

Synthesis and structural characterization of dialkyldithiocarbamate complexes of niobium

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The reaction of alkyne-containing niobium(III) complexes [NbCl₃(dme)(RC≡CR')] (dme = 1,2-dimethoxyethane) with the appropriate Na(S₂CNR'₂) reagents, in a 1:3 molar ratio, afforded the corresponding dialkyldithiocarbamate complexes [Nb(RC≡CR')(S₂CNR'₂)₃] (R = R' = Ph, R'' = Me **1**; R = R' = Ph, R'' = Et **2**; R = R' = R'' = Me **3**; R = R' = Me, R'' = Et **4**; R = R' = Et, R'' = Me **5**; R = R' = R'' = Et **6**; R = R' = SiMe₃, R'' = Me **7**; R = R' = SiMe₃, R'' = Et **8**; R = Ph, R' = Me, R'' = Me **9**). The same complexes were also prepared from the reaction of the appropriate [NbCl₃(bpzm)(RC≡CR')] [bpzm = bis(pyrazol-1-yl)methane] complexes with the corresponding sodium dialkyldithiocarbamates. All complexes were spectroscopically characterized and the dynamic behaviour of some of them was studied by variable-temperature NMR techniques. The molecular structure of complex **9** was also established.

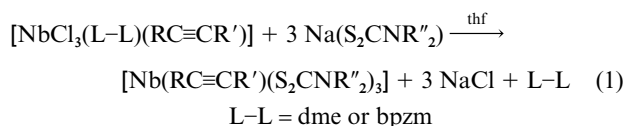
Alkyldithiocarbamate-containing metal complexes are extensively known.¹ With respect to the Group 5 metals, an increasing interest in the formation of this class of complexes has recently been shown. The first such complexes, described in 1965, were synthesized by reaction of the M(NR₂)_x species with CS₂,² and since then several others have been described. The most obvious way to prepare these species is the reaction of metal halides with anhydrous sodium alkyldithiocarbamates and a wide variety of complexes can be isolated depending upon the nature of the solvent, stoichiometry of the reagents, and reaction temperature. Thus, the reaction of Na(S₂CNR₂) with MX_n (M = Nb or Ta; X = Cl or Br; n = 4 or 5) in different solvents afforded the complexes M(S₂CNR₂)_n (n = 4 or 5) and [MX(OR)₂(S₂CNR₂)₂].³ However, the most important family of this class of complexes corresponds to the compounds of stoichiometry ML(S₂CNR₂)₃ (M = Nb or Ta; L = O, S, NR, S₂ or N₂R₂).⁴ Furthermore, it is noteworthy that in all the above-mentioned complexes the metal appears in a higher oxidation state, five, and only a few examples of complexes in lower oxidation states have been described [e.g. several alkyldithiocarbamates of vanadium(III)].⁵

Following our research on alkyne-containing niobium(III) complexes,⁶ and in order to obtain more insight into their dynamic behaviour, we have undertaken new studies on the synthesis of dialkyldithiocarbamate-containing niobium species by the reaction of the complexes [NbCl₃(dme)(RC≡CR')] or [NbCl₃(bpzm)(RC≡CR')] [bpzm = bis(pyrazol-1-yl)methane] with the appropriate sodium dialkyldithiocarbamate salt, Na(S₂CNR'₂). The aim of this work was to investigate the synthesis and the structural characterization of new dialkyldithiocarbamate niobium complexes, [Nb(RC≡CR')(S₂CNR'₂)₃].

Results and Discussion

The reaction of [NbCl₃(dme)(RC≡CR')] or [NbCl₃(bpzm)(RC≡CR')] with the appropriate sodium dialkyldithiocarbamate salts have been attempted. The standard reaction involved the addition of thf to a mixture of the complex and Na(S₂CNR'₂) in a 1:3 molar ratio to give, after stirring for 4 h, solutions from which the different products were isolated,

after appropriate work-up as air-stable solids corresponding to [Nb(RC≡CR')(S₂CNR'₂)₃] **1–9** [equation (1)]. The same



- 1** R = R' = Ph, R'' = Me; **2** R = R' = Ph, R'' = Et;
3 R = R' = R'' = Me; **4** R = R' = Me, R'' = Et;
5 R = R' = Et, R'' = Me; **6** R = R' = R'' = Et;
7 R = R' = SiMe₃, R'' = Me; **8** R = R' = SiMe₃, R'' = Et;
9 R = Ph, R' = R'' = Me

complexes were isolated, together with starting material, when the reactions were carried out in 1:1 or 1:2 molar ratios, indicating that the complexes containing three dithiocarbamate ligands are especially stable. Different types of Group 5 metal-containing complexes with three dithiocarbamate groups have been previously described.⁴ Complexes **1–9** are soluble in polar solvents such as dichloromethane, chloroform and acetone, but insoluble in alkanes.

