ELSEVIER

Journal of Alloys and Compounds 303–304 (2000) 83–93

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

The use of pyrazolylborates as ancillaries for lanthanide complexes

Anna C. Hillier[a], Sung Ying Liu[a], Andrea Sella[a,*], Mark R.J. Elsegood[b]

[a]*Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*
[b]*Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU, UK*

Abstract

$[Sm(Tp^{Me,Me})_2]$ reacts with dichalcogenides to give a series of isoleptic complexes $[Sm(Tp^{Me,Me})_2ER]$ (E=O, S, Se, Te; R=phenyl) which have been structurally characterized. An unusual distortion of the $Tp^{Me,Me}$ for the selenolates is discussed in relation to fluxionality and decomposition mechanisms for these complexes. The fluxional behaviour of $[Sm(Tp^{Me,Me})_2(S_2CNR_2)]$ and $[Sm(Tp^{Me,Me})_2(S\text{-}2\text{-}pyr)]$ is also described. $[Sm(Tp^{Me,Me})_2]$ reacts with $Mn_2(CO)_{10}$ to give $[Sm(Tp^{Me,Me})_2]Mn(CO)_5$ and small amounts of $\{[Sm(Tp^{Me,Me})_2]_2(\mu\text{-}O_2CH)\}Mn(CO)_5$ – effectively the room temperature conversion of CO to formate. The corresponding reaction with $Re_2(CO)_{10}$ yields $[Sm(Tp^{Me,Me})_2]Re(CO)_5$ and $[Sm(Tp^{Me,Me})_2]_2Re_4(CO)_{17}$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Samarium; Pyrazolylborate; X-ray diffraction; Fluxionality; Chalcogenolate

1. Introduction

The reactivity of the lanthanides in low oxidation states has long been dominated by cyclopentadienyl complexes [1]. Ytterbocene and more importantly samarocene complexes have been shown to have a wealth of varied reactivity towards a wide range of substrates. This reactivity stems from the combined reducing power and Lewis acidity of the metal centres themselves as well as from the comparative coordinative unsaturation available in the equatorial wedge of the metallocene. Numerous other ligand systems have been investigated but none so far has gained wide acceptance [2].

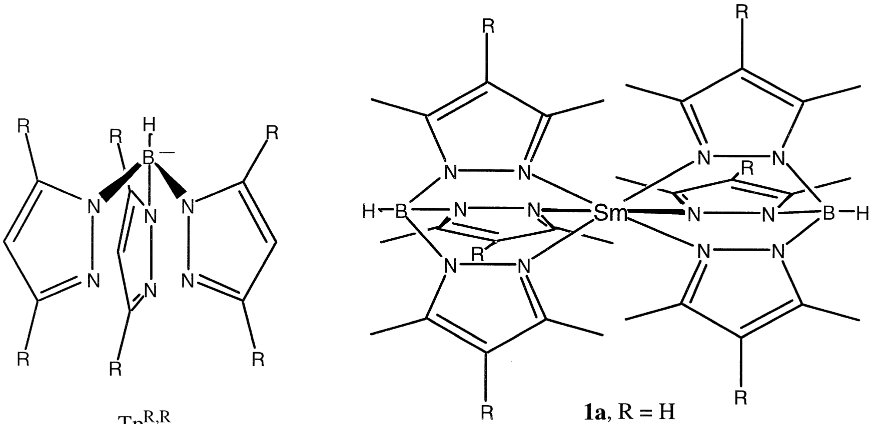
The tris-pyrazolylborates ($Tp^{R,R}$) (Scheme 1) have often been likened to cyclopentadienyls and have been applied to lanthanide chemistry by a number of research groups for some time [3]. Several different sets of series of divalent complexes $[Ln(Tp^{R,R})_2]$ (Ln=Sm, Eu and Yb) have been prepared using the ligands Tp [4], $Tp^{Me,Me}$ [5], $Tp^{Me,Me\text{-}4\text{-}Et}$ [6], $Tp^{Ph,Me}$, $Tp^{thienyl,Me}$ [7] all of which are complexes with tris-coordinated Tp ligands. Attempts to prepare the corresponding complexes using the more sterically demanding $Tp^{tBu,Me}$ ligand result in one ligand adopting a bidentate coordination mode stabilized by a B–H–Ln interaction and exchange is observed between the η^3 and η^2 pyrazolyl groups [7]. The corresponding complexes with $Tp^{2\text{-}py}$ and Tp^{btz} (btz=benzotriazolyl) ligands have proved difficult to isolate in analytically pure form [8].

The reactivity of all of these species is now beginning to be explored, most of the work having focused on the highly insoluble purple complex $[Sm(Tp^{Me,Me})_2]$, **1a**, and its more tractable analogue $[Sm(Tp^{Me,Me,\ 4\text{-}Et})_2]$, **1b**. Thus far no reaction has been observed with comparatively inert small molecules such as CO, unactivated olefins and alkynes, isonitriles etc. On the other hand, electron transfer is observed with more easily reducible substrates such as azobenzene and O_2 which give the corresponding side-bound azobenzene and superoxo complexes $[Sm(Tp^{Me,Me})_2(PhNNPh)]$ [9] and $[Sm(Tp^{Me,Me})_2(O_2)]$ [10] respectively, and TCNE or TCNQ which give salts of the type $[Sm(Tp^{Me,Me})_2]X$ [6]. Reaction with NO results in clean disproportionation to give $[Sm(Tp^{Me,Me})_2(O_2N)]$ [6]. Reaction with the activated alkyne $CF_3C{\equiv}CCF_3$ results in clean C–F bond cleavage giving the corresponding fluoride $[Sm(Tp^{Me,Me})_2F]$ [11]. Similar halocarbon bond cleavage is observed with saturated molecules such as dichloromethane, bromocarbons etc. [6]. Finally, binuclear metal carbonyls such as $[CpM(CO)_3]_2$ (M=Cr, Mo, W) react cleanly with **1a** to give isocarbonyl-bridged heterobimetallics of the type $[Sm(Tp^{Me,Me})_2(\mu\text{-}CO)CpM(CO)_2]$ [12]. The reaction of **1a** with $Co_2(CO)_8$ leads to the formation of the salt $[Sm(Tp^{Me,Me})_2]Co(CO)_4$. These results suggest that there is scope for further investigation of soft bond cleavage.

---

*Corresponding author.

0925-8388/00/$ – see front matter
PII: S0925-8388(00)00655-1



$Tp^{R,R}$

1a, R = H
1b, R = Et

Scheme 1.

