Synthesis and structures of monocyclopentadienylniobium complexes with bi- and tri-dentate dithiolate ligands †

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Reactions of cyclopentadienyl and methylcyclopentadienyl-tetrachloroniobium with thallium(I) 1,3-propanedithiolate yield compounds $[NbCp^x(1,3\text{-}S_2C_3H_6)_2]$ [**1**, $Cp^x = \eta\text{-}C_5H_5$ (Cp); **2**, $Cp^x = \eta\text{-}C_5H_4Me$ (Cp′)]; similar reactions of the thallium(I) derivative of 2,2′-thiodiethanethiol afford $[NbCp^xCl_2\{(SC_2H_4)_2S\}]$ (**3**, $Cp^x = Cp$; **4**, $Cp^x = Cp′$). Reaction of $[NbCp′Cl_4]$ with thallium(I) 2,2′-oxydiethanethiolate produces both $[NbCp′Cl_2\{(SC_2H_4)_2O\}]$ **5** and $[NbCp′O\{(SC_2H_4)_2O\}]$ **6**. Products have been characterised analytically and by NMR spectroscopy; the solid-state structures of **1**, **3**, **5** and **6** have been established by XRD. Compound **1** is five-coordinate, with a distorted four-legged piano-stool geometry, compound **3** is six-coordinate with tridentate thiolate and *cis*-equatorial Cl ligands, compound **5** is also six-coordinate but with *trans*-equatorial Cl ligands, and compound **6** is five-coordinate, approximating to a trigonal bipyramidal geometry with an equatorial oxo ligand. Compounds **1** and **2** are fluxional in solution due to non-rigidity of the twist conformations of the six-membered chelate rings, as shown by VT ^1H NMR spectroscopic studies with $\Delta G^{\ddagger} = 42.7 \pm 1.4$ kJ mol^{-1} (at 231 K) and $\Delta G^{\ddagger} = 43.1 \pm 1.3$ kJ mol^{-1} (at 233 K), respectively, for ring inversion in toluene solutions. Cyclic voltammetric studies on **1** and **2** showed two consecutive, quasi-reversible, reduction processes, attributable to the sequential formation of mono- and di-anionic derivatives; reductions of the other compounds showed less evidence for reversibility. ESR spectra of the initial products of chemical reduction of **1** and **2** in thf, using either a sodium film or cobaltocene as reductant, are typical of those from Nb(IV) species and assigned to the respective mono-anions.

Introduction

The chemistry of monocyclopentadienyl thiolate complexes of the early transition metals has received the attention of several groups of workers in recent years,[1a] including derivatives with unsaturated dithiolene ligands.[1b] A number of monocyclopenta-dienyltitanium complexes with alkane thiolate and dithiolate ligands have been investigated,[1a,2] including work from our laboratories.[3] Related mononuclear derivatives of the Group 6 metals have also been reported,[4,5] and in this area we have previously studied a number of derivatives of Group 6 metals, including anionic complexes of the type $[MoCp(SAr)_4]^-$ (Cp = $\eta\text{-}C_5H_5$, Ar = fluoroaryl group) with four-legged piano-stool geometry, which act as polydentate ligands to large metal cations.[6] These interactions, and related observations on titanium derivatives, suggest potential applications of such polythiolate transition metal complexes as sensors for metal ions.

For group 5 transition metals, a number of monocyclopenta-dienyl polythiolates have been reported for tantalum, *i.e.* $[TaCp^*(dithiolate)_2]$ (Cp* = $\eta\text{-}C_5Me_5$; dithiolate = 1,2-ethene-dithiolate, 1,2-ethanedithiolate, 2,3-*exo*-norbornanedithiolate),[7,8] $[TaCp′(SPh)_4]$ (Cp′ = $\eta\text{-}C_5H_4Me$),[9] $[TaCp^*(S^tBu)_3$-$(O^nBu)]$,[10] and $[TaCp^*(S^tBu)_2(N,N′\text{-}^tBu_2\text{-diazabutadiene})]$;[11] other complexes of the Cp*Ta entity with 2-butanethiolate and with 1,2-ethane and 1,3-propane-dithiolate ligands, as well as rearranged species formed by ensuing C–S bond cleavage reactions, are briefly described in a review.[5] More recently, complexes of the tridentate ligands, 2,2′-thiodiethanethiol and 2,2′-oxydiethanethiol, $[TaCp^*X_2\{(SCH_2CH_2)_2Y\}]$ (X = Cl, Me; Y = S, O), have been characterised and two insertion products of reaction between xylyl*iso*cyanide and $[TaCp^*Me_2\{(SCH_2CH_2)_2O\}]$ have been isolated.[12] Pentamethylcyclopentadienyl-tantalum species with simple sulfido ligands are also known,[5,13] and these may be formed by decomposition of thiolate pre-cursors. Also known is the dinuclear tantalum(II) compound, $[TaCp^*(CO)_2(\mu\text{-}SPh)]_2$.[14]

Monocyclopentadienylniobium thiolates are rarer. We have previously studied arenedithiolate complexes, $[NbCp(S_2Ar)_2]$ (Ar = 1,2-C_6H_4, 3,4-C_6H_3Me) but were unable to isolate analogous mononuclear derivatives containing saturated 1,2-ethanedithiolate ligands, such as $[NbCp(SCH_2CH_2S)_2]$, which appeared to be highly susceptible to hydrolytic decomposition and only dinuclear complexes of monomethylcyclopentadienyl-niobium incorporating terminal or bridging oxo-ligands were structurally characterised.[15] More recently, pentamethylcyclo-pentadienylniobium complexes with sulfur-rich dithiolene ligands, $[NbCp^*(dddt)X_2]$ [dddt = 5,6-dihydro-1,4-dithiine-2,3-dithiolate, X_2 = Cl_2, dddt or dmit (1,3-dithiole-2-thione-4,5-dithiolate)] have been prepared and studied electrochemically.[16] Reported lower oxidation state thiolate complexes of cyclo-pentadienylniobium are mononuclear $[NbCp(PhC_2Ph)(SiPr)_2]$, the related heterobimetallics, $[NbCp(PhC_2Ph)(\mu\text{-}SiPr)_2Mo$-$(CO)_4]$ and $[NbCpCl_2(\mu\text{-}SMe)_2NiCp]$,[17] and the dinuclear compound $[NbCp(CO)_2(\mu\text{-}SMe)]_2$.[18] In this paper we present synthetic, spectroscopic and structural investigations of mono-cyclopentadienylniobium species with the saturated bidentate ligand, 1,3-propanedithiolate, and with the tridentate ligands, 2,2′-thiodiethanethiolate and 2,2′-oxydiethanethiolate.

