Interestingly, only four hydrogen bonds (three C–H–O and one N–H–O) are associated with this group.

Relevance to Biological Chromium. This study represents the first systematic effort to prepare nicotinic acid complexes of chromium(III) with defined, controlled structure. Resulting species are highly water soluble but have limited stability with respect to hydrolysis at neutral pH. Although the poor kinetic stability will preclude in vivo biological assay, in vitro methods that measure the rapid cellular uptake of an appropriate sugar may be feasible. Such bioassay work is in progress.

Spectroscopic work described here should be compared with that reported previously for synthetic complexes (of undefined structure and homogeneity) and for chromium-containing fractions obtained from brewers' yeast.[9] Biologically active yeast fractions reportedly have a UV absorption band at 262 nm reminiscent of that for nicotinic acid.[9] This absorption could well be due to free nicotinic acid or other heterocyclic compounds. However, it must be acknowledged that, on the basis of our model study, a carboxyl-coordinated nicotinic acid complex is expected to have a UV band near 262 nm (with two shoulders as in the free-ligand spectrum). Infrared spectra recorded in the earlier study lack major bands in the 1635- and 1355–1380-cm^{-1} regions, indicating the presence of free nicotinic acid or possibly a nitrogen-coordinated complex. In this regard, further attempts should be made to prepare and examine nitrogen-coordinated species.

Questions have been raised concerning the viability of nicotinic acid as a stable chromium(III) ligand at physiological pH.[13,49] With regard to base hydrolysis, nicotinate confers no particular stability to the ammine and ethylenediamine complexes examined here, and the residue is displaced as a chromium(III) ligand at neutral pH. This is not surprising, in view of the enhanced ligand substitution rates reported for chromium(III) complexes of carboxylates and other oxyanions.[50] Problems with hydrolysis of complexes and protonation of free nicotinic acid precluded quantitative kinetic and thermodynamic evaluations of nicotinic acid coordination. However, the qualitative observations made here offer no support for a carboxyl-bound form of nicotinic acid in physiological chromium(III) complexes.

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Registry No. $[Cr(NA)(NH_3)_5](ClO_4)_2$, 85454-43-9; *cis*-$[Cr(NA)_2(NH_3)_4]ClO_4$, 85454-45-1; *trans*-$[Cr(NAH)_2(NH_3)_4](ClO_4)_3\cdot 2H_2O$, 85454-48-4; *trans*-$[Cr(NA)_2(NH_3)_4]ClO_4$, 85610-71-5; *cis*-$[Cr(NA)_2(en)_2]Br$, 85454-49-5; $[Cr(NH_3)_5(H_2O)](ClO_4)_3$, 32700-25-7; *trans*-$[Cr(NH_3)_4(H_2O)_2](ClO_4)_3$, 21034-95-7; *cis*-$[CrBr(H_2O)(en)_2]Br_2$, 30172-32-8; *cis*-$[Cr(H_2O)_2(en)_2]Br_3$, 15040-49-0; *cis*-$[Cr(NH_3)_4(H_2O)_2]Br_3$, 85454-41-7; *cis*-tetraamminediaquachromium(III) perchlorate, 41733-15-7; *cis*-aquachlorobis(ethylenediamine)chromium(III) bromide, 13966-43-3; nicotinic acid anhydride, 16837-38-0.

Supplementary Material Available: A figure showing molecular packing with hydrogen bonding and listings of anisotropic thermal parameters, calculated hydrogen coordinates and isotropic thermal parameters, least-squares planes, hydrogen bond distances and angles, perchlorate group and pyridinium ring bond distances and angles, and observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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New Nitrene Complexes of Niobium and Tantalum of the Type $M(NR)(S_2CNR'_2)_3$

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Niobium and tantalum nitrene complexes having the formula $M(NR)(S_2CNR'_2)_3$ ($R' = CH_3, CH_2CH_3$) have been prepared from $NbCl_5$ or $TaCl_5$ and $(CH_3)_2SiS_2CNR'_2$ in the presence of excess amine (RNH_2) or hydrazine (R_2NNH_2). A wide variety of aliphatic ($R = CH_3, CH_2CH_2CH_3, CH(CH_3)_2, C(CH_3)_3$) and aromatic amines was used. The structure of one complex ($M = Nb$; $R = p\text{-}CH_3C_6H_4$; $R' = C_2H_5$) was determined at −145 °C by using X-ray diffraction techniques. The complex is monomeric and seven-coordinate and has a distorted pentagonal-bipyramidal geometry. Two dithiocarbamate groups occupy four equatorial coordination sites, and the third group spans an axial and an equatorial site. The Nb atom is displaced 0.30 Å out of plane of the five equatorial sulfur atoms toward the nitrene, which occupies the remaining axial site. The nitrene ligand is only slightly bent at the nitrogen atom ($Nb\text{–}N(4)\text{–}C(41) = 167.4\ (3)°$) with a typical $Nb\equiv N(4)$ distance of 1.783 (3) Å. The NR ligand exerts little, if any, trans influence. The title complex crystallizes in space group *Pbca* with $a = 23.468\ (7)$ Å, $b = 15.485\ (5)$ Å, $c = 16.326\ (5)$ Å, and $Z = 8$. On the basis of 4701 unique reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.038$ and $R_w(F) = 0.048$.

Introduction

Owing to their formal similarity to carbene ligands and their potential synthetic uses, coordinated nitrenes have been studied more intensely in recent years.[2] Electron-rich nitrene complexes of the sort $OsO_2(NR)_2$,[3] $Mo(NR)_2(S_2CNR'_2)_2$,[4] and $TaCl(NR)(PR_3)_4$[8] have been shown to possess reactive NR groups, which are readily removed from the metal under mild conditions; in contrast, most other coordinated nitrenes are tightly bound to the metal and are not readily displaced. Among the first nitrene complexes to be reported are those containing Nb and Ta, $M(NR)(NR_2)_3$ (M = Nb, Ta), which were first prepared from lithium dialkylamides and the metal pentahalides.[5] Improved syntheses and the structure of $Ta(NR)(NMe_2)_3$ have recently appeared.[6]

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In order to study nitrene complexes of niobium and tantalum and compare them with tungsten and rhenium analogues, we have synthesized the group 5A complexes, $M(NR)(S_2CNR'_2)_3$, from the metal pentahalides and trimethylsilyl dithiocarbamates in the presence of excess amine or hydrazine. The structure of one member of the series, $Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$, was determined by using X-ray diffraction techniques. It is claimed that similar complexes can be obtained from the addition of CS_2 to $M(NR)(NR'_2)_3$.[6] Recently, Ta and Nb nitrene complexes have been prepared by the reductive coupling of nitriles using the trivalent metals[7] and from the reaction of metallocarbenes with organic imines.[8]