2. Preparation of chalcogenolates

Only in recent years have a number of research groups begun to explore the chemistry of the lanthanides with the comparatively soft chalcogenolate ligands. Much of the interest in these systems stems from their potential as precursors for the preparation of lanthanide sulfides and selenides which have unusual optical and magnetic properties [13]. In the majority of cases the chalcogenolate ligands act as bridges between two metal centres in dimers or small multimetallic oligomers. Terminal chalcogenolates remain rare and few systems exist where detailed structural comparisons may be made with a view to gaining a deeper understanding of the bonding between the metal and the p-block element.

With this in mind we set out to prepare a series of complexes of the general type $[(Tp^{Me,Me})_2Sm–ER]$. The alkoxide may be prepared by saline metathesis by the reaction of $[(Tp^{Me,Me})_2SmCl]$ with the appropriate alkoxide:

$$[Sm(Tp^{Me,Me})_2Cl] + NaOR \rightarrow [Sm(Tp^{Me,Me})_2OR] + NaCl.$$

In this way it was possible to isolate complexes for $R = C_6H_5$, **2a** and C_6H_4-4-Bu^t, **2b**. The corresponding complexes were not isolated for phenoxides with *ortho* substituents, nor for simple alkoxides, observations we attribute to the excessive steric crowding around the metal centre.

The heavier chalcogenolates could be prepared by reductive cleavage of the appropriate dichalcogenide (REER) (E = S, Se, Te) by **1a** in a manner analogous to that used by Edelmann et al. for the corresponding metallocenes [14]:

$$2[Sm(Tp^{Me,Me})_2] + REER \rightarrow 2[Sm(Tp^{Me,Me})_2ER].$$

These reactions proceed in reasonable yield and give rather moisture sensitive but thermally stable products $[Sm(Tp^{Me,Me})_2ER]$, (ER = SPh, **3a**; SPh-4-Me, **3b**; SePh, **4a**; SePh-4-Bu^t, **4b**; SePh-4-OMe, **4c**; TePh, **5a**). Analogous complexes have also been prepared with the more soluble $[Sm(Tp^{Me,Me,4\text{-}Et})_2]$, **1b**. The selenolates, **4**, were found to be particularly sensitive when left to stand in solution. In this respect they resemble $Sm(Tp^{Me,Me})_2Br$ which has proved remarkably difficult to isolate in synthetically useful yields [15].

The NMR spectra of these complexes are all broadly similar showing the typical pattern for a fluxional $[Sm(Tp^{Me,Me})_2L]$ type system consisting of three singlets in the ratio of 3:3:1 for the protons of the ancillary ligand and appropriate resonances for the hydrogens on the chalcogenolate. In each case the hydrogens are somewhat shifted from their 'expected' positions by the mildly paramagnetic samarium centre. Thus at room temperature the coordination spheres of these complexes are quite mobile. Cooling samples of **2**, **3**, and **5** did not result in any significant change in the appearance of the ^1H NMR spectra apart from gradual changes in the positions of the peaks as a result of the Curie–Weiss dependence of the chemical shifts. In contrast, however, cooling **4a** and **4b** in toluene resulted in the gradual broadening and eventual disappearance of all three peaks associated with the $Tp^{Me,Me}$ ligands into the baseline. By −95°C each peak had resolved into three broad singlets consistent with a seven-coordinate species of effective C_2 symmetry and similar in appearance to the spectrum observed by Takats for $[Sm(Tp^{Me,Me})_2(PhNNPh)]$ [9]. We note that this latter complex does not, however, show evidence for exchange by ^1H EXSY even at 60°C.

With a view to locking the coordination sphere, the dithiocarbamates $[Sm(Tp^{Me,Me})_2(S_2CNR_2)]$ (R = Me, **6a**; Et, **6b**) were prepared by the analogous route using the dithiuram disulfides:

$$2[Sm(Tp^{Me,Me})_2] + (S_2CNR_2)_2 \rightarrow 2[Sm(Tp^{Me,Me})_2(S_2CNR_2)]\ (R = Me, Et).$$