Results and discussion

Complexes with 1,3-propanedithiolate

Reaction of the thallium salt of 1,3-propanedithiol with cyclopentadienyltetrachloroniobium, $[NbCpCl_4]$, in a 2 : 1 molar ratio, in tetrahydrofuran (thf), afforded the dithiolate compound $[NbCp(1,3\text{-}S_2C_3H_6)_2]$ **1** as a deep purple product; a similar reaction using methylcyclopentadienyltetrachloro-niobium as reagent gave $[NbCp′(1,3\text{-}S_2C_3H_6)_2]$ **2**. Isolable in yields of *ca.* 40–55%, pure products **1** and **2** have been charac-terised by elemental analysis and by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy in *d*-chloroform and *d$_8$*-toluene. At ambient tem-

† Electronic supplementary information (ESI) available: NMR data for compounds **1** and **2** in *d$_8$*-toluene; cyclic voltammogram of compound **1**; ESR spectrum of reduced compound **1**. See http://www.rsc.org/suppdata/dt/b2/b209823g/

peratures, both compounds show ¹H resonances of an AA′BB′ spin system for the sulfur-bound methylene hydrogens, with AA′ and BB′ components appearing as two approximate quintets (6–7 Hz splitting) separated by 0.43–0.45 ppm, and ¹H resonances of an AB spin system for the central methylene hydrogens of the thiolate ligand (*i.e.* H^C and H^D in Scheme 1)
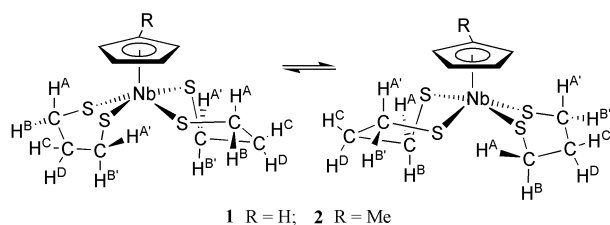
Scheme 1

which appear as a single overlapping multiplet in chlorinated solvents but as two multiplets, separated by *ca.* 0.06 ppm, in toluene. The singlet ¹H resonance of the cyclopentadienyl group of compound **1** and the ¹H resonances of the methyl-cyclopentadienyl ligand of **2** (*i.e.* singlet of the methyl group and AA′BB′ multiplet of the ring-hydrogens) are of the relative intensities corresponding to the molecular formulae. ¹³C{¹H} NMR spectra of compounds **1** and **2** are also in accord with the formulae, showing small shifts (2–3 ppm) to low field for resonances of the thiolate ¹³C nuclei compared to the parent dithiol.

Compounds **1** and **2** are soluble in light petroleum and common organic solvents but are prone to slow decomposition at ambient temperature, more notable for compound **2** and especially in more polar and chlorinated solvents, forming orange and yellow niobium species and liberating organosulfur compounds. Decomposition to free dithiol in solutions, observed by NMR, appears to involve protolysis of the sulfur ligand, but thermal decomposition also occurs, probably *via* C–S bond cleavage. Such cleavage on thermal decomposition is supported by the EI mass spectrum of **1** which, although it includes a small peak for the molecular ion, gave a range of dominant fragmentation ions including the cyclopentadienyl-niobium sulfido species $[NbCpS_x]^+$ (x = 1, 2, 3). Similar C–S fission has been observed in pentamethylcyclopentadienyl tantalum dithiolate compounds.[5]

Low temperature crystallisation of **1** from light petroleum produced small crystals from which only weak X-ray diffraction data could be obtained. Although refinement of the X-ray data was poor‡ this clearly indicated the five-coordinate structure of Fig. 1. The dithiolate ligands are chelating, forming two six-membered rings which adopt twist (skew-boat)[19] conformations with bond lengths Nb–S(1) and Nb–S(2) of 2.441(7) and 2.410(6) Å, Nb–S(3) and Nb–S(4) of 2.420(6) and 2.406(6) Å, and bite angles S(1)–Nb–S(2) and S(3)–Nb–S(4) of 85.0(2) and 86.0(2)°, respectively. Similar Nb–S bond lengths (average 2.450 Å) are found[20] in the binary 1,3-propanedithiolate anion $[Nb(S_2C_3H_6)_3]^-$ in which the ligands also have a twist conformation with an average bite angle of 83.5°. In reported bis- and mono-cyclopentadienylvanadium complexes, 1,3-propane-dithiolate ligands have chair conformations.[21] The coordination geometry around Nb in complex **1** can be considered as a distorted four-legged piano-stool but with the four S-atoms deviating significantly from co-planarity (rms deviation 0.337
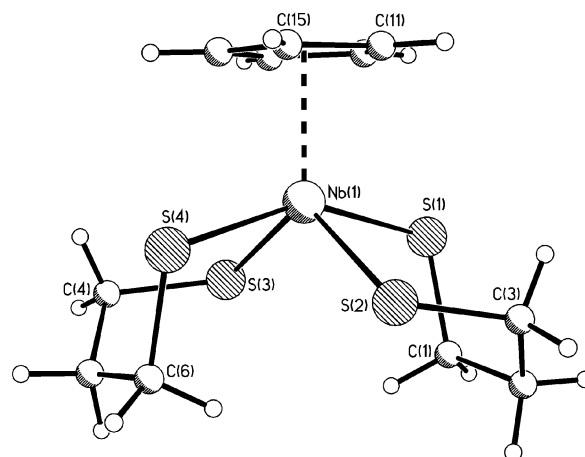
Fig. 1 Molecular structure of compound **1**.

Å); two *trans* S-atoms, one on each dithiolate ligand, are bent further away from the cyclopentadienyl ring [angles Cp–Nb–S(2)/(3) = 122.7(2)°/120.0(2)°(Cp = centroid of ring)] but their S–C bonds are oriented approximately parallel to the ring; the other Cp–Nb–S angles are significantly smaller [Cp–Nb–S(1)/(4) = 103.0(2)/104.8(2)°] and their corresponding S–C bonds are approximately perpendicular to and pointing away from the ring. Note that with angles S(1)–Nb–S(4) = 152.2(2)° and S(2)–Nb–S(3) = 117.3(2)°, an alternative description of the geometry is distorted trigonal bipyramidal, with psuedo-axial ligands S(1) and S(4). This type of distortion and orientation of S–C bonds has previously been reported in the monodentate benzenethiolate complex $[TaCp'(SPh)_4]$, supported by calculations on the model system $[TaCp(SH)_4]$, and explained mainly by the maximisation of π bonding between S π-donor orbitals and empty metal d_{z^2} and d_{xy} orbitals but also partly by steric repulsions between *cis* S-atoms.[9] For compound **1**, the conformation of the six-membered chelate ring may also contribute to the stability of this arrangement, and it is possible that the difficulty in preparing the analogous 1,2-ethane-dithiolate derivatives[15] may arise from an unfavorable conformation of the five-membered rings which destabilises bonding to the metal.