Complexes **1–9** were characterized by standard spectroscopic techniques. Their IR spectra show a characteristic band at ca. 990 cm⁻¹, corresponding to the ν(C=S) of a dithiocarbamate unit co-ordinated in a bidentate fashion⁷ and another band at ca. 360 cm⁻¹ for ν(Nb-S) (see Experimental section). However, it was not possible to observe in the IR spectra the characteristic band for the ν(C≡C) of the co-ordinated alkyne unit, which in the spectra of the starting materials appears as an absorption of medium to weak intensity in the range 1692–1719 cm⁻¹.⁶ However, the NMR spectral data are the most valuable in establishing the structure of the complexes. Proton NMR spectra at room temperature show four sets of resonances for the alkyl group on the dithiocarbamate ligands, which is in accordance with a pentagonal bipyramidal structure in the solid state,⁸ as shown in Fig. 1, where a dithiocarbamate ligand occupies an equatorial-axial disposition and the alkyne ligand a single co-ordination site, although a distorted dodecahedral geometry⁹ where the alkyne, being bidentate, occupies two sites may also be considered (Experimental section); for example, in the ¹H

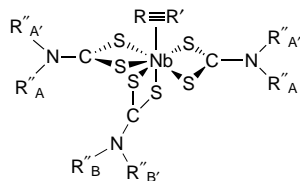


Fig. 1 Molecular structure for complexes 1–9

NMR spectra of those complexes which contain methyl groups in the dithiocarbamate ligands, four single resonances, with relative intensities 1 : 1 : 2 : 2 ($R''_B : R''_B' : R''_A : R''_A'$), are observed. In the spectra of complexes containing ethyl groups the CH_2 protons behave as an AB spin system (Experimental section). The ^{13}C NMR spectra exhibit four resonances for the carbon atoms of the methyl and ethyl groups in those complexes with dimethyl- and diethyl-dithiocarbamate ligands, respectively, as well as two resonances at δ ca. 210, one for the carbon atom of the equatorial dithiocarbamates and the other for the carbon atom of the equatorial-axial dithiocarbamate (see Experimental section). It is noteworthy that at room temperature a static structure is present in the complexes, since in all other dialkyldithiocarbamatoniobium species $[\text{NbL}(\text{S}_2\text{CNR}_2)_3]$ described previously⁴ fluxionality is observed even at low temperature which renders the dialkyldithiocarbamate groups equivalent. However, in complexes 1–9 a similar situation was found at high temperature (see below). With regard to the alkyne moiety, the ^{13}C NMR spectroscopic data for 1–9 (see Experimental section) indicate that it behaves as a four-electron donor.¹⁰ In fact, the chemical shift values at δ ca. 220 are a clear indication that the number of electrons donated per alkyne is four, in such a way that the role of both bonding π_{\parallel} and π_{\perp} orbitals in donating electrons is not in conflict with acceptance of electron density from the niobium centre into the antibonding π^*_{\parallel} orbital of the alkyne. In addition, ^1H and ^{13}C NMR spectra of complexes 1–8 indicate that both halves of the alkyne ligands are equivalent and a simple rotation of the alkyne ligand around the bisector of the metal–alkyne isosceles triangle is proposed to occur. A ^1H – ^{13}C heteronuclear correlation (HETCOR) experiment carried out for complex 4 has allowed us to assign the resonances corresponding to the methyl and methylene carbon atoms of the S_2CNET_2 moiety and distinguish them from those corresponding to the methyl alkyne groups. The proposed structure for complexes 1–9 was unequivocally confirmed by the crystal structure of $[\text{Nb}(\text{PhC}\equiv\text{CMe})(\text{S}_2\text{CNMe}_2)_3]$ 9.

A plot of the molecular structure of complex 9 is presented in Fig. 2. Selected bond lengths and angles are listed in Table 1. In the eight-co-ordination description, where the alkyne ligand occupies two sites, atoms S(1), S(5), S(4) and C(3) occupy the A sites and S(2), S(6), S(3) and C(2) the B sites of a distorted dodecahedron. The three bidentate dimethyldithiocarbamate ligands span three edges, the fourth one being occupied by the alkyne. Interestingly, the average Nb– S_A and Nb– S_B bond lengths are equal (2.60 Å) and, furthermore, there is no preference for Nb– S_A to be longer than Nb– S_B . Indeed, in each set, one short, one intermediate and one long Nb–S bond is found. This is ascribed to the very small bite angle of the phenylpropyne ligand [$\text{C}(2)\text{–Nb–C}(3)$ $36.5(3)^\circ$]. Similar patterns of discrepancy have been observed in other Group 5 metal complexes of the type $\text{M}(\text{S}_2\text{CNR}_2)_3$ - (bidentate ligand).^{4a,h,f}

