New Organolanthanide Complexes containing a σ-Bonded 1,3-Dithiane. Crystal Structures of $[M(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ (M = Lu or Y; thf = Tetrahydrofuran)†

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New complexes of Y and Lu have been synthesized and fully characterized by single-crystal X-ray analysis: $[M(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ (M = Lu **1** or Y **2**, thf = tetrahydrofuran). Both complexes crystallize from pentane at 0 °C. The crystal of **1** has space group $P\bar{1}$ with $a = 11.489(4)$, $b = 14.438(6)$, $c = 20.217(4)$ Å, $\alpha = 94.16(3)$, $\beta = 89.76(2)$ and $\gamma = 97.58(3)°$. Least-square refinements based on 5881 reflections $[I > 2.0\sigma(I)]$ converged to a final $R = 0.072$. Complex **2** crystallizes in orthorhombic unit cell and space group *Pbca* with $a = 14.744(6)$, $b = 21.148(7)$ and $c = 21.472(6)$ Å. Least-squares refinement based on 1570 reflections $[I > 2.0\sigma(I)]$ converged to a final $R = 0.081$. The complexes contain the anion of 1,3-dithiane included into a pentagonal co-ordination ring formed by M (Lu or Y), C, S, Li and Cl atoms. 1,3-Dithiane is σ bonded to the metal (Y or Lu) through the 2-carbon atom. Proton and ^{13}C NMR spectra suggest high conformational stability of the 1,3-dithiane ring in solution at room temperature. The complexes react with protonic acids such as water, $NH(SiMe_3)_2$ and HC≡CPh releasing free 1,3-dithiane and forming corresponding cyclopentadienyl derivatives.

Bis(cyclopentadienyl) complexes of Group 3 metals and lanthanides with σ-bonded hydrocarbyl ligands are known as active catalysts for many processes, leading to the formation of C–E (E = H, C, N, Si or B) bonds.[1] A large number of complexes with hydrocarbyl ligands, bound through sp^3-, sp^2- and sp-hybridized carbon atoms, have been synthesized and structurally characterized.[2,3] However, the majority of cyclopentadienyllanthanide derivatives of strong CH acids comprises various acetylenides,[3,4] while very few data are available on complexes derived from other 'stable' carbanions, capable of forming σ bonds with lanthanide, Sc or Y atoms. Studies of such complexes are needed to find correlations between thermodynamic properties of the parent CH acids and structural parameters and reactivities of corresponding organolanthanides. Lately this has become particularly interesting, after the development of techniques for accurate measurements of the thermochemical parameters of organo-f-element complexes.[5]

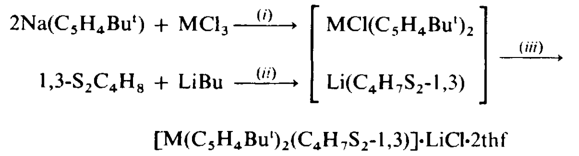
An important group of 'stable' carbanions is formed by the derivatives of heteroatom-stabilized CH acids.[6] One such acid, 1,3-dithiane ($1,3\text{-}S_2C_4H_8$), was introduced into synthetic practice in 1965 by Corey and Seebach,[7] and eventually became one of the most popular so-called 'umpoled synthones'.[8] It can be smoothly metallated with LiMe or LiBu in tetrahydrofuran (thf) at −78 °C giving the carbanion, stabilized by two neighbouring sulfur atoms.[6] Further reactions of this anion with electrophiles, followed by hydrolysis of the 1,3-dithio fragment, provide a convenient route to aldehydes and unsymmetrical ketones.

Though 1,3-dithiane has been extensively used in organic synthesis,[9] very little is known about its potential as a ligand for organometallic chemistry. The ion pair pK_a of 1,3-dithiane has been measured in cyclohexylamine[10] and has a value of 31.1 at 25 °C. This places 1,3-dithiane between relatively strong CH acids, such as acetylenes, and normally non-dissociating hydrocarbons (*e.g.* the pK_a values of phenylacetylene and *tert*-butylacetylene are 25.5 and 23.4 respectively, while for regular hydrocarbons the values are >40).[11] A few complexes of 1,3-dithiane with Si,[12a] Sn[12b] and Ge,[12c] which are the intermediates in synthetic transformations, and also Al[12d] and Ti[12e] have been described, however no structural details were reported. The only example of an isolated and fully characterized analogue is the lithium salt of 2-methyl-1,3-dithiane, co-crystallized with *N,N,N′,N′*-tetramethylethane-1,2-diamine (tmen).[13] Also, structurally related iron dithiacarbene derivatives were recently reported.[14]

In this paper we describe the synthesis and structures of new bis(*tert*-butylcyclopentadienyl) complexes of Lu and Y with σ-bound η^2-co-ordinated 1,3-dithiane.

Results and Discussion

Synthesis.—The general route leading to complexes **1** and **2** is shown on Scheme 1. In both cases two slightly different



$$\left.\begin{array}{l}2Na(C_5H_4Bu^t) + MCl_3 \xrightarrow{(i)} \\ 1,3\text{-}S_2C_4H_8 + LiBu \xrightarrow{(ii)}\end{array}\right. \begin{bmatrix} MCl(C_5H_4Bu^t)_2 \\ Li(C_4H_7S_2\text{-}1,3)\end{bmatrix} \xrightarrow{(iii)}$$

$$[M(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$$

1 M = Lu
2 M = Y

Scheme 1 (*i*) thf, room temperature (r.t.), 5 h; (*ii*) thf, 0 °C, 1 h; (*iii*) 0 °C, 10 h

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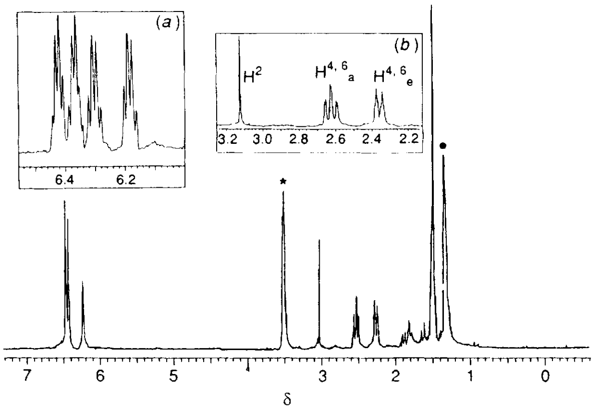
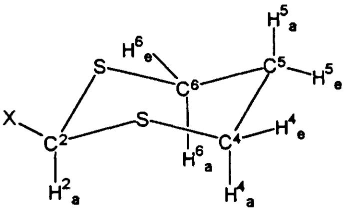


Fig. 1 Proton NMR spectrum of $[Lu(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **1** in C_6D_6. The inserts (*a*) and (*b*) show for a solution in $C_6D_5CD_3$ the cyclopentadienyl protons, and the protons of the 1,3-dithiane ligand respectively (see Scheme 2 for assignment). Peaks marked with * originate from thf



Scheme 2 X = H, Li, $Lu(C_5H_4Bu^t)_2$ **1**, or $Y(C_5H_4Bu^t)_2$ **2**

synthetic procedures, both following the general scheme, have been applied. First, isolated crude precursors of the type $[MCl(C_5H_4Bu^t)_2]\cdot thf$ (M = Lu or Y) were treated with $Li(C_4H_7S_2\text{-}1,3)$, also prepared separately and stored as a solid. However, later we found that generation of both components *in situ* led to only slightly lower yields of the final complexes (45–55%), as compared to the first method (60–65%). In the latter case bis(*tert*-butylcyclopentadienyl)metal chlorides were synthesized directly from the corresponding trichlorides and $Na(C_5H_4Bu^t)$ in thf,[1g] and then mixed with a solution of $Li(C_4H_7S_2\text{-}1,3)$ at −78 °C. The latter reagent was prepared immediately prior to synthesis by the metallation of 1,3-dithiane with LiBu in thf.[15] Compounds **1** and **2**, recrystallized from pentane as white solids, are very soluble in toluene and other aromatic solvents.