In the solid-state, all H-atoms of each chelate ring of compound **1** are in different environments causing the six ¹H nuclei to be magnetically inequivalent. The equivalence of H^A and H^A′ and of H^B and H^B′ in ¹H NMR spectra of compounds **1** and **2** in solution at ambient temperature can be attributed to a facile inversion of the twist conformation adopted by the six-membered rings (see Scheme 1). Variable temperature (−90–+30 °C) ¹H NMR spectra of compounds **1** and **2** in d_8-toluene and d_2-dichloromethane show typical coalescence behaviour for the apparent AA′BB′ systems and separation into four inequivalent resonances at <−50 °C (*e.g.* see Fig. 2) is consistent with the rigid solid-state structure. Also, the complex splitting pattern of the AB-type resonance of H^C and H^D is modified as fluxionality decreases at lower temperatures. At coalescence temperatures for H^A/H^A′ and H^B/H^B′ in d_8-toluene the calculated[22] activation free energies for exchange, $\Delta G^\ddagger_C$, are: 42.7 ± 1.4 kJ mol⁻¹ (at 231 K), for compound **1**; 43.1 ± 1.3 kJ mol⁻¹ (at 233 K), for compound **2**. A similar value for $\Delta G^\ddagger_C$ [41.4 kJ mol⁻¹ (at 222 K)] is found for **1** in the more polar CD_2Cl_2 suggesting that solvent effects on this fluxionality are minor. The barriers are comparable with that for the chair–chair inversion of cyclohexane, although barriers are generally lower for diamine chelating ligands with chair conformations and twist conformations are usually very flexible.[19] The magnitude of the activation barriers in complexes **1** and **2** will, in part, reflect the distorted Nb coordination geometry and the nature of the Nb–S bonds.
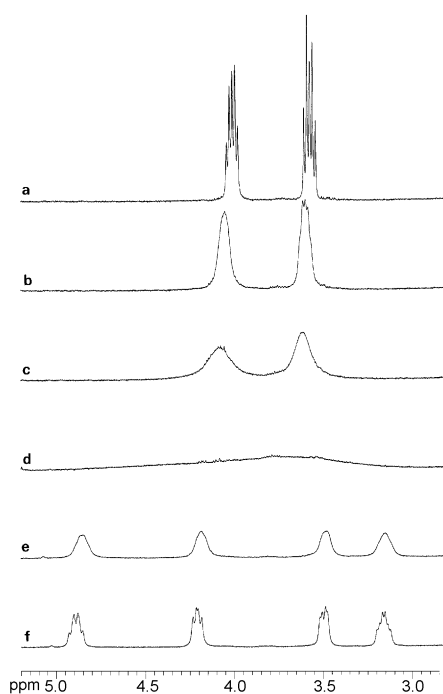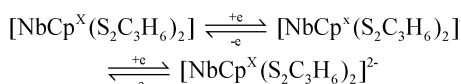
Fig. 2 ^{1}H NMR resonances of the α-CH$_2$ groups of 1,3-propane-dithiolate ligands in compound **2** at various temperatures in d_8-toluene (400 MHz): (a) 30; (b) 0; (c) −20; (d) −40; (e) −70; (f) −80 °C.

Cyclic voltammetric studies of compound **1** in thf show the presence of two reduction processes having well defined cathodic and anodic peaks with $E_{1/2}$ = −0.98 and −2.12 V with values quoted relative to FeCp$_2$$^{1+/0}$ (see Fig. S1, ESI). The anodic–cathodic peak separations, ΔE_{pp}, of *ca.* 100 and 140 mV, respectively, are comparable or less than that of the ferrocene couple recorded under the same experimental conditions and are consistent with two (quasi)reversible redox reactions. Under similar conditions, cyclic voltammetry on compound **2** also shows two reduction processes: the first, $E_{1/2}$ = −1.11 V, with similar characteristics to that of compound **1**, including a ratio of peak-currents close to unity, appears to be reversible; the second with a cathodic peak, E_{pc} = −2.25 V, but with a poorly resolved oxidative peak, indicates less reversibility and probably reflects the lower stability of the methylcyclopentadienylniobium system. These results support the formation of mono- and di-anionic species of Nb(IV) and Nb(III), as in the following equation.

$$[NbCp^X(S_2C_3H_6)_2] \underset{-e}{\overset{+e}{\rightleftharpoons}} [NbCp^x(S_2C_3H_6)_2]^-$$
$$\underset{-e}{\overset{+e}{\rightleftharpoons}} [NbCp^X(S_2C_3H_6)_2]^{2-}$$

Similar reductions have been observed for monocyclopentadienylniobium(v) compounds of arene-1,2-dithiolates at slightly more positive potentials.[15] Bis(dithiolene) complexes of half-sandwich pentamethylcyclopentadienylniobium compounds also show two reductions at more anodic potentials and, in these systems with sulfur-rich ligands, oxidation to radical-cations is noted.[16] Two-step redox processes have also been reported for bis(cyclopentadienyl)niobium compounds with unsaturated dithiolate ligands[23] and for other [NbCp$_2$X$_2$] compounds[24,25] linking Nb(v)–Nb(III) states, although chemical irreversibility has been noted in some cases.

Reductions of compounds **1** and **2** in thf by short contact with a sodium mirror in an evacuated ESR cell produced dark/brownish solutions which gave similar ten-line ESR spectra typical of d^1 niobium(IV) species: g_{iso} = 1.986 and A_{iso}(^{93}Nb) = 0.0097 cm^{-1} for **1** (see Fig. S2, ESI); g_{iso} = 1.987 and A_{iso}(^{93}Nb) = 0.0097 cm^{-1} for **2**. Spectra with the same parameters could also be produced by reduction of the dithiolate precursors with

equimolar amounts of cobaltocene. In accord with the CV investigations, the paramagnetic products are most likely to be the mono-anions [NbCp^x(S$_2$C$_3$H$_6$)$_2$]$^-$, although other insoluble material is also formed in these reactions and attempts to isolate and characterise the pure anions in salts such as [CoCp$_2$][NbCp^x(S$_2$C$_3$H$_6$)$_2$] were unsuccessful. The g_{iso} and A_{iso}(^{93}Nb) values are consistent with the unpaired electron being located mainly on the Nb(IV).[25] ESR spectra obtained by reduction of arenedithiolate complexes have previously been assigned to anions [NbCp(S$_2$Ar)$_2$]$^-$ (Ar = 1,2-S$_2$C$_6$H$_6$, 3,4-S$_2$C$_6$H$_3$Me) for which the g_{iso} values are slightly higher (1.991) and the niobium hyperfine coupling A_{iso}(^{93}Nb) is slightly lower (0.0090 cm^{-1});[15] one factor that could contribute to both of these differences in parameters is an increased spin delocalisation on to the ligands in the unsaturated arenedithiolate systems.[25] It should be noted that similar ESR spectra have also been previously studied for biscyclopentadienylniobium(IV) complexes with sulfur ligands.[23b,25–27]

Complexes with 2,2′-thiodiethanethiolate

Reactions between [NbCpCl$_4$] or [NbCp′Cl$_4$] with more than two molar equivalents of the thallium derivative of 2,2′-thiodiethanethiolate in thf at ambient temperature over three hours led only to the isolation of the partially substituted products [NbCp^{x}Cl$_2${(SC$_2$H$_4$)$_2$S}] (**3**, Cp^x = Cp; **4**, Cp^x = Cp′) in ≥60% yield, with no evidence for significant replacement of all the four chloride ligands.

