

Synthesis and structure of $[\text{Sm}(\eta^5\text{-CpPPh}_2)(\kappa^3\text{-Tp}^{\text{Me}_2})(\text{I})(\text{THF})]$; a samarium complex with four different ligands

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Abstract

The mixed-ligand complex, $[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]$ (**1**), was prepared in moderate yield (55%) by the redox reaction between SmI_2 and $\text{Ti}[\text{CpPPh}_2]$ in THF at ambient temperature followed by direct treatment with KTp^{Me_2} . Complex **1** was fully characterized by elemental analysis, FT-IR, MS and multinuclear NMR (^1H , ^{11}B and ^{31}P) spectroscopies. The solid-state structure was established by single crystal X-ray crystallography. The coordination geometry of the samarium is best described as distorted tetrahedral with the apexes occupied by four different ligands; Tp^{Me_2} , CpPPh_2 , I^- and THF. Variable temperature ^1H -NMR spectroscopic investigation confirmed that the chiral, asymmetric structure is maintained in solution at low temperatures. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The diphenylphosphinocyclopentadienyl ligand (CpPPh_2) has attracted considerable attention due to its unique structure, providing both a phosphorus donor and the cyclopentadienyl moiety. The ligand has been widely used with transition metals [1], f-elements [2], and in the construction of homo- and heterobimetallic complexes [3]. Its application to lanthanide chemistry has afforded the isolation of a series of novel lanthanide metalloligands, viz. organolanthanide complexes containing pendant phosphines [4]. Subsequent treatment of the metalloligands with labile transition metal complexes produced interesting heterobimetallic lanthanide-transition metal containing species [2b,4a-d], prototypical examples include Deacon's $[\text{Me}_2\text{Pt}(\text{Ph}_2\text{PCp})_2\text{Yb}(\text{THF})_2]$ [4a] and $[(\text{CO})_2\text{Ni}(\text{Ph}_2\text{PCp})_2\text{Yb}(\text{THF})_2]$ [4b].

An ongoing research interest in our laboratories is the synthesis and reactivity of lanthanide complexes anchored by hydrotris(pyrazolyl)borates ($\text{Tp}^{\text{R,R}'}$) [5].

The $\text{Tp}^{\text{R,R}'}$ ligand system was first introduced by Trofimenko in 1967 and is now one of the most widely used ligands in metal chemistry [6]. Recently, we synthesized several mixed Tp/Cp lanthanide complexes and found that they either exhibited interesting reactivities [7] or adopted unusual coordination mode of the $\text{Tp}^{\text{R,R}'}$ ligand [8]. In this contribution, we report the synthesis and structure of the mixed $\text{Tp}^{\text{Me}_2}/\text{CpPPh}_2$ complex, $[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]$, which, in addition, has the unusual feature of a samarium center with four different ligands. The solution behavior of the complex is probed by VT ^1H -NMR spectroscopy.

2. Experimental

2.1. General considerations

The starting materials and the complex are air- and moisture-sensitive, therefore, both synthesis and subsequent manipulations were performed under a nitrogen atmosphere with rigorous exclusion of air and moisture by using Schlenk, vacuum line and glovebox techniques. THF (tetrahydrofuran) was dried by refluxing over Na benzophenone ketyl and distilled under nitro-

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gen prior to use. Deuterated solvents were dried over Na/K benzophenone ketyl and then vacuum transferred. SmI_2 [9], $\text{Ti}[\text{CpPPh}_2]$ [1a,10] and KTp^{Me_2} [11] were prepared according to literature procedures. FT-IR spectrum was recorded on a BOMEM MB-100 spectrophotometer. Multinuclear NMR spectra were obtained on a BRUKER AM400 spectrometer. Chemical shifts are reported in ppm relative to TMS (^1H), 85% H_3PO_4 (^{31}P) and $\text{F}_3\text{B}\cdot\text{OEt}_2$ (^{11}B). Mass spectrum was recorded on a AEI MS-50G Spectrometer using EI ionization techniques. Elemental analysis data were provided by the Microanalysis Laboratory, Department of Chemistry, University of Alberta.

