Cleavage of a C–S Bond in $[Nb(SCH_2CH_2S)_3]^-$ Leading to Formation of a Sulfide and a tpdt Ligand in $[NbS(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]^-$

Kazuyuki Tatsumi,* Yoitsu Sekiguchi, and
Akira Nakamura*

Department of Macromolecular Science
Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

Roger E. Cramer* and John J. Rupp†

Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

Received October 24, 1985

As part of our efforts[1] to develop chemistry of group 5 transition metals with S-coordinated ligands, the first homoleptic ethane-1,2-dithiolate complexes of niobium,[2] $[A][Nb(SCH_2CH_2S)_3]$ (A = $Li(thf)_3$ (**1a**), Ph_4P (**1b**),[3] and Et_4N (**1c**)), were synthesized.[4] The coordination sphere defined by the six sulfur atoms of **1c** was found midway between trigonal prismatic and octahedral by X-ray crystallography. Here we report that the complex anion of **1b**,**c**, $[Nb(SCH_2CH_2S)_3]^-$, undergoes an unexpected isomerization generating $[NbS(SCH_2CH_2S)(tpdt)]^-$ (**2**) (tpdt = 3-thiapentane-1,5-dithiolate, $SCH_2CH_2SCH_2CH_2S$), when exposed to water, methanol, or phenol.

As a typical experiment, oxygen-free water vapor (2.8 mmol) was transferred to a concentrated DMF solution containing 1.3 g (1.7 mmol) of **1b** at room temperature and the solution was warmed up to 70 °C with stirring. The color changes gradually from dark red to orange-vermilion and the reaction is complete in 3–5 h. After filtrating off a minor insoluble white residue, removal of solvent in vacuo followed by washing with cold acetonitrile afforded 0.9 g (70%) of analytically pure **2b**.[5] Recrystallization from DMF gave reddish orange crystals of the DMF solvate suitable for X-ray diffraction studies. A similar reaction with **1c** yielded $[Et_4N][NbS(SCH_2CH_2S)(tpdt)]$ (**2c**) as a reddish orange crystalline powder.[5] The compounds **2b** and **2c** are rather stable in the air as solids but decompose into white material in water or by contact with moisture for a prolonged period.

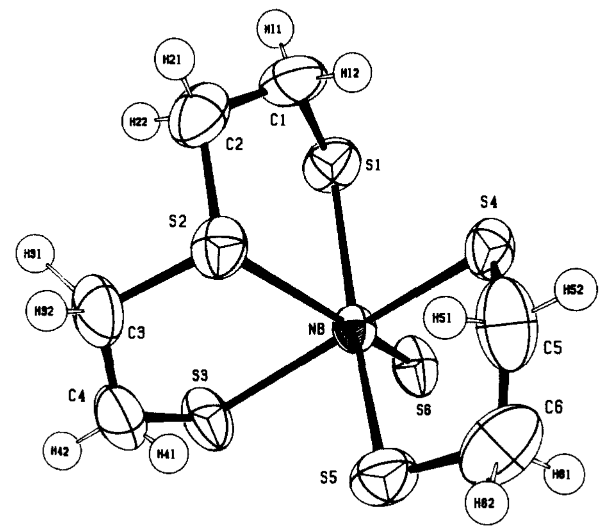


Figure 1, Structure of the complex anion in **2b**, $[NbS(SCH_2CH_2S)(tpdt)]^-$, showing the 50% probability thermal ellipsoids and the atom labeling scheme. Selected bond distances (Å) and angles (deg): Nb–S(1) = 2.455 (3), Nb–S(2) = 2.740 (4), Nb–S(3) = 2.436 (4), Nb–S(4) = 2.467 (4), Nb–S(5) = 2.484 (3), Nb–S(6) = 2.192 (3), S(1)–Nb–S(2) = 78.0 (1), S(2)–Nb–S(3) = 78.5 (1), S(4)–Nb–S(5) = 80.4 (1), S(2)–Nb–S(6) = 162.8 (1).

In the structure of **2b**[6] (Figure 1), sulfide, ethane-1,2-dithiolate, and tpdt surround an Nb atom forming a nearly octahedral geometry. The tpdt ligand orients in such a way that the central sulfur, S(2), the weakest donor among the six sulfur atoms in **2b**, sits in a position trans to the terminal sulfide, which is an understandable choice. The Nb–S distances are diverse ranging from the short Nb═S(6) bond of 2.192 (3) Å to the long Nb—S(2) (in tpdt) bond of 2.740 (4) Å. The trend parallels the change in π donor ability of the coordinated sulfurs. The observed Nb═S(6) bond is somewhat longer than in $NbS(SPPh_3)Cl_3$ (2.114 (4) Å), $[NbS(SPPh_3)Cl_3]_2$ (2.129 (4) Å),[7a] and $NbS(tht)_2Br_3$ (2.09 (8) Å),[7b] rare instances of structurally characterized Nb complexes with terminal sulfides.[7d] The elongation is probably due to the presence of four thiolate sulfur atoms in **2b** donating π electrons to Nb. The Nb—S(2) distance is comparable to those of the Nb—S(tht) and Nb—SMe_2[7c] bonds and the Nb—S(thiolate) lengths are normal.[4]