Focusing on the alkyne ligand, we find short Nb–C bonds [Nb–C(2) 2.080(7), Nb–C(3) 2.086(7) Å] and an elongated C≡C bond [C(2)–C(3) 1.306(9) Å]. It is the only case in the series of tris(dialkyldithiocarbamate) complexes where the A and B sites occupied by the unique ligand are symmetrically bound to the metal. The Nb–C bond lengths indicate multiple bonding. Such bond lengths, as seen in other Group 5 metal complexes,¹⁰ characterise 4e-alkyne ligands.¹² In these complexes the alkyne

Table 1 Bond lengths (Å) and angles ($^\circ$) for compound 9· $\text{C}_6\text{H}_5\text{Me}$

Nb–C(2)	2.080(7)	N(1)–C(11)	1.47(1)
Nb–C(3)	2.086(7)	N(1)–C(12)	1.45(1)
Nb–S(1)	2.630(2)	S(3)–C(13)	1.709(6)
Nb–S(2)	2.578(2)	C(13)–S(4)	1.718(7)
Nb–S(3)	2.631(2)	C(13)–N(2)	1.331(9)
Nb–S(4)	2.567(2)	N(2)–C(14)	1.44(1)
Nb–S(5)	2.599(2)	N(2)–C(15)	1.46(1)
Nb–S(6)	2.600(2)	S(5)–C(16)	1.714(7)
C(2)–C(3)	1.306(9)	C(16)–S(6)	1.708(6)
C(2)–C(1)	1.49(1)	C(16)–N(3)	1.321(9)
C(3)–C(4)	1.470(9)	N(3)–C(17)	1.458(9)
C(4)–C(5)	1.37(1)	N(3)–C(18)	1.450(9)
C(4)–C(9)	1.38(1)	C(100)–C(101)	1.435(6)
C(5)–C(6)	1.40(1)	C(101)–C(102)	1.391(7)
C(6)–C(7)	1.35(1)	C(101)–C(106)	1.380(7)
C(7)–C(8)	1.35(1)	C(102)–C(103)	1.383(8)
C(8)–C(9)	1.38(1)	C(103)–C(104)	1.388(8)
S(1)–C(10)	1.699(8)	C(104)–C(105)	1.372(8)
C(10)–S(2)	1.716(7)	C(105)–C(106)	1.390(8)
C(10)–N(1)	1.322(9)		
C(2)–Nb–C(3)	36.5(3)	Nb–S(2)–C(10)	90.7(3)
S(1)–Nb–S(2)	66.48(6)	Nb–S(3)–C(13)	87.0(3)
S(3)–Nb–S(4)	68.03(6)	S(3)–C(13)–S(4)	116.1(4)
S(5)–Nb–S(6)	66.77(5)	S(3)–C(13)–N(2)	122.1(6)
Nb–C(2)–C(3)	72.0(4)	S(4)–C(13)–N(2)	121.7(5)
Nb–C(3)–C(2)	71.5(4)	Nb–S(4)–C(13)	88.9(2)
Nb–C(3)–C(4)	148.1(5)	Nb–S(5)–C(16)	89.7(2)
C(2)–C(3)–C(4)	140.2(7)	S(5)–C(16)–S(6)	113.4(4)
Nb–S(1)–C(10)	89.4(2)	S(5)–C(16)–N(3)	123.3(5)
S(1)–C(10)–S(2)	113.4(4)	S(6)–C(16)–N(3)	123.3(5)
S(1)–C(10)–N(1)	124.1(6)	Nb–S(6)–C(16)	89.8(3)
S(2)–C(10)–N(1)	122.5(6)		

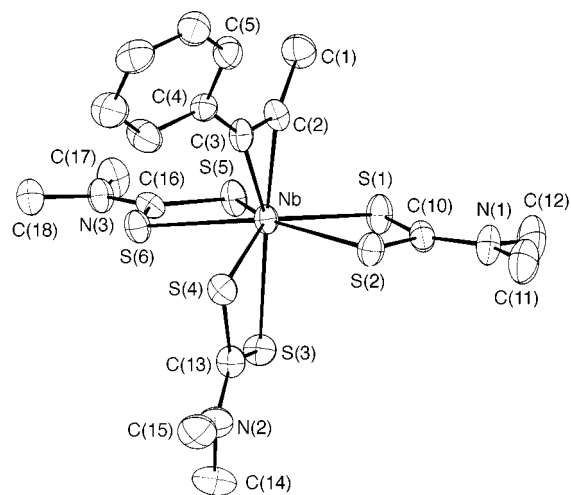


Fig. 2 An ORTEP¹¹ diagram for complex 9

may thus be viewed as a dianion thus oxidizing the metal by two units to give a d^0 niobium(v) centre.