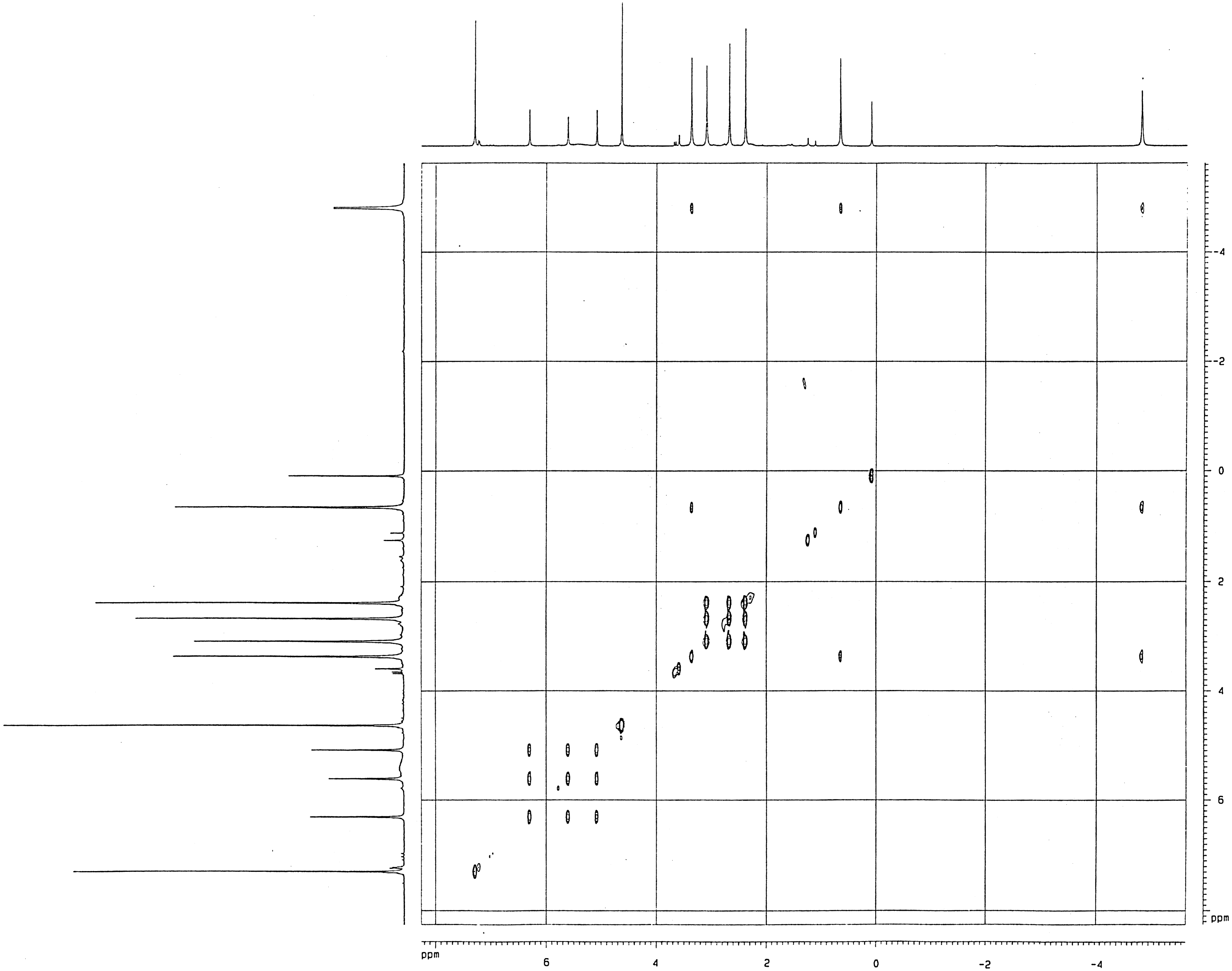


Fig. 1. 400 MHz ^{1}H EXSY NMR spectrum of [(Tp^{Me,Me})$_2$Sm(S$_2$CNMe$_2$)], **6a**, recorded at −10°C.

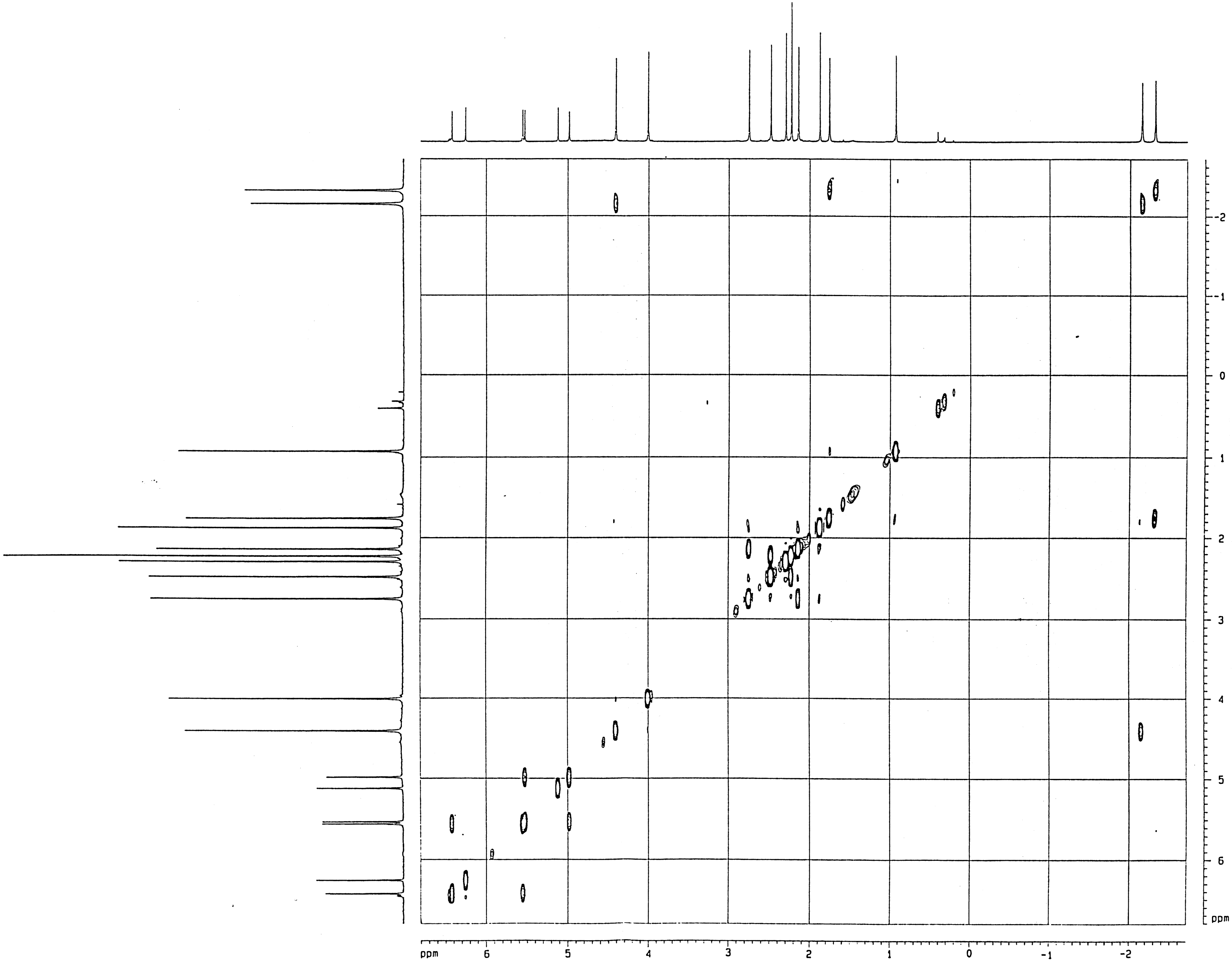
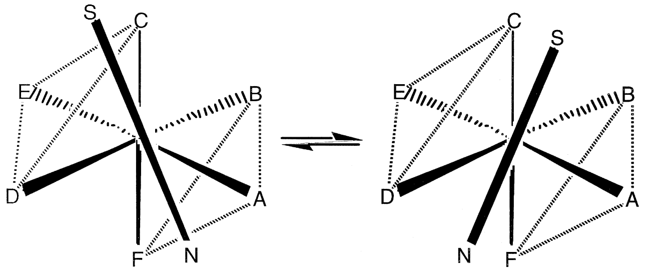


Fig. 2. 500 MHz ^1H EXSY NMR spectrum of $[(Tp^{Me,Me})_2Sm(S\text{-}2\text{-}pyr)]$, **7**, recorded at 20°C.



Scheme 2.

The colourless complexes gave somewhat broad ^{1}H NMR spectra at room temperature but the fluxionality was frozen out by −10°C. The high temperature limit could not be reached in toluene. The ^{1}H EXSY spectrum of **6a** (Fig. 1), recorded at −10°C, shows two cross-peaks for each methyl indicating that the fluxional process consists of simple rotation of the Tp^{Me,Me} group around the B–Sm axis.

