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Tris(indenyl)lanthanum(III) derivatives with two stereogenic centres: crystal structures and solution NMR spectroscopy of the adducts $[(C_9H_7)_3La \cdot L]$ with L = (R)-(+)-methyl-p-tolylsulphoxide and triphenylphosphinoxide

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Abstract

Three new adducts of the type $[(C_9H_7)_3La \cdot L]$ with L = (R)-(+)-methyl-p-tolylsulphoxide **1**, triphenylphosphinoxide **2** and diphenylsulphoxide **3** have been prepared and further characterized. The crystal structures of **1** and **2** were determined from single crystals. **1** crystallizes as one distinct epimeric form with two 'equatorially' and one 'meridionally' oriented C_9H_7 ligands. Space group $P2_1$; cell parameters $a = 838.30(10)$, $b = 966.5(3)$, $c = 1770.5(7)$ pm, $\beta = 90.82(2)^\circ$. Crystals of **2** contain two crystallographically equivalent diastereomers with three disordered but essentially 'equatorial' C_9H_7 ligands. The $P(C_6H_5)_3$ propellers adopt either of two possible enantiomorphic configurations. Space group $R\bar{3}$; cell parameters $a = b = 1451.1(3)$, $c = 3136.6(7)$ pm. The solution ^1H NMR spectra of **1–3** clearly reflect rapid intramolecular motion of the C_9H_7 ligands. The quasi-first-order spectrum of **1** is indicative of significant diastereotopic splitting, displaying a total of seven individual C_9H_7 proton resonances.

Keywords: Lanthanum; Indenyl; Sulphoxides; Triphenylphosphinoxide; Crystal structures; Nuclear magnetic resonance

1. Introduction

Homoleptic tris(indenyl)metal fragments $[(C_9H_7)_3M]^q$ ($q = 0$, M = trivalent rare earth metal; $q = +1$, M = tetravalent actinoid metal) may, in some of their possible conformations, be considered as prochiral (for precise definitions see Ref. [1]). Thus, addition of a fourth (uncharged or anionic) ligand L should afford an enantiomeric pair of $[(C_9H_7)_3La \cdot L]$ complexes of type A as long as all three C_9H_7 ligands are oriented 'head-to-tail' in 'equatorial' positions as shown in Fig. 1(a). Chiral $[(C_9H_7)_3M \cdot L]$ systems should also result from the (already chiral) conformations depicted in Fig. 1(b) and Fig. 1(c), wherein one C_9H_7 ligand is assumed to be oriented 'meridional' (symbolized by a small circle), i.e. with its benzo group either *cisoid* (type B) or *transoid* (type C) to the additional ('axial') M–L bond. $[(C_9H_7)_3M \cdot L]$ systems involving all-*cisoid* (type D) or all-*transoid* (type E) positioned benzo groups (Fig. 1(d)) should, in contrast, be achiral. [Strictly speaking, all configurations in which the main axes of the three equivalent C_9H_7 ligands do not run parallel to the M–L axis should be chiral.]

Owing to the usually facile rotation of indenyl ligands about their (C_5-) ring centre-to-metal axes, all former structural studies were focused on crystalline samples, as crystal packing effects may efficiently reduce most intra- and intermolecular mobility. Table 1 presents a survey of results based on the single-crystal X-ray studies of various tris(indenyl) metal complexes including also derivatives with partially alkylated indenyl ligands. Several examples resembling closely either of the four 'ideal' complex types A, B, C and D may actually be distinguished. The information collected in Table 1 suggests that type D may be favoured in cases of minimal, and type A of maximal, space demand for L and eventual substituents of distinct indenyl H atoms. For instance, the α carbon atoms of L = THF in **16–19** (type A) carry four H atoms which require more space than the two H atoms in the α positions of L = pyridine in complex **12** (type B). Inter-

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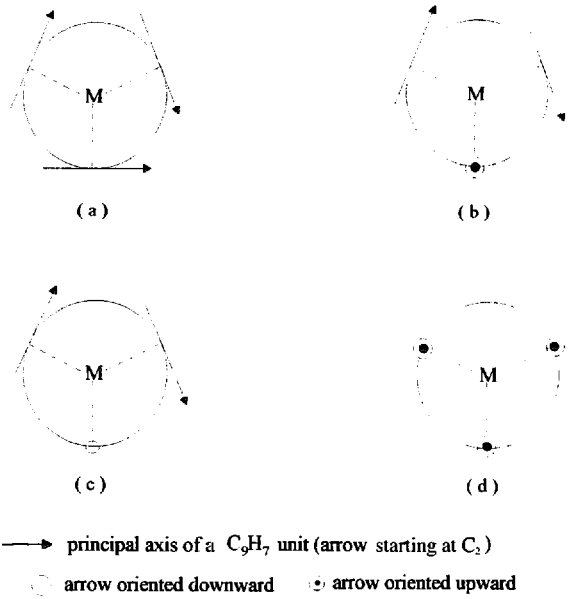

Fig. 1. Schematic description of four alternative conformations of the $(C_9H_7)_3M^n$ fragment.

estingly, the space groups of most of the complexes adopting type A or B are achiral, indicating that the lattices of those principally chiral molecules tend to involve their racemic mixtures. So far, only the complexes **18** and **19** seem to crystallize enantiomerically pure. However, the chiral and acentric space groups $P2_12_12_1$ of the two type D complexes **4** and **5** are unlikely to originate from molecular dissymmetry as long as the point symmetry of an individual molecule is as high as C_{3v}. The dinuclear anions of compounds

Table 1
A survey of the conformational variety of tris(indenyl) metal complexes based on the single crystal X-ray studies

