Reactivity of (η^7-cycloheptatrienyl)(η^5-cyclopentadienyl)M (M = Ti, Nb) toward Dithioacetic Acid: Preparation and Characterization of (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ and (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$

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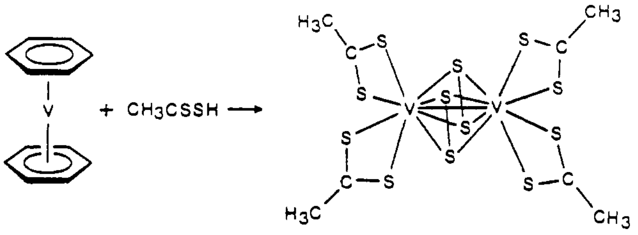
A method for the high-yield syntheses (up to 85%) of the two new compounds (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ (**1**) and (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$ (**2**) from (η^7-C_7H_7)M(η^5-C_5H_5) (M = Ti, Nb) and dithioacetic acid, CH_3CS_2H, is described. Both compounds are characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, mass spectrometry, and X-ray crystallography. Compound **1** crystallizes in orthorhombic space group *Pbca* with $a = 16.964(5)$ Å, $b = 24.545(10)$ Å, $c = 7.832(2)$ Å, $V = 3261(9)$ Å^3, $Z = 8$, $R = 0.0558$, and $R_w = 0.0655$. Compound **1** exists in the crystalline state as discrete seven-coordinate molecules; the coordination environment of the central Ti(IV) atom is a slightly distorted pentagonal bipyramid. A η^5-C_5H_5 ring occupies one axial site, two bidentate dithioacetate groups occupy four equatorial sites, and a third bidentate dithioacetate group spans the remaining axial and equatorial sites. The average equatorial Ti–S distance of 2.619 Å is appreciably longer than the axial Ti–S distance, 2.545(3) Å. Compound **2** crystallizes in space group $P2_1/c$ with $a = 13.365(2)$ Å, $b = 7.906(4)$ Å, $c = 13.710(2)$ Å, $\beta = 96.44(3)°$, $V = 1440(1)$ Å^3, $Z = 4$, $R = 0.038\,49$, and $R_w = 0.054\,75$. Crystals of **2** consist of discrete seven-coordinate molecules; the coordination environment of the central Nb(V) atom is a severely distorted pentagonal bipyramid. A η^5-C_5H_5 ring occupies one axial site, and a "side-on" bonded disulfide, η^2-S_2, occupies two equatorial sites. The remaining positions are occupied by two nonequivalent bidentate dithioacetate ligands. A variable-temperature ^1H NMR study on **2** shows rapid interconversion between the two dithioacetate environments at 47 °C ($\Delta G^{\ddagger} = 17.1 \pm 0.1$ kcal mol^{-1}).

Introduction

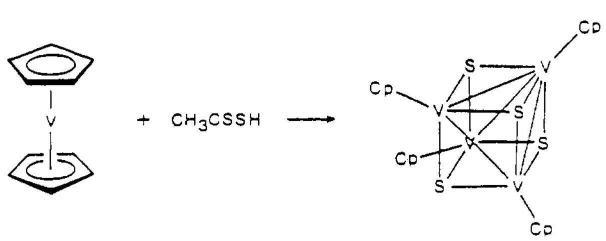
We report a novel entry into a diverse and rich area of sulfur-containing early transition metal complex chemistry. The focal point of our approach was to study the reactivity of various low-valent organometallic sandwich π-complexes toward dithiocarboxylic acids. In general, neither dithioacetic acid nor early transition metal mixed carbocyclic sandwich π-complexes of the formula (η^7-C_7H_7)M(η^5-C_5H_5), where M = Ti or Nb, have been synthetically exploited.[1–3] Dithioacetic acid is readily prepared by a simple Grignard reaction, is easily purified by distillation, and can be stored for several months at approximately −20 °C.[4] Similarly, the well-established organometallic sandwich-type (η^7-cycloheptatrienyl)(η^5-cyclopentadienyl)M (M = Ti and Nb) compounds are readily synthesized and purified by sublimation.[3,5]

Recently, we reported the reaction of bis(benzene)vanadium(0) with dithioacetic acid, CH_3CS_2H, which gives the first example of a simple divanadium tetrakis(dithioacetate), that is, (CH_3CS_2)$_2$V(μ-η^2-S_2)$_2$V(S_2CCH_3)$_2$ containing two symmetrical μ-η^2-S_2 bridges:[6]



An unusual feature of this dimer is the chelating coordination of the dithioacetate ligands at each end of the V–V core; all other M–M bonded dimeric carboxylates, including $Mo_2(\mu\text{-}S_2CR)_4L_2$ where R = CH_3 or Ph and L = THF, contain bridging acidic groups.[7,8]

Additionally, we reported the reaction between vanadocene and dithioacetic acid which produces the tetranuclear cluster [(η^5-C_5H_5)$_4$V$_4$(μ_3-S)$_4$]:[9]



In the present paper, we describe two new reactions involving (η^7-C_7H_7)Ti(η^5-C_5H_5) and (η^7-C_7H_7)Nb(η^5-C_5H_5) with dithioacetic acid. These high-yield syntheses afford (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ (**1**) and (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$ (**2**), respectively (Scheme I). The new compounds are fully characterized by elemental analysis, ^1H and ^{13}C NMR spectroscopy, infrared spectroscopy, mass spectrometry, and X-ray crystallography.

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(1) (a) *Methoden Der Organischen Chemie*; Houben-Weyl: Stuttgart, Germany, 1985; Vol. E5, pp 893–899. (b) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 6, pp 455–456.

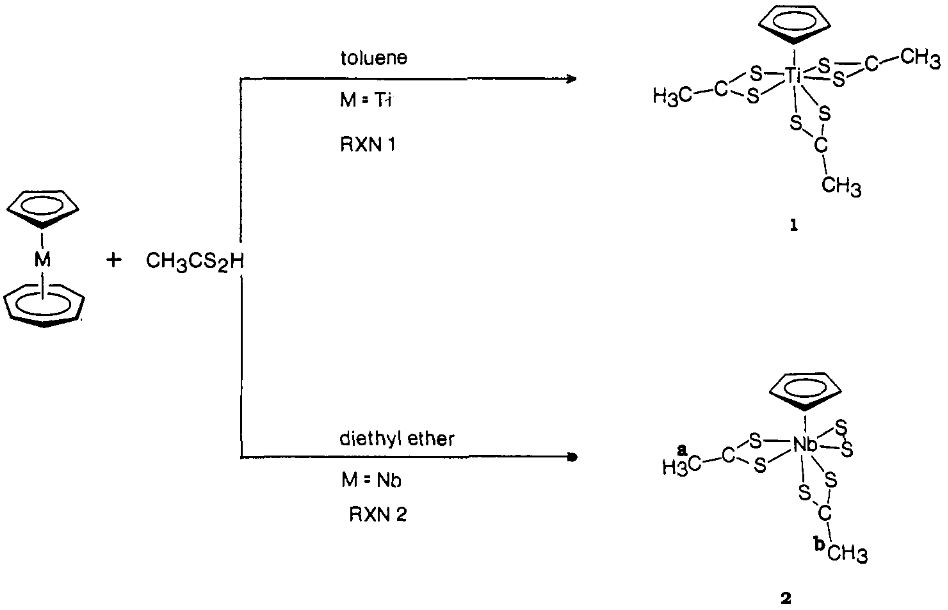
(2) (a) Botrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, Chapter 22. (b) Labinger, J. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, Chapter 25.