Experimental Section

All reactions were carried out in an inert (N_2) atmosphere with dry, freshly distilled solvents. The reaction solutions were only slightly oxygen sensitive but quite sensitive to atmospheric moisture. The final products could be conveniently handled in air as dry crystalline solids. Anhydrous diethyl ether was used directly from sealed cans; benzene was distilled from potassium–benzophenone; methylene chloride was distilled from P_2O_5. All liquid amines were distilled at atmospheric pressure from BaO; solid amines were carefully sublimed; hydrazines were carefully vacuum distilled. Me_3SiCl was distilled under dry nitrogen, and CS_2 was dried over NaOH pellets and finally distilled from P_2O_5. Resublimed $NbCl_5$ and $TaCl_5$ were purchased from Apache Chemical Co., Seward, IL, and used without further purification. Infrared spectra were measured in Fluorolube S-30 or Nujol mulls with a Perkin-Elmer 283 spectrometer and were calibrated with use of a polystyrene film. ^1H NMR spectra were measured in the stated solvents at the specified temperatures with Varian Associates HR-220 and XL-100 spectrometers. Spectra were calibrated with use of internal tetramethylsilane. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, IN. X-ray data collection was carried out with a locally constructed diffractometer consisting of a Picker goniostat interfaced to a Texas Instruments TI980B computer; the attached low-temperature device has been described.[9] The trimethylsilyl dithiocarbamates were prepared by a modified version of the published procedures.[10,11]

Trimethylsilyl Diethyldithiocarbamate. To a 3-L three-necked, round-bottomed flask equipped with a mechanical stirrer, a 250-mL addition funnel, and a reflux condenser was added 1000 mL of anhydrous ether, followed by 346 mL (3.34 mol) of diethylamine. Me_3SiCl, (189 mL, 1.40 mol) was added dropwise to the stirred $HNEt_2/Et_2O$ solution over a period of 1 h. Immediately, a white precipitate formed in the flask, and the temperature of the reaction mixture caused the solvent to gently reflux. After all the Me_3SiCl had been added, the resulting white slurry was vigorously stirred at room temperature for about 2 h. The mixture was filtered and washed with 200 mL (2 × 100 mL) of Et_2O. The filtrate (~1600 mL) yielded a colorless liquid upon solvent removal. Distillation with a 10-in. Vigreaux column yielded 132 g of a colorless liquid that boiled at 122–124 °C. The yield was 62% of Me_3SiNEt_2. ^1H NMR ($CDCl_3$): δ 0.07 (s, 9 H, Me_3Si), 1.00 (t, 6 H, CH_3CH_2N), 2.85 (q, 4 H, CH_3CH_2N).

Me_3SiNEt_2 (132 g, 0.92 mol) was placed in a 500-mL two-necked, round-bottomed flask; a reflux condenser and an addition funnel were attached. While the Me_3SiNEt_2 was being stirred with a magnetic stirrer, CS_2 was added portionwise from the addition funnel. The reaction mixture slowly turned yellow, but little heat was generated. After the addition of CS_2 and an induction period of about 15 min, sufficient heat was produced to cause the solution to reflux and the color of the solution became orange. An ice bath was used to keep the reaction under control. The mixture was stirred under N_2 for 3 h. The resulting orange-red, viscous liquid was distilled under reduced pressure. The desired product was collected at 104–108 °C (1 torr) as an orange liquid with a very pungent smell. The yield was 134 g (66%) of $Me_3SiS_2CNEt_2$. The product decomposed to a white solid after several minutes of exposure to air; the product was stored under argon to prevent decomposition. ^1H NMR ($CDCl_3$): δ 0.55 (s, 9 H, $SiMe_3$), 1.28 (t, 6 H, CH_3CH_2N), 3.39 (q, 4 H, CH_3CH_2N).

Trimethylsilyl Dimethyldithiocarbamate. A 100-g sealed glass ampule of dimethylamine (Eastman) was cooled to −10 °C and then carefully opened. The entire amount was added to 500 mL of anhydrous diethyl ether that was cooled to 0 °C. The remainder of the synthesis followed closely to that of the foregoing compound, giving Me_3SiNMe_2 as a colorless liquid (69% yield) that distilled at 88–90 °C. ^1H NMR ($CDCl_3$): δ 0.33 (s, 9 H, $SiMe_3$), 2.43 (s, 6 H, MMe_2). $Me_3SiS_2CNMe_2$ was subsequently obtained as a yellow liquid from the reaction of Me_3SiNMe_2 and CS_2 according to the above procedure (73% yield). The product distilled at 95–100 °C (10 torr). ^1H NMR ($CDCl_3$): δ 0.52 (s, 9 H, $SiMe_3$), 3.45 (s, 6 H, NMe_2).

Tris(diethyldithiocarbamato)(methylnitrene)niobium. Yellow $NbCl_5$ (2.70 g, 10.0 mmol) was placed in a Schlenk tube under N_2 atmosphere, and 50 mL of freshly distilled benzene was added to give a red suspension. Anhydrous methylamine from a lecture bottle was bubbled through the solution at a vigorous rate. Immediately, the reaction mixture turned bright yellow, with concomitant formation of a fine white solid. Addition of methylamine was continued for about 20 min until further reaction ceased. A solution of 6.85 g $Me_3SiS_2CNEt_2$ in benzene (30 mL) was added rapidly to the reaction mixture. Within minutes, the color of the reaction mixture changed to red. After 24 h of stirring under an N_2 atmosphere, the deep red reaction mixture was filtered, and the filtrate was concentrated on a rotary evaporator to about 10 mL. Then 100 mL of anhydrous ether was slowly added to crystallize the light yellow product. The product was filtered and then washed with Et_2O. Recrystallization from CH_2Cl_2/hexane yielded yellow crystals. The yield was 2.72 g (48%).

Tris(diethyldithiocarbamato)(*n*-propylnitrene)niobium. To the red suspension of $NbCl_5$ (2.50 g, 92.5 mmol) in 50 mL of dry benzene was rapidly added *n*-propylamine (1.80 g, 30.4 mmol). Immediately a white precipitate formed, and the reaction mixture turned yellow. Subsequently, $Me_3SiS_2CNEt_2$ (6.25 g, 28.2 mmol) was added with the aid of a hypodermic syringe. The reaction mixture gradually turned deep red after being stirred under N_2 for 24 h. The mixture was filtered, and the filtrate was concentrated to about 10–15 mL on a rotary evaporator. Hexane was added to crystallize the yellow product. Recrystallization of the crude product from CH_2Cl_2/hexane led to the isolation of yellow-orange crystals. The yield was 2.58 g (47%). **Tris(diethyldithiocarbamato)(isopropylnitrene)niobium** (45% yield) and **tris(diethyldithiocarbamato)(*tert*-butylnitrene)niobium** (58% yield) were prepared similarly.