Number	Compound	Complex type	Space Group	Hapticity [a]	Ref.
4	$[(C_9H_7)_3UCl]$	D	$P2_12_12_1$	η^5	[2]
5	$[(C_9H_7)_3UBr]$	D	$P2_12_12_1$	η^5	[3]
6	$[(C_9H_7)_3UI]$	A	$P2_1/c$	η^5	[4]
7, 8	$[(1,4,7\text{-}Me_3C_9H_4)_3MCl]$ (M = Th, U)	A	$P2_1/c$	η^5	[5,6]
9	$[(1\text{-}EtC_9H_6)_3ThCl]$	A	$P2_1/c$	η^5	[7]
10	$[(1,2,4,5,6,7\text{-}Me_6C_9H)_3UCl]$	C	$P\bar{1}$	η^5	[8]
11	$[(C_9H_7)_3UOCH_2CF_3]$	B [d]	$P2_1/c$	η^5	[9]
12	$[(C_9H_7)Ce \cdot NC_5H_5]$ [b]	C	$Pbac$	η^5	[10]
13–15	$[Na(THF)_6][\{(C_9H_7)_3M\}_2(\mu\text{-}Cl)]$ [c] (M = Pr, Nd, Sm)	B	$P\bar{1}$	η^5	[11,12]
16, 17	$[(C_9H_7)_3M \cdot THF]$ (M = La, Pr)	A [d]	$P2_1/a$	η^5	[13]
18, 19	$[(C_9H_7)_3M \cdot THF]$ (M = Nd, Gd)	A	$P6_3$	η^5	[14]

[a] According to statements in the literature.
[b] NC_5H_5 = pyridine.
[c] THF = tetrahydrofuran.
[d] Crystal structure with two non-equivalent molecules per unit cell.

13–15 are the first tris(indenyl)metal complexes with two stereogenic centres. According to the literature [11,12], only the corresponding *meso* form is realized. In our present study, we wish to extend the series of $[(C_9H_7)_3La \cdot L]$ systems towards the first examples involving another stereogenic centre in the Lewis base molecule L. Commercially available (R)-(+)-methyl-p-tolylsulphoxide (MTSO) was chosen as a promising, unequivocally chiral base, while triphenylphosphinoxide (TPPO) was selected owing to its capability to generate a conformationally quite labile, stereogenic centre by orienting its three phenyl groups in a propeller-like dissymmetric fashion [15–17]. Particular interest will be focused on the potential interplay of the two principally independent chirality centres of the new adducts. To explore the molecular structures adopted outside a crystal lattice, we have also investigated the solution ^1H NMR spectra of the adducts with MTSO **1** and TPPO **2**, as well as of the non-chiral adduct **3** with L = $SO(C_6H_5)_2$ (DPSO).

2. Experimental section

All operations had to be carried out under pure nitrogen using standard Schlenk techniques, and all solvents were dried and distilled over Na–K alloy with benzophenone ketyl. Anhydrous $LaCl_3$ was prepared according to the literature [18], and NaC_9H_7 by treating indene with an excess of Na pearls in THF. $[(C_9H_7)_3La \cdot THF]$ was prepared according to Ref. [19]. The lanthanum content of **1–3** was determined by complexometric titration with EDTA, and the C/H content on a Heraeus CHN-O-Rapid analyser. IR spectra were recorded on a Perkin–Elmer 1720 FT-IR spectrometer. ^1H NMR spectra of **1** were recorded on a Bruker AM 360 spectrometer, and of **2** and **3** on a Varian Gemini 200 MHz instrument.

2.1. Preparation of $[(C_9H_7)_3La \cdot (R)$-(+)-MTSO] (1)

Freshly prepared $[(C_9H_7)_3La \cdot THF]$ (2.203 g, 3.96 mmol) was dried in vacuo at 100 °C for 3 h; after cooling to room temperature, 10 ml of toluene was added under stirring. Within 10 min, (R)-(+)-MTSO (Fluka, 0.62 g, 4 mmol) dissolved in 35 ml of toluene was added under stirring. Very quickly, the reaction mixture became an almost transparent solution. After stirring for one day, filtering (G4 frit), concentration of the filtrate, cooling overnight to ca. 0 °C and drying, colourless crystals were collected (ca. 2.02 g, yield 80%). Decomp. temperature 143–144 °C. Anal. Found: C, 65.05; H, 4.88; La, 22.17. $C_{35}H_{31}OSLa$ Calc.: C, 65.86; H, 4.85; La, 21.76%. IR spectra (KBr pellet, cm^{-1}):

Table 2
Summary of crystal data and details of data collection and refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{35}H_{31}LaOS$	$C_{35}H_{36}LaOP$
Formula weight	638.57	762.62
Temperature (K)	293(2)	293(2)
Diffractometer	Syntex $P2_1$	Syntex $P2_1$
Wavelength (pm)	71.073	71.073
Crystal system	monoclinic	trigonal
Space group	$P2_1$	$R\bar{3}$
Unit cell dimensions (pm)	$a = 838.30(10)$	$a = 1451.1(3)$
	$b = 966.5(3)$	$b = 1451.1(3)$
	$c = 1770.5(7)$	$c = 3136.6(7)$
	$\beta = 90.82°$	$\beta = 90°$
Volume (nm^3)	1.4343(7)	5.769(2)
Z	2	6
Density (calc.) ($mg\,cm^{-3}$)	1.479	1.317
Absorption coefficient (mm^{-1})	1.588	1.184
$F(000)$	644	2316
θ Range for data collection	2.30 to 27.57°	2.81 to 24.99°
Index ranges	$-2 \le h \le 10$	$-2 \le h \le 17$
	$-2 \le k \le 12$	$-2 \le k \le 17$
	$-23 \le l \le 23$	$-41 \le l \le 41$
Reflections collected	5966	4078
Independent reflections	4287 ($R_i = 0.0273$)	2252 ($R_i = 0.0622$)
Data/restraints/parameters	4287/1/347	2249/73/197
Goodness of fit on F^2	1.126	1.079
Final R indices [$I > 2\sigma(I)$] R_1/wR_2	0.0393/0.0973	0.0475/0.1175
R indices (all data) R_1/wR_2	0.0403/0.0987	0.0518/0.1222
Absolute structure parameter	0.01(2)	0.0025(3)
Largest difference peak and hole (nm^{-3})	1097 and −2670	617 and −502

3060(w), 2920(w), 1708(w), 1597(m), 1559(m), 1494(m), 1457(m), 1394(m,sh), 1313(m,br), 1150(s), 1122(w), 1089(s), 1038(s,br), 1018(w), 948(m,br), 915(w,sh), 862(m,sh), 810(s,sh), 767(vs,sh), 719(m,sh), 694(m,sh). ^{1}H NMR (C_6D_6): see Table 7.

