb^V(S)_2(S^tBu)_2]$ (10%). This ratio also was verified by ^{1}H-NMR spectroscopy. The refinement of the structures by full-matrix least-squares methods was based on 2375 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$) for I and 1998 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$) for II. Anisotropic temperature factors were used for all non-hydrogen atoms in I and II with the exception of the minority component sulfido ligands in II that were refined with isotropic temperature factors. At the current stage of refinement on 343 parameters for I and 288 parameters for II, with all atoms present in the asymmetric units, $R_w = 0.062$ and 0.058, respectively, for I and II.

(14) Darensbourg, M. Y.; Bischoff, C. J.; Houliston, S. A.; Pala, M.; Reibenspies, J. *J. Am. Chem. Soc.* **1990**, *112*, 6905–6912.

area from 2.085 (5) Å in $[Nb(S)Cl_4]^-$ [15] to 2.20 Å in $[Nb_6S_{17}]^{4-}$.[3a] The Nb–S stretching vibrations at 492 and 465 cm^{-1} for I and II, respectively, are within or close to the 552–483-cm^{-1} rangereported covered by the Nb=S group.[2b] The reactivity of the Nb=S bond toward electrophilic reagents and the utility of the very reactive I and II as reagents for the development of Nb–S chemistry currently are under investigation in our laboratory.

(15) Muller, U.; Klingelhofer, Z. *Z. Anorg. Chem.* **1984**, *510*, 109.

Acknowledgment. The support of this work by a grant from the National Science Foundation (CHE-9006069) is gratefully acknowledged.

Supplementary Material Available: Tables S1 and S2, containing listings of positional parameters, thermal parameters, and selected distances and angles of I and II (14 pages). Ordering information is given on any current masthead page.