Solutions of 1,3-dithianes and their alkali-metal salts have been studied extensively.[16] However we have not been able to find any literature data on the isolation and characterization of solid $Li(C_4H_7S_2\text{-}1,3)$. This compound precipitates as a white powder from diethyl ether solutions when 1,3-dithiane is treated with 1 equivalent of LiBu at 0 °C. It is highly sensitive towards oxidizers and moisture, but sufficiently stable under pure argon. In contrast, its solutions in thf, decompose rather rapidly even under an inert atmosphere. The ^1H NMR spectra indicate that solutions become contaminated with considerable amounts of free 1,3-dithiane after 1–2 h of storage at room temperature.

NMR Spectroscopy.—Both the complexes described in this paper were characterized by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of the lutetium complex **1** is shown in Fig. 1. The signals of the cyclopentadienyl protons appear as two quartets and one multiplet at δ 6.3–6.6 in C_6D_6 solution. This pattern is quite different from the 'regular' AA'BB' triplet-triplet spectrum of monosubstituted cyclopentadienyl rings, typical for many complexes bearing the $M(C_5H_4Bu^t)_2$ fragment. This is probably due to the asymmetry induced by the third ligand, 1,3-dithiane. Indeed, the same pattern was found, for example, in the spectrum of highly non-symmetric dicyclopentadienyl(dimethylsilyl)titanium(IV) pentasulfide, which was attributed to the existence of a AA'BB'XX'YY' spin system.[17] In the latter complex the Ti atom was incorporated into a six-membered ring together with five sulfur atoms, and the whole ring was fixed in a 'chair' conformation. X-Ray data (see below) show that the 1,3-dithiane rings in both **1** and **2** also predominantly exist in 'chair' conformations, with metal (Lu or Y) atoms occupying equatorial positions, quite similar to the structure suggested for the titanium complex.[17] Interestingly, the spectrum of **1** in $C_6D_5CD_3$ [Fig. 1(*a*)] exhibits much less equivalence and signals of all four cyclopentadienyl protons appear as separate multiplets at δ 6.44, 6.39, 6.32 and 6.19.

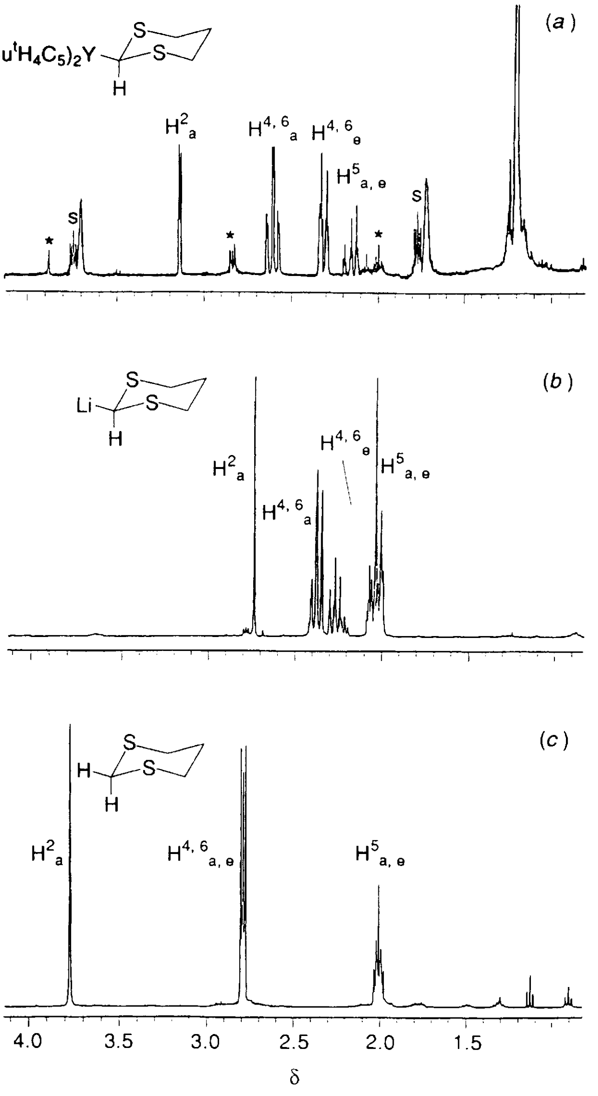


Fig. 2 Proton NMR spectra of complex **2** in C_6D_6 (*a*), $Li(C_4H_7S_2\text{-}1,3)$ (*b*) and free 1,3-dithiane (*c*) in $[^2H_8]$tetrahydrofuran (see Scheme 2 for atom assignment). Peaks marked with s originate from solvents and * marks traces of free 1,3-dithiane

Fig. 1(*b*) shows the part of the spectrum corresponding to the 1,3-dithiane ligand. Fig. 2(*a*) shows the resonances of the dithiane protons in the yttrium complex **2**. The spectra of $Li(C_4H_7S_2\text{-}1,3)$ [Fig. 2(*b*)] and free 1,3-dithiane [Fig. 2(*c*)] are given for comparison. The corresponding chemical shifts and coupling constants are listed in Table 1. In solution at room temperature the ring of free 1,3-dithiane undergoes rapid conformational exchange. The signals of the axial and equatorial protons of atoms C^4, C^6 and C^5 (Scheme 2) are mixed and appear as a characteristic triplet and multiplet at δ 2.78 and 2.01 respectively. The conversion rate is much lower

Table 1 Proton and ^{13}C NMR spectral data

					1,3-Dithiane[b]				
Compound	Solvent	Bu^t	C_5H_4	thf[a]	2	4,6	5	J_{aa}/Hz	J_{ae}/Hz
^1H NMR (δ_H)									
1,3-Dithiane	C_6D_6	—		—	3.34	2.23	1.52		—
	[$^2H_8$]thf	—		—	3.77	2.78	2.01		—
Li($C_4H_7S_2$-1,3)	[$^2H_8$]thf	—		—	2.73	2.36, 2.26	2.25	11.5	2.1
1	C_6D_6	1.59	6.32, 6.52, 6.56	1.42, 3.60	3.31	2.62, 2.36	—	12.2	3.0
	$C_6D_5CD_3$	1.49	6.19, 6.32, 6.39, 6.44	1.41, 3.56	2.86	2.52, 2.24	1.80	13.0	3.1
2	C_6D_6	1.48	6.20, 6.32, 6.48	1.79, 3.57	3.00 (d)[c]	2.18, 2.52	2.10	13.1	3.2
	[$^2H_8$]thf	1.24	5.76, 5.90, 5.98, 6.57	1.72, 3.58	3.07 (d)[d]	2.28, 2.58	—	11.3	3.0
^{13}C NMR (δ_C)				1,3-Dithiane and thf					
1	[$^2H_8$]thf	32.4, 68.4	107.4, 108.6, 109.4, 110.5, 137.7	25.4, 28.1, 30.2, 32.7	42.9 (M–CH)				
2	C_6D_6	32.2, 68.5	107.7, 109.2, 109.9, 111.4, 139.4,	25.3, 27.2, 28.1, 32.4	40.5 (d) (M–CH)[e]				—

[a] Co-ordinated. [b] See schematic diagram of 1,3-dithiane ligand for numbering of hydrogen and carbon atoms. [c] Doublet, $^2J_{YH} = 3.2$ Hz. [d] Doublet, $^2J_{YH} = 3.1$ Hz. [e] Doublet, $^1J_{YC} = 40.8$ Hz.

for metallated 1,3-dithiane. Both theoretical[18] and experimental studies of lithium-1,3-dithianes in solution[16a,b] suggest that the free electron pair is located virtually exclusively in the equatorial position of the ring. Accordingly, only one chair conformation is predominant and thus for substituted dithianes the axial and equatorial H^4, H^5 and H^6 protons should be resolved in the NMR spectrum. Indeed, in the spectrum of the lithiated compound [Fig. 2(*b*)] signals of the axial and equatorial H^4 and H^6 protons appear as two separate groups of triplets at δ 2.36 ($J_{aa} \approx J_{gem} = 11.5$, $J_{ae} = 2.1$) and at 2.26 ($J_{gem} = 11.6$, $J_{ae} \approx J_{ee} = 2.1$ Hz). Obviously the resonance of the H^2 proton is shifted significantly upfield (more than 1 ppm) for the dithiane carbanion, to δ 2.73.