2.2. Preparation of $[(C_9H_7)_3La \cdot OP(C_6H_5)_3]$ (2)

Colourless microcrystals of $[(C_9H_7)_3La \cdot THF]$ (0.47 g, 0.845 mmol) were conditioned as above and suspended in 20 ml of toluene. After cooling to 0 °C and addition of 0.23 g (0.84 mmol) of $OPPh_3$ dissolved in 20 ml of toluene, the initially yellow reaction mixture soon became colourless. After stirring for another 4 h at room temperature, and subsequent warming to ca. 50–60 °C, the sediment was completely dissolved, affording again a bright yellow solution. After filtration and slow cooling, a precipitate consisting of numerous crystals of regular rhombic shape could be isolated (yield > 95%) and dried at 80–100 °C. Decomp. temperature 248–250 °C. Anal. Found: C, 68.63; H, 4.91; La, 18.92. $C_{45}H_{36}OPLa$ Calc.: C, 70.89; H, 4.72; La, 18.22%. [Sample dried, for comparison, only at room temperature. Anal. Found: C, 71.61; H, 5.18. $C_{48.5}H_{40}OPLa$ ($2 \cdot 0.5MePh$) Calc.: C, 73.09; H, 5.14%.] IR (KBr, cm^{-1}): 3055(m), 2884(w), 1704(w,br), 1591(m,sh), 1559(m,sh), 1484(m,sh), 1458(m,sh), 1438(vs), 1393(m,sh), 1361(w), 1328(m,sh), 1312(m), 1259(w), 1184(vs,br), 1121(s,sh), 1094(w), 1071(w), 1027(w), 997(m,sh), 943(w), 915(w), 862(m), 768(s), 755(s), 722(vs), 696(vs), 541(vs,sh). ^{1}H NMR (C_6D_6, room temp.): see Table 7. ^{31}P NMR (in C_6H_6 vs. external 85% H_3PO_4): one singlet at 36.67 ppm.

2.3. Preparation of $[(C_9H_7)_3La \cdot OS(C_6H_5)_2]$ (3)

A solution of 0.105 g (0.52 mmol) of $(C_6H_5)_2SO$ in 15 ml of toluene was added under stirring to a suspension of appropriately conditioned $[(C_9H_7)_3La \cdot THF]$ (vide supra) in 20 ml of toluene. An almost clear mixture was quickly obtained. After stirring for one day,

Table 3
Atom coordinates ($\times 10^4$) and isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **1**, with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
La	9877(1)	9992(1)	7880(1)	31(1)
S(1)	12036(2)	6684(2)	7538(1)	42(1)
O(1)	11890(6)	8254(6)	7559(3)	49(1)
C(1)	10366(7)	10570(8)	9420(3)	46(1)
C(2)	11218(7)	9364(8)	9299(3)	47(1)
C(3)	10176(6)	8223(7)	9229(3)	42(1)
C(4)	8599(6)	8745(6)	9354(3)	38(1)
C(5)	8713(6)	10216(8)	9450(2)	40(2)
C(6)	7305(8)	11000(7)	9576(3)	49(1)
C(7)	5901(7)	10316(8)	9663(4)	54(2)
C(8)	5802(7)	8855(9)	9612(4)	51(2)
C(9)	7126(6)	8077(7)	9451(3)	45(1)
C(11)	10199(7)	12696(8)	7211(3)	48(1)
C(12)	11217(8)	11820(7)	6796(3)	51(1)
C(13)	12516(8)	11492(8)	7279(5)	58(2)
C(14)	12310(8)	12108(8)	7976(4)	57(2)
C(15)	10880(8)	12882(7)	7948(3)	5o(1)
C(16)	8725(10)	13370(8)	7021(5)	65(2)
C(17)	8000(11)	14144(9)	7543(6)	74(2)
C(18)	8608(13)	14303(8)	8260(6)	84(3)
C(19)	10039(12)	13705(8)	8491(4)	70(2)
C(21)	8212(7)	8279(7)	6748(3)	44(1)
C(22)	7759(6)	9653(7)	6516(3)	46(2)
C(23)	6846(6)	10262(6)	7100(3)	46(2)
C(24)	6682(6)	9246(7)	7665(3)	45(1)
C(25)	7542(7)	8041(7)	7477(3)	45(1)
C(26)	8208(7)	10148(12)	5782(3)	58(2)
C(27)	9066(10)	9282(12)	5333(4)	72(2)
C(28)	9527(10)	7945(11)	5564(4)	73(2)
C(29)	9109(8)	7399(9)	6268(4)	60(2)
C(31)	13295(6)	6302(6)	6760(3)	39(1)
C(32)	14115(7)	7355(7)	6402(3)	47(1)
C(33)	15110(7)	6993(8)	5806(3)	51(1)
C(34)	15306(7)	5634(9)	5585(3)	52(1)
C(35)	14495(10)	4613(8)	5966(4)	63(2)
C(36)	13473(7)	4959(12)	6555(3)	56(1)
C(37)	16427(11)	5286(12)	4944(5)	86(3)
C(38)	13452(8)	6280(9)	8278(4)	59(2)