To our knowledge, **2b** and **2c** are the first complexes that carry three distinctive types of sulfur donors at a single metal center; the terminal sulfide, the thiolate type, and the thioether type. They also provide a novel, convenient synthetic entry into niobium(V) sulfides. The preparation of $NbSX_3$ (X = Cl, Br) has been achieved by a careful reaction of NbX_5 and Sb_2S_3 in CS_2,[8] but isolation of pure products is a difficult task and the only well-characterized complexes are the tht or Ph_3PS adducts.[7]

When a carefully dried DMF solution of **1b** was warmed at 70 °C, no discernible isomerization reaction took place even after 10 h as manifested by UV–visible spectroscopy. Upon introduction of dry dioxygen into the DMF solution, an unidentified white product precipitated slowly but there were no signs of **2b** formation. In the light of these results, we hypothesize that an attack of H^+ or ROH (R = H, CH_3, C_6H_5) on a dithiolate sulfur of **1b**,**c** initiates reaction 1, followed by cleavage of the C–S bond and a subsequent rearrangement via, e.g., a carbonium ion intermediate or a concerted pathway, which eventually leads to formation of **2b**,**c** by loss of H^+ or ROH.

The facile C–S bond disruption and the concomitant formation of a terminal sulfide may be a general reaction particularly for

---

† Present address: Department of Chemistry, St. Lawrence University, Canton, New York 13617.

(1) Tatsumi, K.; Takeda, J.; Sekiguchi, Y.; Kohsaka, M.; Nakamura, A. *Angew. Chem.* **1985**, *97*, 355–356; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 332–333.

(2) Benzenedithiolate complexes of Nb and Ta: (a) Martin, J. L.; Takats, J. *Inorg. Chem.* **1975**, *14*, 73–78, 1358–1364. (b) Cowie, M.; Bennet. M. J. *Ibid.* **1976**, *15*, 1589–1595.

(3) The phosphonium salt is solvated by one DMF molecule upon recrystallization from DMF.

(4) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *Angew. Chem.*, in press; *Angew Chem., Int. Ed. Engl.*, in press.

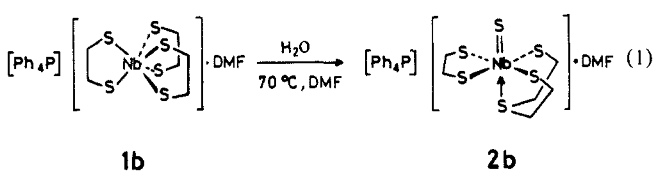
(5) (a) $[Ph_4P][NbS(SCH_2CH_2S)(tpdt)]\cdot DMF$ (**2b**): Anal. Calcd for $C_{33}H_{39}NOPS_6Nb$: C, 50.68; H, 5.04; N, 1.79; S, 24.60. Found: C, 50.81; H, 4.99; N, 1.86; S, 24.54. ^1H NMR (400 MHz, CD_3CN) δ 3.61 (m, 4 H, $SCH_2CH_2SCH_2CH_2S$), 3.26 (dt, 2 H, $SCH_2CH_2SCH_2CH_2S$), 2.21 (dt, 2 H, $SCH_2CH_2SCH_2CH_2S$), 3.20 (s, 4 H, SCH_2CH_2S), 2.89 (s, 3 H, DMF), 2.77 (s, 3 H, DMF), 7.9–8.0 (m, 1 H, DMF), 7.8 (m, 20 H, Ph_4P); UV–vis (λ_{max} (10^{-3} ϵ, M^{-1} cm^{-1}) CH_3CN) 306 nm (9.7), 342 (6.2), 407 (6.3); IR (KBr, Nujol); 493 cm^{-1} (Nb═S); 330 (br, Nb–S). (b) $[Et_4N][NbS(SCH_2CH_2S)(tpdt)]$ (**2c**): Anal. Calcd for $C_{14}H_{32}NS_6Nb$: C, 33.65; H, 6.45; N, 2.80; S, 38.50; Nb, 18.59. Found: C, 33.58; H, 6.50; N, 2.88; S, 37.79; Nb, 18.26. ^1H NMR (100 MHz, CD_3CN) δ 3.63 (m, 4 H, $SCH_2CH_2SCH_2CH_2S$), 3.27 (m, 2 H, $SCH_2CH_2SCH_2CH_2S$), 2.25 (m, 2 H, $SCH_2CH_2SCH_2CH_2S$), 3.23 (s, 4 H, SCH_2CH_2S), 3.19 (q, 8 H, J^{HH} = 7 Hz, $N(CH_2CH_3)_4$), 1.23 (tt, 12 H, $N(CH_2CH_3)_4$); UV–vis (λ_{max} (10^{-3} ϵ, M^{-1} cm^{-1}), CH_3CN) 236 sh nm (14.8), 271 (10.4), 306 (10.8), 340 (6.7), 407 (6.7); IR (KBr, Nujol) 487 cm^{-1} (Nb═S), 330 (br, Nb–S).