Co-ordination of the 1,3-dithiane anion to a larger cationic centre, such as a $Ln(C_5H_4Bu^t)_2$ moiety, substantially affects the positions of the dithiane resonances [Figs. 1(*b*) and 2(*a*)]. This effect may be due partially to the metal-induced spatial magnetic anisotropy: the fragment $Ln(C_5H_4Bu^t)_2$ plays the role of 'shift reagent' for the dithiane anion. In solution the dithiane ring in the complex is fixed in one of two possible chair conformations and the signals of the axial and equatorial H^4 and H^6 protons are separated by more than 0.1 ppm. The values of J_{aa}, J_{gem} and J_{ae}, J_{ee} are very similar in pairs and similar to those found for the lithium derivative (see Table 1). The general pattern of this group of protons is typical for 2-substituted dithianes,[16c,d] occurring as a triplet (axial protons) and a doublet (equatorial protons), both split with small J_{ae} and J_{ee} (2–3 Hz).

We should mention here that X-ray analysis of the yttrium complex **2** (see below) revealed disorder in the positions of one of the two sulfur atoms in the dithiane ligand, with relative occupation factors of 80 and 20%. The corresponding conformations of the dithiane ring are 'chair' and 'boat' respectively (see Table 6 for details). It is interesting, however, that in solution no spectral evidence for the existense of a 'boat' conformation has been found. Probably, stabilization of the 'chair' conformation due to solvation effects makes the 'boat' conformation thermodynamically unfavourable. Our earlier study of the similar complex $[Y(C_5H_5)_2(C_4H_7S_2\text{-}1,3)]\cdot$thf showed, however, two independent groups of dithiane signals in the ^1H NMR spectrum.[19] These probably belong to 'chair' and 'boat' conformations, both present in solution.

The signals of H^5_a and H^5_e in compound **2** appear as several multiplets at around δ 2.1. Although accurate identification of all peaks in this group is difficult, they have somewhat similar shapes and coupling constants. The doublet of the H^2 proton is shifted 0.34 ppm downfield as compared to the corresponding resonance of $Li(C_4H_7S_2\text{-}1,3)$. Obviously the chemical shift of this last proton is mostly dependent upon the nature of the cationic centre present in the molecule. The corresponding peaks are separated by 0.24 ppm for **1** and **2**, while structurally the complexes are very similar (see below). The second-order coupling on atom H^2 ($^2J_{YH} = 3.1$ Hz) is very similar to that measured for the α-hydrogen in $[Y(C_5H_5)_2\{CH(SiMe_3)_2\}]$ ($^2J_{YH} = 2.3$ Hz)[20] and also for the methylene protons in anionic $[Y(C_5Me_5)_2\{CH_2(SiMe_3)\}_2]^-$ ($^2J_{YH} = 2.8$ Hz).[21]

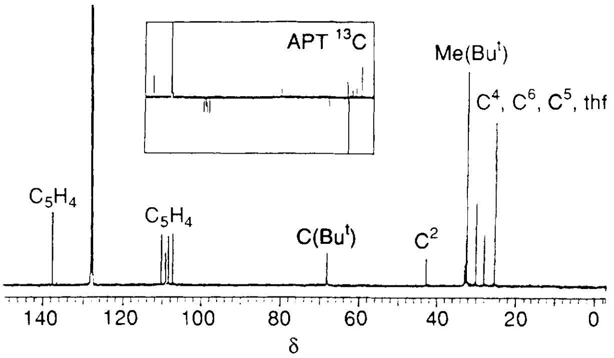


Fig. 3 The ^{13}C NMR spectrum of complex **1**. Insert shows the ^{13}C APT spectrum

The ^{13}C NMR spectrum of a thf solution of complex **1** is shown in Fig. 3 and the chemical shifts are given in Table 1. A more accurate assignment of the carbon resonances has been done with the use of the attached proton test (APT) ^{13}C† technique (spectrum is shown as the insert to Fig. 3). The group of four 'even' resonances in the range δ 24–34 belongs to the C^4(C^6), C^5 atoms of the dithiane ligand and carbons of the co-ordinated thf molecules. However a more detailed assignment cannot be accomplished without additional spectroscopic studies. The aspect worth mentioning here is the presence of a relatively large Y–C coupling in **2** ($^1J_{YC} = 40.8$ Hz), which clearly demonstrates binding of the dithiane to the metal. This coupling is substantially larger than one found for the σ-bonded bis(trimethylsilyl)methyl complex $[Y(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ ($^1J_{YC} = 36.6$ Hz)[20] and bridged methyl complexes $[\{Y(C_5Me_5)_2Me\}_2]$ ($^1J_{YC} = 25$ Hz).[22]

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† In the spectra obtained with this technique the signals of carbons with odd numbers of attached hydrogens turn upside down, while those of carbons with even numbers of hydrogens remain unchanged.

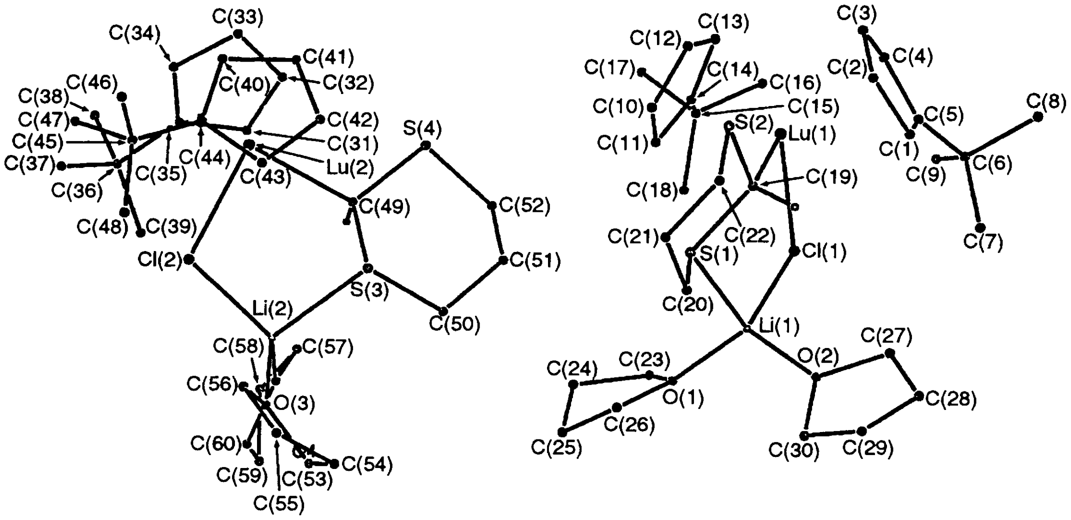


Fig. 4 Perspective view of the two independent molecules in the crystallographic unit of complex **1**