The corresponding reaction with pyridyldisulfide, first carried out by Marques, yields the expected pyridinethiolate complex [Sm(Tp^{Me,Me})$_2$(S-2-pyr)], **7**:

$$2[\mathrm{Sm(Tp^{Me,Me})_2}] + \mathrm{(S\text{-}2\text{-}pyr)_2} \rightarrow 2[\mathrm{Sm(Tp^{Me,Me})_2(S\text{-}2\text{-}pyr)}]$$

which gives a ^{1}H NMR spectrum consistent with a non-fluxional C_1 symmetric species: 12 resonances for the methyl groups and six for the methines, in addition to the peaks associated with the pyridyl group. On warming **7** to 40°C eight of the methyl and four of the methine resonances broaden indicating the onset of fluxionality. A ^{1}H EXSY spectrum of **7** recorded at room temperature (Fig. 2), shows pairwise exchange between four sets of methyls and two pairs of methine hydrogens. This suggests a fluxional mechanism involving a simple gear-locked liberation of the Tp^{Me,Me} ligands and the thiolate allowing for pairwise interchange (vide infra). Thus this low temperature process simply interchanges the pyrazolyl groups A with D and B with E, while C and F remain unique (Scheme 2). When the temperature is raised to 50°C the ^{1}H EXSY spectrum (Fig. 3) now indicates the onset of full rotation of each pyrazolylborate group around the Sm–B axis, as indicated by five cross-peaks for each methyl peak and three for the methines.

3. Structures

It was possible to crystallize examples of each of compounds **2b**, **3b**, **4a**, **5a** and **6b** (Figs. 4–9) which proved to consist of simple seven-coordinate complexes as expected, with two staggered tridentate Tp^{Me,Me} groups and the chalcogenolate rotated away from the methyl group on the ancillary ligand 'below' it. The average M–N and M–E distances are tabulated in Table 1 together with the M–E–C angle. The M–E distances increase steadily, compensated for somewhat by a decrease in M–N distance. The angle at the donor atom decreases steadily in line with values observed for the corresponding hydrides. Although the alkoxide is somewhat bent (153.7(2)°), comparison with other pyrazolylborate alkoxides prepared by reduction of quinones, for example, suggests that this is a very soft potential, strongly affected by steric factors [8,11,16]. Hence the short Ln–O distance may well not reflect strong π-overlap but rather the highly polarized nature of the bond as has been argued recently by Parkin for Zr(IV) [17].

In the case of **4a**, however, a second molecule, **4a**″ with a structure quite distinct from the first was found in the asymmetric unit. **4a**″ has a very significant distortion of one of the pyrazolylborates, a feature also found in the structure of **4b** which showed an extremely similar molecular geometry (Fig. 7). The two structures will therefore be discussed together. While one pyrazolylborate is tridentate with local C_3 symmetry, the second is markedly distorted with one pyrazolyl ring rotated such as to bring both nitrogens into contact with the metal. Such a distortion has been observed before in the case of [U(Tp^{Me,Me})$_2$I] [18], although in both **4a**″ and **4b** the distortion is somewhat more marked. The complex is therefore effectively eight-coordinate and the collapse of one pyrazolylborate ligand may be a reflection of the extreme Lewis acidity of the metal centre which is not compensated for adequately by the chalcogenolate ligand. The distorted ligand appears to be stabilized by a π-interaction between the phenyl groups of the chalcogenolate and one pyrazolyl ring. The wide range of twist angles in these (Table 1) and other related complexes suggests that this distortion is also quite facile.

Our observation of this structural type for **4a**″ and **4b** in the solid state may well account for the fact that it is only for the selenolate that we are able to slow the fluxionality of the coordination sphere sufficiently to observe distinct environments, although the fully distorted C_1 structure is never observed in solution. The impossibility of a π-stacking interaction in the case of the iodide may account for why no slowing of the fluxionality was observed for the related U(III) complex [18]. In addition, the apparent greater instability of this complex towards decomposition or fragmentation may reflect an increased susceptibility to attack when the bond is twisted. Indeed, several research groups have reported the isolation of partially fragmented pyrazolylborate dimers of the type [(Tp^{Me,Me})Ln(μ_2-O)BH(dmpz)$_2$]$_2$ which may result from enhanced hydrolysis at a twisted B–N bond [8,11,16].

The structure of the dithiocarbamate, **6b**, is eight-coordinate as expected, with essentially normal pyrazolylborates and the ligands disposed in an essentially dodecahedral geometry, as shown by simple polytopal analysis. The geometry is therefore extremely similar to other 8-coordi-