Table 4
Atom coordinates ($\times 10^4$) and isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2**, with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq}
La(1)	0	0	2214(1)	69(1)
C(1)	679(5)	−1611(6)	2225(2)	129(8)
C(2)	235(6)	−1703(6)	2623(2)	138(10)
C(3)	−852(6)	−2106(7)	2572(2)	139(10)
C(4)	−1071(5)	−2217(7)	2141(3)	97(6)
C(5)	−134(6)	−1957(7)	1928(2)	91(3)
C(6)	849(9)	−1533(6)	2983(3)	158(7)
C(7)	1907(8)	−1271(9)	2945(4)	203(13)
C(8)	2351(6)	−1179(9)	2547(5)	160(8)
C(9)	1737(5)	−1349(6)	2187(4)	127(6)
C(1′)	694(6)	−1505(6)	2488(3)	108(6)
C(2′)	147(6)	−1947(6)	2114(2)	168(15)
C(3′)	−922(5)	−2287(6)	2183(3)	99(6)
C(4′)	−1027(6)	−2009(7)	2593(3)	105(6)
C(5′)	−37(7)	−1571(8)	2788(2)	129(7)
C(6′)	672(9)	−2078(7)	1772(3)	147(7)
C(7′)	1744(9)	−1767(10)	1804(4)	169(10)
C(8′)	2291(7)	−1325(10)	2177(5)	188(12)
C(9′)	1766(6)	−1194(7)	2520(4)	174(11)
O(1)	0	0	1460(2)	110(2)
P(1)	0	0	990(1)	78(1)
C(21)	−1332(4)	−716(4)	786(1)	77(1)
C(22)	−1692(4)	−310(4)	476(2)	87(1)
C(23)	−2725(5)	−905(6)	323(2)	107(2)
C(24)	−3380(5)	−1894(6)	473(2)	112(2)
C(25)	−3042(5)	−2316(5)	780(3)	119(2)
C(26)	−2028(5)	−1736(5)	936(2)	103(2)
C(1H)	0	0	4431(27)	256(49)
C(2H)	0	0	5000	330(115)

filtration and concentrating the filtrate to half of its initial volume, the transparent solution (containing already a few suspended microcrystals) was cooled to 0 °C. Colourless crystals were isolated after a few days and dried in vacuo between 40 and 60 °C (water bath). Yield 0.32 g (90%). Decomp. temperature 179–180 °C. Anal. Found: C, 67.72; H, 4.58; La, 19.89. $C_{39}H_{31}OSLa$ Calcd.: C, 68.25; H, 4.51; La, 20.24%. IR (KBr pellet, cm^{-1}): 3063(w), 1704(w), 1609(w), 1581(w), 1554(w), 1476(m), 1457(m), 1444(s), 1393(m), 1323(w), 1312(w), 1227(w), 1205(w), 1158(m), 1091(s), 1047(s), 1020(m), 998(m), 942(w), 915(w), 861(w), 768(vs), 757(m), 743(m), 719(m), 695(vs), 590(m), 538(m). ^1H NMR (C_6D_6, 200 MHz, room temp.): see Table 7.

2.4. X-ray crystallography

Suitable single crystals of **1** and **2** were grown from toluene solutions at room temperature or at 0 °C. Selected crystals were positioned in carefully conditioned, and finally sealed, thin-walled Lindemann capillaries. The determination of Laue symmetry and the crystal orientation matrix were carried out by standard techniques making use of X-ray photographs similar to those described by Churchill et al. [20]. Details of relevance for the data collection for **1** and **2** are given in Table 2.

All crystallographic calculations were carried out by means of the SHELX-93 and SHELXTL-PLUS program set [21]. Heavy atoms were found from Patterson maps for **1** and direct methods for **2**, and other non-hydrogen atoms were detected by Fourier techniques. The structures were refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C–H) = 96$ pm. Final refinement of position and thermal parameters (one unique isotropic parameter only for all hydrogen atoms) resulted in $R_1 = 0.0393$, $wR_2 = 0.0973$ for **1** and 0.0475, 0.1175 for **2**. The atomic coordinates of **1** and **2** are given in Tables 3 and 4. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany on quoting the depository numbers CSD-405567(1) and 405568(2).

3. General properties of 1, 2 and 3

For an efficient preparation of all three adducts it has turned out to be favourable to apply 'conditioned' $[(C_9H_7)_3La \cdot THF]$ (see Section 2), i.e. a species strongly depleted in THF. At room temperature the products **1-3** are only weakly soluble in toluene. Their solubility generally increases with temperature, but then decomposition cannot be strictly avoided. CH_2Cl_2 turned out to be a better solvent already at room temperature; however, the ^1H NMR spectra taken in CD_2Cl_2 were clearly indicative of more facile decomposition than in toluene.

The sulphoxide adducts **1** and **3** are thermally more labile than the phosphinoxide adduct **2**. Thus, the decomposition temperature of the latter exceeds those of the former by at least 50 deg. Moreover, even under N_2, crystals of **1** and **3** tend to darken slowly at their surfaces. The wavenumbers of the ν(SO) absorptions of **1** and **3** (1038 and 1047 cm^{-1}) do not differ significantly from those of the uncoordinated sulphoxides (1048 of free MTSO and 1072/1037 cm^{-1} of free DPSO [22]). Correspondingly, the ν(PO) absorption of **2** appears at 1184 cm^{-1}, only slightly below that of free TPPO (1195 cm^{-1} [15,23]). More strongly coordinated TPPO may even absorb around 1050 cm^{-1} (e.g. $[UCl_4(TPPO)_2]$ 1045–1057 cm^{-1} [24]). The chemical shift of the ^{31}P nucleus of **2** (36.67 ppm in C_6D_6) indicates weak deshielding relative to free TPPO (29.3 ppm [25]), probably because of a slightly more positive charge on the phosphorus atom in the lanthanum complexes.