Tris(diethyldithiocarbamato)(*tert*-butylnitrene)tantalum. $TaCl_5$ (7.47 g, 20.8 mmol) was dissolved in 150 mL of benzene to form a yellow solution. Then, *tert*-butylamine (6.6 mL, 62.7 mmol) was added rapidly. Immediately, the reaction mixture turned yellow-orange. Subsequently, $Me_3SiS_2CNEt_2$ (14.0 g, 63.2 mmol) was added with the aid of a hypodermic syringe. The color of the reaction mixture rapidly darkened, and the light brown reaction mixture was then refluxed for 4 h; a bright orange reaction mixture was obtained. The reaction mixture was filtered, and the remaining solid was washed with CH_2Cl_2 until the filtrate was colorless. The washings and the filtrate were combined, and most of the solvent was removed on a rotary evaporator. Ether was added to induce the crystallization of the product, which was subsequently collected by filtration and washed with hexane. Recrystallization from CH_2Cl_2/Et_2O yielded 9.2 g (79%) of pale yellow microcrystals. **Tris(dimethyldithioicarbamato)(*tert*-butylnitrene)tantalum** (89% yield), **tris(dimethyldithiocarbamato)(*tert*-butylnitrene)niobium** (70% yield), and **tris(dimethyldithiocarbamato)(*p*-tolylnitrene)niobium** (63% yield) were prepared similarly.

Tris(diethyldithiocarbamato)(*p*-tolylnitrene)niobium. $NbCl_5$ (2.85 g, 10.5 mmol) was partially dissolved in 60 mL of dry benzene to form a red suspension. Freshly sublimed *p*-toluidine crystals (3.43 g, 31.7 mmol) were dissolved in 20 mL of benzene, and the solution was added to the $NbCl_5$ suspension. Instantaneously, white fumes were formed with a fleeting appearance of a greenish yellow color, which gradually developed into dark red. After 30 min the color stabilized, and 6.94 g (31.6 mmol) of $Me_3SiS_2CNEt_2$ was added. The reaction mixture darkened slightly and was then stirred under N_2 for about 18 h at room temperature. The mixture was filtered on a coarse glass fritted funnel that contained a layer of Celite. The red filtrate was con-

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Table I. Summary of Crystallographic Data

compd	$Nb(NC_7H_7)(S_2CN(C_2H_5)_2)_3$
formula	$C_{22}H_{37}N_4NbS_6$
formula weight	642.86
a, Å	23.468 (7)
b, Å	15.485 (5)
c, Å	16.326 (5)
V, Å^3	5933
Z	8
space group	D_{2h}^{15}-$Pbca$
cryst size, mm	0.24 × 0.26 × 0.40
cryst vol, mm^3	1.9×10^{-2}
cryst shape	orthorhombic prism with {001}, {110}, and {111} faces
radiation	Mo Kα, λ = 0.710 69 Å, monochromatized by using highly oriented graphite
D, g/cm^3	1.439 (calcd) 1.42 (2) (obsd) at 25 °C
temp, °C	−145 (5)
μ, cm^{-1}	8.118
aperture	2.5 mm wide × 3.5 mm high
takeoff angle, deg	2.0
scan speed, deg/min	3.0
scan range	0.90° below Kα_1 to 0.85° above Kα_2
bkgd counting, s	10
2θ limits, deg	4.0–55.0
no. of variables	298
total unique data	7423
unique data with $I_o > 3\sigma(I_o)$	4701
error in observn of unit wt, e	1.23
$R(F)$	0.038
$R_w(F)$	0.048

Table II. Positional Parameters for the Atoms in $Nb(NC_7H_7)(S_2CN(C_2H_5)_2)_3$

atom	x^a	y	z
Nb	0.357187 (14)	0.094923 (20)	0.352328 (19)
S(11)	0.25437 (4)	0.07305 (6)	0.30257 (6)
S(12)	0.35043 (4)	−0.01024 (6)	0.22801 (6)
S(21)	0.29201 (4)	0.19719 (6)	0.43500 (6)
S(22)	0.41336 (4)	0.20290 (6)	0.44270 (6)
S(31)	0.45926 (4)	0.08669 (6)	0.29819 (6)
S(32)	0.37964 (4)	0.21593 (6)	0.23714 (6)
N(1)	0.24264 (15)	−0.06583 (20)	0.20574 (19)
N(2)	0.34875 (13)	0.32416 (19)	0.51307 (18)
N(3)	0.49172 (13)	0.21756 (19)	0.20424 (19)
N(4)	0.36526 (13)	0.00288 (19)	0.41693 (18)
C(11)	0.27750 (17)	−0.00898 (22)	0.23965 (23)
C(21)	0.35100 (15)	0.25190 (24)	0.47008 (21)
C(31)	0.44806 (15)	0.17907 (21)	0.24164 (22)
C(41)	0.37887 (16)	−0.07498 (23)	0.45304 (21)
C(42)	0.34634 (15)	−0.14952 (25)	0.43690 (24)
C(43)	0.35904 (17)	−0.22644 (24)	0.47522 (25)
C(44)	0.40437 (16)	−0.23346 (25)	0.52982 (23)
C(45)	0.43661 (16)	−0.16049 (26)	0.54447 (23)
C(46)	0.42481 (15)	−0.08246 (24)	0.50729 (22)
C(47)	0.41763 (21)	−0.3169 (3)	0.57341 (28)
C(12)	0.18085 (19)	−0.06231 (28)	0.22099 (27)
C(13)	0.15021 (21)	−0.0106 (4)	0.1550 (4)
C(14)	0.26470 (20)	−0.13582 (27)	0.15317 (26)
C(15)	0.27967 (21)	−0.21522 (27)	0.2030 (3)
C(22)	0.40148 (17)	0.37145 (24)	0.53333 (23)
C(23)	0.42371 (19)	0.42554 (28)	0.46286 (29)
C(24)	0.29484 (17)	0.36218 (26)	0.54210 (24)
C(25)	0.28120 (19)	0.44779 (28)	0.5020 (3)
C(32)	0.55117 (17)	0.18677 (26)	0.21335 (25)
C(33)	0.56560 (21)	0.11576 (29)	0.15381 (29)
C(34)	0.48412 (18)	0.29620 (25)	0.15433 (25)
C(35)	0.49633 (22)	0.37663 (27)	0.2023 (3)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

centrated under vacuum, and hexane was added to precipitate the crude, yellow product. Recrystallization of this product from benzene/hexane yielded large, yellow prismatic crystals (4.33 g, 57%). ^{1}H NMR and elemental analyses revealed that one benzene molecule was present for each Nb. The product was also recrystallized from CH_2Cl_2/hexane as solvent-free crystals. **Tris(diethyldithiocarbamato)((*p*-methoxyphenyl)nitrene)niobium** (48% yield) and **tris(diethyldithiocarbamato)(phenylnitrene)niobium** (68% yield) were similarly prepared.

Tris(diethyldithiocarbamato)((dimethylamino)nitrene)niobium. To the red suspension of $NbCl_5$ (2.00 g, 7.40 mmol) in 60 mL of benzene was added 1,1-dimethylhydrazine (1.10 g, 18.3 mmol). Immediately, evolution of white fumes and simultaneous precipitation of green-brown solid took place; the liquid phase of the reaction mixture was light green. Subsequently, $Me_3SiS_2CNEt_2$ (5.10 g, 23.1 mmol) was added rapidly, and gradually the reaction mixture became deep wine red. It was stirred under N_2 for about 24 h at room temperature. After filtration, the red filtrate was concentrated under vacuum, and hexane was added to precipitate a reddish brown product. The crude material was carefully recrystallized from CH_2Cl_2/hexane to afford 2.56 g (58%) of orange crystals. $Nb(NN(CH_2)_5)(S_2CNEt_2)_3$ (44% yield), $Nb(NNMePh)(S_2CNEt_2)_3$ (45% yield), $Nb(NNMePh)(S_2CNMe_2)_3$ (56% yield), and $Nb(NNMe_2)(S_2CNMe_2)_3$ (62% yield) were all analogously prepared.