(3) Demerseman, B.; Dixneuf, P. H.; Douglade, J.; Mercier, R. *Inorg. Chem.* **1982**, *21*, 3942–3947.

(4) Houben, J.; Pohl, H. *Chem. Ber.* **1907**, *40*, 1303–1305.

(5) van Oven, H. O.; Groenenboom, C. J.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1974**, *81*, 379–384.

Scheme I



The titanium compound, **1**, is the first example of an group IV (4) organometallic complex possessing dithioacetate ligands. The niobium complex, **2**, is the first example of a group V (5) organometallic complex possessing dithioacetate ligands and is also the first example of a monocyclopentadienylniobium complex containing a "side-on"-bonded disulfide group, η^2-S_2. Finally, the preparation of (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$, is the first reported reaction of (η^7-cycloheptatrienyl)(η^5-cyclopentadienyl)niobium. This particular reaction demonstrates a new and facile synthetic method whereby a classical organometallic compound, namely, (η^7-C_7H_7)Nb(η^5-C_5H_5), is utilized as an entry into the underdeveloped chemistry of niobium.

Experimental Section

General Procedures. All operation of moisture- and air-sensitive materials were performed under an inert atmosphere using standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in a Vacuum Atmospheres Co. drybox equipped with a HE-493 dri-train. Solvents were freshly distilled from sodium benzophenone ketyl prior to use. Solutions were transfered via stainless steel cannulae and/or syringes. Titanium tetrachloride and niobium pentachloride (Strem Chemicals Inc.) were used without additional purification. Dithioacetic acid,[8] (η^7-C_7H_7)Ti(η^5-C_5H_5),[7] and (η^5-C_5H_5)NbCl$_4$[10] were prepared according to literature methods. (η^7-C_7H_7)Nb(η^5-C_5H_5) was prepared by a new procedure which is described below.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Inc. (Knoxville, TN). Proton NMR spectra were recorded on either a Varian T-60, Varian FT-80A, or a Bruker AC300F (300 MHz) spectrometer. Carbon-13 NMR spectra were recorded on a Varian FT-80A or a Bruker AC300F (300 MHz) spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer 599B spectrophotometer. Electron impact mass spectra (MS) were recorded on a Finnigan TSQ-45 mass spectrometer via a solid insertion probe. Magnetic measurements were determined at room temperature on a MSB1 Johnson Matthey magnetic susceptibility balance. Corrections for diamagnetism were made using Pascal's constants.

Preparation of (η^7-C_7H_7)Nb(η^5-C_5H_5).[11] A powder addition funnel was charged with (η^5-C_5H_5)NbCl$_4$ (10.0 g, 33.4 mmol) and attached to a 250 mL two-necked flask containing anhydrous FeCl$_3$ (0.34 g, 2.1 mmol) and magnesium turnings (3.62 g, 150 mmol). While stirring, 150 mL of THF and deaerated cycloheptatriene (8.9 g, 97 mmol) were added to the flask. The (η^5-C_5H_5)NbCl$_4$ was added slowly to the contents of the flask. Throughout the addition, the temperature of the reaction flask was maintained between 45 and 55 °C. The mixture gradually became dark brown. Once the addition was complete, the mixture was heated for 2 h at 58–63 °C. During this time, precipitation of a dark brown solid occurred. After stirring for additional 72 h at room temperature, the solvent was removed and the resulting dark gray residue dried for 18 h under vacuum. Sublimation at 150–160 °C (10^{-2} mmHg) produced maroon crystals of (η^7-C_7H_7)Nb(η^5-C_5H_5). Yield: 2.80 g (34%) [lit. 5%].[5] Anal. Calcd (found) for $C_{12}H_{12}Nb$: C, 57.85 (57.58); H, 4.86 (4.75). IR (KBr, cm^{-1}): 3350 (m), 3020 (m), 2920 (w, br), 1593 (w), 1583 (w), 1440 (w), 1420 (m), 1260 (w), 1232 (m), 1190 (w), 1170 (w), 1103 (m), 1005 (s), 950 (s), 893 (m), 850 (s), 800 (s), 780 (s, br), 700 (m), 390 (s), 380 (s). MS (solid probe, 70 eV): *m/e* 294 M$^+$ (100%, $C_{12}H_{12}Nb^+$), 248 (5%, $C_{12}H_{11}Nb^+$), 247 (34%, $C_{12}H_{10}Nb^+$), 245 (2%, $C_{12}H_8Nb^+$), 223 (4%, $C_{10}H_{10}Nb^+$), 222 (1%, $C_{10}H_9Nb^+$), 221 (7%, $C_{10}H_8Nb^+$), 220 (1%, $C_{10}H_7Nb^+$), 219 (2%, $C_{10}H_6Nb^+$), 171 (16%, $C_6H_6Nb^+$), 170 (3%, $C_6H_5Nb^+$), 169 (14%, $C_6H_4Nb^+$), 168 (1%, $C_6H_3Nb^+$), 158 (3%, $C_5H_5Nb^+$), 157 (1%, $C_5H_4Nb^+$), 156 (1%, $C_5H_3Nb^+$), 145 (1%, $C_4H_4Nb^+$), 144 (2%, $C_4H_3Nb^+$), 143 (4%, $C_4H_2Nb^+$), 142 (1%, C_4HNb^+), 132 (2%, $C_3H_3Nb^+$), 131 (3%, $C_3H_2Nb^+$), 130 (2%, C_3HNb^+), 119 (1%, $C_2H_2Nb^+$), 118 (1%, C_2HNb^+), 91 (<1%, $C_7H_7^+$), 78 (<1%, $C_6H_6^+$), 65 (1%, $C_5H_5^+$). $\chi_M = 1.18 \times 10^{-3}$ emu/mol at 293 K; μ_{eff} = 1.66 BM [lit. 1.73 BM].[5]

Preparation of (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ (1). A solution of (η^7-C_7H_7)Ti(η^5-C_5H_5) (0.55 g, 2.7 mmol) in 75 mL toluene was treated with redistilled dithioacetic acid (2.0 g, 21.7 mmol). The color of the solution immediately changed from blue to green-brown. The solution was stirred for 3 days at room temperature. The resulting orange-brown solution was concentrated to one-fifth of the original volume. Heptane (50 mL) was added, and the solution cooled in a dry ice/acetone bath for 1 h to precipitate a light orange solid. The solid was collected on a frit, washed with two 5 mL aliquots of heptane, and dried under vacuum. Recrystallization from toluene/heptane (v/v 25/75) afforded bright yellow crystalline **1**. Yield: 0.40 g (83.3%). Anal. Calcd (found) for $C_{11}H_{14}S_6Ti$: C, 34.18 (33.71); H, 3.66 (3.84). ^{1}H NMR (C_6H_6): δ 2.38 (s, 6H), 2.47 (s, 3H), 5.83 (s, 5H). ^{13}C NMR (C_6H_6): δ 41.9, 42.1, 133.7, 213.9, 214.5. IR (KBr, cm^{-1}): 3113 (w), 3096 (w), 2966 (w), 2948 (w), 1443 (m), 1434 (m), 1413 (m), 1403 (sh), 1353 (s), 1345 (sh), 1266 (m), 1262 (m), 1158 (sh), 1153 (vs), 1140 (vs), 1070 (m), 1026 (m), 1019 (s), 868 (vs), 851 (s), 843 (m), 840 (m), 824 (vs), 456 (m), 401 (m),

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(6) Duraj, S. A.; Andras, M. T.; Kibala, P. A. *Inorg. Chem.* **1990**, *29*, 1231–1234.

(7) (a) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: London, 1983. (b) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (c) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1988.

(8) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowsk, J. C. *Acta Chem. Scand.* **1978**, *A32*, 663–671.