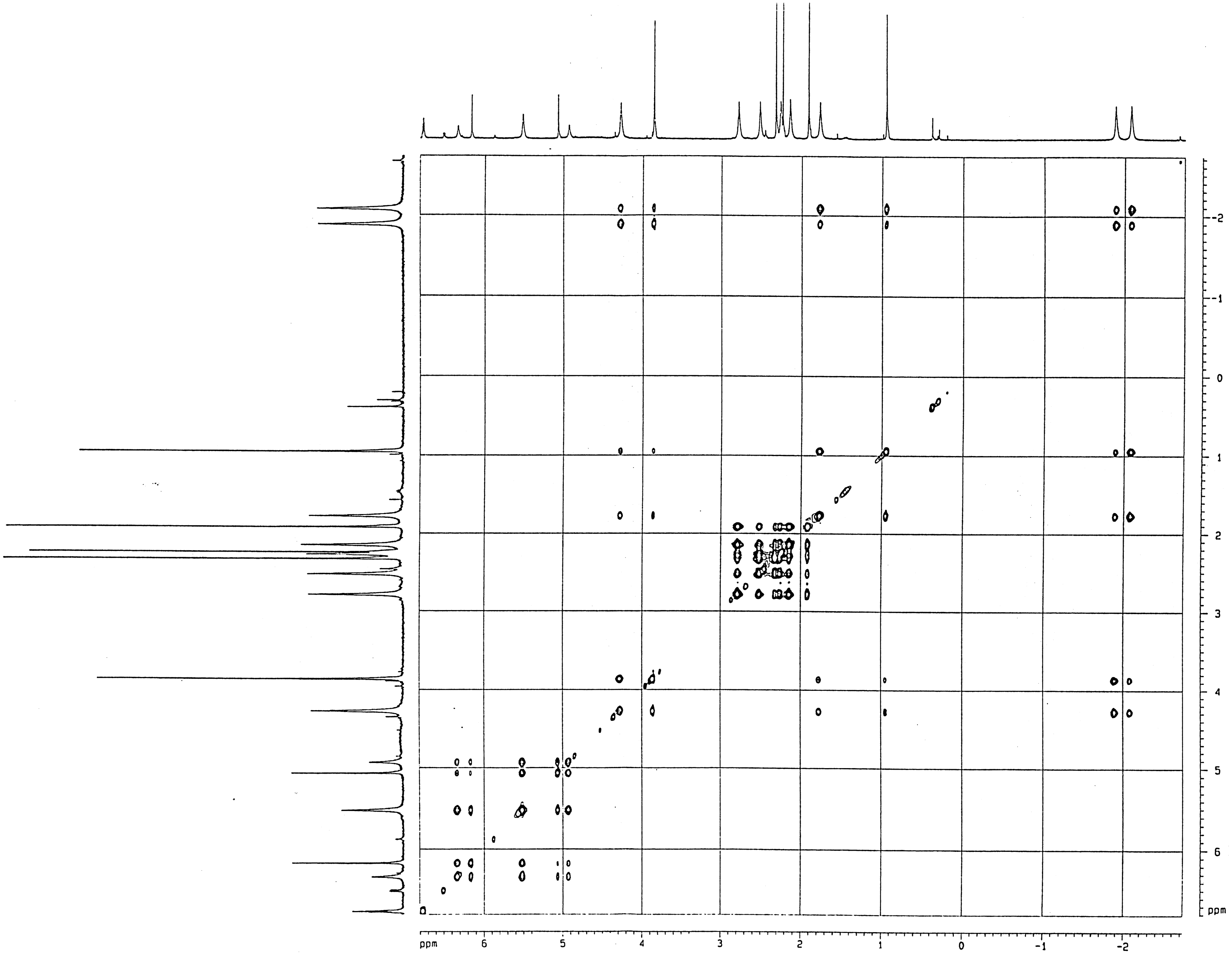


Fig. 3. 500 MHz ^{1}H EXSY NMR spectrum of [(Tp^{Me,Me})$_2$Sm(S-2-pyr)], **7**, recorded at 50°C.

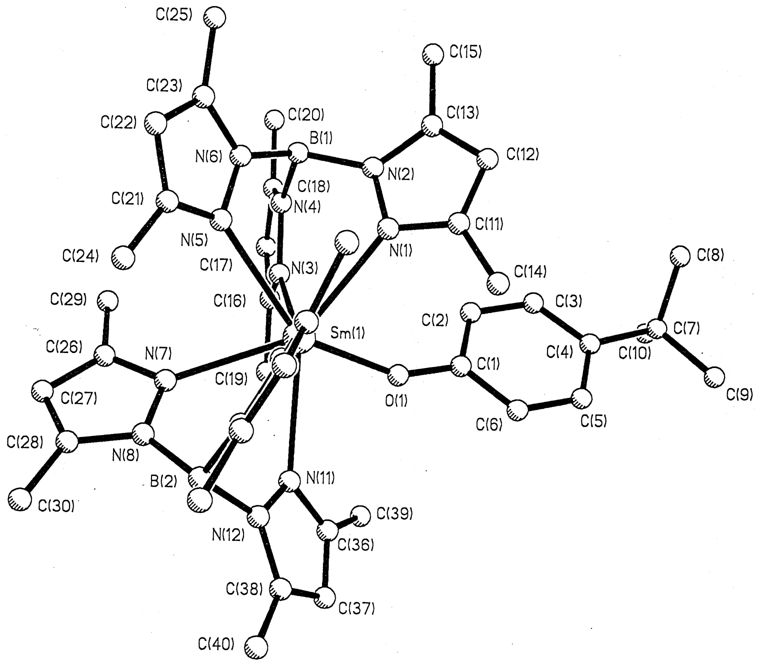


Fig. 4. Molecular structure of [(Tp^{Me,Me})$_2$SmOPh-4-Bu^t], **2b**, hydrogens omitted.

nate Tp^{Me,Me} complexes [19]. Assuming the geometry of **7** to be similar to that of **6b**, the low temperature fluxional process observed in solution for the former is presumably the result of interconversion of two DOD forms passing through a BCTP intermediate [16].

Finally, the reaction of **1** with excess PhTeTePh, or alternatively of **5a** with one or more equivalents of PhTeTePh yielded the salt [Sm(Tp^{Me,Me})$_2$](TePh)$_3$, **8**, which contains the unprecedented (PhTe)$_3^-$ anion. The anion is almost linear (172.92(3)°), unsymmetrical (Te–Te: 2.939(2), 3.113(1) Å) and may be considered as an adduct of PhTe$^-$ with PhTeTePh. As such it is therefore an analogue of I$_3^-$ stabilized in the solid state by the [Sm(Tp^{Me,Me})$_2$]$^+$ cation. Indeed, the corresponding salt [(Tp^{Me,Me})$_2$Sm]I$_3$, **9**, may be prepared by reaction of [(Tp^{Me,Me})$_2$Sm] with excess iodine. Attempts to prepare a

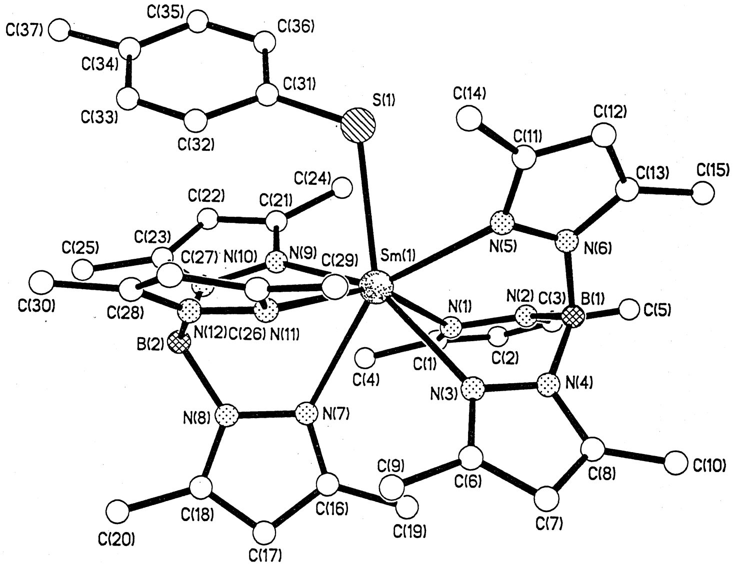


Fig. 5. Molecular structure of [(Tp^{Me,Me})$_2$SmSPh-4-Me], **3b**, hydrogens omitted.

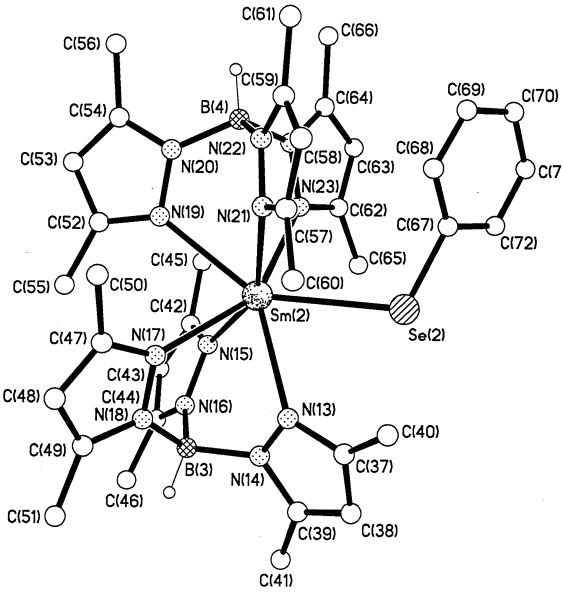


Fig. 6. Molecular structure of [$(Tp^{Me,Me})_2SmSePh$], **4a′**, hydrogens omitted.

selenium analogue were unsuccessful as were attempts to prepare mixed telluroselenolates. Reactions to prepare mixed iodo-tellurides only led to recovery of the insoluble [$(Tp^{Me,Me})_2Sm$]I in good yields.