3 R = H; **4** R = Me
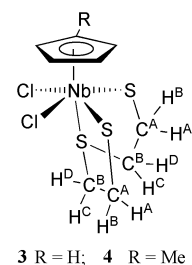
A related tantalum compound [TaCp*Cl$_2${(SC$_2$H$_4$)$_2$S}] has recently been reported.[12] Compounds **3** and **4** have been characterised by elemental analysis and by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. ^{1}H NMR spectra of **3** or **4** show typical resonances for Cp or Cp′ rings, respectively, and a set of multiplets assignable to four inequivalent hydrogens of the 2,2′-thiodiethanethiolate ligand with the correct relative intensities. In light of the X-ray structure determination of **3** (*vide infra*), the resonances can be assigned to nuclei H^A–H^D in each of the two ethylene units which, in solution, appear to be equivalent and related by a plane of symmetry, as indicated in the structural formula; two of the four resonances overlap giving a complex band centred at *ca.* 4.0 ppm and were assigned by ^{1}H–^{13}C correlation to two H-atoms on *vic*-C atoms, C^A and C^B. Variable temperature ^{1}H NMR spectra of compound **3** in CD$_2$Cl$_2$ over the range −90 to +30 °C showed no change, other than minor broadening of the multiplets at low temperatures, so that there must be a low barrier to any fluxionality of a less symmetrical structure, as found in the crystal. ^{13}C{^{1}H} NMR spectra of **3** and **4** also contained the expected resonances but the two resonances of the thiolate ligand at *ca.* 43 and 44 ppm could not be unambiguously assigned to specific atoms C^A and C^B. Compound **3** showed a well defined parent ion in its EI mass spectrum as well as fragment ions arising from loss of chloride and from decomposition of the thiolate ligand by cleavage of C–S bonds.

A dark purple crystal of **3** obtained from dichloromethane–light petroleum was structurally analysed by X-ray diffraction. Fig. 3 shows a perspective view of the structure and Table 1 lists selected geometrical parameters. The mononuclear compound exists as discrete molecules in the crystal and contains a *fac*-tridentate trisulfur ligand and two *cis*-Cl ligands. If the Cp

Table 1 Selected bond lengths (Å) and angles (°) for [NbCpCl₂-{(SCH₂CH₂)₂S}] **3**

Nb(1)–Cp	2.1138(4)	Nb(1)–S(1)	2.4383(13)
Nb(1)–S(2)	2.6113(13)	Nb(1)–S(3)	2.4518(13)
Nb(1)–Cl(1)	2.5068(14)	Nb(1)–Cl(2)	2.5060(12)
S(1)–C(1)	1.812(5)	S(2)–C(2)	1.806(5)
S(2)–C(3)	1.820(5)	S(3)–C(4)	1.810(5)
C(1)–C(2)	1.494(7)	C(3)–C(4)	1.529(7)
Cp–Nb(1)–S(1)	99.12(3)	Cp–Nb(1)–S(2)	178.82(3)
Cp–Nb(1)–S(3)	101.03(4)	Cp–Nb(1)–Cl(1)	105.85(4)
Cp–Nb(1)–Cl(2)	105.37(3)	S(1)–Nb(1)–S(2)	79.84(4)
S(1)–Nb(1)–S(3)	93.90(5)	S(1)–Nb(1)–Cl(1)	154.96(5)
S(1)–Nb(1)–Cl(2)	90.39(4)	Cl(1)–Nb(1)–S(2)	75.17(4)
Cl(2)–Nb(1)–S(2)	74.14(4)	S(3)–Nb(1)–Cl(1)	83.27(5)
S(3)–Nb(1)–Cl(2)	152.22(5)	S(3)–Nb(1)–S(2)	79.63(4)
C(2)–C(1)–S(1)	113.2(3)	C(1)–C(2)–S(2)	112.3(4)
C(4)–C(3)–S(2)	108.8(4)	C(3)–C(4)–S(3)	111.1(4)

Cp = Centroid of cyclopentadienyl ring.
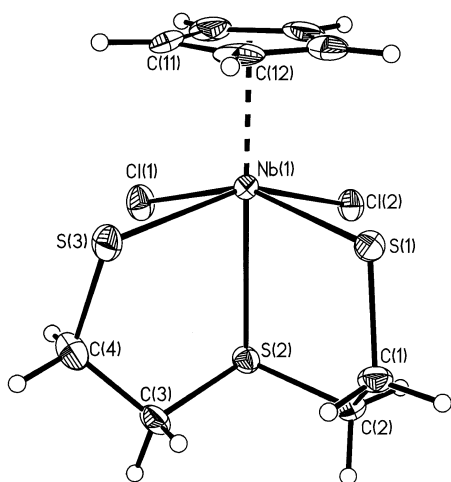
Fig. 3 Molecular structure of compound **3** (50% probability displacement ellipsoids).

ring is considered to occupy one site, the Nb atom is formally six-coordinate with a distorted octahedral arrangement of ligands. The Cp ligand is *trans* to the central S atom of the tridentate ligand [angle Cp–Nb–S = 178.82(3)°]. Angles between the Cp ligand and the other four *cis*-coordinated atoms are in the range 99.1–105.9°. These four ligand atoms are essentially coplanar (rms deviation 0.0105 Å) and this plane lies 0.5428(8) Å below Nb and at an angle of 5.2(3)° to the Cp plane. The two *cis*-Nb–Cl bonds are essentially equal with an average length of 2.5064 Å, and the two *cis*-thiolato Nb–S bonds (mean length 2.4451 Å) are shorter than the thioether Nb–S(2) bond of 2.6113(13) Å. Overall, the structural parameters of **3** are similar to those of [TaCp*Cl₂{(SC₂H₄)₂S}] but do show significant variations.[12] It may be noted that one five-membered ring of the tridentate ligand adopts an envelope and the other a twist conformation placing all H-atoms in different environments so that the more symmetrical structure deduced from the ¹H NMR spectrum in solution is probably the result of facile interconversion between these conformations.

The two *cis*-Cl ligands in compounds **3** and **4** are potentially available for introduction of other ligands by nucleophilic substitution, although in preparations of **3** and **4** with excess 2,2′-thiodiethanethiolate in thf at ambient temperature over several hours this displacement did not occur. Compound **3** and >5 molar equivalents of thallium(ɪ) 2,2′-thiodiethanethiolate suspended in toluene at 60 °C over 4 days did produce toluene-soluble products which, on the basis of ¹H NMR analysis, appeared to include the bis-dithiolate [NbCp{(SCH₂CH₂)₂S}₂] but this was not isolated as a pure product. Similarly, a prolonged reaction of **3** with excess thallium(ɪ) 1,3-propane-

dithiolate formed a toluene-soluble product, probably containing the mixed dithiolate compound [NbCp{(SCH₂-CH₂)₂S}(1,3-S₂C₃H₆)], but incompletely characterised.