Crystals of **2** dried only at room temperature always contained some toluene. This conclusion is supported by ^1H NMR spectroscopic results, elemental analysis (after only moderate or extensive drying) and some corresponding X-ray features. Drying at ca. 100 °C led to complete removal of the solvent molecules, however, under these conditions already part of the coordinated TPPO sublimed off too [26].

4. Crystal structure of $[(C_9H_7)_3La \cdot MTSO]$ (1)

Although the crystal structures of at least four representatives of the general type $[(C_5H_5)_3Ln \cdot OSR^1R^2]$ (Ln = lanthanoid element) have been determined (Ln = La, R^1, R^2 = Me [27]; Ln = Pr, Yb, R^1 = Me, R^2 = p-MeC_6H_4; Ln = Pr, R^1 = 2-Me-C_5H_3N, R^2 = p-MeC_6H_4 [28]), the structure of **1** appears to be the first one of a related sulphoxide adduct to be reported in the open literature. Data of relevance for the crystal structure are collected in Table 2, and one perspective of the molecular structure of **1** is presented in Fig. 2. In accordance with the involvement of the pure (R)-(+)-enantiomer of MTSO, the lattice of **1** adopts a chiral space group ($P2_1$, see Table 2). The likewise chiral complex $[(C_5H_5)_3Pr \cdot PTSO]$ (PTSO = (R)-(+)-2-pyridyl-p-tolylsulphoxide) was found to crystallize in the same space group. The structures of the latter three complexes will be sumitted for publication in this journal in due course.) A closer inspection of the structure of **1** (see Fig. 2) leaves no doubt that the molecular conformation should be attributed to type C of Table 1 (see also Fig. 1). Apparently, both the methyl group and the free electron pair of the sulphur atom prevent the

MTSO ligand from sterically adopting a position *cisoid* to the benzo group of the 'meridional' C_9H_7 ligand. The unique molecule present in the unit cell is devoid of any significant disorder, confirming the statement that only one distinct epimeric form of **1** is realized. The corresponding alternative epimer whose two 'equatorial' C_9H_7 ligands are rotated (relative to those of **1**) by angles of 180° about their (C_5-) ring normals is probably sterically more congested and hence likely to be less concentrated in solution.

Selected intramolecular distances and bond angles of **1** are listed in Table 5. The sulphoxide ligand is coordinated to the strongly oxygenophilic La^{3+} ion exclusively via its oxygen atom (non-bonding La · · · S distance 372.7 pm). The La–O distance exceeds that found in $[(C_5H_5)_3La \cdot DMSO]$ (DMSO = dimethylsulphoxide) by only 3.4 pm [27], but is about 12 pm shorter than the La–O bond in $[(C_5H_5)_3La \cdot THF]$ [29]. The S–O bond is elongated by only 3.0 pm relative to that in free MTSO [30]. The La–O–S angle of 138.1(3)° (Table 5) compares well with the Ln–O–S angles reported for $[(C_5H_5)_3Pr \cdot MTSO]$ (143.1(1)° [28]), $[La(DMSO)_4(NO_3)_3]$ (132.6 and 141.1° [31]) and $[Pr(DMSO)_4(NO_3)_3]$ (132.5 and 137.1° [32]). The La–C distances (see Table 5) range between 279.4(5) and 308.2(5) pm and match well with those reported for $[(C_5H_5)_3La \cdot L]$ complexes with L = DMSO and THF [27,29]. Although the two ring carbon atoms belonging to both the C_5 and the C_6 fragment of each C_9H_7 ligand are as usual slightly more distant from the metal ion than the three 'pure' C_5 carbon atoms, all three indenyl ligands of **1** can be considered as η^5-coordinated. The configuration of the chiral OSMe(p-tolyl)

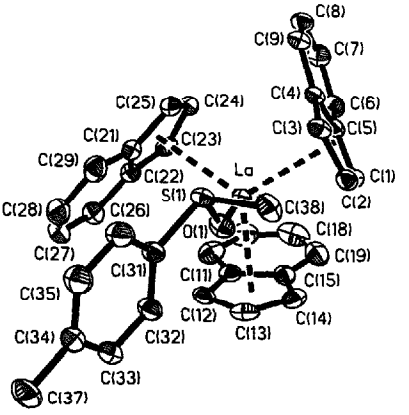

Fig. 2. Molecular structure of **1** viewed along its O–La axis.

Table 5
Selected bond lengths (pm) and bond angles (°) for **1**

La–O(1)	245.3(5)	La–C(1)	280.8(5)
La–C(2)	280.4(5)	La–C(3)	294.5(5)
La–C(4)	208.2(5)	La–C(5)	296.8(4)
La–C(11)	288.4(7)	La–C(12)	285.1(6)
La–C(13)	286.3(6)	La–C(14)	289.2(7)
La–C(15)	292.0(7)	La–C(21)	293.7(6)
La–C(22)	299.4(5)	La–C(23)	288.6(5)
La–C(24)	279.4(5)	La–C(25)	280.3(6)
La–Cen1	255.3	La–Cen2	262.1
La–Cen3	261.7	S(1)–O(1)	152.3
S(1)–C(31)	178.5(5)	S(1)–C(38)	179.8(7)
C(1)–C(2)	138.5(10)	C(1)–C(5)	142.9(8)
C(2)–C(3)	141.1(10)	C(3)–C(4)	143.6(7)
C(4)–C(9)	140.6(8)	C(4)–C(5)	143.4(9)
C(5)–C(6)	142.3(8)	C(6)–C(7)	136.1(9)
C(7)–C(8)	141.7(13)	C(8)–C(9)	137.4(9)
C(11)–C(12)	141.4(10)	C(11)–C(15)	142.8(9)
C(11)–C(16)	143.3(11)	C(12)–C(13)	141.3(10)
C(13)–C(14)	138.4(11)	C(14)–C(15)	141.3(10)
C(15)–C(19)	144.1(11)	C(16)–C(17)	134.2(13)
C(17)–C(18)	137(2)	C(18)–C(19)	138.7(14)
C(21)–C(29)	142.4(9)	C(21)–C(25)	143.3(8)
C(21)–C(22)	143.9(10)	C(22)–C(23)	142.3(8)
C(22)–C(26)	144.1(8)	C(23)–C(24)	141.0(8)
C(24)–C(25)	141.2(9)	C(26)–C(27)	136.6(13)
C(27)–C(28)	141(2)	C(26)–C(29)	140.3(12)
C(34)–C(37)	152.0(8)		
O(1)–La–Cen1	96.2	O(1)–La–Cen2	98.3
O(1)–La–Cen3	101.1	Cen1–La–Cen2	118.3
Cen2–La–Cen3	114.8	Cen1–La–Cen3	120.3
S(1)–O(1)–La	138.1(3)	O(1)–S(1)–C(31)	105.9(3)
O(1)–S(1)–C(38)	104.5(4)	C(31)–S(1)–C(38)	97.2(3)
C(36)–C(31)–S(1)	118.2(4)	C(32)–C(31)–S(1)	120.3(4)