2.2. Synthesis of $[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]$ (**1**)

In the glovebox, solid $\text{Ti}[\text{CpPPh}_2]$ (0.226 g, 0.50 mmol) was added in several portions to a stirred solution of SmI_2 in THF (0.05 M, 10.0 ml, 0.50 mmol). The color of solution changed immediately from deep blue to orange and a black precipitate (metallic Ti) formed. After the reaction mixture had been stirred for 10 h, a THF solution (15 ml) of KTp^{Me_2} (0.168 g, 0.50 mmol) was added dropwise. The resultant mixture was stirred for another 10 h. A clear yellow solution was obtained after removal of the insoluble materials (metallic Ti and KI) by centrifugation. Concentration and subsequent cooling the solution at -40°C afforded a greenish yellow crystalline product in ca. 55% yield (0.24 g). $^1\text{H-NMR}$ (THF- d_8 , δ , ppm, -60°C): 8.74, 8.65, 8.53, 7.60 (all singlets, 1H, $\text{C}_5\text{H}_4\text{PPh}_2$), 7.20, 6.90, 6.78, 6.60, 5.40 (s_{br} , s_{br} , m, m, m, 3H, 2H, 1H, 2H, 2H, $\text{CpP}(\text{C}_6\text{H}_5)_2$), 6.65, 5.57, 5.52 (s, s, s, 1H, 1H, 1H, 4-*pz-H*), 4.76 (br, 1H, B-*H*), 2.76, 2.33, 2.24, 2.18, 2.13, 1.92 (all singlets, 3H, 3- and 5-*pz-CH}_3), the resonances of coordinated THF overlap with the residual peaks of THF- d_8 . $^1\text{H-NMR}$ (THF- d_8 , δ , ppm, 80°C): 10.62, 9.95 (s, s, 2H, 2H, $\text{C}_5\text{H}_4\text{PPh}_2$), 6.95 (m, 6H, *p*- and *m*-Ph-*H*), 6.69 (m, 4H, *o*-Ph-*H*), 5.48 (s, 3H, 4-*pz-H*), 2.40, 2.15 (s, s, 9H, 9H, 3- and 5-*pz-CH}_3). $^1\text{H-NMR}$ (toluene- d_8 , δ , ppm, -50°C): 9.73, 8.82, 8.65, 8.01 (all singlets, 1H, $\text{C}_5\text{H}_4\text{PPh}_2$), 6.74, 6.59, 6.02 (m, m, m, 1H, 2H, 2H, *p*-, *o*- or *m*-(C_6H_5) PPhCp , proton resonances of the second phenyl group could not be identified due to overlap with the residual peaks of toluene- d_8 around 7.0 ppm), 6.40, 5.32, 4.90 (s, s, s, 1H, 1H, 1H, 4-*pz-H*), 3.52, 1.35 (s_{br} , s_{br} , 4H, 4H, OC_4H_8), 2.48, 1.93, 1.84 (s, s, s, 6H, 9H, 3H, 3- and 5-*pz-CH}_3). $^1\text{H-NMR}$ (toluene- d_8 , δ , ppm, 90°C): 10.80, 10.10 (s, s, 2H, 2H, $\text{C}_5\text{H}_4\text{PPh}_2$), 5.24 (s, 3H, 4-*pz-H*), 2.77, 1.04 (s_{br} , s_{br} , 4H, 4H, OC_4H_8), 2.18, 2.05 (s, s, 9H, 9H, 3- and 5- CH_3), the peaks of phenyl groups overlap with the residual peaks of toluene- d_8 around 7.0 ppm. $^{31}\text{P}\{^1\text{H}\}$ -NMR (toluene- d_8 , δ , ppm, 25°C) -18.14 (s). $^{11}\text{B}\{^1\text{H}\}$ -NMR (toluene- d_8 , δ , ppm, 25°C): -7.91 (s, $\Delta\nu_{1/2} = 235\text{Hz}$). FT-IR (KBr, cm^{-1}): 2564 ($\nu_{\text{B-H}}$). MS (EI, *m/e*): 72.1***

($[\text{THF}]^+$), 183.0 ($[\text{PPh}_2]^+$), 649.8 ($[\text{Sm}(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]^+$), 698.0 ($[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})]^+$), 746.2 ($[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]^+$). Anal. Found: C, 48.38; H, 4.49; N, 9.18. Calc. for $\text{C}_{36}\text{H}_{44}\text{BIN}_6\text{OPSm}$: C, 48.26; H, 4.95; N, 9.38%.