4. Transition metal carbonyl reactions

The reaction of **1a** with transition metal carbonyls has led to a number of unexpected products. With $Mn_2(CO)_{10}$ the corresponding salt, [$(Tp^{Me,Me})_2Sm$][$Mn(CO)_5$], **10**, can be isolated. However, in addition a second product, a salt of $Mn(CO)_5^-$ containing the unusual formate-bridged cation [$(Tp^{Me,Me})_2Sm]_2(\mu\text{-}O_2CH)]^+$, **11**, was also isolated as a minor side-product (Fig. 10). The difficulties we have experienced in developing a reliable prep of this complex are consistent with the reaction occurring as a result of attack by adventitious water, and are complicated by the possibility of hydrolysis of the pyrazolylborate itself (as described earlier). The reaction is presumed to proceed (Scheme 3) via the formation of $HMn(CO)_5$ by protonation of $Mn(CO)_5^-$. This species is in equilibrium with the isomeric formyl which is activated towards nucleophilic attack by adventitious water by coordination to the Lewis acidic samarium centre. β-elimination from this bimetallic complex generates a terminal formate which crystallizes after the binding for a further $[(Tp^{Me,Me})_2Sm]^+$ unit. Thus this reaction represents a rare example of how cooperative interactions between a transition metal and a lanthanide can give rise to the unusual room temperature conversion of CO to formate.

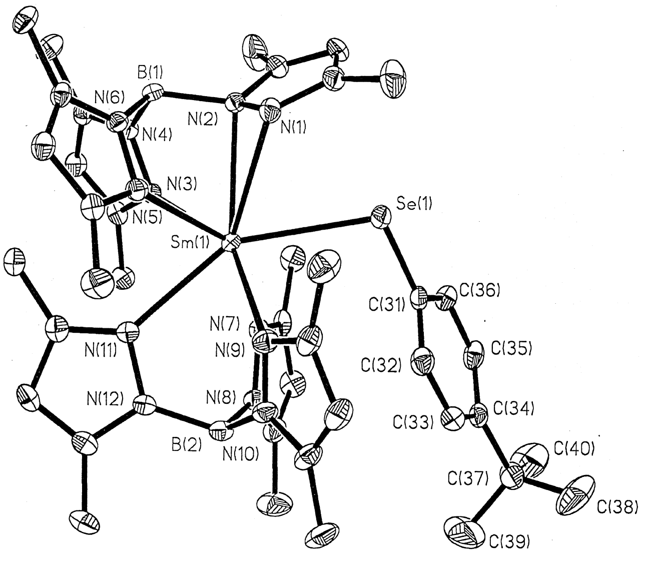


Fig. 7. Molecular structure of [$(Tp^{Me,Me})_2SmSePh\text{-}4\text{-}Bu^t$], **4b**, hydrogens omitted.

$Re_2(CO)_{10}$ does not react with **1a** at room temperature in toluene. On warming however it is possible to isolate the salt [$(Tp^{Me,Me})_2Sm$]$Re(CO)_5$, **12**, as yellow blocks in fairly low yield. Their formation is however accompanied by the formation of a reddish pink product. Better yields can be obtained if the temperature is maintained above 80°C in the presence of two equivalents of the rhenium starting material. This complex, which could not however be structurally characterized, was identified as [$(Tp^{Me,Me})_2Sm]_2[Re_4(CO)_{17}$], **13**. Slow crystallization from toluene yielded the corresponding protonated cluster, [$(Tp^{Me,Me})_2Sm$][$HRe_4(CO)_{17}$], **14**, in which the rhenium core adopts a spike-triangular arrangement. The formation of these unusual clusters is presumed to relate to the slowness of the electron transfer from the highly insoluble **1a**, which allows time for the $Re(CO)_5^-$ anion to react with additional $Re_2(CO)_{10}$ (Scheme 4).

5. Half sandwich complexes

The large size of the lanthanides and their lability leads to rapid ligand exchange and/or the formation of oligomeric coordination/organometallic complexes unless the coordination sphere is heavily saturated by sterically demanding ligands. One of the 'holy grails' of molecular lanthanide chemistry is therefore to prepare functionalizable heteroleptic complexes. Attempts to prepare such complexes using cyclopentadienyl-based ancillaries are often complicated by ligand redistribution. The non-planar Tp ligands offer the potential for preparing such complexes. Indeed we and others have prepared both divalent [20] and trivalent halides [21]. The successful preparation of these complexes depends rather crucially on the nature of the Tp ligand and the conditions used in their preparation. Thus $Tp^{t\text{-}Bu,Me}$ gives tractable products with Sm(II) and Yb(II): for example, half-sandwich complexes of the lanthanides have been prepared by metathesis of

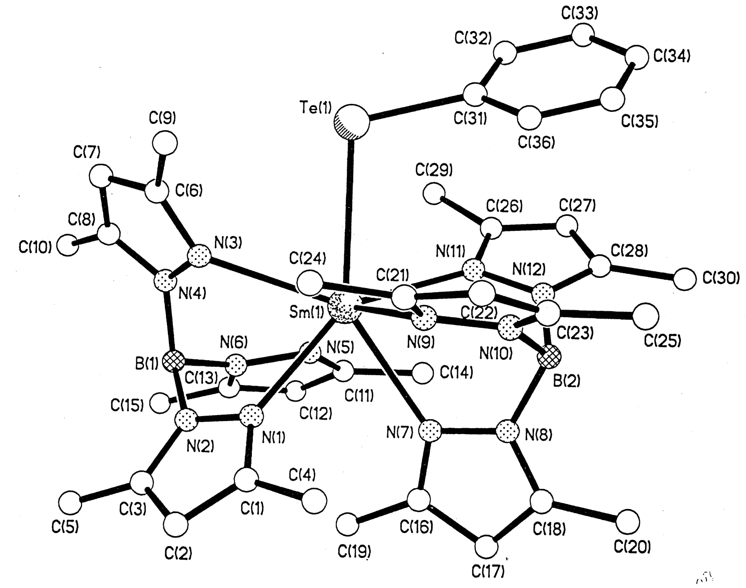


Fig. 8. Molecular structure of [$(Tp^{Me,Me})_2$SmTePh], **5**, hydrogens omitted.