(9) Duraj, S. A.; Andras, M. T.; Rihter, B. *Polyhedron*, **1989**, *8*, 2763–2767.

(10) Cardoso, A. M.; Clark, R. J. H.; Moorehouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156–1160.

(11) Modification of the procedure reported for (η^7-C_7H_7)Ti(η^5-C_5H_5); see ref 3.

Table I. Crystallographic Data for **1** and **2**

	1	**2**
mol formula	$C_{11}H_{14}S_6Ti$	$C_9H_{11}NbS_6$
mol wt	386.52	404.48
space group (No.)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
a, Å	16.964 (5)	13.365 (2)
b, Å	24.545(10)	7.906(4)
c, Å	7.832(2)	13.710(2)
β, deg		96.44(3)
V, Å^3	3261(9)	1440(1)
Z	8	4
ρ_{calcd}, g/cm^3	1.575	1.866
T, °C	20	23
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	12.389	16.103
transm coeff	1.024–0.9854	1.0816–0.9949
$R^{a,c}$	0.0558	0.038 49
$R_w{}^{b,c}$	0.0655	0.054 75

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|)^2$. [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{par})]^{1/2}$.

378 (w), 358 (m), 328 (w), 305 (w), 290 (w). MS (solid probe, 40 eV): *m/e* 386 M^+ (<1%, $C_{11}H_{14}S_6Ti^+$), 295 (60%, $C_9H_{11}S_4Ti^+$), 294 (5%, $C_9H_{10}S_4Ti^+$), 293 (5%, $C_9H_9S_4Ti^+$), 204 (5%, $C_7H_8S_2Ti^+$), 203 (21%, $C_7H_7S_2Ti^+$), 202 (1%, $C_7H_6S_2Ti^+$), 113 (2%, $C_5H_5Ti^+$), 91 (1%, $C_2H_3S_2^+$), 59 (100%, $C_2H_3S^+$), 58 (1%, $C_2H_2S^+$).

Yellow prismatic X-ray crystallographic-quality crystals were obtained by slow diffusion of heptane into a concentrated toluene solution of (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ (**1**) over a few weeks. Alternatively, crystallographic-quality crystals of **1** were grown by slow diffusion of a heptane solution of dithioacetic acid into a toluene solution of (η^7-C_7H_7)Ti(η^5-C_5H_5).

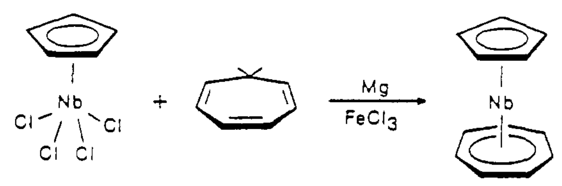
Preparation of (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$ (2). A solution of (η^7-C_7H_7)Nb(η^5-C_5H_5) (0.82 g, 3.3 mmol) in 60 mL diethyl ether was treated with redistilled dithioacetic acid (1.0 g, 11 mmol). The light brown solution immediately became darker brown. The solution was stirred for 4 days at room temperature. During this time, precipitation of an orange solid occurred. The resulting orange solid was collected on a frit, washed with 5 mL of heptane, and dried under vacuum. Recrystallization from toluene/heptane (v/v 20/80) afforded dark red-brown crystalline **2**. Yield: 1.11 g (83%). Anal. Calcd (found) for $C_9H_{11}NbS_6$: C, 26.72 (27.03); H, 2.74 (2.79). ^{1} NMR (C_6H_6): δ 2.12 (s, 3H), 2.14 (s, 3H), 5.26 (s, 5H). ^{13}C NMR (C_6H_6): δ 41.9, 42.6, 108.8, 239.3, 243.5. IR (KBr, cm^{-1}): 3095 (m), 3060 (m), 2970 (w), 2350 (w), 1787 (w), 1700 (w), 1473 (m), 1430 (m), 1412 (w), 1350 (m), 1252 (s), 1245 (sh), 1207 (w), 1167 (vs), 1143 (s), 1097 (w), 1017 (m), 930 (w), 865 (vs), 855 (vs), 840 (sh), 835 (vs), 830 (vs), 802 (s), 670 (w), 618 (w), 542 (s), 455 (m), 450 (m), 386 (s), 335 (s), 330 (sh). MS (solid probe, 70 eV): *m/e* 404 M^+ (<1%, $C_9H_{11}NbS_6^+$), 340 (<1%, $C_9H_{11}NbS_4^+$), 313 (<1%, $C_7H_8NbS_4^+$), 93 (<1%, Nb^+), 91 (<1%, $C_2H_3S_2^+$), 76 (<1%, CS_2^+), 65 (2%, $C_5H_5^+$), 64 (6%, $C_5H_4^+$), 59 (100%, $C_2H_3S^+$), 58 (<17%, $C_2H_3S^+$).

Red-brown prismatic X-ray crystallographic-quality crystals were obtained by slow diffusion of heptane into a toluene-ether solution of (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$ (**2**) over several weeks. Alternatively, crystallographic-quality crystals of **2** were grown by slow diffusion of a heptane solution of dithioacetic acid into a toluene solution of (η^7-C_7H_7)Nb(η^5-C_5H_5).

X-ray Crystallography. Pertinent crystallographic data for **1** and **2** are summarized in Table I. Selected crystals of **1** and **2** measuring 0.1 mm × 0.26 mm × 0.4 mm and 0.49 mm × 0.51 mm × 0.51 mm, respectively, were mounted in glass capillaries and mounted on an Enraf-Nonius CAD-4 automated diffractometer. Intensity measurements were performed using graphite-monochromatized Mo Kα radiation. Unit cell parameters were determined from least-squares refinement of 25 reflections obtained from an automatic centering program. Intensity data were collected with the ω–2θ technique in the range $4° \leq 2\theta \leq 50°$. For **1**, a total of 2248 independent reflections were collected in the region of h = 0 to 22, k = 0 to 31, l = 0 to 12. For **2**, a total of 3045 reflections were recorded for h = 0 to 17, k = 0 to 10, l = –17 to 17. Of the total reflections, 1443 and 2782 unique reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ were used, respectively, in the calculations of structure factors. Three standard reflections were measured every 60 min. Intensities were corrected for Lorentz, polarization and absorption effects.

All calculations were performed on a PDP-11/60 computer using software from the Enraf-Nonius Structure Determination Package PLUS.[12] The positions of the titanium atom and six sulfur atoms in **1** were determined using MULTAN.[13] Interpretation of a Patterson map led to the location of the niobium atom in **2**. The remaining non-hydrogen atoms were located and refined through a series of difference Fourier maps and full-matrix least-squares refinements. All of the non-hydrogen atoms were refined anisotropically.

Scheme II



Tables of anisotropic thermal parameters and complete bond distances and angles for **1** and **2** are provided as supplementary material.

Results and Discussion

Synthesis and Spectroscopic Characterization of 1 and 2. In order to begin this investigation, high-yield syntheses of the organometallic sandwich π-complexes (η^7-C_7H_7)M(η^5-C_5H_5) (M = Ti, Nb) were required. The preparation of the titanium sandwich followed literature procedure.[3] However, the reported procedure (5% yield) for the niobium analogue was of little synthetic value to our studies.[5] As a result, we developed an improved synthesis (34% yield) by modifying the procedure reported for the titanium complex (Scheme II). Thus, cyclopentadienylniobium tetrachloride, (η^5-C_5H_5)$NbCl_4$, reacts with cycloheptatriene, (C_7H_8), in the presence of magnesium metal and a trace amount of anhydrous iron(III) chloride to produce (η^7-C_7H_7)M(η^5-C_5H_5) in 34% yield.