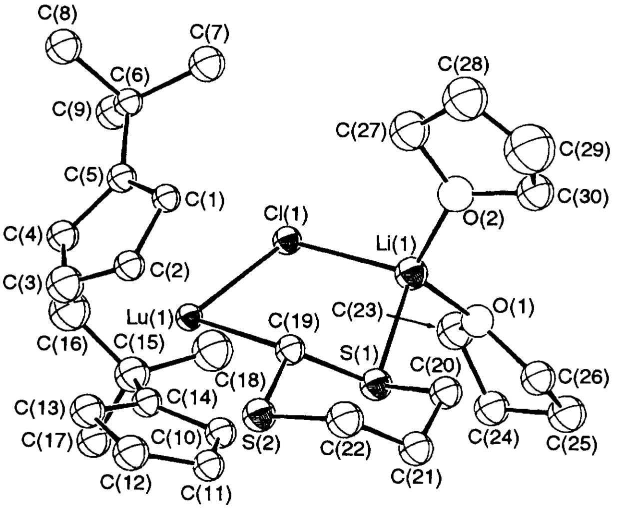


Fig. 5 An ORTEP diagram of the molecular structure of complex **1**

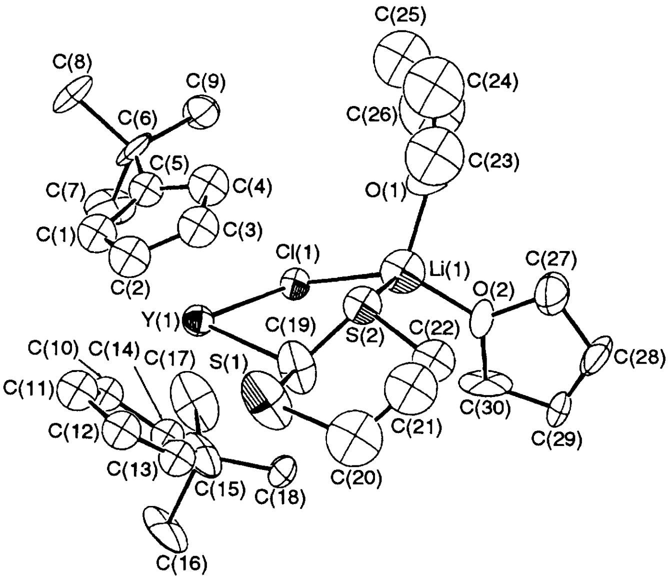


Fig. 6 An ORTEP diagram of the molecular structure of complex **2**

Molecular structures of $[M(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ (M = Lu **1** *or* Y **2**).—The structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction analysis. Table 2 gives selected bond distances (Å) and angles (°) and Table 3 torsion angles and puckering coordinates[23] for selected cyclic fragments of the structures.

Both compounds co-crystallize with LiCl and two thf molecules, the lanthanide metals thus achieving co-ordinative saturation. The crystal structure of **1** consists of two crystallographically independent molecules (see Fig. 4) with practically identical structures. The only difference is the relative orientation of the thf molecules, bound to the Li atom. The Li–O distances vary from 1.86(4) to 1.93(5) Å. An ORTEP[24] plot of one of the molecules is given in Fig. 5.

The Lu atom is bound to two $C_5H_4Bu^t$ rings in a η^5 fashion. The C_5H_4 rings in both independent complexes are practically flat within the standard deviations. The Lu–C(η^5) distances exhibit significant dispersion varying from 2.56(2) to 2.70(2) Å. The longest distance (averaged over four rings) is between Lu and the carbon atom attached to Bu^t, while the shortest one is to the carbon atom in position 3 (or 4), relative to the Bu^t substituent. These distances are within the range of values observed for other bis(cyclopentadienyl)lutetium organometallics.[3,25] The ring centroid–metal–ring centroid angles Cp(1)–Lu–Cp(2) are 128.6(6) and 130.1(7)° for the two molecules, also typical for bent bis(cyclopentadienyl)lutetium complexes. The co-ordination polyhedra formed around the lanthanide centres in various organolanthanides usually have pseudo-tetrahedral geometry with ring centroids located in the corner positions. In general the orientation of the $C_5H_4Bu^t$ ligands in both molecules of **1** follows this pattern, though the bulky Bu^t groups are located on one side of the plane drawn through the Cp centroids and Lu atom. This asymmetry causes a small shift of the centroids from the corner positions of a regular tetrahedron.

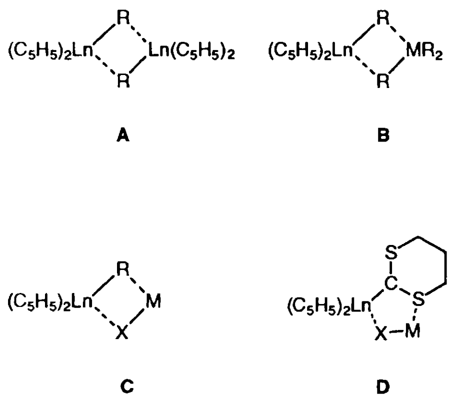
The molecular structure of the yttrium complex **2** (Fig. 6) is similar to that of **1**. The distances characterizing the location of the cyclopentadienyl ligands are in general slightly larger, whereas the ring centroid–metal–ring centroid angle is 126.5(8)°, slightly lower than for **1**. All values are in a good agreement with data obtained from structures of other yttrocene derivatives.[20–22,26]

The 1,3-dithiane fragment is present in complex **1** in the 'chair' conformation. Although in complex **2** the sulfur atom is bound to lithium, it is disordered with site occupation factors of 0.80(1) for S(2) and of 0.20(1) for S(2a). This disorder leads to the presence of 1,3-dithiane in two 'chair' (80%) and 'boat' (20%), conformations, also increasing the displacement

Table 2 Selected interatomic distances (Å) and angles (°) for $[Lu(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **1** and $[Y(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **2**

1[a]		**2**	
$C_5H_4Bu^t$ [C(1)–C(5)]			
Lu–Cp(1)[b]	2.34(2)	Y(1)–Cp(1)	2.36(3)
⟨Lu–C(η^5)⟩	2.63(2)	⟨Y(1)–C(η^5)⟩	2.65(3)
C(5)–C(6)	1.55(3)	C(5)–C(6)	1.48(4)
$C_5H_4Bu^t$ [C(10)–C(14)]			
Lu–Cp(2)	2.32(2)	Y(1)–Cp(2)	2.39(3)
⟨Lu–C(η^5)⟩	2.61(2)	⟨Y(1)–C(η^5)⟩	2.68(3)
C(14)–C(15)	1.51(3)	C(14)–C(15)	1.51(4)
1,3-Dithiane, LiCl and thf			
Lu–Cl	2.570(5)	Y(1)–Cl(1)	2.638(6)
Lu···S(1)	3.510(6)	Y(1)···S(1)	3.54(1)
Lu···S(2)	3.568(6)	Y(1)···S(2)	3.55(1)
Li–O(1)	1.92(4)	Li(1)–O(1)	1.90(6)
Li–O(2)	1.89(4)	Li(1)–O(2)	1.90(5)
S(1)–C(19)	1.77(2)	S(1)–C(19)	1.71(3)
S(1)–C(20)	1.83(2)	S(1)–C(20)	1.90(4)
S(2)–C(19)	1.76(2)	S(2)–C(19)	1.76(3)
S(2)–C(22)	1.82(3)	S(2)–C(22)	1.87(3)
C(20)–C(21)	1.54(4)	C(20)–C(21)	1.30(5)
C(21)–C(22)	1.48(4)	C(21)–C(22)	1.42(4)
Cp(1)–Lu(1)–C(19)	104.1(7)	Cp(1)–Y(1)–C(19)	106.9(8)
Cp(2)–Lu(1)–C(19)	105.8(7)	Cp(2)–Y(1)–C(19)	103.8(8)
Cp(1)–C–C(Bu^t)[c]	167(2)	Cp(1)–C–C(Bu^t)[c]	176(2)
Cp(2)–C–C(Bu^t)[c]	172(2)	Cp(2)–C–C(Bu^t)[c]	168(3)
Lu(1)–Cl(1)–Li(1)	107(1)	Y(1)–Cl(1)–Li(1)	106(1)
Lu(1)–C(19)–S(1)	111.5(10)	Y(1)–C(19)–S(1)	115(1)
Lu(1)–C(19)–S(2)	113.5(10)	Y(1)–C(19)–S(2)	111(2)
Cl(1)–Lu(1)–C(19)	89.8(5)	Cl(1)–Y(1)–C(19)	88.3(6)
Cl(1)–Li(1)–S(1)	99(1)	Cl(1)–Li(1)–S(2)	102(2)
Cl(1)–Li(1)–O(1)	114(2)	Cl(1)–Li(1)–O(1)	114(2)
Cl(1)–Li(1)–O(2)	112(2)	Cl(1)–Li(1)–O(2)	118(2)
S(1)–C(19)–S(2)	111.5(10)	S(1)–C(19)–S(2)	111(2)
S(1)–Li(1)–O(1)	104(2)	S(2)–Li(1)–O(1)	102(2)
S(1)–Li(1)–O(2)	114(2)	S(2)–Li(1)–O(2)	116(2)
S(1)–C(20)–C(21)	112(2)	S(2)–C(22)–C(21)	111(2)
C(20)–C(21)–C(22)	115(2)	C(20)–C(21)–C(22)	122(3)
C(21)–C(22)–S(2)	116(2)	C(21)–C(20)–S(1)	116(3)
C(22)–S(2)–C(19)	101.5(10)	C(20)–S(1)–C(19)	103(2)