fragment in **1** corresponds to that of free (R)-(+)-MTSO. Moreover, the angles O–S–C(Me), O–S–C(tolyl) and C(Me)–S–C(tolyl) of 104.5(4), 105.9(3) and 97.2(3)° respectively are practically identical with those (105.5, 106.5 and 97.6° respectively) of uncoordinated (R)-(+)-MTSO [30]. Finally, the Flack parameter, 0.0084, of **1** (with e.s.d. 0.0207, expected value 0 within 3 e.s.d.s for correct absolute structure) confirms identical absolute configurations, and is in agreement with the findings of Axelord et al. [33] and de la Camp and Hope [30].

5. Crystal structure of $[(C_9H_7)_3La \cdot TPPO]$ (2)

In spite of a widespread application of the TPPO ligand, even in lanthanoid chemistry, the crystal structure of only one representative of the complex type $[(C_5H_5)_3M \cdot TPPO]$ **20** has been described in a Ph.D. Thesis (M = Yb [34]). The related tris(indenyl) complex **2** crystallizes, in contrast to **1** and **20**, in the non-chiral space group $R\bar{3}$ (Table 2), although its molecular structure (Fig. 3) is obviously of type A. Hence, both

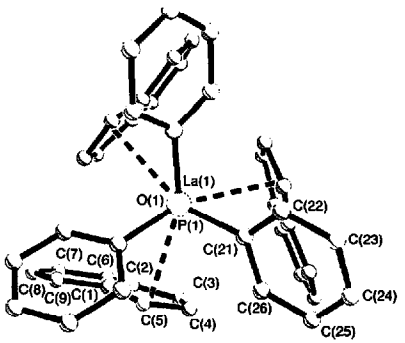

Fig. 3. Molecular structure of 2 viewed along the P–O–La axis for one case of disorder only.

enantiomers of the stereogenic $(C_9H_7)_3LaO$ fragment must be present in the unit cell of **2**. Owing to a strictly linear La–O–P backbone, each molecule possesses one C_3 axis as a dominating symmetry element, so that not only all three C_9H_7 ligands, but likewise the three phosphorus-bonded C_6H_5 groups, become crystallographically equivalent. Each $OP(C_6H_5)_3$ fragment is as usual propeller-shaped [15–17], acting as a second stereogenic centre of the molecule, so that in fact two crystallographically equivalent diastereomers should result. In view of the very special nature of the two stereogenic centres of **2**, we did not, however, make use here of the fundamental Cahn–Ingold–Prelog rules [35,36] to assign the two diastereomers appropriately as an (R,S)/(S,R) or (S,S)/(R,R) pair. [Correspondingly, also, the prefixes 'threo-' and 'erythro-' (for pairs of diastereomers with two stereogenic centres) do not appear applicable here to arrive at a meaningful differentiation.]

The two diastereomers of **2** contain non-disordered $OP(C_6H_5)_3$ propellers whose configurations behave exactly as mutual mirror images (Fig. 4). After Bradley et al. [15] had briefly mentioned the alternative configurations of the PPh_3 fragment, Dunitz and coworkers [37,38] studied extensively the configurations of free and coordinated TPPO. More recently, Brunner et al. [17] have drawn attention to the potential chirality of the PPh_3 fragment again. In one case, they have succeeded in studying single crystals of both epimers with respect to the two TPPO configurations of a ruthenium half-sandwich complex with three stereogenic centres. Interestingly, most of the reported crystal structures of TPPO-containing metal complexes, including that of **20**, have turned out to involve TPPO units in either a right- or left-helical configuration only.

Unlike the three phenyl groups, all indenyl ligands of **2** turn out to be strongly disordered. For this reason, the C_5 units were considered for the calculation as fixed, regular pentagons, and the C_6 units as fixed regular hexagons respectively. Fig. 5 explains the actual mode of disorder for one of the two diastereomers of **2**. Optimal convergence resulted for an occupancy factor of 0.5. Similar situations are frequently found in the literature, one strongly related example being the dinuclear $[\{(C_9H_7)_3Nd\}_2Cl]$ anion of compound **14** [12], wherein only the two 'meridionally' oriented indenyl ligands are disordered. In **2**, the C_5 centre of situation (a) of Fig. 5 deviates from the C_5 centre of situation (b) by 43.7 pm (deviation of the two corresponding centres of the adjacent C_6 unit 141.9 pm!). Related C_9H_7 units in the disordered positions (a) and (b) are no longer coplanar.