Under mild conditions, the reactions between (η^7-C_7H_7)M(η^5-C_5H_5) (M = Ti, Nb) and excess dithioacetic acid, CH_3CS_2H, yield two new mononuclear complexes, (η^5-C_5H_5)Ti(S_2CCH_3)$_3$ (**1**) and (η^5-C_5H_5)Nb(η^2-S_2)(S_2CCH_3)$_2$ (**2**), respectively, (Scheme I). Gas chromatographic and mass spectrometric analyses of the reaction mixtures were performed in order to determine the fate of the η^7-C_7H_7 ring. For reaction 1, the chromatogram revealed the presence of **1**, dithioacetic acid, toluene and cycloheptatriene, C_7H_8. The presence of C_7H_8 was confirmed by matching the resulting mass spectrum to the NIST Library spectrum of 1,3,5-cycloheptatriene. It may be argued, that in (η^7-C_7H_7)Ti(η^5-C_5H_5) the η^7-C_7H_7 ring is negatively charged, i.e., η^7-$C_7H_7^-$.[14,15] Thus, a $\eta^7 \rightarrow \eta^1$ rearrangement of the anionic ring followed by protonation may be postulated for the formation of C_7H_8 in reaction 1.

However, the chromatogram of reaction 2 contained peaks attributed to **2**, dithioacetic acid, and dicycloheptatrienyl, (C_7H_7)$_2$. The resulting mass spectrum of the (C_7H_7)$_2$ was matched to the corresponding spectrum of bi-2,4,6-cycloheptatrien-1-yl (i.e., dicycloheptatrienyl) in the NIST Library. Thus, we believe, that some, if not all, of the liberated cycloheptatrienyl undergoes a coupling type reaction producing (C_7H_7)$_2$ under the reported conditions. Dicycloheptatrienyl is also a side-product in the preparation of (η^7-C_7H_7)Mo(CO)$_2$I from [(η^7-C_7H_7)Mo(CO)$_3$]BF_4 and NaI.[16]

The ^{1}H and ^{13}C NMR spectra of the two new compounds, recorded at ambient probe temperature, show the expected results. For both complexes, the spectra are consistent with a pentagonal

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(12) *Structure Determination Package PLUS*; Enraf-Nonius: Delft, The Netherlands, 1983.

(13) Main, P.; Fiske, S. J.; Hill, S. E.; Lessinger, L.; Germain, G.; Ceclercq, J. P.; Woolfson, M. M. *MULTAN: A System of Computer Programs for Automatic Solution of Crystal Structures from X-Ray Diffraction Data*; University of York: York, England, 1982.

(14) .Sharma, K. M.; Anand, S. K.; Multani, R. K.; Jain, B. D. *J. Organomet. Chem.* **1970**, *21*, 389–390.

(15) King, R. B.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 5263–5264.

(16) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; p 64.

Table II. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Ti(1)	0.30667(8)	0.37542(6)	0.0593(2)	2.28(3)
S(1)	0.2177(2)	0.42856(9)	−0.1586(4)	3.26(5)
S(2)	0.2177(2)	0.31421(9)	−0.1352(4)	3.44(6)
S(3)	0.3630(1)	0.27653(9)	0.0717(4)	3.31(5)
S(4)	0.4513(1)	0.3679(1)	0.1757(4)	3.47(5)
S(5)	0.3740(2)	0.4687(9)	0.0026(4)	3.50(5)
S(6)	0.3889(1)	0.3761(1)	−0.2125(4)	3.26(5)
C(1)	0.1799(6)	0.3814(4)	0.198(1)	3.7(2)
C(2)	0.2213(7)	0.3367(4)	0.272(1)	4.6(3)
C(3)	0.2920(6)	0.3566(4)	0.362(1)	4.2(3)
C(4)	0.2929(6)	0.4154(4)	0.340(1)	4.1(3)
C(5)	0.2262(6)	0.4301(4)	0.240(1)	3.9(2)
C(6)	0.1798(5)	0.3702(3)	−0.230(1)	3.0(2)
C(7)	0.1157(5)	0.3672(4)	−0.362(1)	3.5(2)
C(8)	0.4478(6)	0.2999(4)	0.155(1)	3.3(2)
C(9)	0.5143(5)	0.2631(4)	0.204(1)	4.2(2)
C(10)	0.4118(5)	0.4416(4)	−0.175(1)	3.4(2)
C(11)	0.4621(6)	0.4741(4)	−0.300(2)	4.7(3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

bipyramidal coordination environment around the respective metal center. In the ^1H NMR spectrum of **1**, two distinct CH_3 resonances are observed at 2.27 and 2.38 ppm, with relative intensities of 2:1. These are assigned to the nonequivalent equatorial and spanning dithioacetate groups, respectively. The single resonance at 5.83 ppm is assigned to the protons of the π-bonded $\eta^5\text{-}C_5H_5$ ring. This spectrum is in accord with a stereochemically rigid configuration of **1** on the NMR time scale. There is a limited number of seven-coordinate complexes for which slow-exchange spectra are observed.[17,18]

Although the ^1H and ^{13}C NMR spectra of **2** resemble the corresponding spectra of **1**, interpretation of the spectra is not as straightforward. For example, in the ^1H NMR of **2**, two singlet resonances (2.12 and 2.14 ppm) of equal intensity are assigned to the CH_3 protons of the two nonequivalent dithioacetate ligands (see **2**, Scheme I). We believe, based upon the structural properties of **2** and the corresponding spectrum of **1**, the downfield resonance is due to the spanning dithioacetate group (^{b}Me in **2**, Scheme I); however, a definite assignment for the resonances is not possible. The sharp singlet at 5.26 ppm is assigned to the protons of the π-bonded $\eta^5\text{-}C_5H_5$ ring.

At 47 °C the two CH_3 resonances for **2** coalesce; this behavior is indicative of rapid interconversion between the two CH_3 environments at this temperature. As the temperature is lowered, the original spectrum is again observed. The free energy of activation at coalescence ($\Delta G^* = 17.1 \pm 0.1$ kcal mol^{-1}) is comparable to ΔG^* of similar complexes (e.g.: $Rh(PPh_3)(S_2CNMe_2)_3$, 17.2 ± 0.2 kcal mol^{-1}; $Mo(NO)(S_2CNMe_2)_2$, 18.5 ± 0.2 kcal mol^{-1}; $Mo(NO_2)(S_2CNMe_2)_2$, 20.6 ± 0.1 kcal mol^{-1}; $W(NO)(S_2CNMe_2)_2$, 20.8 ± 0.1 kcal mol^{-1}).[19]

The general features of the infrared spectrum of **1** are similar to those of analogous seven-coordinate titanium(IV) dithiocarbamato complexes.[20,21] Titanium–sulfur stretching vibrations occur between 267 and 435 cm^{-1} for dithiols, xanthates and dithiocarbamates.[22-24] We assign the band at 358 cm^{-1} to the ν(Ti–S) stretching vibration. The IR spectrum of **1** also includes absorption bands characteristic of π-bonded $\eta^5\text{-}C_5H_5$ rings at 3096, 1443, 1019 and 824 cm^{-1}.[25]

Table III. Selected Bond Distances (Å) and Angles (deg) for **1**[a]