Cyclic voltammetric investigations of compounds **3** and **4** in thf revealed two well resolved, successive reduction waves, with peak potentials (*vs.* FeCp₂¹⁺/⁰): E_{pc} = −1.25 and −1.54 V for **3**; E_{pc} = −1.29 and −1.57 V for **4**. These can be attributed to the formation of the respective mono- and di-anionic species but the reductions were associated with smaller, broader oxidative waves on the reverse scan: E_{pa} = −1.13 and −1.40 V for **3**; E_{pc} = −1.16 and −1.42 V for **4**. Therefore, at scan rates around 0.1 V s⁻¹, these redox processes are non-reversible. The difference between this electrochemical behaviour and that of compounds **1** and **2** could be due to the presence in the former species of chloride ligands, since halide ions are known to dissociate from reduced cyclopentadienylmetal halides.[25]

Complexes with 2,2′-oxydiethanethiolate

Reaction of [NbCp′Cl₄] with an excess of the thallium salt of 2,2′-oxydiethanethiolate in thf at ambient temperature gave a mixture of two main products in good overall yield and in *ca.* 2 : 1 molar ratio. The more soluble product was separated by extraction into toluene and was characterised on the basis of X-ray crystallography, NMR spectroscopy and analysis as [NbCp′O{(SCH₂CH₂)₂O}], **6**. The other product was recrystallised from dichloromethane–light petroleum and shown by similar techniques to be [NbCp′Cl₂{(SCH₂CH₂)₂O}], **5**.
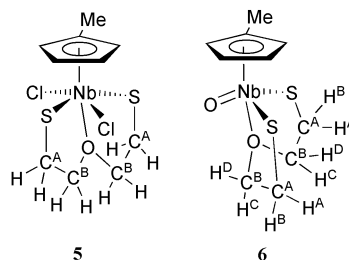

Compound **5**, formed by displacing two Cl ligands with the dithiolate, has a similar stoichiometry to the trisulfur ligand complexes **3** and **4** and is also analogous to the reported tantalum species [TaCp*Cl₂{(SCH₂CH₂)₂O}].[12] Analytical data support the formulation, but samples did retain small amounts of dichloromethane as confirmed by NMR spectra of the product. Integration of the ¹H NMR spectrum also conformed with the 1 : 1 stoichiometry of Cp′ and dithiolate ligands but the two 1 : 2 : 1 triplet resonances for the four sets of methylene hydrogens indicated a more symmetrical geometry of 2,2′-oxydiethanethiolate than for 2,2′-thiodiethanethiolate in **3** and **4** and, in accord with the solid state structure, can be assigned to Hᴬ and Hᴮ of the ligand with a *mer*-tridentate coordination mode as indicated in the structural formula, also containing *trans*-Cl ligands. A similar structure was also inferred for [TaCp*Cl₂{(SCH₂CH₂)₂O}] on the basis of its ¹H NMR spectrum.[12] This structure is consistent with the ¹³C{¹H} NMR spectrum which contains two resonances for equivalent pairs of O- and S-bonded methylenic C-atoms shifted to lower field by 9 and 14 ppm, respectively, compared to the related resonances of free 2,2′-oxydiethanethiol.

A dark red/brown crystal of non-solvated compound **5** was subjected to X-ray diffraction at 160 K. The crystal contains isolated molecules, depicted in Fig. 4, with selected geometrical parameters given in Table 2. The niobium is formally six-coordinate. The Cp′ ligand is *trans* to the coordinated O-atom of the 2,2′-oxydiethanethiolate [angle Cp′–Nb–O = 179.37(9)°] and the two Cl ligands are also *trans*, with angle Cl(1)–Nb–Cl(2) = 153.90(5)°. The tridentate S₂O-donor ligand spans *mer*-coordination sites with angles S–Nb–O = 77.36(9) and

Table 2 Selected bond lengths (Å) and angles (°) for [NbCp′Cl₂-{(SCH₂CH₂)₂O}] **5**

Nb(1)–Cp	2.1127(5)	Nb(1)–O(1)	2.245(4)
Nb(1)–S(2)	2.4252(14)	Nb(1)–S(1)	2.4278(14)
Nb(1)–Cl(1)	2.4988(13)	Nb(1)–Cl(2)	2.5162(13)
O(1)–C(3)	1.448(6)	O(1)–C(2)	1.459(6)
S(1)–C(1)	1.825(6)	S(2)–C(4)	1.818(6)
C(1)–C(2)	1.512(8)	C(3)–C(4)	1.495(8)
Cp–Nb(1)–O(1)	179.37(9)	Cp–Nb(1)–S(2)	102.09(4)
O(1)–Nb(1)–S(2)	77.36(9)	Cp–Nb(1)–S(1)	102.87(4)
O(1)–Nb(1)–S(1)	77.69(9)	S(2)–Nb(1)–S(1)	154.98(5)
O(1)–Nb(1)–Cl(1)	77.40(10)	S(2)–Nb(1)–Cl(1)	87.53(5)
S(1)–Nb(1)–Cl(1)	88.78(5)	Cp–Nb(1)–Cl(2)	103.76(4)
O(1)–Nb(1)–Cl(2)	76.54(10)	S(2)–Nb(1)–Cl(2)	85.30(4)
S(1)–Nb(1)–Cl(2)	87.22(4)	C(3)–O(1)–C(2)	111.3(4)
C(3)–O(1)–Nb(1)	119.5(3)	C(2)–O(1)–Nb(1)	119.7(3)
C(1)–S(1)–Nb(1)	101.74(19)	C(4)–S(2)–Nb(1)	102.24(18)
C(2)–C(1)–S(1)	110.6(4)	O(1)–C(2)–C(1)	106.3(4)
O(1)–C(3)–C(4)	107.6(4)	C(3)–C(4)–S(2)	110.5(4)

Cp = Centroid of cyclopentadienyl ring.
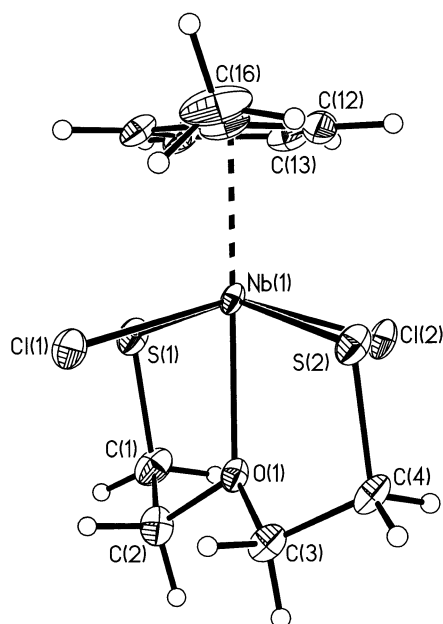
Fig. 4 Molecular structure of compound **5** (50% probability displacement ellipsoids).

77.69(9)°, and both of the five-membered rings of this ligand have envelope conformations; the apparent equivalence of pairs of methylene H-atoms observed by ¹H NMR in solution can be attributed to facile inversion of these rings. The two S and two Cl atoms lie essentially on a plane situated below the Nb atom {0.5445(8)Å} and parallel to the Cp′ ring {interplanar angle = 0.30(20)°}; both S atoms lie on the same side of this plane [deviations: S(1), 0.0203(7) and S(2), 0.0210(7) Å] as the Nb atom, and the Cl atoms both lie on the other side of the plane and are displaced by the same magnitude [Cl(1), 0.0204(7) and Cl(2), 0.0209(7) Å]. The Nb–S bonds of 2.4252(14) and 2.4278(14) Å are marginally shorter than the terminal Nb–S bonds of compound **3**, the average Nb–Cl bond length (2.5075 Å) is comparable to that of compound **3**, and the Nb–O distance is 2.245(4) Å. It is interesting that the structurally characterised six-coordinate dimethyl compound [TaCp*Me₂-{(SCH₂CH₂)₂O)}] has a different isomeric form with *fac*-coordinated S₂O-ligand and *cis*-Me groups.[12]

Compound **6** was shown by X-ray structural determination (*vide infra*) to contain a terminal oxygen ligand. The stoichiometry was consistent with the integrated ¹H NMR spectrum and with the elemental analysis, although analytical samples

had retained *ca*. 0.5H₂O, the presence of which was confirmed by NMR spectroscopy. The source of the oxo-ligand in compound **6** has not been proven but is very likely to be hydrolysis by adventitious water in the reaction mixture possibly originating from incompletely dried thallium dithiolate. Both halogen and thiolate ligands of early transition metal complexes are susceptible to hydrolysis and the incorporation of oxygen as ligands to such metals during the preparation of thiolate derivatives has been reported previously.[4,5,15] Four separate multiplets in the ¹H NMR spectrum of **6** are assignable to pairs of hydrogens Hᴬ–Hᴰ of the tridentate 2,2′-oxydiethanethiolate related by an apparent plane of symmetry in an overall distorted trigonal bipyramidal structure, as illustrated. The ¹³C{¹H} NMR spectrum also includes two resonances for equivalent pairs of atoms Cᴬ and Cᴮ, both at lower fields than the related resonances in free 2,2′-oxydiethanethiol but at higher fields than those observed for compound **5**.