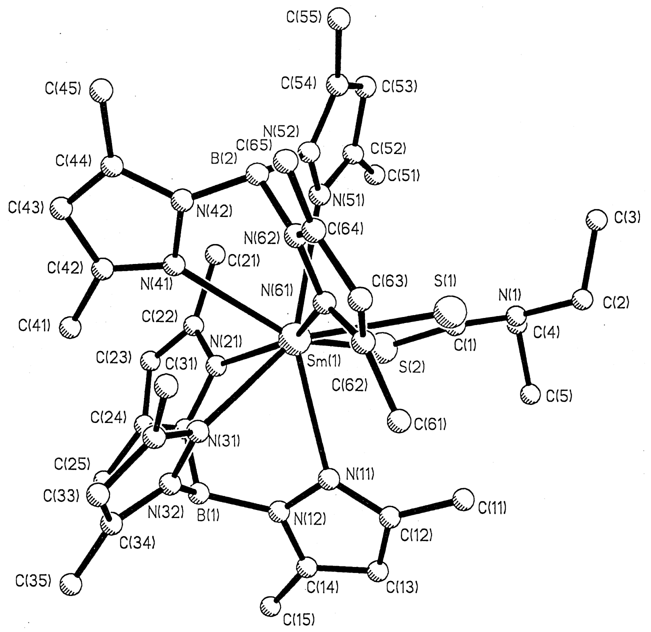


Fig. 9. Molecular structure of [$(Tp^{Me,Me})_2Sm(S_2CNEt_2)$], **6b**, hydrogens omitted.

[$SmTp^{t\text{-}Bu,Me}I(thf)_2$] with Na[$CpMo(CO)_3$] yielding a tetrametallic species [$Sm(Tp^{t\text{-}Bu,Me})(thf)CpMo(CO)(\mu\text{-}CO)_2]_2$ [22].

The preparation of trivalent complexes using $Tp^{t\text{-}Bu,Me}$ appears to result in ligand fragmentation and no tractable products can be isolated. Although the corresponding divalent complexes with the less encumbered ligand $Tp^{Me,Me}$ has been prepared [11], the complex is unstable in solution redistributing to give the highly insoluble **1a** or its ytterbium analogue.

For the trivalent lanthanides the corresponding halide [$Y(Tp^{Me,Me})Cl_2(THF)$] can be isolated in high yields provided they are not left in solution for extended periods [8,23]. These may be derivatized and hydrocarbyls have been prepared [21]. We have prepared borohydride derivatives by saline metathesis:

$$[Ln(Tp^{Me,Me})Cl_2(THF)] + 2MBH_3R \rightarrow [Ln(Tp^{Me,Me})(BH_3R)_2(THF)] + 2MCl$$

$$(Ln = Y, Sm;\ M = Na,\ R = H;\ M = Li,\ R = Ph).$$

Table 1
Selected bond lengths and angles for [$Sm(Tp^{Me2})_2(EPh)$]

E	*d*(Sm–E) Å	*d*($Sm–N_{av}$) Å	Sm–E–C (°)	Max. B–N–N–Sm torsion (°)
O (**2b**)	2.138(8)	2.572(4)	153.7(2)	26.8
S (**3b**)	2.827(1)	2.531(6)	114.6(1)	34.4
Se (**4a′**)	2.9390(3)	2.543(5)	110.97(8)	16.7
Se (**4a″**)	2.9621(3)	2.552(4)	111.18(8)	83.7
Se (**4b**)	2.9457(3)	2.566(4)	108.29(9)	91.3
Te (**5**)	3.1874(4)	2.538(4)	104.83(13)	47.7

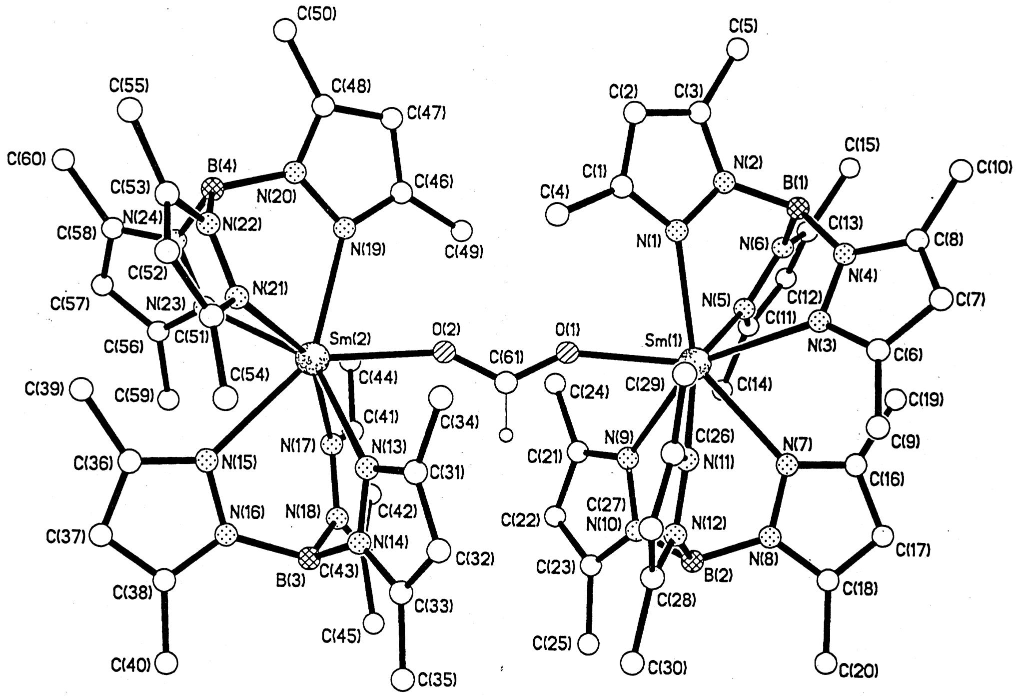
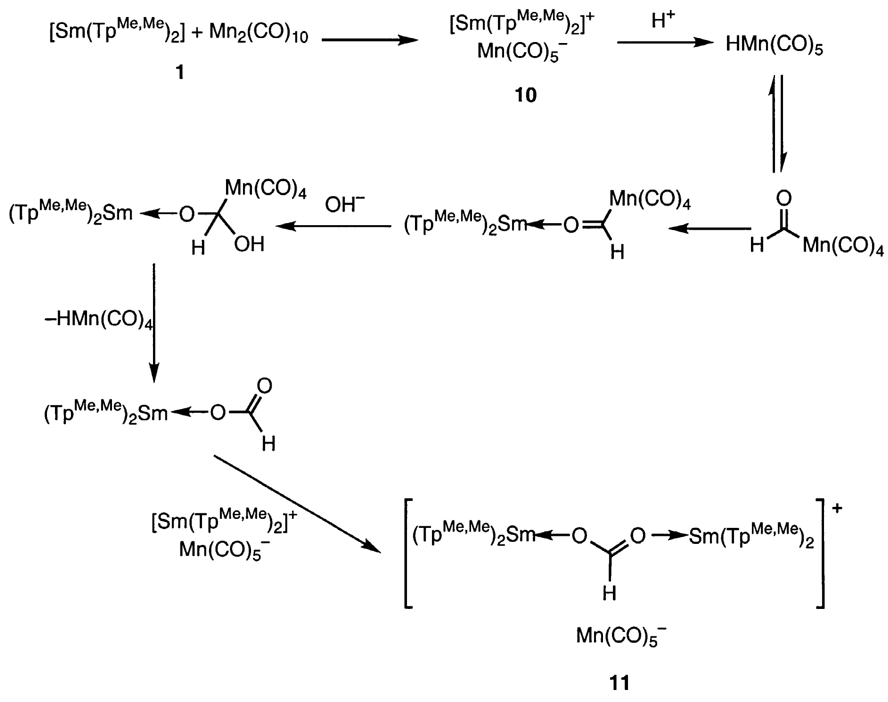
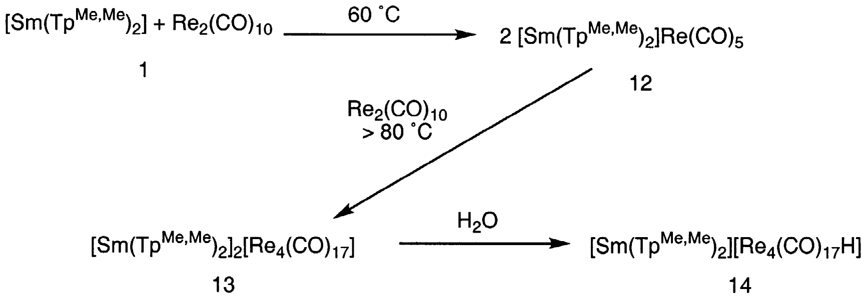