[a] The parameters are averaged over the two independent molecules in the unit cell. [b] Cp = Centroid of C_5H_4 ring. [c] Calculated for Cp(1)–C(5)–C(6) or Cp(2)–C(14)–C(15).

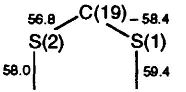


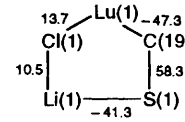
Scheme 3

parameters of the carbon atoms in the 1,3-dithiane and thf fragments of the complex (see Table 3).

Table 3 Torsion angles (°) and puckering parameters* for selected rings of complexes **1** and **2**

Complex **1** (parameters averaged over two independent molecules)

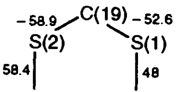


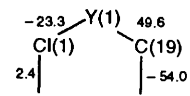


q_2 = 0.056, φ_2 = 17.2
q_3 = 0.691
Q = 0.693, θ = 4.6

q_2 = 0.689
φ_2 = 50.2

Complex **2**
(*a*) Rings, including atom S(2) with site occupation factor 0.80

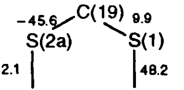


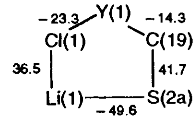


q_2 = 0.157, φ_2 = 319.4
q_3 = 0.623
Q = 0.643, θ = 14.1

q_2 = 0.664
φ_2 = 211.5

(*b*) Rings including atom S(2a) with site occupation factor 0.20





q_2 = 0.690, φ_2 = 119.7
q_3 = −0.007
Q = 0.690, θ = 90.6

q_2 = 0.688
φ_2 = 106.9

* Ln and C(19) are referred as the first atoms in the five- and six-membered rings respectively. Parameters defined in ref. 23; q_2, q_3 and Q measured in Å, φ_2 and θ in degrees.

The most interesting feature of complexes **1** and **2** is certainly a pentagon, formed by the central metal (Lu or Y) atom, 1,3-dithiane and a molecule of LiCl. Usually, if a hydrocarbyl ligand is bulky enough to cover a lanthanide ion and thus prevent co-crystallization, monomeric structures, such as, for example $[Lu(C_5Me_5)_2\{CH(SiMe_3)_2\}]$ [1b] are formed. However, more typically bis(cyclopentadienyl)lanthanide hydrocarbyls form either dimers such as $[\{Y(C_5H_5)_2Me\}_2]$ [22] (Scheme 3, **A**), or co-crystallize with other metal hydrocarbyls, as in $[(C_5H_5)_2Y(\mu\text{-}Me)_2AlMe_2]$ [27] (Scheme 3, **B**). Also, complexes with alkali-metal salts, as in $[Yb(C_5Me_5)_2Me]\cdot LiCl\cdot 2Et_2O$ [28] (Scheme 3, **C**), are commonly formed. This behaviour is mainly due to the strong tendency of lanthanide ions to saturate their co-ordination environment. In all cases the central core of the resulting complex is tetragonal, with bridging halogen or carbon atoms, and metal atoms occupying the opposite corners. 1,3-Dithiane complexes also co-crystallize with LiCl, however the existence of sulfur atoms in the vicinity of both metals allows the formation of less-strained pentagonal metallacycles (Scheme 3, **D**).

In complex **1** the metallacycle has the slightly distorted twist conformation, with the axis drawn through the Cl atom. For complex **2** the 'chair' conformation of the 1,3-dithiane fragment corresponds to the 'envelope' conformation of the metallacycle with its apex at C(19), while the 'boat' conformation of 1,3-dithiane corresponds to the metallocycle with its apex at Li (Table 3).

The values of angles Cl–Ln–C (dithiane) are 90.8(5) and 88.2(5)° for the two independent molecules of complex **1** and 88.3(6)° for **2**, which is less than typically obtained for complexes with two bridging halogen atoms[3] (94.6–97.7°). The distances between the metal and 1,3-dithiane ligand M–C(19), 2.45(2) Å for **1** and 2.47(3) Å for **2**, are close to those reported for dimeric alkyl complexes, 2.54 Å for $[\{\mathrm{Y(C_5H_5)_2Me}\}_2]$,[27] and for bridging complexes with LiMe, 2.46 Å for $[\mathrm{Li(tmen)}][\mathrm{Lu(C_5H_5)_2(\mu\text{-}Me)_2}]$.[29] For comparison, the distance between Li and the σ-bound carbon atom in the lithium-2-methyl-1,3-dithiane centrosymmetric dimer[13] was found to be 2.186 Å. This is 0.27 Å shorter than the corresponding Lu–C bond in **1**. The latter value is still 0.1 Å greater than the difference in crystallographic radii for Li (0.68 Å) and Lu (0.85 Å).

Another edge of the pentagon is formed by a LiCl molecule and the Li–Cl contacts in complexes **1** and **2** are 2.34(4) and 2.33(5) Å respectively. The corresponding bonds in complexes of type $\mathrm{Ln(C_5R_5)_2X{\cdot}LiX{\cdot}2solv}$ (X = halide, solv = solvent, R = H or Me, $\mathrm{R_5}$ = $\mathrm{H_4Me}$ or $\mathrm{H_4Bu^t}$, *etc.*) usually vary in the narrow range of 2.39–2.41 Å.[3] The Lu–Cl distance in **1** is 2.570(5) Å, very close to the 2.59 Å reported for $[\mathrm{Yb(C_5Me_5)_2Cl}]{\cdot}\mathrm{LiCl}{\cdot}2\mathrm{Et_2O}$.[30] The Li atoms in **1** and **2** complete their co-ordination tetrahedrons by binding to one of the sulfur atoms of the 1,3-dithiane ligand. The distances of these contacts are 2.45(4) Å in **1** and 2.40(5) (higher occupation site) and 2.61(6) Å (lower occupation site) in **2** respectively. The binding virtually has no influence on the geometry of the 1,3-dithiane in complex **1**, which remains fixed in a regular chair conformation with the Lu atom located in the equatorial position of the ring, and the same is true for the dominant conformation of 1,3-dithiane in **2**.