The La–O distance in **2** (Table 6) is even slightly shorter than in **1** and in the complex $[\{Me_3Si)_2N\}_3La \cdot TPPO]$ [15] (by 6.6 and 1.8 pm). Moreover, the La–O distance in **2** exceeds the Yb–O distance in $[(C_5H_5)_3Yb \cdot TPPO]$ [34] by 12.7 pm, which difference is significantly smaller than that of the ionic radii of La^{3+} and Yb^{3+} (ca. 17.2 pm). The O–P distance in **2** of 148.6 pm is almost unchanged compared with that of free TPPO (149.1–149.4 pm [38], 146–147 pm [39]). In view of the strict linearity of the La–O–P backbone, the La–O bond in **2** might even profit from additional O → La

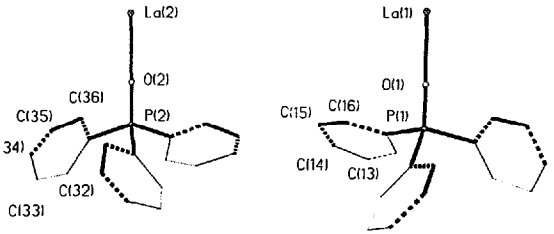

Fig. 4. Schematic view of the two enantiomeric configurations of the PPh_3 fragment in **2**.

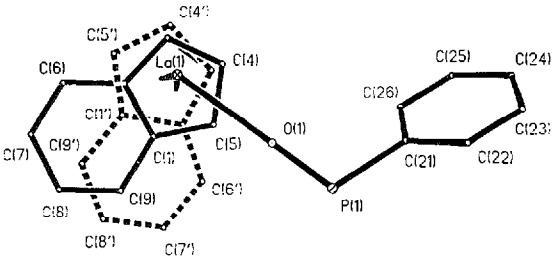

Fig. 5. Schematic representation of the two cases of disorder of one indenyl fragment of complex **2**. Dotted lines, situation (b).

π-donor contributions. In $[(C_5H_5)_3Yb \cdot TPPO]$, the Yb–O–P angle is significantly more 'acute' than in **2** (161.8° [34]). The five La–C distances in **2** vary between 269.6 and 295.6 pm (Table 6).

According to the elemental analyses and ^1H solution NMR spectra, crystals of **2** dried at room temperature should contain non-bonded solvent (i.e. toluene) molecules. In fact, crystallographically, two extra 'atoms' have been detected on the C_3 axis of each molecule. The appearance of additional 'atom'-like features on the electron density map is most probably due to strongly disordered 'guest' molecules. Situations like this are quite common and may be met particularly when the refinement converges towards a comparatively high R value [40].

6. Solution ^1H NMR spectroscopy

Our interest in the solution NMR spectra of the two title complexes **1** and **2**, as well as of the related diphenyl sulphoxide (DPSO) adduct **3**, was mainly due to the question of whether any of the distinct molecular conformations detectable in the crystalline state would still be retained in solution. In Fig. 6, a survey of the ^1H NMR spectra of **1**, **2** and **3** (solvent C_6D_6) is shown for the spectral range 5.5 to 8.0 ppm, wherein all resonances of the indenyl protons should appear. Strictly speaking, all three spectra are of higher order, although the following discussion will refer tentatively to a quasi-first-order appearance. While up to ca. 6.8 ppm only the resonances of the three C_5 protons are seen, the subrange above ca. 6.8 ppm is partially perturbed by the extra resonances of different aryl groups (i.e. of p-tolyl in the case of **1** and phenyl in the case of **2** and **3**). Below 5.5 ppm only complex **1** displays the two equally intense methyl resonances of its MTSO ligand (see Table 7). In contrast to samples of **2** dried at 100 °C, solutions of crystals dried only at room temperature gave rise to an additional signal at 2.11 ppm (solvent C_6D_6), which has been ascribed to toluene molecules contained in the crystals. The relative intensity of this extra resonance suggests the composition $2 \cdot 0.5$MePh (vide supra). In CD_2Cl_2 solution, still another resonance occurs between 3.0 and 3.5 ppm, which is tentatively assigned to free indene, or to an indene derivative. Nevertheless, a set of resonances typical of indenyl units appears throughout at slightly higher fields than in C_6D_6 solution. The phenyl resonances are, on the contrary, shifted towards lower field. The resonance patterns of **2** and **3** strongly resemble those expected, and actually reported [41,42], for complexes with rapidly (on the NMR timescale) rotating C_9H_7 ligands. Owing to this intramolecular motion, each C_9H_7 skeleton becomes symmetrical with respect to a mirror plane passing its C2 atom (Fig. 6). Consequently, in addition to one doublet and one triplet for the three C_5 protons, one AA'BB' multiplet consisting essentially of two well-separated quasi-quartets (due to the four benzo protons) appear. In contrast, owing to the presence of a dissymmetric sulphur atom, the virtual mirror planes are absent in adduct **1**, and the resonances of the pairwise prochiral indenyl protons H1/H3, H4/H7 and H5/H6 experi-

Table 6
Selected bond lengths (pm) and bond angles (°) for **2**

La(1)–O(1)	238.7(6)	O(1)–P(1)	148.6(6)
P(1)–C(21)	179.5(5)	C(21)–C(26)	139.2(7)
C(21)–C(22)	137.6(7)	C(22)–C(23)	139.1(8)
C(23)–C(24)	135.1(9)	C(24)–C(25)	136.3(9)
C(25)–C(26)	137.0(9)		
disorder a		disorder b	
La(1)–C(1)	295.6(6)	La(1)–C(1')	295.6(6)
La(1)–C(2)	295.5(6)	La(1)–C(2')	295.5(6)
La(1)–C(3)	289.3(8)	La(1)–C(3')	289.3(8)
La(1)–C(4)	279.6(9)	La(1)–C(4')	279.6(9)
La(1)–C(5)	289.3(8)	La(1)–C(5')	289.3(8)
La(1) ··· R51	265.1	La(1) ··· R52	265.1
R51 ··· R52	43.7	R61 ··· R62	141.9
P(1)–O(1)–La(1)	180.0	O(1)–P(1)–C(21)	111.02(14)
C(21)–P(1)–C(21a)	107.9		
O(1)–La(1)–R51	95.6	O(1)–La(1)–R52	105.1
R51–La(1)–R51a	119.1	R52–La(1)–R52a	113.5
R61–R51–La(1)	97.1	R62–R52–La(1)	96.8
R51–La(1)–R52	9.5		