Crystallographic Information. The crystal handling and data collection were similar to those described previously.[4] Owing to the small absorption coefficient, no absorption correction was performed. A careful check of F_o and F_c in the final refined model indicated that no extinction correction was necessary. Anomalous dispersion terms for Nb and S were included in F_c. Owing to intermittent instrument failure, 24 reflections had to be discarded; no effort was made to recollect these data. An additional 7 reflections were discarded because the backgrounds were highly unsymmetric. The structure was solved by using a Patterson synthesis to locate the metal atom and difference Fourier syntheses to locate all the remaining atoms including all 37 hydrogen atoms. The H atom positions were idealized, and they were included as fixed contributions in the final anisotropic refinements. A statistical analysis of the trends of the quantity $\sum w(|F_o| - |F_c|)^2$ as a function of observed structure amplitudes, diffractometer setting angles, and Miller indices showed nothing unusual and indicated that the weighting scheme was adequate. A final difference Fourier synthesis showed no significant residual electron density; the largest peak at 0.7 e/Å^3 was located near the niobium atom. Of the reflections with $3\sigma(F_o^2) > F_o^2$, only one had $F_o^2 - F_c^2 > 4\sigma(F_o^2)$ (Table I).

The final positional and thermal parameters of the atoms appear in Tables II and S-I; the root-mean-square amplitudes of vibration are given in Table S-III.[13] Table S-II[13] contains the positional and thermal parameters for the hydrogen atoms. Table S-IV contains bond distances and bond angles of the niobium complex.[13] A listing of the observed and calculated structure amplitudes for those data used in the refinements is available.[13]

Discussion

Syntheses. When $NbCl_5$ was allowed to react with 3–4 equiv of a primary amine and an anhydrous source of dialkyldithiocarbamate, modestly good yields of $Nb(NR)(S_2CNR'_2)_3$ ($R' = CH_3, C_2H_5$) resulted (eq 1). A full

$$NbCl_5 + 3RNH_2 + 3Me_3SiS_2CNR'_2 \rightarrow Nb(NR)(S_2CNR'_2)_3 + 3Me_3SiCl + 2RNH_3^+Cl^- \quad (1)$$

range of amines was used including methyl-, *n*-propyl-, isopropyl-, and *tert*-butylamines as well as aromatic amines; only *p*-nitroaniline and *p*-chloroaniline failed to produce isolable products (see Table III). These complexes are stable to oxygen and atmospheric moisture in the solid state; in solution they are moisture sensitive. NMR spectroscopic studies of the filtered reaction mixtures conclusively showed the presence of large amounts of Me_3SiCl and small amounts of Me_3SiNHR. The benzene-insoluble ammonium chlorides, $RNH_3^+Cl^-$, were compared to authentic samples for positive identification. The presence of too much amine (>5 equiv), did not seem to alter the reaction too much, as judged from visual observations, but isolated yields were distinctly lower. Usually the reactions were carried out at ambient temperature

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(13) See paragraph at end of paper regarding supplementary material.

Table III. Physical, Spectroscopic, and Analytical Data for Niobium and Tantalum Nitrene Complexes

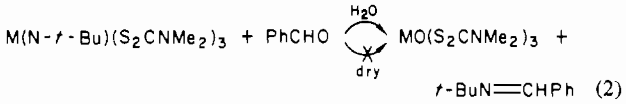
	elemental analyses, % found (calcd)				^{1}H NMR resonances,[c] ppm	
compd[a] (color)				ν(CN),[b] cm^{-1}	NR	$S_2CNR'_2$
$Nb(NMe)(S_2CNEt_2)_3$ (yellow)	C	33.99	(33.86)	1495	3.58 (s) CH_3	1.27 (t) 6 × CH_3
	H	5.96	(5.82)	1485		3.88 (q) 6 × CH_2
	N	9.64	(9.88)			
Nb(N-*n*-Pr)$(S_2CNEt_2)_3$ (orange-yellow)	C	36.55	(36.30)	1508	0.93 (t) CH_3	1.27 (t) 6 × CH_3
	H	6.41	(6.22)	1488	1.62 (sx) $NCH_2\mathit{CH}_2$	3.90 (q) 6 × CH_2
	N	9.11	(9.41)		3.56 (t) $N\mathit{CH}_2CH_2$	
Nb(N-*i*-Pr)$(S_2CNEt_2)_3$ (orange-yellow)	C	36.69	(36.30)	1505	1.16 (d) 2 × CH_3	1.26 (t) 6 × CH_3
	H	6.19	(6.22)	1492	3.84 (sp) CH	3.85 (q) 6 × CH_2
	N	9.42	(9.41)			
Nb(N-*t*-Bu)$(S_2CNEt_2)_3$ (yellow)	C	37.63	(37.44)	1505	1.23 (s) 3 × CH_3	1.28 (t) 6 × CH_3
	H	6.35	(6.40)	1488		3.86 (q) 6 × CH_2
	N	9.08	(9.19)			
Ta(N-*t*-Bu)$(S_2CNEt_2)_3$ (pale yellow)	C	32.50	(32.71)	1511	1.21 (s) 3 × CH_3	1.27 (t) 6 × CH_3
	H	5.51	(5.59)	1496		3.77 (q) 6 × CH_2
	N	7.69	(8.03)			
$Nb(NPh)(S_2CNEt_2)_3$ (yellow)	C	40.46	(40.06)	1497	7.1 (m) C_6H_5	1.25 (t) 6 × CH_3
	H	5.82	(5.56)	1475		3.81 (q) 6 × CH_2
	N	8.41	(8.90)			
Nb(*p*-NC_6H_4OMe)$(S_2CNEt_2)_3$ (yellow)	C	40.29	(40.06)	1503	3.73 (s) CH_3	1.28 (t) 6 × CH_3
	H	5.91	(5.61)	1486	6.88 (qt) C_6H_4	3.87 (q) 6 × CH_2
	N	8.21	(8.50)			
Nb(*p*-NC_6H_4Me)$(S_2CNEt_2)_3$[d] (yellow)	C	41.46	(41.06)	1501	2.30 (s) CH_3	1.27 (t) 6 × CH_3
	H	5.82	(5.75)	1495	7.00 (qt) C_6H_4	3.84 (q) 6 × CH_2
	N	8.41	(8.71)			
Nb(N-*t*-Bu)$(S_2CNMe_2)_3$ (yellow)	C	29.99	(29.74)	1530 (br)	1.24 (s) 3 × CH_3	3.35 (s) 6 × CH_3
	H	5.08	(5.18)			
	N	10.51	(10.67)			
Nb(*p*-NC_6H_4OMe)$(S_2CNMe_2)_3$ (yellow)	C	33.72	(33.42)	1533 (br)	3.71 (s) CH_3	3.33 (s) 6 × CH_3
	H	4.48	(4.38)		6.84 (qt) C_6H_4	
	N	9.91	(9.74)			
Nb(*p*-NC_6H_4Me)$(S_2CNMe_2)_3$ (yellow)	C	40.98	(40.79)	1535 (br)	2.22 (s) CH_3	3.34 (s) 6 × CH_3
	H	5.88	(5.55)		6.79 (qt) C_6H_4	
	N	9.90	(10.02)			
Ta(N-*t*-Bu)$(S_2CNMe_2)_3$ (pale yellow)	C	25.09	(25.48)	1546	1.22 (s) 3 × CH_3	3.25 (s) 6 × CH_3
	H	4.32	(4.11)	1540		
	N	9.33	(9.14)			
$Nb(NNMe_2)(S_2CNEt_2)_3$ (orange)	C	34.20	(34.23)	1492	2.85 (s) 2 × CH_3	1.25 (t) 6 × CH_3
	H	6.18	(6.04)	1484		3.85 (q) 6 × CH_2
	N	11.96	(11.74)			
$Nb(NNMePh)(S_2CNEt_2)_3$ (red)	C	40.40	(40.12)	1495	3.36 (s) CH_3	1.24 (t) 6 × CH_3
	H	5.87	(5.77)	1490	7.1 (m) C_6H_5	3.86 (q) 6 × CH_2
	N	10.94	(10.64)			
$Nb(NN(CH_2)_5)(S_2CNEt_2)_3$ (orange)	C	38.02	(37.74)	1504	1.8 (m) 3 × CH_2	1.23 (t) 6 × CH_3
	H	6.41	(6.29)	1487	3.4 (br) 2 × CH_2	3.82 (q) 6 × CH_2
	N	11.12	(11.01)			
$Nb(NNMe_2)(S_2CNMe_2)_3$ (red)	C	25.68	(25.80)	1528 (br)	2.84 (s) 2 × CH_3	3.34 (s) 6 × CH_3
	H	4.88	(4.72)			
	N	13.43	(13.68)			
$Nb(NNMePh)(S_2CNMe_2)_3$ (red)	C	33.11	(33.50)	1536 (br)	3.38 (s) CH_3	3.34 (s) 6 × CH_3
	H	4.50	(4.57)		7.2 (m) C_6H_5	
	N	12.01	(12.21)			