Reactions.—We examined the reactivity of dithiane complexes **1** and **2** towards other protonic acids, such as water, HC≡CPh and $\mathrm{NH(SiMe_3)_2}$. All acids chosen have higher $\mathrm{p}K_\mathrm{a}$ values than that of free 1,3-dithiane. The reactions were carried out in sealed glass vials in thf or benzene solutions and the organolanthanide complexes were always present in excess. In all cases the reaction progress was monitored by ^{1}H NMR spectroscopy.

The addition of water to the complexes caused immediate release of 1,3-dithiane. The changes in positions of the $\mathrm{Bu^t}$ and $\mathrm{C_5H_4}$ signals were indicative of the formation of hydroxo derivatives, probably similar to the recently reported dimeric complex $[\{\mathrm{Lu[1,3\text{-}(Me_3Si)_2C_5H_3]_2(\mu\text{-}OH)}\}_2]$.[31] The less acidic HC≡CPh reacts with complex **2** at room temperature in benzene, leading to the formation of free 1,3-dithiane and a new bis(*tert*-butylcyclopentadienyl)yttrium acetylenide complex. The resonances of the *o*- (δ, 6.94, d), *p*- (7.36, t) and *m*-protons (7.47, t) are close to those recently reported for $[\{\mathrm{La(C_5Me_5)_2}\}_2(\mu\text{-}\mathrm{PhC_4Ph})]{\cdot}2(\mathrm{C_6H_5Me})$.[32] However the question of whether two phenylacetylene fragments in this complex are coupled to each other by a C=C bond, giving a trienediyl structure as in $[\{\mathrm{Sm(C_5Me_5)_2}\}_2(\mu\text{-}\mathrm{PhC_4Ph})]$[33] and $[\{\mathrm{Ce(C_5Me_5)_2}\}_2(\mu\text{-}\mathrm{Bu^tC_4Bu^t})]$,[34] or they form independent asymmetrically bridging, σ-bonded acetylide links, as in $[\{\mathrm{Er(C_5H_5)_2(C{\equiv}CBu^t)}\}_2]$[4a] and $[\{\mathrm{Sm(C_5H_4Bu^t)_2(C{\equiv}CPh)}\}_2]$,[4c] cannot be answered in this case without actual structural studies. However, when the complexes contain non- or mono-substituted ligands, as in our case, structures of the latter type seem to form more often.

The reaction of complex **2** with $\mathrm{NH(SiMe_3)_2}$ in benzene requires more rigorous conditions. After heating the reaction mixture at 60 °C for a few hours the spectrum showed signals of a new complex $[\mathrm{Y(C_5H_4Bu^t)_2}\{\mathrm{N(SiMe_3)_2}\}]$ complex and of released free 1,3-dithiane. By analogy with the known $[\mathrm{Y(C_5Me_5)_2}\{\mathrm{N(SiMe_3)_2}\}]$ complex[20] and considering the large steric volume of the hexamethyldisilazide ligand, we believe that the resulting compound has a monomeric structure. The signal of the silazide methyls appears at δ 0.15, only slightly different from that reported for $[\mathrm{Y(C_5Me_5)_2}\{\mathrm{N(SiMe_3)_2}\}]$ (δ 0.14). The cyclopentadienyl part of the spectrum has a conventional AA′BB′ shape with two triplets at δ 6.04 and 6.23.

The reactivity of complexes **1** and **2** allows them to be considered as convenient precursors for organolanthanides with ligands derived from protonic acids stronger than 1,3-dithiane. Further investigation of the reactivity of 1,3-dithiane organolanthanide complexes is in progress.

Experimental

General Considerations.—The compounds described in this paper are extremely air and moisture sensitive. All manipulations were carried out using Schlenk and vacuum-line techniques. Solutions of highly reactive chemicals were transferred using 1.5 mm stainless-steel cannulas by applying an extra pressure of argon. Argon (*High Purity* Grade, RossGaz, Moscow) was purified as described previously[35] by passing through a set of columns filled with copper–Kieselguhr, maintained at 200 °C, CrO–$\mathrm{SiO_2}$[36a] and 4 Å molecular sieves. Toluene, benzene, thf, diethyl ether and all NMR solvents ($\mathrm{C_6D_5CD_3}$), $\mathrm{C_6D_6}$ and [$^2\mathrm{H_8}$]tetrahydrofuran were distilled from Na or Na–K alloy and stored in vacuum in specially made storage bulbs over sodium–benzophenone. Pentane was distilled from $\mathrm{P_2O_5}$ and stored over Na–K alloy in vacuum. All solvents were vacuum transferred into the reaction flasks or NMR tubes, which were charged with the solid compounds immediately prior to use. Vaseline oil, used for manipulation with crystals under anaerobic conditions, was kept at 100 °C in vacuum (10^{-2}–10^{-3} Torr; 1 Torr ≈ 133 Pa) over Na–K alloy for 3–4 h, then cooled and saturated with argon. Ampoules containing dried crystals for X-ray analysis held under vacuum were opened in a glass under a layer of oil, so the crystals were coated with oil immediately and thus protected from oxygen and moisture. The protection offered by the thin (less than 0.5 mm) layer of oil was good enough to keep sensitive crystals in good shape for the few hours needed to perform all necessary manipulations. The compounds $\mathrm{LuCl_3}$ and $\mathrm{YCl_3}$ were prepared by heating the corresponding hexahydrates with an excess of $\mathrm{NH_4Cl}$ in vacuum.[36b] 1,3-Dithiane was prepared by $\mathrm{BF_3}$-

Table 4 Crystal and data collection parameters for complexes **1** and **2***

	1	**2**
Formula	$\mathrm{C_{30}H_{49}ClLiLuO_2S_2}$	$\mathrm{C_{30}H_{49}ClLiO_2S_2Y}$
M	723.2	637.1
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pbca*
a/Å	11.489(4)	14.744(6)
b/Å	14.438(6)	21.148(7)
c/Å	20.217(4)	21.472(6)
α/°	94.16(3)	90
β/°	89.76(2)	90
γ/°	97.58(3)	90
U/Å^3	3328(2)	6695(4)
D/g cm^{-3}	1.443	1.264
μ(Mo-Kα)/cm^{-1}	32.0	19.7
F(000)	1472.0	2688.0
Size/mm	0.8 × 0.7 × 0.4	0.5 × 0.5 × 0.4
T/°C	−60	−80
Scan method	ω–2θ	ω
Total data	8143	3479
Unique data	7978	3479
Observed data [$I > 2\sigma(I)$]	5881	1570
Number of parameters	696	260
R	0.072	0.081
R'	0.071	0.083
Goodness of fit	7.28	7.88
Largest shift/e.s.d., final cycle	0.06	0.09
Largest peak/e Å^{-3}	2.0	0.7

* Details in common: λ(Mo–Kα) 0.710 73 Å; 2θ range 2–50°; $w = 1/\sigma^2(F)$.