(6) Crystal data for **2b**: Crystal size 0.15 × 0.24 × 0.66 mm, monoclinic, space group $P2^1/c$, a = 17.923 (4) Å, b = 12.602 (2) Å, c = 16.972 (2) Å, β = 111.83 (2)°, V = 3558 (1) Å^3, ρ_{calcd} = 1.402 g cm^{-3}, Z = 4, μ(Mo K_α) = 6.82 cm^{-1}, 2246 observed reflections $I > 3\sigma(I)$, 3289 measured reflections, 162 refined parameters, R = 0.0502, R_w = 0.0476. The structure was refined using the SHELX program with non-hydrogen atoms anisotropically and all hydrogen atoms but those for DMF isotropically refined, where the phenyl groups of the cation were treated as rigid groups.

(7) (a) Drew, M. G. B.; Fowles, G. W. A.; Hobson, R. J.; Rice, D. A. *Inorg. Chim. Acta* **1976**, *20*, L35–L36. (b) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1983**, 2251–2256. tht, tetrahydrothiophene. (c) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Ibid.* **1984**, 1087–1090. (d) Very recently the reactions of $Na(S_2CNEt_2)$ with NbX_5 (X = Cl, Br) were found to give $NbS(S_2CNEt_2)_3$: Drew, M. G. B.; Rice, D. A.; Williams, D. M. *Ibid*, **1985**, 1821–1828. See also: Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 3809–3812.

(8) Fowles, G. W. A.; Hobson, R. J.; Rice, D. A.; Shanton, K. J. *J. Chem. Soc., Chem. Commun.* **1976**, 552–553.

0002-7863/86/1508-1358$01.50/0



(1)

1b **2b**

early-transition-metal thiolates.[9] Our finding provides useful information relevant to the mechanism of industrially important hydrodesulfurization processes promoted by, e.g., commercial Co-Mo/Al_2O_3 catalysts.[10] The mechanism of reaction 1 and reactivity of **2b**,**c** are under investigation.

Acknowledgment. We thank the Japan Society for the Promotion of Science and the NSF that enabled us to carry out the joint research under the Japan-United States Cooperative Science Program between K. Tatsumi and Akira Nakamura at Osaka University and J. W. Gilje and R. E. Cramer at University of Hawaii. R.E.C. is also thankful for partial support NSF, Grant CHE 8210244.

Supplementary Material Available: Positional and thermal parameters, bond distances, and bond angles for **2b** (5 pages). Ordering information is given on any current masthead page.

---

(9) (a) $Cp_2Nb(BH_4)$ was found to react with *t*-BuSH yielding $(Cp_2Nb)_2(\mu\text{-}S)_2$ presumably via a thiolate-bridged intermediate $(Cp_2Nb)_2(\mu\text{-}S\text{-}t\text{-}Bu)_2$ and subsequent loss of the *t*-Bu group: Skripkin, Yu. V.; Eremenko, I. L.; Pasynskii, A. A.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285-292. (b) It has been known that the hydrocarbon linkage of the dithiolate ligands in, e.g., $(CpMo)_2\text{-}(\overline{S\ S})_2$ undergoes an exchange reaction with alkenes and alkynes: DuBois, M. R.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245-5252. (c) Interestingly, reaction of $K_2[ReCl_6]$ with excess of ethane-1,2-dithiolate in methanol produces $[ReS(SCH_2CH_2S)_2]^-$: Blower, P. J.; Dilworth, J. R; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L225-L226.

(10) For example, see: Mitchell, P. C. H. "Catalysis"; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1.