[a] Abbreviations: Me = CH_3, Et = C_6H_5, Ph = C_6H_5, *t*-Bu = $C(CH_3)_3$, *i*-Pr = $CH(CH_3)_2$, *n*-Pr = $CH_2CH_2CH_3$. [b] Infrared spectra measured in Nujol and Fluorolube mulls; ν(CN) is for dithiocarbamate; br = broad. [c] Measured at ambient temperature in $CDCl_3$ with tetramethylsilane as internal standard: s = singlet, d = doublet ($^3J_{HH} \simeq 7$ Hz), t = triplet ($^3J_{HH} \simeq 7$ Hz), q = quartet ($^3J_{HH} \simeq 7$ Hz), sx = sextet ($^3J_{HH} \simeq 7$ Hz), sp = septet ($^3J_{HH} \simeq 7$ Hz), m = multiplet, qt = AA'BB' quartet ($^3J_{HH} \simeq 8$ Hz; $^5J_{HH}$ = small). [d] Anal. for Nb(*p*-NC_6H_4Me)$(S_2CNEt_2)_3 \cdot C_6H_6$: C, 46.49 (46.60); H, 6.39 (5.99); N, 7.48 (7.77).

(~25 °C), but refluxing benzene was used to promote the reactions in some cases, especially when $TaCl_5$ was used instead of the niobium halide. Having an anhydrous, hydrocarbon-soluble source of dithiocarbamate was important. The use of "anhydrous" $NaS_2CNR'_2$ in THF did not give the desired products. Freshly recrystallized $AgS_2CNR'_2$ gave poor yields, $TlS_2CNR'_2$ gave better yields (~40–50%), but $Me_3SiS_2CNR'_2$ produced the best yields with the easiest purification of products.

We noted that the filtered reaction mixtures were usually dark red at the end of the reactions, yet the complexes were yellow to orange. The presence of Me_3SiNHR in the reaction suggested that HCl may also be present. Indeed, yellow benzene solutions of $Nb(NR)(S_2CNR'_2)_3$ all turned deep red when anhydrous HCl, HBr, or HO_3SCF_3 was added. All protonation reactions were perfectly reversible when base (Et_3N) was added. In one case, we were able to isolate a red oil from the reaction of Nb(N-*t*-Bu)$(S_2CNMe_2)_3$ with HO_3SCF_3. Titration with a standardized solution of Et_3N produced nearly a quantitative yield of the starting complex while consuming 1.1 equiv of base/equiv of Nb. Low-temperature ^{1}H NMR spectra of the red oil showed a sharp *t*-Bu singlet slightly shifted downfield from that in the starting complex and major changes in the dithiocarbamate region of the spectrum. In the absence of more information, we speculate that the acid protonated one of the dithiocarbamate ligands producing a six-coordinate complex. Efforts to displace one dithiocarbamate ligand with HCl forming $NbCl(NR)(S_2CNR'_2)_2$ were unsuccessful. Alkylating agents such as CH_3I, $CH_3OSO_2CF_3$, CH_3OSO_2F, and $(CH_3)_3O^+PF_6^-$ also produced red solutions with $Nb(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$, but no pure products could be isolated.

Tantalum nitrene complexes, $TaCl_3(NR)(THF)_2$[7,8] and $Ta(NBu)(NMe_2)_3$,[6] are reported to react with ketones and aldehydes, forming organic imines and tantalum oxo complexes. However, $Ta(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$ and its Nb analogue will *not react* with dry, freshly distilled benzaldehyde in refluxing benzene (8 h). No $MO(S_2CNR'_2)_3$ or PhCH=N-*t*-Bu is formed (eq 2). However, small amounts of moisture



$$M(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3 + PhCHO \xrightarrow[\text{dry}]{H_2O} MO(S_2CNMe_2)_3 + t\text{-}BuN{=}CHPh \quad (2)$$

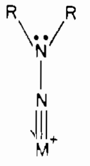
M = Nb, Ta

slowly hydrolyze the Nb–N-*t*-Bu complex, forming free *t*-$BuNH_2$, which then condenses with the benzaldehyde to form the imine.