Ti(1)–S(1)	2.625(3)	Ti(1)–C(4)	2.417(10)
Ti(1)–S(2)	2.618(3)	Ti(1)–C(5)	2.382(10)
Ti(1)–S(3)	2.610(3)	C(6)–S(1)	1.668(9)
Ti(1)–S(4)	2.623(3)	C(6)–S(2)	1.691(9)
Ti(1)–S(5)	2.598(3)	C(8)–S(3)	1.682(10)
Ti(1)–S(6)	2.545(3)	C(8)–S(4)	1.678(10)
Ti(1)–C(1)	2.413(10)	C(10)–S(5)	1.669(11)
Ti(1)–C(2)	2.403(11)	C(10)–S(6)	1.680(9)
Ti(1)–C(3)	2.431(10)		
S(1)–Ti(1)–S(2)	64.89(8)	S(3)–Ti(1)–S(6)	80.59(9)
S(3)–Ti(1)–S(4)	65.12(8)	S(4)–Ti(1)–S(5)	73.17(9)
S(5)–Ti(1)–S(6)	67.07(9)	S(4)–Ti(1)–S(6)	77.22(9)
S(1)–Ti(1)–S(3)	134.2(1)	S(1)–C(6)–S(2)	113.7(6)
S(1)–Ti(1)–S(4)	143.0(1)	S(3)–C(8)–S(4)	133.9(6)
S(1)–Ti(1)–S(5)	72.76(9)	S(5)–C(10)–S(6)	116.1(6)
S(1)–Ti(1)–S(6)	76.59(9)	S(1)–C(6)–C(7)	123.6(7)
S(2)–Ti(1)–S(3)	72.48(9)	S(2)–C(6)–C(7)	122.6(7)
S(2)–Ti(1)–S(4)	134.5(1)	S(3)–C(8)–C(9)	122.7(7)
S(2)–Ti(1)–S(5)	131.3(1)	S(4)–C(8)–C(9)	123.4(7)
S(2)–Ti(1)–S(6)	80.4(1)	S(5)–C(10)–C(11)	122.8(7)
S(3)–Ti(1)–S(5)	131.7(1)	S(6)–C(10)–C(11)	121.0(8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

In the infrared spectrum of **2**, several bands below 600 cm^{-1} may be assigned by analogy to other niobium–sulfur containing complexes. These include the ν(Nb–S) stretching vibrations at 386, 335 and 330 cm^{-1} and the ν(S–S) vibration of the $\eta^2\text{-}S_2$ group at 542 cm^{-1}.[23,26,27] In addition, the bands at 3095, 1473, 1017 and 830 cm^{-1} are assigned to the π-bonded $\eta^5\text{-}C_5H_5$ ring.[25]

The mass spectra of **1** and **2** indicate that both complexes exist in the gas phase as mononuclear species. A weak molecular ion is present in both spectra, and nothing is observed at higher masses. In the mass spectrum of **1**, the most abundant metal-containing fragments result from the loss of one dithioacetate ligand [*m/e* 295 $(\eta^5\text{-}C_5H_5)Ti(S_2CCH_3)_2^+$, 60%] and the loss of two dithioacetate ligands and an additional hydrogen [*m/e* 203 $(\eta^5\text{-}C_5H_5)Ti(S_2CCH_2)^+$, 21%]. The base peak is due to CH_3CS^+, the resonance-stabilized dithioacetate − S ion.

In the mass spectrum of **2**, only two weak (<1%) metal-containing fragments are present. The first fragment results from the loss of the $\eta^2\text{-}S_2$ ligand, $(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}S_2)(S_2CCH_3)_2^+$. The second fragment results from the loss of one dithioacetate ligand, $(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}S_2)(S_2CCH_3)^+$. The strongest peaks in the spectrum arise from the ligands and their decomposition products. The base peak is, again, the resonance stabilized dithioacetate − S ion, CH_3CS^+.

Crystal Structure of $(\eta^5\text{-}C_5H_5)Ti(S_2CCH_3)_3$ (1). The final atomic positional and equivalent isotropic displacement parameters are listed in Table II. Selected interatomic distances and angles are given in Table III. A view of the entire molecular unit is depicted in Figure 1, which also defines the atomic labeling scheme.

Compound **1** exists in the crystalline state as discrete seven-coordinate molecules. In each molecule, the coordination ge-

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[17] Steffen, W. L.; Chun, H. K.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 3498–3502.

[18] Bruder, A. H.; Fay, R. C.; Lewis, D. F.; Sayler, A. A. *J. Am. Chem. Soc.* **1976**, *98*, 6932–6938.

[19] Davis, R.; Hill, M. N. S.; Holloway, C. E.; Johnson, B. F. G.; Al-Obaidi, K. H. *J. Chem. Soc. A* **1971**, 994–999.

[20] Bhat, A. N.; Fay, R. C.; Lewis, D. F.; Lindmark, A. F.; Strauss, S. H. *Inorg. Chem.* **1974**, *13*, 886–892.

[21] Alyea, E. C.; Ramaswamy, B. S.; Bhat, A. N.; Fay, R. C. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 399–403.

[22] Kwoka, W.; Moyer, R. O., Jr.; Lindsay, R. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1889–1892.

[23] Martin, J. L.; Takats, J. *Inorg. Chem.* **1975**, *14*, 73–78.

[24] Bradley, D. C.; Gitlitz, M. H. *J. Chem. Soc. A* **1969**, 1152–1156.

[25] Nakamota, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 391.

[26] For ν(Nb–S) vibrations see: (a) Moore, F. W.; Larson, M. L. *Inorg. Chem.* **1967**, *6*, 998–1003. (b) Tatsumi, K.; Sekiguchi, Y.; Nakamura, A.; Cramer, R. E.; Rupp, J. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 86–87. (c) Casey, A. T.; Mackey, D. J.; Martin, R. L.; White, A. H. *Aust. J. Chem.* **1972**, *25*, 477–492.

[27] For ν(S–S) vibrations due to side-on-bonded $\eta^2\text{-}S_2$ groups see: (a) Migot, J. L.; Sala-Pala, J.; Guerchias, J. E. *J. Organomet. Chem.* **1983**, *243*, 427–436. (b) Treichel, P. M.; Werber, G. P. *J. Am. Chem. Soc.* **1968**, *90*, 1753–1756. (c) Muller, A.; Nolte, W. O.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 279.

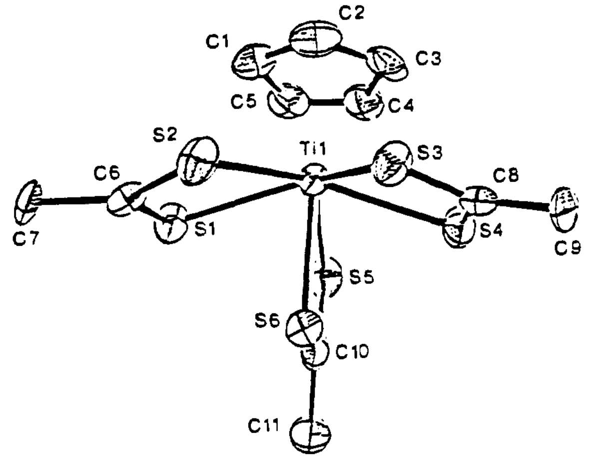

Figure 1. ORTEP drawing of the $(\eta^5\text{-}C_5H_5)Ti(S_2CC_6H_5)_3$ molecule, **1**, showing 50% thermal ellipsoids and the atomic labeling scheme.

ometry of the central Ti(IV) atom is a slightly distorted pentagonal bipyramid. A $\eta^5\text{-}C_5H_5$ group occupies one axial site, two bidentate dithioacetate ligands occupy four of the five equatorial sites, and the remaining axial and equatorial coordination sites are spanned by a third bidentate dithioacetate ligand. Pentagonal bipyramidal geometry is reported[28] to be the preferred configuration for seven-coordinate complexes of the type M(chelate)$_3$X where X participates in a relatively strong M-X covalent bond.[29] For example, $Ti(S_2CNMe_2)_3Cl$,[30] $VO(S_2CNEt_2)_3$,[29] $Mo(S_2CNBu_2)_3NO$,[30] and $(\eta^5\text{-}C_5H_5)Zr(S_2CNMe_2)_3$[18] possess pentagonal bipyramidal geometry.