2.3. X-ray diffraction data collection and structure determination of $[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]\cdot 0.5\text{C}_6\text{H}_6$ (**1**· $0.5\text{C}_6\text{H}_6$)

X-ray quality crystals of $1\cdot 0.5\text{C}_6\text{H}_6$ were obtained from a benzene solution by slow evaporation of benzene solvent at ambient temperature. Crystals were protected using Paratone-N oil (Hampton Research), which allowed crystal selection and mounting to be performed in air. A yellow crystal of approximate dimensions $0.26 \times 0.14 \times 0.05$ mm was mounted on a glass fiber (the oil functioned as adhesive) and transferred to a Bruker P4/R4/SMART 1000 CCD diffractometer. The X-ray diffraction data were collected at -80°C using Mo- K_α radiation. The unit cell parameters were obtained from a least-squares refinement of 8104 centered reflections. The systematic absences indicated the space group to be $P2_1/n$ (no. 14). The data were corrected for absorption through use of the SADABS procedure.

The structure of **1** was solved using the direct method program SHELXS-86 [12] and the refinement was completed using the program SHELXL-93 [13]. Hydrogen atoms were assigned positions based on the geometries of their attached carbon or boron atoms, and were given thermal parameters of 20% greater than those of the attached atoms. The final model for $1\cdot 0.5\text{C}_6\text{H}_6$ was refined to values of $R_1(F) = 0.0327$ (for 5813 data with $F_o^2 > 2\sigma(F_o^2)$) and $wR_2(F^2) = 0.0666$ (for all 7532 independent data). See Table 1 for the details of the data collection and structure determination.

3. Results and discussion

3.1. Synthesis and characterization of $[\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})]$ (**1**)

The logical synthesis of the mixed ligand complex **1** would involve treatment of ' $\text{Sm}(\text{CpPPh}_2)\text{I}_2$ ' or ' $\text{Sm}(\text{Tp}^{\text{Me}_2})\text{I}_2$ ' with KTp^{Me_2} or NaCpPPh_2 , respectively. However, currently there are no reports of $\text{Ln}(\text{CpPPh}_2)_2\text{X}_2\text{L}_n$ (Ln = lanthanide element, X = halide, L = neutral ligand) type complexes, only a number of $\text{Ln}(\text{CpPPh}_2)_2\text{XL}_n$ complexes have been described [4e-g]. And, despite the fact that $\text{Ln}(\text{Tp}^{\text{Me}_2})\text{Cl}_2\text{L}_n$ complexes have been prepared [14] and some, such as $[\text{Nd}(\text{Tp}^{\text{Me}_2})\text{Cl}_2\text{L}]$ (**2**) (L = 4,4'-di-*tert*-butyl-2,2'-bipyridine) [14d] and $[\text{Yb}(\text{Tp}^{\text{Me}_2})\text{Cl}_2(\text{THF})]$ (**3**) [14e], are structurally characterized, they are often isolated

either in low yield (**2**, 16%) or are subject to ligand rearrangement and/or ligand redistribution reactions.

Table 1
The details of X-ray data collection and structure determination of $1 \cdot 0.5C_6H_6$