Color changes indicate that the addition of primary amines to $NbCl_5$ yields $RNH_3^+Cl^-$ and an intermediate, which subsequently reacts with $Me_3SiS_2CNR'_2$ to give the isolated products. We did not isolate the intermediates; however, their properties are consistent with their formulation as $NbCl_3(NHR)_2(NH_2R)$, which was isolated by Carnell and Fowles from $NbCl_5$ and excess RNH_2 (eq 3).[14] Whether these intermediates rearrange to form complexes like $NbCl_3(NR)(NH_2R)_2$ before or after reaction with the dithiocarbamate is uncertain at present. It should be noted that $NbOCl_3(solvent)_2$ and $TaCl_3(NR)(solvent)_2$ are known to exist in nonprotic, donor solvents.[8,15]

$$NbCl_5 + 5RNH_2 \rightarrow NbCl_3(NHR)_2(NH_2R) + 2RNH_3^+Cl^- \quad (3)$$

In a reaction analogous to (1), 1,1-disubstituted hydrazines produce R_2NN complexes. These complexes have physical and spectroscopic properties similar to those of the RN complexes except that they are red. The ^1H NMR spectral characteristics of $Nb(NNMePh)(S_2CNMe_2)_3$ and $Mo(NNMePh)(S_2CNMe_2)_3^+$[16] are so similar that we believe them to be isostructural. The structure of a very similar Mo complex, $Mo(NNEtPh)(S_2CN(CH_2)_4)_3^+$, shows a distorted pentagonal-bipyramidal geometry with a nitrogen atom occupying an apical site and a nearly linear Mo–N–N arrangement for the nitrogen ligand, whose structure is best described by a hybrid of I and II. The R_2NN complexes could be reversibly protonated with strong acids, but again pure products could not be isolated.



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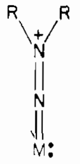

II

The spectroscopic data for $M(NR)(S_2CNR'_2)_3$ complexes are all consistent with a seven-coordinate, pentagonal-bipyramidal geometry as determined from X-ray diffraction studies (vide infra). ^1H NMR spectra indicate that the complexes are fluxional at ambient temperature (~30 °C). All three dithiocarbamate ligands produce a single pattern (singlet for S_2CNMe_2; triplet + quartet for S_2CNEt_2), as does the NR ligand. $Nb(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$ was studied at −48 °C; the *t*-Bu singlet (9 H) remained unchanged but the S_2CNMe_2 (18 H) singlet split into four singlets of areas 3 H, 6 H, 6 H, and 3 H (see Figure 1). At −48 °C, $Nb(NNMe_2)(S_2CNMe_2)_3$ gave similar results while the spectrum of $Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$ at low temperature gave an extremely complex pattern for the ethyl groups, which can be interpreted as overlapping A_2X_3 and ABX_3 patterns. The chemical shifts for the NR protons are nearly the same as those for the respective hydrogen atoms in the free amines with the exception of the protons on the carbon atom attached to N. These proton resonances are shifted downfield by about 1 ppm. The chemical shifts of the protons in NCH_3 ligands vary widely depending on the nature of the metal–nitrogen interaction as shown by the following list: $ReCl_3(NCH_3)(PPh_3)_2$, 0.4 ppm; $Re(NCH_3)(S_2CNMe_2)_3$, 2.2 ppm; $Re(OCH_3)(NCH_3)(S_2CNMe_2)_2$, 2.4 ppm; H_2NCH_3, 2.5 ppm; $Nb(NCH_3)(S_2CNEt_2)_3$, 3.6 ppm; $WF_4(NCH_3)(NCCH_3)$, 5.5 ppm. It seems that metals with higher formal oxidation states, with fewer valence d electrons, and with more electron-withdrawing coligands induce downfield chemical shifts in attached NCH_3 ligands.

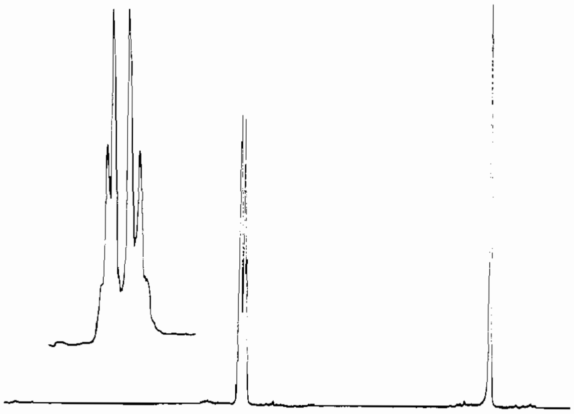

Figure 1. Proton NMR spectrum (220 MHz) of $Nb(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$ in $CDCl_3$ at −48 °C.

The infrared spectra indicate that all three dithiocarbamate ligands in $M(NR)(S_2CNR'_2)_3$ are bidentate. A careful comparison[17] of the spectra of $Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$ and $Re(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$ shows that the Nb complex has only bidentate dithiocarbamate ligands while the Re complex contains both bidentate and unidentate ligands. The same comparison between $Mo(NO)(S_2CNEt_2)_3$[18] (only bidentate) and $Ru(NO)(S_2CNEt_2)_3$[19] (bidentate + unidentate) leads to the same results and corroborates our conclusions about the Nb complex. The presence of two C–N stretching frequencies in the Nb and Ta complexes is consistent with the presence of two types of bidentate dithiocarbamates, axial–equatorial and equatorial–equatorial. We were not able to identify the $Nb{\equiv}N$ stretching frequency. A comparison of $NbO(S_2CNEt_2)_3$[20] and $Nb(NPh)(S_2CNEt_2)_3$ shows a medium strong band for the NPh complex at 1351 cm^{-1}, which is not obviously assignable to a phenyl mode. For comparison's sake, we observe that bands in the following compounds are seen to shift 25–30 cm^{-1} upon ^{15}N substitution: $TaCl_3(NPh)(THF)_2$, 1365 cm^{-1};[8] $TaCl_3(NPh)(PEt_3)_2$, 1345 cm^{-1};[7] $W(CO)(NPh)(S_2CNMe_2)_2$, 1344 cm^{-1};[21] $ReCl_3(NPh)(PPh_3)_2$,

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Table IV. Selected Metal-Sulfur Bond Distance (Å) Data for Heptacoordinate Tris(dithiocarbamato) Complexes, $MX(S_2CNR_2)_3$

complex[a]	unique ligand A $M-S_{ax}$	 B $M-S_{eq}$	other $M-S_{eq}$ C (4 values, av)	A minus B	A minus C	ref
$Nb(NTo)(S_2CNEt_2)_3$	2.707	2.607	2.575	0.100	0.132	this work
$NbO(S_2CNEt_2)_3$	2.753	2.594	2.569	0.159	0.184	22
$TaS(S_2CNEt_2)_3$	2.682	2.538	2.561	0.144	0.121	*b*
$MoN(S_2CNEt_2)_3$	2.852	2.509	2.526	0.343	0.326	23
$Mo(NO)(S_2CNBu_2)_3$	2.568	2.463	2.519	0.105	0.049	18
$Mo(NS)(S_2CNEt_2)_3$	2.600	2.487	2.52	0.113	0.08	23
$Mo(NNPh)(S_2CNMe_2)_3$	2.611	*f*	2.514[g]		0.097	*c*
$MoO(S_2CNEt_2)_3^+$	2.630	2.506	2.481	0.124	0.149	*d*
$Mo(NNEtPh)(S_2CN(CH_2)_4)_3^+$	2.55	2.48	2.50	0.07	0.05	16
$Re(CO)(S_2CNEt_2)_3$	2.518	2.433	2.483	0.085	0.035	*e*

[a] Abbreviations: Me = CH_3, Et = C_2H_5, Bu = *n*-C_4H_9, To = *p*-$CH_3C_6H_4$. [b] Peterson, E. J.; von Dreele, R. B.; Brown, T. M. *Inorg. Chem.* **1978,** *17*, 1410. [c] Butler, G.; Chatt, J.; Leigh, G. J.; Smith, A. R. P.; Williams, G. A. *Inorg. Chim. Acta* **1978,** *28*, L165. [d] Dirand, J.; Richard, L; Weiss, R. *Transition Met. Chem. (N.Y.)* **1975,** *1*, 2. [e] Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1974,** 486. [f] Value not reported. [g] Average of five equatorial distances.