Two factors contribute to the slight deviation of the Ti(IV) coordination environment from ideal pentagonal bipyramidal geometry. First, the Ti atom is displaced 0.622 Å from the equatorial plane in the direction of the $\eta^5\text{-}C_5H_5$ group (Table IV, plane 2). Second, within the equatorial plane, the S–Ti–S angles vary from the ideal pentagonal angle of 72°. The maximum deviation of the interligand S–Ti–S angles is approximately 7° and that of the intraligand S–Ti–S angles is 1°.

Molecules of **1** are located at general position in space group *Pbca* and lack crystallographic symmetry; however, C_s-*m* point group symmetry is approximated. The centroid of the $\eta^5\text{-}C_5H_5$ ligand (Cent Cp), the Ti atom, and the sulfur atoms (S_5 and S_6) of the spanning dithioacetate group all lie in a quasi-mirror plane (Table IV, plane 3). The two equatorial dithioacetate groups are symmetrically located around this plane. The quasi mirror plane is orthogonal to the equatorial plane (Table IV, planes 3 and 2, respectively); the dihedral angle between the two planes is 90.2°. In addition, the plane of the $\eta^5\text{-}C_5H_5$ ring and the equatorial plane (Table IV, planes 1 and 2, respectively) are nearly parallel; the dihedral angle between the two planes is 1.3°.

The five equatorial Ti–S bond lengths range from 2.598 to 2.625 Å. The variations are such as to maintain the quasi-mirror symmetry of the molecule. That is, symmetrically related Ti–S_1 and Ti–S_4 bonds are essentially equal (2.625(3) and 2.623(3) Å, respectively), as are Ti–S_2 and Ti–S_3 (2.618(3) and 2.610(3) Å, respectively). The axial Ti–S distance, (Ti–S_6, 2.545 Å), is appreciably shorter (by 0.07 Å) than the average bond length of the five equatorial Ti–S distances, 2.615 Å. Similar findings are reported for other pentagonal bipyramidal chelated-type Ti(IV) structures.[18,28,31–33] The average equatorial Ti–S distance, 2.615 Å, is significantly longer than previously reported average Ti–S distance (e.g.: $(Et_4N)_2Ti(S_2C_3H_4)_3$, 2.43 Å;[33] $(\eta^5\text{-}C_5H_5)_2TiS_5$, 2.44 Å;[34] $Ti(S_2CNMe_2)_3Cl$, 2.512 Å[17]). However, the analogous dithiocarbamato complex, $(\eta^5\text{-}C_5H_5)Ti(S_2CNMe_2)_3$, possesses an average Ti–S distance of comparable length, 2.611 Å.[17] Fay at al.[17] suggest that the electronic and steric requirements of the monodentate ligand, X, in M(chelate)$_3$X complexes contribute to the weakening and subsequent lengthening of the Ti–S bonds.

Within the dithioacetate ligands, the bond distances and angles are in agreement with values found in other early transition metal bidentate dithioacetate complexes.[35–37] The average C–S bond length, 1.678 Å, is approximately intermediate between the sum of the Pauli single bond radii and the double bond radii (C—S, 1.81 Å; C=S, 1.61 Å),[38] and demonstrates the presence of delocalized π-bonding in the CS_2 fragment of the ligand. However, within individual molecules of **1**, there are several structural differences between the two types of dithioacetate groups (i.e., equatorial and spanning): (1) the "bite" of the spanning ligand is larger than the "bite" of the equatorial ligands (2.84 Å vs 2.81 and 2.82 Å); (2) the S–Ti–S angle of the spanning ligand is larger (by 2.06°) than the corresponding angles of the equatorial ligands (67.07° vs 64.89 and 65.12°); (3) the S–C–S angle of the spanning ligand is larger than the corresponding angles of the equatorial ligands (116° vs 113.7 and 113.9°); and (4) the average C–S–Ti angle of the spanning ligand is smaller (by 2.2°) than the average C–S–Ti angle in the equatorial ligands (88.4° vs 90.6°).

The $\eta^5\text{-}C_5H_5$ ring is strictly planar; the largest displacement of a carbon atom from the mean plane of the ring is 0.005 Å (Table IV, plane 1). Within the ring, the average C–C bond length, 1.449 Å, is in accordance with the expected value of 1.42 Å and with C–C bond lengths in similar π-bonded $(\eta^5\text{-}C_5H_5)Ti$ complexes.[2a] The C–C–C angles are all within 2.4° from the 108° angle of an ideal pentagon.

Fay et al.[17] report a range of 2.31–2.43 Å for Ti–C bond lengths in π-bonded $(\eta^5\text{-}C_5H_5)Ti$ complexes. As a consequence of the crowding in the Ti(IV) coordination sphere in compound **1**, the average Ti–C distance of 2.409 Å, falls in the upper limit of this range. The Ti atom is 2.070 Å from the center of the $\eta^5\text{-}C_5H_5$ ring (Table IV, plane 1).

The distances between adjacent sulfur atoms in the equatorial plane are appreciably less than the van der Waals contact, i.e., 3.43 Å.[18] The S···S distances range from an average value of 2.81 Å for the intraligand contacts (i.e., S_1–S_2 and S_3–S_4) to an average value of 3.10 Å for the interligand contacts (i.e., S_2–S_3, S_4–S_5, and S_1–S_5). The three interligand S···S contacts are comparable to those found in $Ti(S_2CNMe_2)_3Cl$, 2.951, 3.088, and 3.101 Å.[17] Brennan and Bernal[39] report similar findings for seven-coordinate $Mo(S_2CNBu_2)_3NO$. They suggest the short S···S contacts, ranging from 2.809 to 3.080 Å are indicative of ligand–ligand interactions that stabilize the equatorial pentagonal plane of the Mo complex.

Crystal Structure of $(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}S_2)(S_2CCH_3)_2$ (2). The final atomic positional and equivalent isotropic displacement parameters are listed in Table V. Selected interatomic distances and angles are given in Table VI. A view of the entire molecular unit is depicted in Figure 2, which also defines the atomic labeling scheme.

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(28) Lewis, D. F.; Fay, R. C. *J. Am. Chem. Soc.* **1974**, *96*, 3843–3845.

(29) Henrick, K.; Raston, C. L.; White, A. H. *J. Am. Chem. Soc., Dalton Trans.* **1976**, 26–28.

(30) Alyea, E. C.; Bradley, D. C.; Lappert, M. F.; Sanyer, A. R. *Chem. Commun.* **1969**, 1065–1065.

(31) Park, J. J.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3636–3644.

(32) von Dreele, R. B.; Stezowski, J. J.; Fay, R. C. *J. Am. Chem. Soc.* **1971**, *93*, 2887–2892.

(33) Dorfman, J. R.; Rao, C. P.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 453–454.

(34) Epstein, E. F.; Bernal, I.; Kopf, H. *J. Organomet. Chem.* **1971**, *26*, 229–245.

(35) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. J. *J. Chem. Soc., Dalton Trans.* **1975**, 2079–2082.

(36) Bonamico, M.; Dessy, G.; Fares, V.; Scaramuzza, L. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1258–1263.

(37) Fanfani, L.; Nunzi, A.; Zanazzi, P. F.; Zanzari, A. R. *Acta Crystallogr.* **1972**, *B28*, 1298–1302.