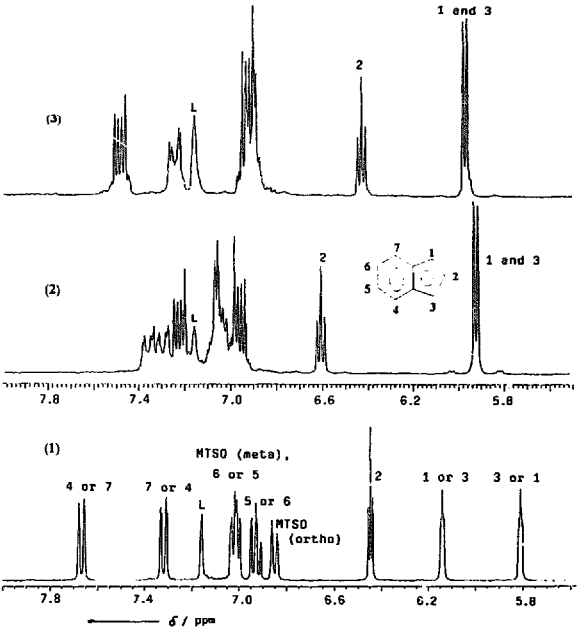

Fig. 6. Comparison of the ^{1}H NMR spectra of **1**, **2** and **3** between 5.6 and 8.0 ppm (L: resonance of C_6D_6 of 98% D). Numbers of corresponding ring carbon atoms are noted except for the phenyl/benzo resonance ranges of **2** and **3**.

Table 7
Survey of observed ^{1}H NMR data for **1**, **2** and **3** (all measurements at room temperature)

Compound	Resonances of C_9H_7 protons δ (ppm)				Resonances of protons of base L δ (ppm)	
	H-1 and/or 3	H-2	H-4 and/or 7	H-5 and/or 6	CH_3	$C_6H_{4/5}$
1 (360 MHz, C_6D_6)	5.81 (s, 3H) [a]	6.44 (t, 3H) [a]	7.32 (d, 3H) [a]	6.93 (t, 3H) [a]	1.94 (s, 3H, S-bonded)	6.84 (d, 2H) [c]
	6.14 (s, 3H) [a]	J_{HH} = 3.35 Hz	J_{HH} = 8.20 Hz	J_{HH} = 7.4 Hz	1.80 (s, 3H, -C_6H_4-bonded)	J_{HH} = 8.07 Hz
			7.66 (d, 3H) [a]	7.01 (t, 3H) [a]		6.99–7.04 (d, 2H) [c,d]
			J_{HH} = 8.22 Hz	J_{HH} = 7 Hz		
2 (200 MHz, C_6D_6)	5.92 (d, 6H)	6.60 (t, 3H)	7.22 (q, 6H) [a]	6.95 (q, 6H) [a]		7.05 (m, 9H) [e]
	J_{HH} = 3.36 Hz	J_{HH} = 3.37 Hz	J_{HH} ≈ 3 Hz [b]	J_{HH} ≈ 3 Hz [b]		7.33 (m, 6H) [d]
2 (200 MHz, CD_2Cl_2)	5.62 (d, 6H)	6.20 (t, 3H)	7.05 (q, 6H) [a]	6.84 (q, 6H) [a]		
	J_{HH} = 3.36 Hz	J_{HH} = 3.34 Hz	J_{HH} ≈ 3 Hz [b]	J_{HH} ≈ 3 Hz [b]		7.54 (m, 15H) [e]
3 (200 MHz, C_6D_6)	5.97 (d, 6H)	6.43 (t, 3H)	7.84 (q, 6H)	6.90 (m, 6H)		6.89 (m, 6H) [c,e]
	J_{HH} = 3.36 Hz	J_{HH} = 3.37 Hz	J_{HH} ≈ 3 Hz [b]	J_{HH} = 3 Hz [b]		7.24 (dd, 4H) [d]
						J_{HH} = 7.65 Hz

[a] Idealized designation of multiplicity.
[b] Averaged value only.
[c] Covered partially by indenyl resonances.
[d] Protons in *ortho* positions to S or P atoms.
[e] Protons in *meta* and/or *para* positions.

ence diasterotopic splitting. Thus, the initial doublet of the atoms H1 and H3 (to be seen in the spectra of **2** and **3**) is split into two separate resonances of some faint additional structuring. Moreover, the C_6 proton multiplet separates into two quasi-doublets (of H4/H7) and two triplets (of H5/H6). The resulting quasi-first-order spectrum of **1** is similar to that of the recently reported [43] complex $[O\{SiMe_2C_9H_6\}_2ZrCl_2]$, **21**, tetramethyl in which two indenyl ligands are connected by a disiloxane bridge. Interestingly, the diasterotopic splitting of the proton pairs H1/H3 and H4/H7 of **1** is of the same magnitude as in **21** (0.33 vs. 0.34 ppm), suggesting that the chiral sulphur atom influences both the C_5 and the C_6 portions of the ligand similarly, probably owing to intramolecular C_9H_7 rotation. A resonance pattern very similar to that displayed by complex **1** is in fact also expected for a strictly rigid type A complex. In the presence of (R)-(+)-MTSO, however, two very similar, but not strictly identical, spectra of different intensity should occur, as two chemically slightly different epimers are expected to coexist in solution. The observation of a spectrum of one singular species only confirms that at least at room temperature, rapid epimerization (owing to intramolecular ligand mobility) takes place in solution. Unfortunately, the low solubility of all three complexes **1–3** in deuterated solvents principally suitable for low temperature NMR studies has so far not admitted any NMR experiments below room temperature.

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