If the alkyne is considered to occupy a single co-ordination site, in a pentagonal bipyramidal geometry, two dialkyldithiocarbamate ligands occupy the equatorial plane and their four sulfur atoms are virtually coplanar. The third dithiocarbamate ligand spans the remaining equatorial site S(4) and an axial site S(3), *trans* to the alkyne. For this ligand Nb– S_{ax} is relatively long [2.631(2) Å], and markedly longer than Nb– S_{eq} [2.567(2) Å], a feature that has also been ascribed to the presence of multiple metal–ligand bonding in the *trans* position.^{4f,9} The *trans* influence of 4e-alkyne ligands has been noted previously.^{12a} As suggested elsewhere, 4e-alkyne and imide ligands are very similar.¹³ Indeed, the true (*p*-tolylimido)niobium(v) complex $[\text{Nb}(\text{S}_2\text{CNET}_2)_3(=\text{NC}_6\text{H}_4\text{Me}-4)]$ has been synthesized^{4f} and its molecular structure reveals high similarities with that of 9.

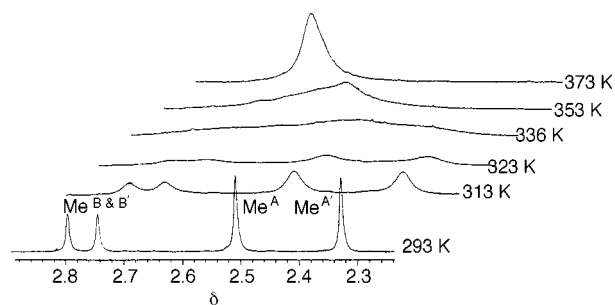


Fig. 3 Methylthiocarbamate region in the variable-temperature ^1H NMR spectrum of complex **3**

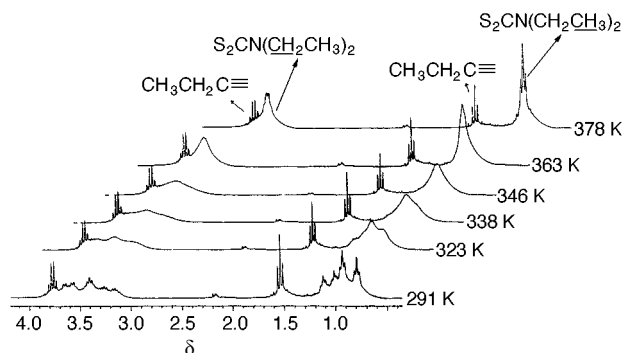


Fig. 4 Ethylthiocarbamate and acetylene region in the variable-temperature ^1H NMR spectra of complex **6**

Variable-temperature NMR studies for complexes **3**, **4**, **5**, **6** and **7** were carried out in order to elucidate the dynamic behaviour in solution. It has been established that at high temperatures the three dialkylthiocarbamate groups are equivalent indicating that a fast exchange between them takes place. However, when the temperature was lowered, even to 188 K, the alkyne ligand in the complexes remained fluxional and therefore it was not possible to block its rotation, indicating that low energy barriers to alkyne rotation are involved¹⁰ in a similar behaviour to that previously described for complexes $[\text{NbCl}_3(\text{bpzm})(\text{RC}\equiv\text{CR}')]_3$.⁶ For complex **3** when the temperature was raised, see Fig. 3, two independent coalescences for the methyl groups of equatorial-axial (B,B') and equatorial (A,A') dithiocarbamate ligands were observed (at lower temperature for B,B') and finally a broad singlet at 373 K for all the methyl groups appeared. The different coalescence values may be due to the differences in Δv ($\Delta v_{\text{B,B}'} < \Delta v_{\text{A,A}'}$). In the variable-temperature NMR spectra for complexes **5** and **7** a similar situation was found and a broad singlet was observed at 373 and 378 K, respectively. The studies for complexes **4** and **6** are a little more complicated because of the multiplicity of signals for the ethyl groups. Fig. 4 shows the variable-temperature NMR spectra for **6** where it can be seen that both a triplet and quadruplet appear at 378 K for all equivalent ethyl groups.

Conclusion

This study has revealed that the niobium complex $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]_3$ or $[\text{NbCl}_3(\text{bpzm})(\text{RC}\equiv\text{CR}')]_3$ reacts readily with 3 equivalents of the appropriate sodium dialkylthiocarbamate salts, giving rise to the alkyne complexes $[\text{Nb}(\text{RC}\equiv\text{CR}')(\text{S}_2\text{CNR}'_2)_3]$. The NMR spectroscopic studies reveal a static structure and a fluxional behaviour for the dithiocarbamate and alkyne ligands respectively at room temperature, although a dynamic behaviour of the former was observed at high temperatures. We believe that the results reported offer a significant advance in the chemistry of alkyne-containing niobium complexes, and work in this field is ongoing.