(38) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(39) Brennan, T. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 282–291.

Table IV

Least-Squares Mean Planes for **1**[a]

plane no.	atoms	*A*	*B*	*C*	*D*
1	C(1), C(2), C(3), C(4), C(5)	0.5351	–0.1102	–0.8376	–0.6904
2	S(1), S(2), S(3), S(4), S(5)	0.5209	–0.1025	–0.8474	1.9938
3	Cent Cp, S(5), S(6), Ti(1)	–0.7988	0.2982	–0.5225	–1.6483
4	S(1), S(2), S(3), S(4), Ti(1)	0.5478	–0.0117	–0.8365	2.7744
5	S(5), S(6), C(10), C(11), Ti(1)	–0.8095	0.2891	–0.5110	–1.8061

Atoms and Their Displacements (Å) from the Planes

plane 1	C(1), –0.005(10); C(2), 0.004(10); C(3), –0.001(10); C(4), –0.003(10); C(5), 0.005(11); Ti(1), 2.070(2); S(1), 2.548(3); S(2), 2.704(3); S(3), 2.767(3); S(4), 2.639(3); S(5), 2.800(3); S(6), 4.598(3)
plane 2	S(1), –0.095(3); S(2), 0.037(3); S(3), 0.043(3); S(4), –0.098(3); S(5), 0.114(3); S(6), 1.907(3); Ti(1), –0.622(2)
plane 3	Cent Cp, 0.001; S(5); 0.000(3); S(6), 0.001(2); Ti(1), –0.002(2)
plane 4	S(1), 0.0165(3); S(2), 0.044(3); S(3), 0.050(3); S(4), 0.162(3); S(5), 0.549(3); S(6), 2.124(3); Ti(1), –0.421(2)
plane 5	Ti(1), 0.021(2); S(5), –0.015(3); S(6), –0.016(2); C(10), –0.016(2); C(11), 0.0025(11)

Dihedral Angles (deg) between Least-Squares Planes

plane 1	plane 2	angle	plane 1	plane 2	angle	plane 1	plane 2	angle
1	4	5.7	2	3	90.2	3	4	90.2
1	2	1.3	2	4	5.5	3	5	1.0
1	5	92.1	2	5	91.1	4	5	91.1

[a] The equations of the planes are in the form $Ax + By + Cz = D$, where *A*, *B*, *C*, and *D* are constants and *x*, *y*, and *z* are orthogonalized coordinates.

Table V. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	*x*	*y*	*z*	B,[a] $Å^2$
Nb(1)	0.70210(2)	0.18529(4)	0.11940(2)	2.468(5)
S(1)	0.83492(8)	0.3377(1)	0.23734(7)	3.46(2)
S(2)	0.16343(7)	0.6464(1)	0.96808(7)	3.36(2)
S(3)	0.70045(7)	0.4615(1)	0.45058(7)	3.45(2)
S(4)	0.14740(8)	0.4804(1)	0.39380(7)	3.82(2)
S(5)	0.30276(9)	0.5354(1)	0.22321(7)	4.42(2)
S(6)	0.36994(9)	0.4066(1)	0.34096(8)	4.48(2)
C(1)	0.8883(3)	0.4166(5)	0.1423(3)	3.44(7)
C(2)	0.9783(3)	0.5314(6)	0.1571(4)	5.0(1)
C(3)	0.1917(3)	0.4372(5)	0.5086(3)	3.43(7)
C(4)	0.1401(4)	0.1808(5)	0.0726(4)	4.82(9)
C(5)	0.6326(4)	0.4648(6)	0.0959(6)	7.3(2)
C(6)	0.5892(4)	0.3623(7)	0.0159(4)	5.9(1)
C(7)	0.4702(3)	0.7477(7)	0.4453(5)	5.8(1)
C(8)	0.5346(4)	0.2734(8)	0.1525(5)	7.1(1)
C(9)	0.5976(4)	0.4054(7)	0.1792(4)	6.5(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VI. Selected Bond Distances (Å) and Angles (deg) for **2**[a]

Nb(1)–S(1)	2.564(1)	Nb(1)–C(6)	2.402(5)
Nb(1)–S(2)	2.631(1)	Nb(1)–C(7)	2.423(5)
Nb(1)–S(3)	2.587(1)	Nb(1)–C(8)	2.435(5)
Nb(1)–S(4)	2.605(1)	Nb(1)–C(9)	2.431(5)
Nb(1)–S(5)	2.469(1)	C(1)–S(1)	1.674(4)
Nb(1)–S(6)	2.489(1)	C(1)–S(2)	1.668(4)
S(1)–S(2)	2.031(2)	C(3)–S(3)	1.689(4)
Nb(1)–C(5)	2.405(5)	C(3)–S(4)	1.654(4)
S(1)–Nb(1)–S(2)	65.78(3)	S(3)–Nb(1)–S(5)	124.63(4)
S(3)–Nb(1)–S(4)	65.67(3)	S(3)–Nb(1)–S(6)	80.43(4)
S(5)–Nb(1)–S(6)	48.36(4)	S(4)–Nb(1)–S(5)	81.87(4)
S(1)–Nb(1)–S(3)	135.30(3)	S(4)–Nb(1)–S(6)	77.61(4)
S(1)–Nb(1)–S(4)	81.41(3)	S(1)–C(6)–S(2)	115.2(2)
S(1)–Nb(1)–S(5)	76.03(4)	S(3)–C(3)–S(4)	114.7(2)
S(1)–Nb(1)–S(6)	122.40(3)	S(1)–C(1)–C(2)	121.6(3)
S(2)–Nb(1)–S(3)	75.92(3)	S(2)–C(1)–C(2)	123.2(3)
S(2)–Nb(1)–S(4)	73.1(3)	S(3)–C(3)–C(4)	122.1(3)
S(2)–Nb(1)–S(5)	136.67(4)	S(4)–C(3)–C(4)	123.1(3)
S(2)–Nb(1)–S(6)	148.00(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

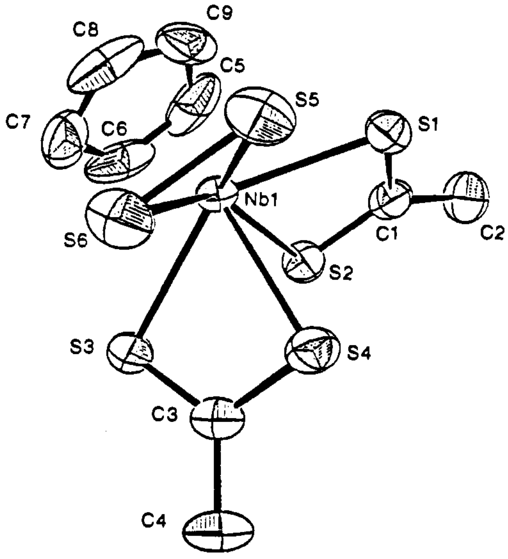

Figure 2. ORTEP drawing of the $(\eta^5\text{-}C_5H_5)Nb(\eta^2\text{-}S_2)(S_2CC_6H_5)_2$ molecule, **2**, showing 50% thermal ellipsoids and the atomic labeling scheme.

Compound **2** exists in the crystalline state as discrete seven-coordinate molecules. In each molecule, the coordination geometry around the central Nb(V) atom is a severely distorted pentagonal bipyramid. A $\eta^5\text{-}C_5H_5$ ring occupies one axial site; a "side-on"-bonded disulfide, $\eta^2\text{-}S_2$, occupies two equatorial sites; and a bidentate dithioacetate ligand occupies two other equatorial sites. The remaining axial and equatorial sites are spanned by a second bidentate dithioacetate group.