First Photochemical Envelope Isomerization of a Late-Transition-Metal 1,3-Butadiene Complex: A Triple Stereochemical Labeling Experiment

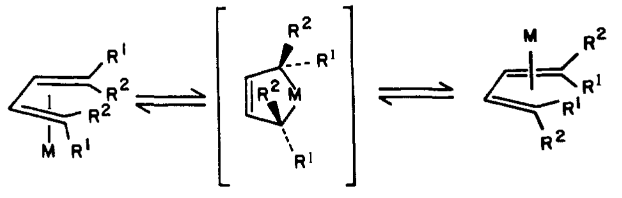
Bruce Eaton, Joseph A. King, Jr., and K. Peter C. Vollhardt*

Department of Chemistry, University of California
Berkeley, California 94720
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

Received October 7, 1985

Several reports have appeared[1] concerning a fundamentally new *thermal* isomerization reaction of *early*-transition-metal η^4-butadiene complexes in which exo and endo substituents at C-1 and/or C-4 exchange positions (e.g., **1** ⇄ **3**, Scheme I). A common intermediate that has been proposed in these transformations is the metallacyclopent-3-ene **2** characteristic of a so-called "envelope flip" process. However, mechanistic evidence for this rare species has been scarce and stepwise pathways, such as those involving (perhaps concerted) reversible butadiene-cyclobutene closures[2] and others,[3] have not been ruled out. We report here the first *photochemical* isomerization of this type, the first to be observed for a late transition metal (e.g., cobalt), and a stereochemical experiment clearly linking simultaneous double exo-endo exchange with a switch of the metal from one π face of the ligand to the other (inversion at the metal) as required by Scheme I.

Scheme I



1 **2** **3**

Our experiment took its motivation from the observation that while the η^5-CpCo complex of 1,4-*cis,cis*-dideuteriobutadiene (**1**) (M = CpCo, R^1 = H, R^2 = D) underwent stereorandomization at temperatures above 140 °C, irradiation at −96 °C with a krypton ion laser (406, 413, 415 nm) led to rapid and *stereospecific* equilibration with (η^4-1,4-*trans,trans*-dideuteriobutadiene)cyclopentadienylcobalt (3) (M = CpCo, R^1 = H, R^2 = D), none of the cis,trans isomer being detectable.[3,4] The stereochemistry of both reactions was ascertained by oxidative demetalation (Fe^{3+}), which was shown to be stereospecific, and Raman analysis of the free ligand.[5] While this experiment was consistent with an envelope flip, which necessitates such a double exchange, the unique feature of inversion with respect to the ligand π system had to be proven by an additional experiment. For this purpose, we chose to prepare the two diastereomers **4** and **5** bearing three stereochemical labels. Scheme I requires diastereoisomerization with concomitant deuterioisomerization, e.g., **4** ⇄ **6** and **5** ⇄ **7**, whereas any pathway involving retention at the metal would lead to equilibrations **4** ⇄ **7** and **5** ⇄ **6**.

The required chiral and stereospecifically labeled ligand was made as shown in Scheme II. The crucial features of the sequence are benzylation of 1-(trimethylsilyl)butyne[6] via its anion,[7] regio- and stereoselective hydrosilylation-deuteriodesilylation,[8] stereospecific bromination[9] of a 2-deuterio-1-alkyl-1-silylethene, stereospecific palladium-catalyzed coupling[10] of a deuterated vinyl bromide with *trans*-1-(tributylstannyl)-2-(trimethylsilyl)ethene,[11] and the stereospecific deuteriodesilylation of a 1,3-diene to give the target structure.[12] Its stereochemistry was unambiguously confirmed by complexation to cobalt [$CpCo(CH_2{=}CH_2)_2$,[13] pentane, 25°C, 4h] to give **4** and **5** (1:1, 75%, the stereochemical

---

(1) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858; *Ann. N.Y. Acad. Sci.* **1977**, *295*, 186. (b) Yasuda, H.; Tatsumi; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120 and the references therein. (c) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71. (d) Erker, G.; Engel, K.; Krüger, C.; Tsay, Y.-H.; Samuel, E.; Vogel, P., *Z. Naturforsch., B* **1985**, *40b*, 150.

(2) See: Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15. Grimme, W.; Köser, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 5919 and the references therein.

(3) A topologically similar but thermal and catalytic isomerization effected by Ni^0 has been postulated to proceed through η^3-allyl intermediates: Graham, C. R.; Stephenson, L. M. *J. Am. Chem. Soc.* **1977**, *99*, 7098.

(4) King, J. A., Jr. Ph.D. Thesis, UC Berkeley, 1983. The ligand was prepared as in: Stephenson, L. M.; Gemmer, R. V.; Current, S. P. *J. Org. Chem.* **1977**, *42*, 212.

(5) Stephenson, L. M.; Gemmer, R. V.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8620.

(6) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J., Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(7) Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 111.

(8) Hurdlik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155.

(9) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1977**, *7*, 475. For a review, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(10) In analogy to: Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. Professor Stille has kindly informed us about work in his group concerned with the analogous coupling of vinyl iodides: Labadie, S. S. Ph.D. Thesis, Colorado State University, 1983.

(11) After: Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480; but modified by using AIBN as initiator (2d) to avoid contamination by the cis isomer.

(12) All new compounds gave satisfactory analytical and/or spectral data.

(13) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005.

0002-7863/86/1508-1359$01.50/0