Experimental

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were obtained in the region 4000–200 cm^{-1} , using a Perkin-Elmer 883 spectrophotometer, ^1H and ^{13}C NMR spectra on a Varian Unity FT-300 spectrometer and referenced to the residual deuterated solvent. The sodium dialkylthiocarbamates were provided by Fluka Chemical and the complexes $[\text{NbCl}_3(\text{dme})(\text{RC}\equiv\text{CR}')]_3$ were prepared as reported previously.¹⁴

Preparations

[Nb(PhC≡CPh)(S₂CNMe₂)₃] 1. To a mixture of $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CPh})]$ (0.50 g, 1.07 mmol) or $[\text{NbCl}_3(\text{bpzm})(\text{PhC}\equiv\text{CPh})]$ (0.56 g, 1.07 mmol) and $\text{Na}(\text{S}_2\text{CNMe}_2)$ (0.46 g, 3.21 mmol) was added thf (50 cm^3). The suspension was stirred for 6 h at room temperature, then evaporated to dryness and the residue extracted with toluene ($3 \times 50 \text{ cm}^3$). The resulting suspension was filtered through Celite giving an orange-red solution which was evaporated to dryness giving complex **1** as an orange solid. Yield 83% (Found: C, 44.02; H, 4.68; N, 6.79. $\text{C}_{23}\text{H}_{28}\text{N}_3\text{NbS}_6$ requires C, 43.76; H, 4.43; N, 6.65%). ^1H NMR (C_6D_6 , 295 K): δ 8.27–7.31 (m, 10 H, Ph), 2.66 (s, 6 H, $\text{R}''_{\text{B}} + \text{R}''_{\text{B}'}$), 2.22, 2.36 (s, 12 H, $\text{R}''_{\text{A}} + \text{R}''_{\text{A}'}$). ^{13}C - $\{^1\text{H}\}$ NMR: δ 212.7 (C≡C), 209.9 ($\text{S}_2\text{CN}_{\text{ax-eq}}$), 203.7 ($\text{S}_2\text{CN}_{\text{eq-eq}}$), 141.7–127.9 (Ph), 40.6, 40.0 ($\text{R}''_{\text{B}} + \text{R}''_{\text{B}'}$), 39.1, 38.6 ($\text{R}''_{\text{A}} + \text{R}''_{\text{A}'}$). IR (Nujol, cm^{-1}): 362s [$\nu(\text{Nb-S})$] and 991s [$\nu(\text{C}\equiv\text{S})$].

[Nb(PhC≡CPh)(S₂CNEt₂)₃] 2. The synthetic procedure was the same as for complex **1**, using $[\text{NbCl}_3(\text{dme})(\text{PhC}\equiv\text{CPh})]$ (0.50 g, 1.07 mmol) and $\text{Na}(\text{S}_2\text{CNEt}_2)$ (0.55 g, 3.21 mmol), giving **2** as an orange solid. Yield 87% (Found: C, 48.34; H, 5.59; N, 6.09. $\text{C}_{29}\text{H}_{40}\text{N}_3\text{NbS}_6$ requires C, 48.67; H, 5.58; N, 5.87%). ^1H NMR (C_6D_6 , 295 K): δ 0.58, 0.67 [t, $^3J = 7.0$, 12 H, $\text{CH}_3(\text{R}''_{\text{A}} + \text{R}''_{\text{A}'})$], 0.83, 0.91 [t, $^3J = 7.0$ Hz, 6 H, $\text{CH}_3(\text{R}''_{\text{B}} + \text{R}''_{\text{B}'})$], 3.02, 3.15, 3.20, 3.45 [q, 12 H, $\text{CH}_2(\text{R}''_{\text{A}}\text{R}''_{\text{A}'} + \text{R}''_{\text{B}} + \text{R}''_{\text{B}'})$] and 7.28–8.13 (m, 10 H, Ph). ^{13}C - $\{^1\text{H}\}$ NMR: δ 213.1 (C≡C), 209.2 ($\text{S}_2\text{CN}_{\text{ax-eq}}$), 203.5 ($\text{S}_2\text{CN}_{\text{eq-eq}}$), 143.1–127.4 (Ph), 45.1, 44.4, 44.0, 43.3, $[\text{CH}_2(\text{R}''_{\text{A}}\text{R}''_{\text{A}'} + \text{R}''_{\text{B}}\text{R}''_{\text{B}'})]$, 12.2 [$\text{CH}_3(\text{R}''_{\text{A}} + \text{R}''_{\text{A}'})$], $\text{CH}_3(\text{R}''_{\text{B}} + \text{R}''_{\text{B}'})$). IR (cm^{-1}): 361s [$\nu(\text{Nb-S})$] and 1003s [$\nu(\text{C}\equiv\text{S})$].