Table 5 Atom coordinates for non-hydrogen atoms of $[Lu(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **1**

Atom	x	y	z	Atom	x	y	z
Lu(1)	0.1360(1)	0.2501(1)	0.4078(0)	Lu(2)	0.6132(1)	0.7471(1)	0.0956(0)
Li(1)	0.421(4)	0.075(3)	0.378(2)	Li(2)	0.887(4)	0.554(3)	0.127(2)
Cl(1)	0.3359(5)	0.1763(4)	0.4553(2)	Cl(2)	0.8146(5)	0.6779(4)	0.0519(2)
S(1)	0.2848(5)	0.1213(5)	0.2849(3)	S(3)	0.7025(6)	0.5323(4)	0.1826(3)
S(2)	0.0290(6)	0.1533(5)	0.2670(3)	S(4)	0.5376(6)	0.6601(5)	0.2575(3)
O(1)	0.570(1)	0.104(1)	0.3429(7)	O(3)	1.014(1)	0.580(1)	0.1779(8)
O(2)	0.415(1)	−0.049(1)	0.4081(8)	O(4)	0.932(2)	0.439(1)	0.0858(8)
C(1)	0.024(2)	0.128(1)	0.4780(9)	C(31)	0.695(2)	0.873(1)	0.1658(9)
C(2)	−0.055(2)	0.180(2)	0.431(1)	C(32)	0.571(3)	0.876(2)	0.176(1)
C(3)	−0.083(2)	0.271(2)	0.449(1)	C(33)	0.503(2)	0.910(2)	0.115(1)
C(4)	−0.009(2)	0.283(1)	0.504(1)	C(34)	0.598(2)	0.929(1)	0.071(1)
C(5)	0.050(2)	0.192(2)	0.5257(9)	C(35)	0.706(2)	0.908(1)	0.0981(8)
C(6)	0.107(2)	0.166(2)	0.592(1)	C(36)	0.829(2)	0.935(2)	0.069(1)
C(7)	0.182(2)	0.071(2)	0.593(1)	C(37)	0.825(2)	0.924(2)	−0.005(1)
C(8)	0.009(2)	0.151(2)	0.644(1)	C(38)	0.816(3)	1.043(2)	0.081(1)
C(9)	0.183(2)	0.239(2)	0.613(1)	C(39)	0.935(2)	0.876(2)	0.104(1)
C(10)	0.260(2)	0.364(2)	0.338(1)	C(40)	0.431(2)	0.765(2)	0.018(1)
C(11)	0.165(2)	0.347(2)	0.296(1)	C(41)	0.397(2)	0.724(2)	0.082(1)
C(12)	0.059(3)	0.387(2)	0.326(1)	C(42)	0.452(3)	0.632(2)	0.091(1)
C(13)	0.088(2)	0.433(2)	0.388(1)	C(43)	0.531(2)	0.612(2)	0.034(1)
C(14)	0.213(2)	0.421(1)	0.392(1)	C(44)	0.514(2)	0.694(2)	−0.012(1)
C(15)	0.284(2)	0.466(2)	0.440(1)	C(45)	0.556(2)	0.700(2)	−0.082(1)
C(16)	0.222(3)	0.467(2)	0.505(1)	C(46)	0.454(3)	0.691(3)	−0.125(1)
C(17)	0.285(2)	0.566(2)	0.415(1)	C(47)	0.604(3)	0.799(2)	−0.098(1)
C(18)	0.409(3)	0.414(2)	0.445(2)	C(48)	0.649(3)	0.625(2)	−0.094(1)
C(19)	0.146(2)	0.134(2)	0.3250(9)	C(49)	0.658(2)	0.649(2)	0.199(1)
C(20)	0.276(2)	0.023(2)	0.236(1)	C(50)	0.748(2)	0.473(2)	0.264(1)
C(21)	0.174(2)	0.041(2)	0.186(1)	C(51)	0.645(2)	0.485(2)	0.313(1)
C(22)	0.056(3)	0.051(2)	0.218(1)	C(52)	0.602(3)	0.582(2)	0.326(1)
C(23)	0.626(3)	0.180(2)	0.363(1)	C(53)	0.983(3)	0.352(2)	0.119(1)
C(24)	0.684(2)	0.216(2)	0.303(1)	C(54)	0.914(3)	0.279(2)	0.100(2)
C(25)	0.709(3)	0.134(2)	0.261(1)	C(55)	0.876(3)	0.313(2)	0.032(1)
C(26)	0.607(2)	0.083(2)	0.276(1)	C(56)	0.865(3)	0.414(2)	0.030(1)
C(27)	0.334(3)	−0.079(2)	0.458(1)	C(57)	1.006(2)	0.646(2)	0.229(1)
C(28)	0.333(3)	−0.183(2)	0.447(2)	C(58)	1.122(4)	0.674(3)	0.232(2)
C(29)	0.394(4)	−0.200(3)	0.392(2)	C(59)	1.209(3)	0.590(3)	0.217(1)
C(30)	0.470(2)	−0.130(2)	0.376(1)	C(60)	1.134(3)	0.549(2)	0.167(1)

Table 6 Atom coordinates for non-hydrogen atoms of $[Y(C_5H_4Bu^t)_2(C_4H_7S_3\text{-}1,2)]\cdot LiCl\cdot 2thf$ **2**

Atom	x	y	z	Atom	x	y	z
Y(1)	0.7557(2)	0.1431(1)	0.6615(1)	C(12)	0.745(2)	0.154(1)	0.781(1)
Cl(1)	0.8352(4)	0.0668(3)	0.5811(3)	C(13)	0.824(2)	0.121(1)	0.774(1)
S(1)	0.8918(9)	0.2733(5)	0.7081(5)	C(14)	0.793(2)	0.059(1)	0.753(1)
S(2)	0.9338(7)	0.2261(4)	0.5866(4)	C(15)	0.837(2)	−0.004(2)	0.747(1)
S(2a)*	0.981(2)	0.186(2)	0.637(2)	C(16)	0.847(3)	−0.031(2)	0.815(1)
O(1)	0.919(1)	0.151(1)	0.450(1)	C(17)	0.799(2)	−0.051(1)	0.705(1)
O(2)	1.067(1)	0.0928(9)	0.5285(9)	C(18)	0.940(2)	0.004(2)	0.724(1)
Li(1)	0.948(3)	0.127(2)	0.533(2)	C(19)	0.895(2)	0.208(1)	0.662(1)
C(1)	0.588(2)	0.183(1)	0.643(1)	C(20)	1.010(3)	0.308(2)	0.700(2)
C(2)	0.641(2)	0.237(1)	0.651(1)	C(21)	1.041(3)	0.313(2)	0.643(1)
C(3)	0.700(2)	0.244(1)	0.601(1)	C(22)	1.048(2)	0.260(1)	0.603(1)
C(4)	0.679(2)	0.194(1)	0.561(1)	C(23)	0.934(3)	0.205(3)	0.422(3)
C(5)	0.611(2)	0.155(1)	0.586(1)	C(24)	0.858(3)	0.217(3)	0.399(3)
C(6)	0.569(1)	0.099(1)	0.556(1)	C(25)	0.837(4)	0.167(3)	0.364(2)
C(7)	0.576(2)	0.042(1)	0.601(1)	C(26)	0.870(4)	0.120(2)	0.405(2)
C(8)	0.467(1)	0.114(2)	0.541(1)	C(27)	1.130(2)	0.109(2)	0.481(1)
C(9)	0.616(2)	0.082(1)	0.495(1)	C(28)	1.220(2)	0.108(2)	0.508(2)
C(10)	0.698(2)	0.062(1)	0.750(1)	C(29)	1.209(2)	0.067(2)	0.560(1)
C(11)	0.671(2)	0.121(1)	0.766(1)	C(30)	1.112(2)	0.059(2)	0.574(1)

* Disordered sulfur atom; occupation S(2):S(2a) = 4:1.

catalysed condensation of propane-1,3-dithiol and dimethoxymethane.[37] It was recrystallized from methanol and dried in vacuum prior to use. Propane-1,3-dithiol was synthesized by hydrolysis of propane-1,3-diyldiisothiouronium dichloride,[38] prepared from 1,3-dichloropropane and thiourea.[39] *tert*-Butylcyclopentadiene was synthesized according to ref. 40 from C_5H_6 and Bu^{t}Cl and converted into the sodium salt in 84% yield by treatment with an equimolar amount of $Na[N(SiMe_3)_2]$ in ether. It was stored in a Schlenk tube under argon. The NMR spectra were recorded on a Varian VXR-400 spectrometer and referenced to residual protons in deuteriated solvents. Initial determination of the stoichiometry of the complexes was performed by GC analysis of hydrolysed complexes on a Chrom-5 (Prague) chromatograph (3 m SE-30 column), using 1,4-dichlorobenzene or adamantane as internal standards. Complexes were hydrolysed with aqueous methanol, extracted with ether and dried over Na_2SO_4 prior to analysis. The lanthanide contents were assayed by titration (ethylenediaminetetracetic acid, xylenol orange).