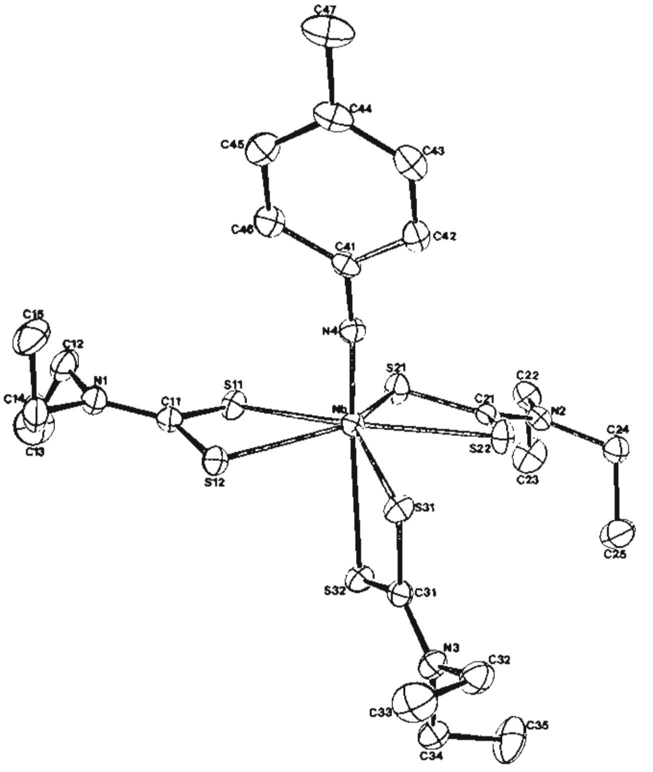

Figure 2. Drawing of a molecule of $Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$. Hydrogen atoms have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

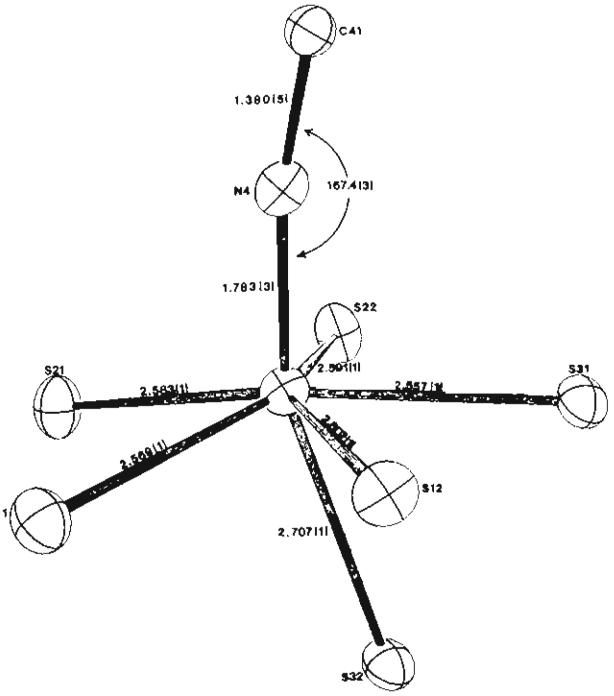

Figure 3. Coordination sphere of $Nb(p\text{-}NC_6H_4CH_3)(S_2CNEt_2)_3$. Only atoms attached to the metal, Nb, and C(41) are shown. Vibrational ellipsoids are drawn at the 50% probability level. The following are averaged structural values: S–C (6 values) = 1.717 Å, C⩦N (3 values) = 1.326 Å, C–N (6 values) = 1.476 Å, C–C (aliphatic, 6 values) = 1.512 Å, C–C (aromatic, 6 values) = 1.390 Å, S–Nb–S (3 values) = 67.13°. See Table S-IV[13] for detailed values.

1347 cm^{-1};[17] $ReCl(NPh)(S_2CNMe_2)_2$, 1353 cm^{-1}.[17] We are not sure whether these bands represent Nb≡N stretches or N—C(phenyl) stretches, but the latter is implicated by the unusually high energies of absorption and by the absence of appreciable variation with changing metals and coligands.

Description of the Structure. The structure of $Nb(N\text{-}p\text{-}CH_3C_6H_4)(S_2CNEt_2)_3$ consists of distinct, well-separated monomers. The niobium atom is seven-coordinate, and the complex displays a distorted pentagonal-bipyramidal geometry as shown in Figure 2. The nitrene ligand occupies one of the apical positions while the equatorial bonding sites are occupied by the four sulfur atoms of two bidentate dithiocarbamate ligands that lie in the equatorial plane and a fifth sulfur atom from the third bidentate dithiocarbamate ligand that spans an equatorial and the remaining axial position. Significant distortions from idealized C_{5v} symmetry arise in part from the small bite angle of the dithiocarbamate ligands (see Table S-IV and Figure 3). There are no significant intermolecular nonbonded contacts, the shortest being H1C23⋯H1C23 at 2.45 Å. All three dithiocarbamate ligands have typical structural parameters usually seen for these ligands. The niobium atom lies 0.298 (3) Å above the least-squares plane containing the five equatorial sulfur atoms. The angle described by N(4)–Nb–S(32) measures 160.67 (10)°; the S(32) position is distorted from the ideal position by the chelate.

The axial sulfur atom possesses the longest Nb–S bond length in the complex at 2.707 (1) Å, significantly longer than the remaining Nb–S distances, which lie in the range 2.557 (1)–2.607 (1) Å (mean 2.581 Å). This lengthening of the axial sulfur–metal distance can be seen in other heptacoordinate tris(dithiocarbamate) transition-metal complexes (see Table IV). This Nb–S(32) bond length is 0.046 Å shorter than the Nb–S(axial) distance of 2.753 (4) Å in $NbO(S_2CNEt_2)_3$.[22] It is also significantly shorter than the Mo–S(axial) bond

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length of 2.852 (3) Å in $MoN(S_2CNEt_2)_3$.[23] This is especially noteworthy considering the smaller atomic radius of molybdenum. The structural data in Table IV indicate that the axial sulfur–metal bond in the seven-coordinate $MX(S_2CNR_2)_3$ complexes undergoes a lengthening owing to the inability of the sulfur chelate to fully span axial and equatorial positions. This lengthening is dependent upon the size of the metal and increases from about 0.03 Å for Tc and Re to 0.06 Å for Mo and W to 0.12 Å for Nb and Ta. On the basis of this, the trans influence of the π-bonded axial ligands can then be estimated from these data: N (0.25–0.30) > O (0.05–0.10) > NR, S (~0.00).