Fig. 10. Molecular structure of the cation from $[(Tp^{Me,Me})_2Sm]_2(\mu\text{-}O_2CH)]Mn(CO_5)$, **11**.



Scheme 3.



Scheme 4.

Structural and reactivity studies are currently in progress.

6. Conclusions

Our studies together with those of Marques and Takats suggest that the reactivity of **1** is significantly depressed relative to the corresponding metallocenes $[Sm(\eta\text{-}C_5Me_5)_2]$ presumably as a result of the shielding afforded by the interlocking methyl groups. The pyrazolylborate ligands do however offer a steric control which results in the isolation of a number of unusual complexes and structures. In addition the extreme steric congestion in the 8-coordinate systems permits the observation and separation of two distinct polytopal rearrangements. We have prepared a series of terminal isoleptic chalcogenolate complexes. The isolation of **13** and **14** suggests that samarium(II) reagents may be a useful alternative to the alkali metals and benzophenone ketyl for the synthesis of higher transition carbonyl clusters. In this respect the $[(Tp^{Me,Me})_2Sm]^+$ cation has advantages over the metallocenes because the steric crowding round the metal tends to suppress the coordination of the lanthanide to the carbonyl groups as was observed previously by Andersen et al. [24].

Acknowledgements

We are grateful to the EPSRC for a studentship to ACH (GR/K11338) and for provision of the X-ray diffractometer. We thank Prof. W. Clegg for use of the X-ray diffractometer and associated computer programs and facilities. We are grateful to Dr. Abil Aliev for assistance with recording the NMR spectra, to Prof. J. Takats and Dr. N. Marques for helpful discussions, to Drs. D.A. Tocher and S. McWhinnie for gifts of disulfides and diselenides.

References

[1] H. Schumann, J.A. Meese-Marktscheffel, L. Esser, Chem. Rev. 95 (1995) 865–986.
[2] F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466–2488.
[3] I. Santos, N. Marques, N. J. Chem. 19 (1995) 551–571.
[4] A. Domingos, J. Marcalo, N. Marques, A.P. Dematos, A. Galvao, P.C. Isolani, G. Vicentini, K. Zinner, Polyhedron 14 (1995) 3067–3076.
[5] G.H. Maunder, A. Sella, D.A. Tocher, J. Chem. Soc. Chem. Commun. (1994) 885–886.
[6] G.H. Maunder, Ph.D. Thesis, University of London, 1995.
[7] X.W. Zhang, R. McDonald, J. Takats, N. J. Chem. 19 (1995) 573–585.
[8] A. Sella, unpublished observations.
[9] J. Takats, X.W. Zhang, V.W. Day, T.A. Eberspacher, Organometallics 12 (1993) 4286–4288.
[10] X.W. Zhang, G.R. Loppnow, R. McDonald, J. Takats, J. Am. Chem. Soc. 117 (1995) 7828–7829.
[11] J. Takats, personal communication.
[12] A.C. Hillier, S.-Y. Liu, A. Sella, O. Zekria, M.R.J. Elsegood, J. Organomet. Chem. 528 (1997) 209–215.
[13] F. Nief, Coord. Chem. Rev. 178–180 (1998) 13–81.
[14] A. Recknagel, M. Noltemeyer, D. Stalke, U. Pieper, H.-G. Schmidt, F.T. Edelmann, J. Organomet. Chem. 411 (1991) 347.
[15] S.-Y. Liu, Ph.D. Thesis, University of London, 1996.
[16] N. Marques, personal communication.
[17] W.A. Howard, T.M. Trnka, G. Parkin, Inorg. Chem. 34 (1995) 5900–5909.
[18] Y.M. Sun, R. McDonald, J. Takats, V.W. Day, T.A. Eberspacher, Inorg. Chem. 33 (1994) 4433–4434.
[19] R.J.H. Clark, S.Y. Liu, G.H. Maunder, A. Sella, M.R.J. Elsegood, J. Chem. Soc., Dalton Trans. (1997) 2241–2247.
[20] G.H. Maunder, A. Sella, D.A. Tocher, Chem. Commun. (1994) 2689–2690.
[21] D.P. Long, P.A. Bianconi, J. Am. Chem. Soc. 118 (1996) 12453–12454.
[22] A.C. Hillier, A. Sella, M.R.J. Elsegood, J. Chem. Soc., Dalton Trans. (1998) 3871–3874.
[23] C. Apostolidis, A. Carvalho, A. Domingos, B. Kanellakopulos, R. Maier, N. Marques, A.F. de Matos, J. Rebizant, Polyhedron 18 (1998) 263–272.
[24] J.M. Boncella, R.A. Andersen, J. Chem. Soc. Chem. Commun. (1984) 809.