A solvent free, dark red crystal of **6** was obtained from dichloromethane–light petroleum and subjected to X-ray diffraction at 160 K. The crystal contains two crystallographically independent molecules, the largest difference (<0.5 Å) between them is in the relative positions of the methyl substituents on the Cp rings. The structure of one molecule is depicted in Fig. 5 and selected bond distances and angles for
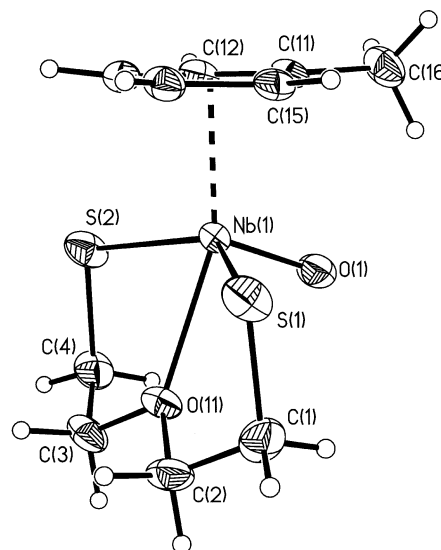
Fig. 5 Molecular structure of compound **6** (50% probability displacement ellipsoids).

both forms (molecules 1 and 2) are given in Table 3. The compound is formally five-coordinate and may be considered to have a distorted trigonal bipyramidal geometry with apical Cp′ group and O-donor from the S₂O-tridentate 2,2′-oxydiethanethiolate ligand, and with an oxo-ligand and two thiolate functions in the equatorial plane. However, the plane containing the two S-atoms and the terminal O-atom lies 0.4756(11) Å below the Nb atom and the S–Nb–S angle [136.06(5)° or 138.13(4)°] is larger than the S–Nb–O(terminal) angles (102.77–105.65°). Also, the angle between axial ligands, Cp′–Nb–O [157.46(8) or 156.85(8)°] deviates considerably from 180° unlike the Cp′–Nb–O angle in compound **5** or Cp–Nb–S angle in compound **3**. The S₂O-ligand adopts a *fac*-coordination mode with Nb–O distance [2.351(3) or 2.342(3) Å] and Nb–S distances (2.4651–2.4761 Å), all somewhat larger than corresponding bonds in compounds **5** and **3**. The Nb–O(terminal) bond length [1.734(3) or 1.735(3) Å] is shorter, as expected for a formal double bond, and is the same as the mean value of 1.735 Å found previously in [Nb₂(μ-η¹:η²-1,2-S₂C₂H₄)₂Cp′₂O-(S₂C₂H₄)].[15] As in complex **5**, the two five-membered rings of the tridentate S₂O-ligand have adopted envelope conformations.

Table 3 Selected bond lengths (Å) and angles (°) for [NbCp′O{(SCH₂CH₂)₂O}] **6**

	Molecule 1		Molecule 2	
	Nb(1)–O(1)	1.734(3)	Nb(2)–O(2)	1.735(3)
	Nb(1)–Cp(1)	2.1535(6)	Nb(2)–Cp(2)	2.1678(6)
	Nb(1)–O(11)	2.351(3)	Nb(2)–O(12)	2.342(3)
	Nb(1)–S(1)	2.4732(13)	Nb(2)–S(3)	2.4743(13)
	Nb(1)–S(2)	2.4761(13)	Nb(2)–S(4)	2.4651(13)
	S(1)–C(1)	1.813(5)	S(3)–C(8)	1.819(5)
	S(2)–C(4)	1.814(5)	S(4)–C(5)	1.820(5)
	O(11)–C(2)	1.455(6)	C(6)–O(12)	1.460(5)
	O(11)–C(3)	1.441(6)	C(7)–O(12)	1.448(5)
	C(1)–C(2)	1.494(7)	C(5)–C(6)	1.499(7)
	C(3)–C(4)	1.500(7)	C(7)–C(8)	1.488(7)
	O(1)–Nb(1)–Cp(1)	111.89(11)	O(2)–Nb(2)–Cp(2)	112.33(10)
	O(1)–Nb(1)–O(11)	90.65(13)	O(2)–Nb(2)–O(12)	90.82(12)
	Cp(1)–Nb(1)–O(11)	157.46(8)	Cp(2)–Nb(2)–O(12)	156.85(8)
	O(1)–Nb(1)–S(1)	104.45(13)	O(2)–Nb(2)–S(3)	104.62(11)
	Cp(1)–Nb(1)–S(1)	98.90(4)	Cp(2)–Nb(2)–S(3)	98.53(3)
	O(11)–Nb(1)–S(1)	74.38(8)	O(12)–Nb(2)–S(3)	74.20(8)
	S(1)–Nb(1)–S(2)	136.06(5)	S(4)–Nb(2)–S(3)	138.13(4)
	O(1)–Nb(1)–S(2)	105.65(13)	O(2)–Nb(2)–S(4)	102.77(11)
	Cp(1)–Nb(1)–S(2)	98.71(3)	Cp(2)–Nb(2)–S(4)	99.61(4)
	O(11)–Nb(1)–S(2)	74.03(8)	O(12)–Nb(2)–S(4)	74.34(8)
	C(1)–S(1)–Nb(1)	99.38(17)	C(8)–S(3)–Nb(2)	101.46(16)
	C(4)–S(2)–Nb(1)	100.34(17)	C(5)–S(4)–Nb(2)	99.13(16)
	C(3)–O(11)–C(2)	110.6(3)	C(7)–O(12)–C(6)	110.8(3)
	C(3)–O(11)–Nb(1)	122.6(3)	C(7)–O(12)–Nb(2)	121.9(3)
	C(2)–O(11)–Nb(1)	122.2(3)	C(6)–O(12)–Nb(2)	122.4(3)

Cp(1), Cp(2) = Centroids of cyclopentadienyl rings.