[Nb(MeC≡CMe)(S₂CNMe₂)₃] 3. As for complex **1** using $[\text{NbCl}_3(\text{dme})(\text{MeC}\equiv\text{CMe})]$ (0.50 g, 1.45 mmol) and $\text{Na}(\text{S}_2\text{CNMe}_2)$ (0.62 g, 4.36 mmol), giving **3** as an orange solid. Yield 75% (Found: C, 30.62; H, 4.68; N, 8.45. $\text{C}_{13}\text{H}_{24}\text{N}_3\text{NbS}_6$ requires C, 30.79; H, 4.83; N, 8.28%). ^1H NMR (C_6D_6 , 295 K): δ 3.27 (s, 6 H, MeC≡), 2.77, 2.75 (s, 6 H, $\text{R}''_{\text{B}} + \text{R}''_{\text{B}'}$), 2.50, 2.35 (s, 12 H, $\text{R}''_{\text{A}} + \text{R}''_{\text{A}'}$). ^{13}C - $\{^1\text{H}\}$ NMR: δ 217.0 (C≡C), 211.3 ($\text{S}_2\text{CN}_{\text{ax-eq}}$), 205.0 ($\text{S}_2\text{CN}_{\text{eq-eq}}$), 39.7, 39.3 ($\text{R}''_{\text{B}} + \text{R}''_{\text{B}'}$), 38.1, 37.4 ($\text{R}''_{\text{A}} + \text{R}''_{\text{A}'}$), 19.7 (MeC≡). IR (Nujol, cm^{-1}): 354s [$\nu(\text{Nb-S})$] and 992s [$\nu(\text{C}\equiv\text{S})$].

[Nb(MeC≡CMe)(S₂CNEt₂)₃] 4. As for complex **1** using $[\text{NbCl}_3(\text{dme})(\text{MeC}\equiv\text{CMe})]$ (0.50 g, 1.45 mmol) and $\text{Na}(\text{S}_2\text{CNEt}_2)$ (0.75 g, 4.36 mmol), giving **4** as an orange solid. Yield 70% (Found: C, 38.37; H, 5.96; N, 6.52. $\text{C}_{19}\text{H}_{36}\text{N}_3\text{NbS}_6$ requires C, 38.54; H, 6.08; N, 7.10%). ^1H NMR (C_6D_6 , 295 K): δ 0.67, 0.80 [t, $^3J = 7.0$, 12 H, $\text{CH}_3(\text{R}''_{\text{A}} + \text{R}''_{\text{A}'})$], 0.92, 1.05 [t, $^3J = 7.0$ Hz, 6 H, $\text{CH}_3(\text{R}''_{\text{B}} + \text{R}''_{\text{B}'})$], 3.12 (s, 6 H, MeC≡), 3.18, 3.32, 3.30, 3.45 [q, 12 H, $\text{CH}_2(\text{R}''_{\text{A}}\text{R}''_{\text{A}'} + \text{R}''_{\text{B}}\text{R}''_{\text{B}'})$]. ^{13}C - $\{^1\text{H}\}$ NMR: δ 216.2 (C≡C), 209.7 ($\text{S}_2\text{CN}_{\text{ax-eq}}$), 203.7 ($\text{S}_2\text{CN}_{\text{eq-eq}}$), 45.3, 44.6, 44.0, 43.8 [$\text{CH}_2(\text{R}''_{\text{A}}\text{R}''_{\text{A}'} + \text{R}''_{\text{B}}\text{R}''_{\text{B}'})$], 19.6 (MeC≡), 12.4 [$\text{CH}_3(\text{R}''_{\text{A}} + \text{R}''_{\text{A}'})$], $\text{CH}_3(\text{R}''_{\text{B}} + \text{R}''_{\text{B}'})$). IR (Nujol, cm^{-1}): 360s [$\nu(\text{Nb-S})$] and 1007s [$\nu(\text{C}\equiv\text{S})$].