Crystal data	
Formula	$C_{39}H_{47}BIN_6OPSm$
Formula weight	934.86
Crystal dimensions (mm)	$0.26 \times 0.14 \times 0.05$
Crystal system	Monoclinic
Space group	$P2_1/n$ (a nonstandard setting of $P2_1/c$ (no. 14))
Unit cell parameters	
a (Å)	13.2486 (7)
b (Å)	19.6829 (11)
c (Å)	16.1407 (9)
β (°)	109.5551 (12)
V (Å ³)	3966.2 (4)
Z	4
ρ_{calc} (g cm ⁻³)	1.566
μ (mm ⁻¹)	2.337
Data collection and refinement conditions	
Diffractometer	Bruker P4/RA/SMART 1000 CCD ^a
Radiation (λ [Å])	Graphite-monochromated Mo-K α (0.71073)
Temperature (°C)	-80
Scan type	ϕ Rotations (0.3°)/ ω scans (0.3°) (30 s exposures)
Data collection 2θ limit (°)	51.50
Total data collected	21059 ($-16 \leq h \leq 16$, $-23 \leq k \leq 24$, $-19 \leq l \leq 19$)
Independent reflections	7532
Number of observations	5813 [$F_o^2 \geq 2\sigma(F_o^2)$]
Structure solution method	Direct methods (SHELXS-86)
Refinement method ^b	Full-matrix least-squares on F^2 (SHELXL-93)
Absorption correction method	SADABS
Range of transmission factors	0.7868–0.5017
Data/restraints/parameters	7532 [$F_o^2 \geq -3\sigma(F_o^2)$]/0/457
Goodness-of-fit (S) ^c	0.944 [$F_o^2 \geq -3\sigma(F_o^2)$]
Final R indices ^d	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0327
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0666
Largest difference peak and hole (e Å ⁻³)	0.863 and -0.987

^a Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

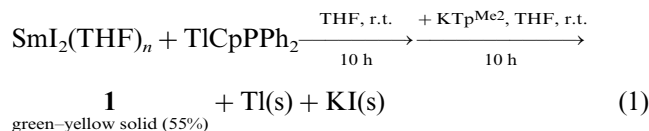
^b Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R -factors wR_2 and all goodnesses of fit S are based on F_o^2 ; conventional R -factors R_1 are based on F_o , with F_o set to zero for negative F_o^2 . The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 , and is not relevant to the choice of reflections for refinement. R -factors based on F_o^2 are statistically about twice as large as those based on F_o , and R -factors based on all data will be even larger.

^c $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0246P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^d $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

Thus complex **3** gave $[Yb(Tp^{Me_2})Cl_2(Me_2pzH)]$ and $[Yb(Tp^{Me_2})Cl_3][Me_2pzH_2]$ and attempts to derivatize $Sm(Tp^{Me_2})Cl_2L$ by Cp^- , RO^- , Et_2N^- or R^- failed, due to ligand redistribution [14b].

In an attempt to prepare $Sm(CpPPh_2)_2 \cdot nTHF$ the reaction of SmI_2 with $TiCpPPh_2$ in THF was carried out. The anticipated redox reaction occurred immediately, as evidenced by color change from deep blue to orange, but attempts to isolate the pure phosphinocyclopentadienyl complex failed. However, direct treatment of the reaction mixture with KTp^{Me_2} , followed by simple workup, afforded pure **1** in moderate yield (Eq. 1).



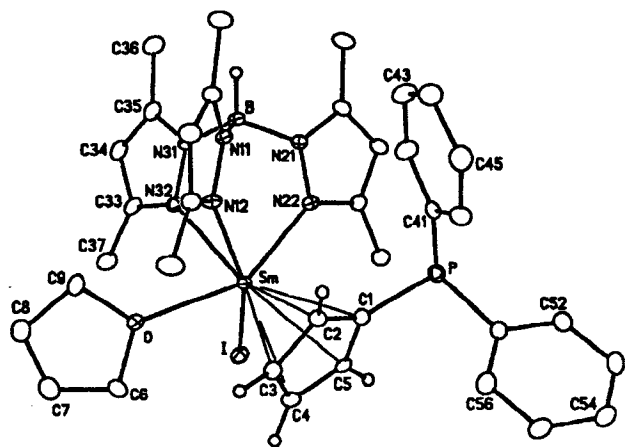
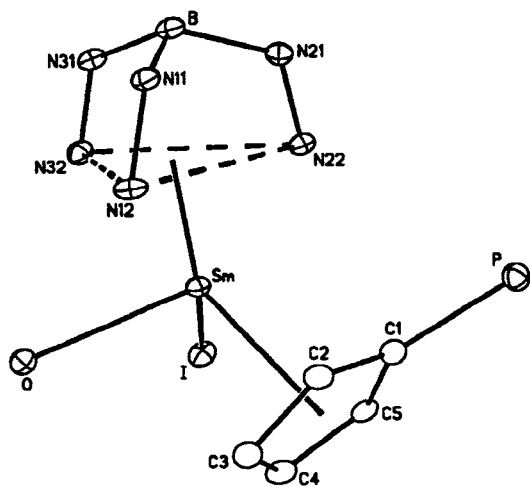
The mixed ligand complex **1** is air- and moisture-sensitive, however it is stable both in the solid state and in solution under an inert atmosphere. Thus repeated crystallization, which proved to be necessary to obtain X-ray quality single crystals, gave the same material; no decomposition or ligand redistribution reaction were observed, which often plague mixed-ligand lanthanide complexes.