The presence of a bound nitrene (imido) ligand is the most salient feature of the title complex. The Nb–N(4)–C(41) angle of 167.4 (3)° noticeably deviates from linearity. This bending is probably caused by the uneven overlap of the nitrogen π orbitals (p_x, p_y) with the metal's π system, which is axially unsymmetric due to the arrangement of the sulfur chelates. The bending around N(4) is in a plane that contains Nb, N(4), and the midpoint of the S(12)–S(31) vector with the phenyl group tilted toward these sulfur atoms. The Nb–N(4) bond distance of 1.783 (3) Å can be compared with that of one other structurally characterized niobium nitrene complex; in the 16-electron complex $[LCl_4NbNC(Me){=}C(Me)NNbCl_4L]^{2-}[(Ph_3P)_2N]^+{}_2$ ($L = CH_3CN$)[24] the Nb–NR bond length is 1.752 (6) Å. The Nb–NR distance in our $Nb(NC_7H_7)(S_2CNEt_2)_3$ is lengthened by approximately 0.03 Å. This lengthening is partly due to steric effects caused by the higher coordination number of the metal. That the above dimeric compound is a 16-electron complex with an empty d orbital also could have an effect on the observed Nb–N distance by facilitating the dative π donation from nitrogen to niobium as a result of increased positive charge on the metal. Three tantalum nitrene complexes have been structurally characterized and have Ta–N distances in the range 1.75–1.77 Å.[6,7,26] The Nb–N(4) bond length in $Nb(NC_7H_7)(S_2CNEt_2)_3$ should be regarded as a Nb≡NR triple bond. The bond length is 0.08 Å longer than the well-established Re≡NR triple-bond length of 1.70 Å, found in structurally characterized rhenium complexes.[2] Since the relative metallic radius of niobium (and tantalum) is 0.06 Å greater than that of rhenium, one would expect a niobium–nitrogen triple-bond length of 1.76 Å for a six-coordinate 18-electron complex; an additional lengthening for seven-coordination would also be expected. There is an unusually close similarity in the seven-coordinate complexes, $MoCl_2(NR)(S_2CNR'_2)_2$[3] and $Nb(NR)(S_2CNCNR'_2)_3$. Both have distorted pentagonal-bipyramidal geometries, slightly bent NR ligands (M–N–R ≃ 168°), and nearly identical metal–nitrogen bond orders (Nb–N > Mo–N by 0.049 Å; Nb radius > Mo radius by 0.046 Å).

Since the molecular structure of $NbO(S_2CNEt_2)_3$ has been determined, one can compare the Nb–O bond length with the Nb≡NR bond length in $Nb(NC_7H_7)(S_2CNR_2)_3$. One finds that the Nb≡O bond length of 1.74 (1) Å is 0.04 Å shorter than the Nb≡NR bond length. This difference compares well with the 0.033-Å difference observed in the seven-coordinate complexes, $MoCl_2(NPh)(S_2CNEt_2)_2$[4] and $MoOCl_2(S_2CNEt_2)_2$.[25] Similarly, the Ta≡O bond length in $TaO(N\text{-}i\text{-}Pr_2)_3$[2] is 0.04 Å shorter than the Ta≡NR bond length in $Ta(N\text{-}t\text{-}Bu)(NMe_2)_3$.[6]

In light of the apparent stability of 16-electron Nb and Ta nitrene complexes, we thought that we might be able to prepare *trans*-$NbCl(NR)(S_2CNR'_2)_2$. Indeed, a deficiency of dithiocarbamate in the reaction procedures leads to different products, but none could be isolated in a pure state. Similarly, we tried to use nitrogen compounds other than RNH_2 and R_2NNH_2 to prepare Nb and Ta complexes. The use of anhydrous NH_3, $RNHNH_2$, or $PhCH{=}NNH_2$ produced vigorous reactions, but pure products could not be isolated. Furthermore, we note that the addition of anhydrous N_2H_4/Et_3N to $NbCl_5$ or $TaCl_5$ followed by $Me_3SiS_2CNMe_2$ produced deep red solutions whose NMR spectra seemed to indicate the presence of a single metal-containing species. Although satisfactory elemental analyses have not been obtained as yet for the red crystalline solids, the analyses are not inconsistent with formulations such as $(HN)M(S_2CNMe_2)_3$ or $[(-N)M(S_2CNMe_2)_3]_2$. Using different synthetic routes, Schrock and co-workers have prepared related complexes, $[(-N)TaCl_3L_2]_2$ ($L = PEt_3$, THF),[12,26] and shown them to be thermally stable.

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Registry No. $Nb(NMe)(S_2CNEt_2)_3$, 85565-28-2; $Nb(N\text{-}n\text{-}Pr)(S_2CNEt_2)_3$, 85565-29-3; $Nb(N\text{-}i\text{-}Pr)(S_2CNEt_2)_3$, 85565-30-6; $Nb(N\text{-}t\text{-}Bu)(S_2CNEt_2)_3$, 85565-31-7; $Ta(N\text{-}t\text{-}Bu)(S_2CNEt_2)_3$, 85565-32-8; $Nb(NPh)(S_2CNEt_2)_3$, 85565-37-3; $Nb(p\text{-}NC_6H_4OMe)(S_2CNEt_2)_3$, 85565-36-2; $Nb(p\text{-}NC_6H_4Me)(S_2CNEt_2)_3$, 85565-35-1; $Nb(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$, 85565-33-9; $Nb(p\text{-}NC_6H_4OMe)(S_2CNMe_2)_3$, 85565-43-1; $Nb(p\text{-}NC_6H_4Me)(S_2CNMe_2)_3$, 85565-34-0; $Ta(N\text{-}t\text{-}Bu)(S_2CNMe_2)_3$, 84416-70-6; $Nb(NNMe_2)(S_2CNEt_2)_3$, 85565-38-4; $Nb(NNMePh)(S_2CNEt_2)_3$, 85565-40-8; $Nb(NN(CH_2)_5)(S_2CNEt_2)_3$, 85565-39-5; $Nb(NNMe_2)(S_2CNMe_2)_3$, 85565-42-0; $Nb(NNMePh)(S_2CNMe_2)_3$, 85565-41-9; AgS_2CNMe_2, 15278-94-1; AgS_2CNEt_2, 1470-61–7; TlS_2CNMe_2, 14930-31-5; TlS_2CNEt_2, 18756-72-4; Me_3SiNEt_2, 996-50-9; $Me_3SiS_2CNEt_2$, 18881-57-7; Me_3SiNMe_2, 2083-91-2; $Me_3SiS_2CNMe_2$, 18140-13-1; methylamine, 74-89-5; *n*-propylamine, 107-10-8; isopropylamine, 75-31-0; *tert*-butylamine, 75-64-9; *p*-toluidine, 106-49-0; 1,1-dimethylhydrazine, 57-14-7; 1,1-methylphenylhydrazine, 618-40-6; aniline, 62-53-3; *p*-anisidine, 104-94-9; *N*-aminopiperidine, 2213-43-6.

Supplementary Material Available: Tables S-I–S-IV, showing anisotropic thermal parameters, parameters for H atoms, root-mean-square amplitudes of vibration, and bond distances and angles, and a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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