Conclusions

Mononuclear half-sandwich niobium(v) compounds with selected bi- and tri-dentate saturated dithiolate ligands can be synthesised and are relatively stable. Bis-1,3-propanedithiolate complexes of cyclopentadienyl and methylcyclopentadienyl-niobium(v), [NbCpˣ(S₂C₃H₆)₂], have a distorted four-legged piano-stool geometry and exhibit fluxional inversion of the six-membered chelate rings in solution; cyclic voltammetric studies indicate that sequential reduction of these complexes to mono- and di-anionic species can occur and paramagnetic niobium(ıv) species resulting from chemical reduction show ESR spectra consistent with the unpaired electron occupying a mainly metal-based orbital. The isolation of bis-1,3-propanedithiolate complexes of cyclopentadienylniobium(v) contrasts with the relative instability of comparable bis-1,2-ethanedithiolate derivatives and may reflect a more effective stabilisation by the conformation of the larger six-membered chelate rings. Complexes of cyclopentadienyl or methylcyclopentadienyl-dichloroniobium(v) with tridentate thio- or oxy-dithiolate ligands, [NbCpˣCl₂{(SC₂H₄)₂X}], have distorted octahedral geometries and form isomeric structures with *fac* (X = S, Cpˣ = Cp) or *mer* (X = O, Cpˣ = Cp′) coordination of the dithiolate. The tendency of such niobium(v) thiolate complexes to undergo hydrolysis is exemplified by the isolation of the five-coordinate oxo-complex, [NbCp′O{(SC₂H₄)₂O}], with approximate trigonal bipyramidal geometry.

Experimental

Reactions and operations were conducted under an atmosphere of dry, oxygen-free nitrogen gas, using Schlenk techniques. Solvents were thoroughly dried, using sodium (toluene), sodium–benzophenone (diethyl ether, tetrahydrofuran, petroleum ether) or calcium hydride (dichloromethane), and freshly distilled before use. Light petroleum ether had a boiling range of 60–80 °C. Starting materials [NbCpCl₄] and [NbCp′Cl₄] were prepared by a literature method.[28] 1,3-Propanedithiol, 2,2′-thiodiethanethiol, 2,2′-oxydiethanethiol and thallium(ı) acetate were obtained commercially (Aldrich) and used as supplied.

Thallium dithiolates were obtained as precipitates by reaction of thallium(ı) acetate with the appropriate dithiol in methanol; these dithiolates were washed with diethyl ether and light petroleum, and dried *in vacuo* at ambient temperature before use. The ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AC 200 spectrometer (at *ca.* 17 °C) and in some cases on a DPX 400 spectrometer (at variable temperatures, as stated) using SiMe₄ as internal reference. EI mass spectra were measured on an upgraded VG MS9 instrument. Cyclic voltammograms were recorded at ambient temperature, at various scan rates (data quoted for 0.1 V s⁻¹), on thf solutions containing 0.1M NBuⁿ₄PF₆ as supporting electrolyte using platinum micro-electrodes and the ferricenium/ferrocene couple as standard; no compensation was made for solution IR drop and under these conditions ΔE_{pp} 150 mV for FeCp₂¹⁺/⁰. ESR spectra were measured at ambient temperature on a JEOL PE1 X band spectrometer, using diphenylpicrylhydrazyl as reference and a Bruker NMR field marker. Elemental analyses were carried out at Heriot-Watt University.

Preparations

[Nb(η-C₅H₅)(1,3-S₂C₃H₆)₂] 1. A suspension of 1,3-(TlS)₂C₃H₆ (1.17 g, 2.26 × 10⁻³ mol) in thf (15 cm³) was slowly added to [NbCpCl₄] (0.34 g, 1.13 × 10⁻³ mol) in thf (30 cm³) and the resulting mixture was stirred at room temperature for 3 h. The red colour changed to deep purple. Removal of solids by filtration and washing with thf (30 cm³), followed by evaporation of solvent from the combined filtrate and washings *in vacuo* yielded a dark purple solid. Recrystallisation from light petroleum afforded pure [NbCp(S₂C₃H₆)₂] (0.17 g, 41%). Found: C, 35.75; H, 4.66; C₁₁H₁₇S₄Nb requires C, 35.67; H, 4.63%. ¹H NMR (CDCl₃); δ 2.05 (m, AB system, 4H, SCH₂C*H₂*), 3.65 (m, AA′ component, 4H, SCH*H*), 4.00 (m, BB′ component, 4H, SC*H*H), 6.41 (s, 5H, C₅H₅). [¹H NMR (C₆D₅CD₃, 400 MHz, 30 °C), see ESI]. EI MS, *m/z* of significant ions: 370 (1.4%, M⁺), 296 (5%, [M − C₃H₆S]⁺), 264–2 (2–5%, [M − C₃H₆₋₈S₂]⁺), 254 (3%, [C₅H₅NbS₃]⁺), 222 (12%,[C₅H₅NbS₂]⁺), 190 (9%, [C₅H₅NbS]⁺), 108 (63%, [C₃H₈S₂]⁺), 74 (61%, [C₃H₆S]⁺), (also higher mass ions *m/z*: 470, 396).

Table 4 Crystal and structure refinement data

	3	**5**	**6**
Empirical formula	$C_9H_{13}Cl_2NbS_3$	$C_{10}H_{15}Cl_2NbOS_2$	$C_{10}H_{15}NbO_2S_2$
Formula weight	381.18	379.15	324.25
Temperature/K	160(2)	160(2)	160(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a/Å	7.9070(11)	14.3244(11)	7.695(2)
b/Å	12.4590(15)	12.0161(11)	13.098(3)
c/Å	13.1460(12)	7.8488(8)	13.984(3)
α/°	90	90	64.180(11)
β/°	90	104.510(9)	75.090(14)
γ/°	90	90	87.720(15)
Volume/Å^3	1295.1(2)	1307.9(2)	1221.8(5)
Z	4	4	4
Absorption coefficient/mm^{-1}	1.789	1.623	1.304
$F(000)$	760	760	656
Crystal size/mm^3	0.08 × 0.32 × 0.20	0.08 × 0.30 × 0.14	0.10 × 0.42 × 0.24
Reflections collected	1826	3062	5044
Independent reflections	1671 [R(int) = 0.0366]	2257 [R(int) = 0.0622]	4082 [R(int) = 0.0406]
Absorption correction	Empirical	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1671/0/136	2257/0/145	4082/0/272
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0297$, $wR2 = 0.0724$	$R1 = 0.0448$, $wR2 = 0.1152$	$R1 = 0.0373$, $wR2 = 0.0909$
R indices (all data)	$R1 = 0.0327$, $wR2 = 0.0742$	$R1 = 0.0629$, $wR2 = 0.1340$	$R1 = 0.0480$, $wR2 = 0.0970$

[Nb(η-C₅H₄CH₃)(1,3-S₂C₃H₆)₂] 2. A suspension of 1,3-(TlS)₂C₃H₆ (1.64 g, 3.20 × 10⁻³ mol) in thf (15 cm³) was slowly added to [NbCp′Cl₄] (0.49 g, 1.56 × 10⁻³ mol) in thf (30 cm³) and the resulting mixture was stirred at room temperature for 3 h to produce a purple solution. Removal of solids by filtration through Celite and evaporation of solvent from the filtrate *in vacuo* yielded a dark purple, oily product. Recrystallisation from light petroleum gave purple solid, [NbCp′(S₂C₃H₆)₂] (0.33 g, 55%). Found: C, 37.11; H, 5.11; $C_{12}H_{19}S_4Nb$ requires C, 37.49; H, 4.98%. ¹H NMR (CDCl₃); δ 2.04 (m, AB system, 4H, SCH₂C*H₂*), 2.30 (s, 3H, CH₃), 3.64 (m, AA′ component, 4H, SCH*H*), 3.98 (m, BB′ component, 4H, SC*H*H), 6.27 (AA′BB′ system, 4H, C₅*H₄*Me). ¹³C{¹H} NMR (CDCl₃); δ 16.1 (CH₃), 25.1 (SCH₂*C*H₂), 40.7 (S*C*H₂), 110.4 (CH, Cp′), 113.1 (CH, Cp′), 133.4 (C-1, Cp′). [¹H and ¹³C{¹H} NMR (C₆D₅CD₃), see ESI].