Formulation of **1** is based on elemental analysis, IR, and multinuclear (¹H, ¹¹B, ³¹P) NMR spectroscopies. The B–H stretching vibration at 2564 cm⁻¹ is close to that in $[Sm(\kappa^3-Tp^{Me_2})_2(\eta^2-O_2)]$ (2543 cm⁻¹) [15] and almost identical to the frequency (2565 cm⁻¹) observed for the κ^3 -coordinated Tp^{Me_2} ligand in $[Sm(\kappa^3-Tp^{Me_2})(\kappa^2-Tp^{Me_2})(Cp)]$ [7], and therefore indicates a κ^3 -coordinated Tp^{Me_2} ligand in **1**. A single peak is observed in the ³¹P{¹H}-NMR spectrum at -18.14 ppm, in the normal range for a non-coordinated phosphine group of $CpPPh_2$ containing lanthanide complexes [4]. The room temperature ¹H-NMR spectrum, although confirming the presence of a THF ligand, showed only very broad peaks with no structural information. To reveal the details of the molecular geometry, and to confirm the connectivity of the Tp^{Me_2} and $CpPPh_2$ ligands, a single crystal of **1** was subjected to an X-ray diffraction study.

3.2. Solid-state structure of



The molecular structure and atom numbering scheme of complex **1** are shown in Fig. 1. As postulated from the IR and ³¹P-NMR spectra, the molecule contains $\kappa^3-Tp^{Me_2}$ ligand and the phosphine group of the $CpPPh_2$ remains uncoordinated, the cyclopentadienyl ring of the latter ligand is bonded to the samarium in a symmetrical η^5 -fashion. The coordination sphere of the Sm(III) center is completed by an iodide ligand and a

Fig. 1. ORTEP drawing of the molecular structure of **1**.Fig. 2. The core structure of **1** with the tetrahedral geometry emphasized.Table 2
Selected bond distances (Å) and angles (°) in **1**

Bond distances			
Sm–N12	2.514(3)	Sm–C1	2.818(4)
Sm–N22	2.474(3)	Sm–C2	2.773(4)
Sm–N32	2.603(3)	Sm–C3	2.732(4)
Sm–I	3.1400(3)	Sm–C4	2.741(4)
Sm–O	2.475(3)	Sm–C5	2.774(4)
B–N11	1.539(3)	P–C1	1.824(4)
B–N21	1.542(3)	P–C41	1.847(4)
B–N31	1.528(3)	P–C51	1.839(4)
Bond angles			
I–Sm–N12	59.76(7)	O–Sm–N12	80.26(9)
I–Sm–N22	95.98(7)	O–Sm–N22	149.49(9)
I–Sm–N32	88.18(7)	O–Sm–N32	77.45(9)
I–Sm–O	88.46(7)		
N12–Sm–N22	85.74(10)	N11–B–N21	113.8(3)
N12–Sm–N32	73.04(10)	N11–B–N31	111.4(3)
N22–Sm–N32	72.55(10)	N21–B–N31	108.5(3)

THF molecule. Although the formal coordination number of samarium is eight, the coordination geometry, like that of the bent samarocene complexes $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{THF})_2]$ [16], $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{THF})_2][\text{BPh}_4]$ [17], and $[\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{I})(\text{THF})]$ [18], is best described as distorted tetrahedral. A simplified diagram emphasizing this view is shown in Fig. 2. The four apexes of the tetrahedron are occupied by the centroid of the CpPPh_2 ligand (Cp_{cent}) and that of the N12N22N32 triangle of Tp^{Me_2} ligand (Tp_{cent}), the iodide and the THF oxygen atom. Since the four ‘apex-ligands’ are different the Sm(III) center is chiral. The molecule crystallizes in the centric space group ($P2_1/n$) and hence comprises a racemic mixture of both enantiomers.