[Nb(EtC≡CEt)(S₂CNMe₂)₃] 5. As for complex **1** using $[\text{NbCl}_3(\text{dme})(\text{EtC}\equiv\text{CEt})]$ (0.50 g, 1.34 mmol) and $\text{Na}(\text{S}_2\text{CNMe}_2)$

CNMe₂) (0.56 g, 4.04 mmol), giving **5** as an orange solid. Yield 81% (Found: C, 33.50; H, 5.25; N, 7.78. C₁₅H₂₈N₃NbS₆ requires C, 33.67; H, 5.23; N, 7.84%). ¹H NMR (C₆D₆, 295 K): δ 1.57 (t, 6 H, ³J = 7.5, CH₃CH₂C≡), 2.33, 2.49 (s, 12 H, R''_A + R''_{A'}), 2.77, 2.74 (s, 6 H, R''_B + R''_{B'}), 3.86 (q, 4 H, ³J = 7.5 Hz, CH₃CH₂C≡). ¹³C-{¹H} NMR: δ 221.0 (C≡C), 211.0 (S₂CN_{ax-eq}), 204.1 (S₂CN_{eq-eq}), 40.7, 40.1 (R''_B + R''_{B'}), 39.1, 38.6 (R''_A + R''_{A'}), 29.3 (CH₃CH₂C≡) and 14.0 (CH₃CH₂C≡). IR (Nujol, cm⁻¹): 360s [ν(Nb–S)] and 997s [ν(C≡S)].

[Nb(EtC≡CEt)(S₂CNEt₂)₃ 6. As for complex **1** using [NbCl₃(dme)(EtC≡CEt)] (0.50 g, 1.34 mmol) and Na(S₂CNEt₂) (0.7 g, 4.04 mmol), giving **6** as an orange solid. Yield 77% (Found: C, 40.25; H, 6.30; N, 6.75. C₂₁H₄₀N₃NbS₆ requires C, 40.73; H, 6.46; N, 6.78%). ¹H NMR (C₆D₆, 295 K): δ 1.55 (t, 6 H, ³J = 7.5 Hz, CH₃CH₂C≡), 0.66, 0.78 [t, ³J = 7.1, 12 H, CH₃(R''_A + R''_{A'})], 0.88, 1.01 [t, ³J = 7.1, 6 H, CH₃(R''_B + R''_{B'})], 3.30, 3.40, 3.70 [q, 12 H, CH₂(R''_AR''_{A'} + R''_BR''_{B'})], 3.84 (q, 4 H, ³J = 7.5 Hz, CH₃CH₂C≡). ¹³C-{¹H} NMR: δ 12.5 (CH₃CH₂C≡), 219.6 (C≡C), 210.1 (S₂CN_{ax-eq}), 203.7 (S₂CN_{eq-eq}), 45.3, 44.6, 44.0, 43.3 [CH₂(R''_AR''_{A'} + R''_BR''_{B'})], 29.7 (CH₃-CH₂C≡) 14.4 [CH₃(R''_A + R''_{A'})], CH₃(R''_B + R''_{B'}) and 12.5 (CH₃CH₂C≡). IR (Nujol, cm⁻¹): 358s [ν(Nb–S)] and 1000s [ν(C≡S)].

[Nb(Me₃SiC≡CSiMe₃)(S₂CNMe₂)₃ 7. As for complex **1** using [NbCl₃(dme)(Me₃SiC≡CSiMe₃)] (0.50 g, 1.09 mmol) and Na(S₂CNMe₂) (0.47 g, 3.26 mmol), giving **7** as an orange solid. Yield 70% (Found: C, 32.76; H, 5.65; N, 6.50. C₁₇H₃₆N₃NbS₆Si₂ requires C, 32.76; H, 5.77; N, 6.73%). ¹H NMR (C₆D₆, 295 K): δ 2.24, 2.47 (s, 12 H, R''_A + R''_{A'}), 2.74, 2.71 (s, 6 H, R''_B + R''_{B'}). ¹³C-{¹H} NMR: δ 2.1 (Me₃SiC≡), 228.2 (C≡C), 212.6 (S₂CN_{ax-eq}), 204.7 (S₂CN_{eq-eq}), 39.8, 39.2 (R''_B + R''_{B'}), 37.9, 37.4 (R''_A + R''_{A'}) and 0.74 (s, 18 H, Me₃SiC≡). IR (Nujol, cm⁻¹): 365s [ν(Nb–S)] and 994s [ν(C≡S)].

[Nb(Me₃SiC≡CSiMe₃)(S₂CNEt₂)₃ 8. As for complex **1** using [NbCl₃(dme)(Me₃SiC≡CSiMe₃)] (0.50 g, 1.09 mmol) and Na(S₂CNEt₂) (0.56 g, 3.26 mmol), giving **8** as a blue-green solid. Yield 78% (Found: C, 38.83; H, 6.58; N, 5.89. C₂₃H₄₈N₃NbS₆Si₂ requires C, 39.05; H, 6.78; N, 5.93%). ¹H NMR (C₆D₆, 295 K): δ 0.73 (s, 18 H, Me₃SiC≡), 0.59, 0.76 [t, ³J = 7.0, 12 H, CH₃(R''_A + R''_{A'})], 0.85, 0.97 [t, ³J = 7.1 Hz, 6 H, CH₃(R''_B + R''_{B'})], 2.90, 3.20, 3.40, 3.45 [q, 12 H, CH₂(R''_AR''_{A'} + R''_BR''_{B'})]. ¹³C-{¹H} NMR: δ 227.3 (C≡C), 211.5 (S₂CN_{ax-eq}), 203.7 (S₂CN_{eq-eq}), 45.2, 44.4, 43.7, 43.1 [CH₂(R''_AR''_{A'} + R''_BR''_{B'})], 12.4 [CH₃(R''_A + R''_{A'})], CH₃(R''_B + R''_{B'}), 2.1 (Me₃SiC≡). IR (Nujol, cm⁻¹): 364s [ν(Nb–S)] and 1009s [ν(C≡S)].