[Nb(η-C₅H₅)Cl₂{(SC₂H₄)₂S}] 3. The thallium derivative, 1,3-(TlSC₂H₄)₂S (3.05 g, 5.44 × 10⁻³ mol), suspended in thf (15 cm³), was added to [NbCpCl₄] (0.59 g, 2.0 × 10⁻³ mol) in thf (30 cm³) and the mixture stirred for 3 h at room temperature. Filtration through Celite of the reaction mixture, followed by removal of the solvent from the filtrate *in vacuo*, gave a dark purple solid which was recrystallised from dichloromethane–light petroleum to afford crystalline [NbCpCl₂{(SC₂H₄)₂S}] (0.48 g, 63%). Found: C, 28.03; H, 3.66; $C_9H_{13}Cl_2S_3Nb$ requires C, 28.36; H, 3.44 %. ¹H NMR (CDCl₃); δ 3.4 (m, 2H, C*H*HS), 3.85 (m, 2H, SC*H*H), 4.0 (complex m, 4H, SC*H*HC*H*H), 6.94 (s, 5H, C₅*H₅*). ¹³C{¹H} NMR (CDCl₃); δ 42.9 (CH₂), 44.5 (CH₂), 118.7 (C₅H₅). EI MS, *m/z* significant ions (³⁵Cl): 380 (3%, M⁺), 352 (9%, [M − C₂H₄]⁺), 345 (5%, [M − Cl]⁺), 286 (14%, [M − C₂H₆S₂]⁺), 254 (13%, [C₅H₅NbS₃]⁺), 92 (100%, C₂H₄S₂]⁺).

[Nb(η-C₅H₄Me)Cl₂{(SC₂H₄)₂S}] 4. Using a similar procedure to that described above, [NbCp′Cl₄] (0.60 g, 1.9 × 10⁻³ mol) and (TlSC₂H₄)₂S (3.0 g, 5.3 × 10⁻³ mol) afforded purple, crystalline [NbCp′Cl₂{(SC₂H₄)₂S}] (0.45 g, 60%). Found: C, 30.31; H, 3.82. $C_{10}H_{15}Cl_2S_3Nb$ requires C, 30.39; H, 3.83%. ¹H NMR (CDCl₃); δ 2.57 (s, 3H, CH₃), 3.36 (m, 2H, C*H*HS), 3.8 (m, 2H, SC*H*H), 3.97 (complex m, 4H, SC*H*HC*H*H), 6.50 (~t, 2.5 Hz, 2H, AA′ component of C₅*H₄*Me), 6.93 (~t, 2.5 Hz, 2H, BB′ component of C₅*H₄*Me). ¹³C{¹H} NMR (100.6 MHz, CDCl₃; 25 °C); δ 16.8 (CH₃), 42.7 (CH₂), 44.0 (CH₂), 117.8 (CH, Cp′), 119.3 (CH, Cp′), 134.5 (C-1, Cp′).

[Nb(η-C₅H₄Me)Cl₂{(SC₂H₄)₂O}] 5 and [Nb(η-C₅H₄Me)-O{(SC₂H₄)₂O}] 6. The thallium derivative, (TlSC₂H₄)₂O (2.2 g, 4.0 × 10⁻³ mol) suspended in thf (15 cm³) was added to [NbCp′Cl₄] (0.60 g, 1.9 × 10⁻³ mol) in thf (30 cm³) and the mixture stirred at room temperature for 3 h to form a dark red solution. Filtration through Celite and evaporation of solvent from the filtrate *in vacuo* yielded a solid mixture (*ca.* 1 : 2 mol ratio) of the two title compounds as major products. Extraction of the mixture with toluene (*ca.* 30 cm³), evaporation of the filtered solution to dryness, and recrystallisation of the resulting solid from dichloromethane–light petroleum afforded rust-red solid [NbCp′O{(SC₂H₄)₂O}] 6 (0.26 g, 41%). Found: C, 36.07; H, 4.64. $C_{10}H_{15}S_2NbO_2·0.5H_2O$ requires: C, 36.04; H, 4.84%. ¹H NMR (CDCl₃); δ 2.12 (s, 3H, CH₃), 3.20 (m, 2H, SC*H*H), 3.43 (m, 2H, SC*H*H), 3.72 (m, 2H, OC*H*H), 4.61 (m, 2H, OC*H*H), 6.02 (~t, 2.4 Hz, 2H, AA′ component of C₅*H₄*Me), 6.13 (~t, 2.4 Hz, 2H, BB′ component of C₅*H₄*Me) [also δ 1.57 (s, *ca.* 1H, 0.5H₂O)]. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C); δ 14.2 (CH₃), 32.0 (CH₂S), 77.7 (CH₂O), 111.5 (CH, Cp′), 111.9 (CH, Cp′), 125.0 (C-1, Cp′). The toluene-insoluble residue of the initial product was recrystallised from dichloromethane–light petroleum to give brown solid [NbCp′-Cl₂{(SC₂H₄)₂O}] 5 (0.16 g, 22%). Found: C, 31.00; H, 3.91. $C_{10}H_{15}Cl_2S_2NbO·0.1CH_2Cl_2$ requires: C, 31.29; H, 3.95%. ¹H NMR (CDCl₃); δ 2.62 (s, 3H, CH₃), 3.91 (t, 5.6 Hz, 4H, SCH₂), 4.94 (t, 5.6 Hz, 4H, OCH₂), 6.50 (~t, 2.6 Hz, 2H, AA′ component of C₅*H₄*Me), 6.86 (~t, 2.6 Hz, 2H, BB′ component of C₅*H₄*Me) [also: δ 5.30 (s, *ca.* 0.2H, 0.1CH₂Cl₂)]. ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25 °C); δ 17.3 (CH₃), 38.4 (CH₂S), 81.3 (CH₂O), 117.0 (CH, Cp′), 117.8 (CH, Cp′), 132.3 (C-1, Cp′).

X-Ray data collection and crystal structure determinations

Single crystals of compounds **3**, **5** and **6** were grown by slow diffusion of dichloromethane solutions with light petroleum at −15 °C; small single crystals of compound **1** were grown from light petroleum at −15 °C. For X-ray data collection, crystals were mounted on a glass fibre, data collected with a Siemens P4 diffractometer[29] at 160 K, cooled by an Oxford Cryosystems Cryostream. Details of the crystal structure determinations are given in Table 4.

CCDC reference numbers 194705–194707 for **3**, **5** and **6** respectively.

See http://www.rsc.org/suppdata/dt/b2/b209823g/ for crystallographic data in CIF or other electronic format.

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