Some important bond distances and angles are given in Table 2, and Table 3 shows a comparison between the metrical parameters of **1** and the related $[\text{Sm}(\text{C}_5\text{Me}_5)_2\text{I}(\text{THF})]$ [18] complex. The Sm–N distances range from 2.474(3) to 2.603(3) Å, and are similar to those observed in other eight-coordinate Tp^{Me_2} anchored Sm(III) complexes. For instances, $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\text{PhN}=\text{NPh})]$ [19] has Sm–N(Tp^{Me_2}) distances ranging from 2.512(8) to 2.669(10) Å, and $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\eta^2\text{-O}_2)]$ [15] from 2.488(3) to 2.647(3) Å. The Sm– Cp_{cent} separation (2.494 Å) is almost the same as the perpendicular distance from Sm to the Cp ring (2.493 Å), indicating a symmetrical bonding of the Cp moiety to Sm(III). The Sm–C distances vary from 2.732(4) to 2.818(4) Å with a mean value of 2.768(4) Å which is close to that observed in $[\text{Sm}(\text{Tp}^{\text{Me}_2})_2(\eta^5\text{-Cp})]$ (2.79 Å) [7], and is in the range of 2.68–2.88 Å reported for Sm–C bond distances for eight-coordinate Sm(III) complexes [20]. The Sm–O distance of 2.473(3) Å is normal and compares favorably with the average Sm–O(THF) distance of 2.48(2) Å compiled by Evans for eight-coordinate permethylcyclopentadienyl Sm(III)

Table 3
Comparisons of metrical parameters in **1** and $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{I})(\text{THF})]$ [18]^a

	1	$[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{I})(\text{THF})]$
Sm–I (Å)	3.1400(3)	3.043(2), 3.053(2)
Sm–O (Å)	2.475(3)	2.45(1) 2.45(1)
Sm–Centroid (Å)	1.758(Tp^{Me_2}) 2.494(Cp)	2.47, 2.46 2.44, 2.45
Centroid–Sm–Centroid (°)	134.3	136 137
Centroid–Sm–I (°)	118.7(Tp^{Me_2}) 98.7(Cp)	106.2(2), 106.1(2) 104.7(2), 106.4(2)
Centroid–Sm–O (°)	102.5(Tp^{Me_2}) 103.9(Cp)	105.7, 104.2 104.4, 104.6
I–Sm–O (°)	88.46(7)	88.8(3) 90.5(3)

^a There are two independent molecules in the unit cell.

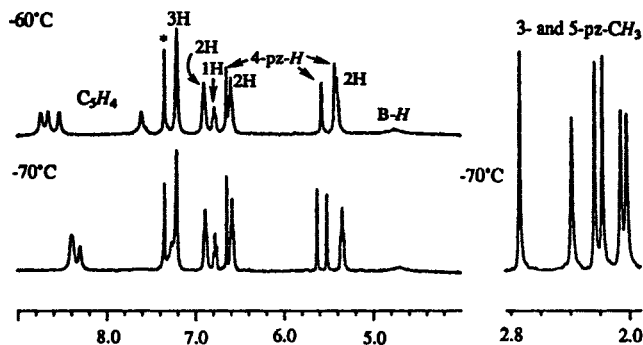


Fig. 3. The $^1\text{H-NMR}$ spectra of **1** in $\text{THF-}d_8$ at -60°C (range 4.0–9.0 ppm) and -70°C (ranges 4.0–9.0 and 2.0–2.8 ppm); *impurity in $\text{THF-}d_8$.