The five equatorial sulfur atoms (i.e., S_1, S_2, S_3, S_5, and S_6) are not coplanar, nor are they coplanar with the Nb atom (Table VII, plane 2). The Nb atom is displaced 0.643 Å from the mean plane of the five equatorial sulfur atoms. Within the equatorial plane, several S–Nb–S angles deviate appreciably from the 72° of an ideal pentagon. A particularly small S–Nb–S angle, 48.36°, results from the "side-on"-bonded $\eta^2\text{-}S_2$ ligand. Obviously, the relatively short disulfide S–S distance (S_5-S_6, 2.031(2) Å), severely restricts the S_5–Nb–S_6 angle. Also, the rigid "bite" of the equatorial dithioacetate group limits the S_1–Nb–S_2 angle to 65.78°. The relatively large interligand S–Nb–S angles (av 77.46°) compensate for the smaller intraligand S–Nb–S angles in this plane. For $NbO(S_2CNEt_2)_3$, a seven-coordinate dithiocarbamato complex, an average interligand S–Nb–S value of 67.3° is reported.[40]

The side-on bonding of the $\eta^2\text{-}S_2$ ligand to the Nb(V) atom is symmetrical with virtually identical Nb–S distances, 2.469(1)

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(40) Dewan, J. C.; Kepert, D. L.; Rasyon, C. L.; Taylor, D.; White, A. H.; Masien, E. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2082–2086.

Table VII. Least-Square Mean Planes for **2**[a]

plane no.	atoms	*A*	*B*	*C*	*D*
1	C(5), C(6), C(7), C(8), C(9)	–0.7622	0.6309	–0.1446	4.2057
2	S(1), S(2), S(3), S(4), S(5), S(6)	–0.7868	0.6108	–0.0888	–7.1309

Atoms and Their Displacement (Å) from the Planes

plane 1	C(5), –0.0036; C(6), 0.0022; C(7), –0.0004; C(8), –0.0017; C(9), –0.0030; Nb(1), 2.118; S(1), 2.8045; S(2), 2.5786; S(3), 2.6980; S(4), 4.6624; S(5), 2.9411; S(6), 2.8060
plane 2	S(1), 0.01770; S(2), –0.01418; S(3), 0.04817; S(5),0.0295; S(6), –0.0542; Nb(1), –0.6428

Dihedral Angles (deg) between Least-Squares Planes

plane 1	plane 2	angle
1	2	3.68

[a] The equations of the planes are in the form $Ax + By + Cz = D$, where A, B, C, and D are constants and x, y, and z are orthogonoalized coordinates.

and 2.489(1) Å. The average Nb–S(η^2-S_2) distance of 2.479 Å is comparable to those found in related complexes.[41–43] The average dithioacetate Nb–S distance of 2.597 Å is significantly longer than those reported for similar dithiolato complexes (i.e., $Nb(S_2C_6H_4)_3^-$, 2.441 Å;[44] and $Nb(SCH_2CH_2S)_3^-$, 2.434 Å[26b]), and only slightly longer than the Nb–S single bond distance of 2.575 Å reported for $[NbCl_3SSPPh_3]_x$ (x = 1, 2).[45]

The average Nb–C bond distance, 2.42(1) Å, is comparable to those found in other π-bonded (η^5-C_5H_5)Nb complexes.[43] However, within the individual Nb–C distances in **2**, there are significant differences. Specifically, the Nb–C_5 and Nb–C_6 bond lengths (2.405(5) and 2.402(5) Å, respectively) are appreciably shorter than the remaining Nb–C distances (see Table VI). In addition, a complementary difference in the C–C bond distances in the η^5-C_5H_5 ring is also observed. The C_5–C_6 bond length, 1.433(8) Å, is significantly longer than the average value of all the η^5-C_5H_5 ring C–C distances, i.e., 1.373(15) Å. Together, these differences suggest the presence of a strong steric interaction between the π-bonded η^5-C_5H_5) ring and the side-on-bonded η^2-S_2 ligand. This interaction results in the tilting of the axial η^5-C_5H_5 ring away from the equatorial η^2-S_2.

The η^5-C_5H_5 ring is strictly planar; the largest displacement of a carbon atom from the mean plane of the ring is 0.004 Å (Table VII, plane 1). Within the ring, the average C–C bond length, 1.373(15) Å, is in agreement to those in similar π-bonded (η^5-C_5H_5)Nb complexes (e.g.: $(\eta^5\text{-}C_5H_5)_2Nb(\eta^2\text{-}S_2)(CH_3)$, 1.39 Å; $(\eta^5\text{-}C_5H_5)_2Nb(CH_3)(CS_2)$, 1.36 Å).[41] The C–C–C bond angles are within 1.9° of the 108° angle for an ideal pentagon. The average C–C–C bond angle is 108°.

Within the dithioacetate ligand, the average bond distances and angles (i.e.: C–C, 1.50 Å; C–S, 1.67 Å; S–C–S, 115°; S–C–C, 122.5°) are in accord with values found in related complexes.[37,39] The average C–S bond distance is approximately intermediate between the C–S single and double bond distances (1.81 and 1.61 Å, respectively). This intermediacy confirms the presence of delocalized π-bonding in the CS_2 portion of the bidentate ligand. There are no major structural differences between the two types of dithioacetate ligands in **2**.

As in **1**, the distances between adjacent sulfur atoms comprising the equatorial plane in **2** are appreciably less than the van der Waals contact, that is 3.45 Å.[18] The S···S distances range from the intraligand distances of 2.031 and 2.82 Å (S_5–S_6 and S_1–S_2, respectively) to the average value of 3.17 Å for the interligand contacts, (i.e., S_1–S_5, S_2–S_3, and S_3–S_6).

Concluding Remarks

In summary, our synthetic, spectroscopic, and crystallographic studies of compounds **1** and **2** contain several points of interest. The utility of dithioacetic acid, CH_3CS_2H, as a precursor to the $CH_3CS_2^-$ ligand is clearly demonstrated. Under mild reaction conditions, desulfurization (or partial desulfurization) of dithioacetic acid occurs. Further work is in progress to better understand the role of the acid in the formation of the η^2-S_2 liganding unit in **2**. Preliminary results show that dithiobenzoic acid, $C_6H_5CS_2H$, reacts with vanadocene to give a mixed-valence hexanuclear vanadium cluster.[46]

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Supplementary Material Available: Figure S, showing the mass spectral match for **1** and **2**, Figure T, showing variable-temperature proton NMR spectra for **2**, Table S1, containing full details of crystallographic data and data collection for **1** and **2**, and tables of anisotropic displacement parameters and complete bond distances and angles for **1** and **2** (10 pages). Ordering information is given on any current masthead page.

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(41) Mercier, R.; Douglade, J.; Amaudrut, J.; Sala-Pala, J.; Guerchais, J. *Acta Crystallogr.* **1980**, *B36*, 2986–2991.

(42) Drew, M. G. B.; Rice, D. A.; Williams, D. M. *J. Chem. Soc., Dalton Trans.* **1983**, 2251–2256.

(43) Holloway, C. E.; Melnik, M. *J. Organometal. Chem.* **1986**, *303*, 1–38.

(44) Bennett, M. J.; Cowie, M.; Martin, J. L.; Takats, J. *J. Am. Chem. Soc.* **1973**, *95*, 7504–7505.

(45) Drew, M. G. B.; Fowles, G. W. A.; Hobson, R. J. *Inorg. Chim. Acta* **1976**, *20*, L35–L36.

(46) Andras, M. T. Ph.D. Dissertation, Cleveland State University, 1990.