X-Ray Crystallography.—Single X-ray-quality crystals of complexes **1** and **2** were obtained from pentane solutions at -10 °C. Crystals were placed under a layer of specially prepared vaseline oil (see above), glued on a glass fibre, and quickly transferred directly into the cold nitrogen stream of the LT-1 low-temperature unit mounted on a Enraf-Nonius CAD-4 diffractometer interfaced to a IBM-PC/386 computer and equipped with a graphite monochromator and Mo-Kα radiation source. Table 4 contains the crystallographic data for both complexes.

For complex **1** a triclinic unit cell was derived by least-squares refinement of 24 of the strongest reflections with 2θ angles in the range 24–30°. The space group $P\bar{1}$ was assumed and then confirmed by the successful solution and refinement of the structure. Crystal and/or instrumental instability was monitored by the intensity of three reference reflections, measured every 2 h, and two standard reflections were used for the orientation control and checked every 200. The net intensities of the collected data were corrected for Lorentz and polarization effects. A Patterson map was solved to locate the positions of both Lu atoms. The remaining non-hydrogen atoms were obtained from Fourier-difference syntheses. All non-hydrogen atoms were refined isotropically. The hydrogen atoms were introduced in their calculated positions assuming a C–H bond length of 0.96 Å. Methyls of Bu^t substituents were refined as rigid top-like groups. The structure was refined by block-diagonal least squares to a final $R = 0.072$. A DIFABS empirical absorption correction[41] was applied to the data. Highest peaks in the final difference synthesis were located within 1.12 Å of the Lu atoms. Atomic coordinates are given in Table 5.

In a similar manner, an orthorhombic unit cell was derived for complex **2**. The space group *Pbca* was obtained by examination of systematic absences. The structure was solved by the direct method which revealed the locations of the Y atom and the atoms co-ordinated to it. Subsequent Fourier synthesis revealed other non-hydrogen atoms. Carbon atoms of cyclopentadienyl rings were rigidly fixed as planar pentagons and were refined isotropically. The S(2) atom which was found to be disordered over two positions (80 and 20% occupancy) and the Li atom were also refined isotropically. Other non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were calculated as before. The structure was refined by full-matrix least squares to a final $R = 0.081$. A DIFABS empirical absorption correction was applied. The highest peak in the final difference synthesis was located in the vicinity of atom S(2). Final atomic coordinates are given in Table 6.

All calculations were carried out on an IBM-PC/486 computer with the programs SHELX 76,[42] SHELXS 86[43] and local programs for calculations of geometrical data.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparations.—$Li(C_4H_7S_2\text{-}1,3)$. A 1.23 mol dm^{-3} hexane solution (8.13 cm^3) of LiBu (10 mmol) was syringed into a Schlenk tube with a solution of 1,3-dithiane (1.2 g, 10 mmol) in diethyl ether (25 cm^3) at 0 °C. A white residue formed and the mixture was allowed to react for 1 h at room temperature. The solvent was removed by cannula and the resulting white powder was washed three times with pentane and dried in vacuum. Yield 1.24 g, 98%.

$[Lu(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **1**. A mixture of $Na(C_5H_4Bu^t)$ (0.87 g, 6.07 mmol) and $LuCl_3$ (0.85 g, 3.03 mmol) in thf (80 cm^3) was stirred at r.t. for 5 h. In a separate Schlenk tube a solution of 1.23 mol dm^{-3} LiBu (2.6 cm^3, 3.1 mmol) was added to a solution of 1,3-dithiane (0.36 g, 3.03 mmol) in thf (20 cm^3) at 0 °C by syringe and the mixture was allowed to react for 1 h. Both flasks were cooled to -78 °C and the solution of $Li(C_4H_7S_2\text{-}1,3)$ was added to the first mixture by cannula. The temperature was raised slowly to 0 °C and the mixture was left to react overnight. The solvent was removed in vacuum, pentane (200 cm^3) was added and the clear pentane extract was transferred by cannula to a separate tube. The volume was reduced to 30 cm^3 and a white amorphous residue formed upon cooling the mixture to -20 °C. It was filtered off, washed once with cold pentane and dried in vacuum. The GC analysis of a hydrolysed portion of the complex and lanthanide titration results agreed with the suggested stoichiometry for **1**. Yield: 0.96 g, 44%.

$[Y(C_5H_4Bu^t)_2(C_4H_7S_2\text{-}1,3)]\cdot LiCl\cdot 2thf$ **2**. Complex **2** was synthesized from $Na(C_5H_4Bu^t)$ (0.98 g, 6.8 mmol), YCl_3 (0.66 g, 3.4 mmol) and 1,3-dithiane (0.41 g, 3.4 mmol) using essentially the same procedure as for **1**. The product was extracted with toluene (100 cm^3) after drying the reaction mixture in vacuum. The toluene volume was reduced to 15 cm^3 and the complex was precipitated by addition of pentane (5 cm^3) and cooling the mixture to -20 °C. The white residue was dried giving 1.2 g of **2** (56%). The stoichiometry was confirmed by GC analysis and lanthanide content titration.

Reaction of Complex **1** *with Water.*—A solution of complex **1** (0.046 g, 6.4×10^{-5} mol) in $[^2H_8]$tetrahydrofuran was mixed with a solution containing water (1.5×10^{-5} mol) in the same solvent in a sealed glass tube. The mixture was transferred to a connected NMR tube, sealed separately and taken to the NMR spectrometer. (Only the signals which belong to the reaction products are given.) δ_H(400 MHz, solvent $[^2H_8]$tetrahydrofuran) 6.55 (t, 4 H, C_5H_4), 6.36 (t, 4 H, C_5H_4), 3.77 (s, 2 H, 1,3-dithiane), 2.78 (t, 4 H, 1,3-dithiane), 2.01 (m, 2 H, 1,3-dithiane) and 1.39 (s, 18 H, Bu^t).

Reactions of Complex **2**.—*With* PhC≡CH. A solution of complex **2** (0.044 g, 6.9×10^{-5} mol) in C_6D_6 was mixed with a C_6D_6 solution containing PhC≡CH (2.0×10^{-5} mol). The mixture was transferred to an NMR tube and subjected to spectral analysis. δ_H(400 MHz, solvent C_6D_6) 7.47 (t, 2 H, *m*-H of Ph), 7.36 (t, 1 H, *p*-H of Ph), 6.94 (d, 2 H, *o*-H of Ph), 6.69 (t, 4 H, C_5H_4), 6.48 (t, 4 H, C_5H_4), 3.34 (s, 2 H, 1,3-dithiane), 2.23 (t, 4 H, 1,3-dithiane), 1.52 (m, 2 H, 1,3-dithiane) and 1.26 (s, 18 H, Bu^t).

With $NH(SiMe_3)_2$. A solution of complex **2** (0.051 g, 8.0×10^{-5} mol) in C_6D_6 was mixed with a C_6D_6 solution containing $NH(SiMe_3)_2$ (3.0×10^{-5} mol). The mixture was transferred to an NMR tube and subjected to spectral analysis. δ_H(400 MHz, solvent C_6D_6) 6.23 (t, 4 H, C_5H_4), 6.04 (t, 4 H, C_5H_4), 3.34 (s, 2 H, 1,3-dithiane), 2.23 (t, 4 H, 1,3-dithiane), 1.52 (m, 2 H, 1,3-dithiane), 1.22 (s, 18 H, Bu^t) and 0.15 (s, 18 H).

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