complexes [20]. However the Sm–I distance, 3.1400(3) Å, is longer than those compiled by Xie et al. [21] in related eight-coordinate Sm(III) complexes; [$\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{I})(\text{THF})$], 3.043(2) and 3.053(2); [$\text{Sm}(\text{tBuCp})_2(\text{I})(\text{THF})$], 3.045 Å; [$\text{Sm}(\text{MeOCH}_2\text{CH}_2\text{Cp})_2(\text{I})$], 3.119(1) Å; and [$\text{Sm}(\text{MeOCH}_2\text{CH}_2\text{Cp})(\text{I})_2(\text{THF})_2$], 3.08(1) and 3.092(1) Å. Reference to Table 3 shows that, with the exception of the significantly longer Sm–I distance and the smaller $\text{Cp}_{\text{cent}}\text{–Sm–I}$ angle in **1**, the corresponding metrical parameters between **1** and [$\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{I})(\text{THF})$] are very close. The lengthening of the Sm–I bond in **1** is most probably attributable to the congested nature of the Sm(III) center due to the bulky Tp^{Me_2} ligand. It is interesting that steric congestion results in weakening of the Sm–I interaction while the Sm–O(THF) distance, and hence bonding, remains normal.

3.3. Variable temperature $^1\text{H-NMR}$ investigation

Since the room temperature $^1\text{H-NMR}$ spectrum was uninformative and in order to verify whether the chiral, non-symmetric solid state structure will be maintained in solution, the $^1\text{H-NMR}$ spectra were recorded at low temperatures. Fig. 3 shows the spectra in $\text{THF-}d_8$ at -60°C (range 4.0–9.0 ppm) and at -70°C (ranges 4.0–9.0 and 2.0–2.8 ppm). It is clear that the broad, almost featureless room temperature spectrum has resolved into a series of relatively sharp signals, their number and relative intensity are as expected from the solid state structure. Thus at high field the six peaks with relative intensity 3H are due to the six chemically non-equivalent pyrazolyl 3/5-Me groups; three sharp 1H signals in the low field region can be assigned to the pyrazolyl 4-H protons. Due to the chiral nature of **1** all four C_5H_4 hydrogens are different, irrespective of the rotation of the ligand around samarium, and indeed four 1H signals are seen at -60°C in the 7.4–8.8 ppm range. Curiously one of the peak is well separated from the other three. For similar reason the two phenyl

groups are diastereotopic [22] and, assuming rapid P–Ph rotation, should give rise to six signals in a 2:2:2:2:1:1 ratio for the *ortho*-, *meta*- and *para*-hydrogens, respectively. In practice we observe five signals at -60°C , one at 7.20 ppm corresponding to 3H presumably is the result of accidental overlap of two signals. In order to identify the signals due to the coordinated THF ligand the spectra were recorded in $\text{toluene-}d_8$. Only two broad peaks were observed at all temperatures between 0°C (3.48 and 1.37 ppm) and -90°C (3.53 and 1.29 ppm), the temperature dependence being due to the presence of the paramagnetic Sm(III) center. Here too we presume that the simple appearance is due to accidental overlap of resonances of a more complex THF pattern expected from the asymmetric structure of **1**. Finally we note that although the low temperature $^1\text{H-NMR}$ spectra are consistent with the maintenance of the chiral, asymmetric solid state structure in solution, the spectra above room temperature, both in $\text{THF-}d_8$ and $\text{toluene-}d_8$, undergo changes which signal the onset of rapid dissociation of coordinated THF ligand and loss of stereochemical integrity. At 90°C in $\text{toluene-}d_8$, the $^1\text{H-NMR}$ spectrum shows only one set of Tp^{Me_2} , C_5H_4 , Ph and THF resonances.

4. Summary

The mixed $\text{Tp}^{\text{Me}_2}/\text{CpPPh}_2$ samarium complex, [$\text{Sm}(\text{CpPPh}_2)(\text{Tp}^{\text{Me}_2})(\text{I})(\text{THF})$] **1**, containing four different ligands, has been synthesized and fully characterized. X-ray analysis confirmed the chiral, monomeric structure with uncoordinated Ph_2P group. Although the asymmetric solid state structure is maintained in solution at low temperatures, above room temperature loss of coordinated THF ligand results in loss of stereochemical integrity. Complex **1** is a potentially versatile metal-ligand for the synthesis of heterobimetallic samarium-transition metal complexes or mixed $\text{Tp}^{\text{Me}_2}/\text{CpPPh}_2$ samarium complexes by salt metathesis of the iodide ligand.

5. Supplementary material

Atomic coordinates, bond lengths and angles, thermal parameters, and structure factor amplitudes have been deposited at the Cambridge Crystallographic Data Center CCDC no. RA100600. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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