[Nb(PhC≡CMe)(S₂CNMe₂)₃ 9. As for complex **1** using [NbCl₃(dme)(PhC≡CMe)] (0.50 g, 1.23 mmol) and Na(S₂CNMe₂) (0.53 g, 3.70 mmol), giving **9** as an orange solid. Yield 90% (Found: C, 37.63; H, 4.51; N, 7.35. C₁₈H₂₆N₃NbS₆ requires C, 37.98; H, 4.56; N, 7.38%). ¹H NMR (C₆D₆, 295 K): δ 3.14 (s, 3 H, MeC≡), 3.09, 3.14 (s, 12 H, R''_A + R''_{A'}), 3.47, 3.42 (s, 6 H, R''_B + R''_{B'}) and 7.25–7.83 (m, 5 H, ≡CPh). ¹³C-{¹H} NMR: δ 222.5, 210.1 (C≡C), 208.7 (S₂CN_{ax-eq}), 204.1 (S₂CN_{eq-eq}), 140.4–127.7 (≡CPh), 40.9, 40.3 (R''_B + R''_{B'}), 39.4, 38.8 (R''_A + R''_{A'}) and 20.5 (MeC≡). IR (Nujol, cm⁻¹): 360s [ν(Nb–S)] and 992s [ν(C≡S)].

Crystallography

Crystals of complex **9** were grown from a solution of toluene by slow evaporation of solvent. A detailed summary of the experimental and refinement data is presented in Table 2. The data collection at 293 K was performed on an IPDS STOE diffractometer using graphite-monochromatized Mo-K α radiation (λ 0.710 73 Å). The structure was solved by direct methods using SIR 92¹⁵ and subsequent Fourier-difference

Table 2 Crystal data, data collection and refinement parameters for 9-C₆H₅Me

Chemical formula	C ₂₅ H ₃₄ N ₃ NbS ₆
<i>M</i>	661.83
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.372(2)
<i>b</i> /Å	28.914(4)
<i>c</i> /Å	11.456(2)
β /°	98.11(2)
<i>U</i> /Å ³	3073(1)
<i>Z</i>	4
<i>D</i> _c /g cm ⁻³	1.43
μ /cm ⁻¹	0.79
<i>F</i> (000)	1362
Crystal size/mm	0.3 × 0.4 × 0.4
Crystal shape, colour	Block, red
2 θ Range/°	2.9–48.4
<i>hkl</i> Ranges	–10 to 10, 0–33, 0–13
No. reflections used for cell post-refinement	2000
No. measured reflections	18 192
No. independent reflections	4614
No. reflections used [<i>I</i> > 3 σ (<i>I</i>)]	2556
<i>R</i> _{merge}	0.1167
<i>R</i>	0.0473
<i>R</i> '	0.0546
Goodness of fit*	1.174
No. parameters	317
Residual density (minimum, maximum)/e Å ⁻³	–0.40, +0.88

* $[\sum(|F_o - F_c|)^2 / (N_o - N_p)]^{1/2}$ where *N*_o, *N*_p = number of observables and parameters.

maps. No absorption corrections were made. The refinement on *F* was carried out with the CRYSTALS package.¹⁶ One molecule of toluene was found in the asymmetric unit. Hydrogen atoms were included as fixed contributors (C–H 0.96 Å) with isotropic thermal parameters fixed 20% higher than those of the carbon atom to which they were connected. Their positions were recalculated after each cycle of refinement. All non-hydrogen atoms were anisotropically refined. The toluene molecule was constrained to lie planar with C–C–C angles of 120.0(5)°, C–C bond lengths of 1.40(1) Å within the aromatic ring, and a length of 1.50(1) Å for the exocyclic C–C bond. Refinements in three blocks were carried out by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where *F*_o and *F*_c are the observed and calculated structure factors. Convergence was reached with $R = \sum(|F_o| - |F_c|) / \sum |F_o| = 0.0473$ and $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2]^{1/2} = 0.0546$.

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