

Polyhedron 21 (2002) 1579-1588



www.elsevier.com/locate/poly

## Scandium halide complexes of phosphine- and arsine-oxides: synthesis, structures and <sup>45</sup>Sc NMR studies

Nicholas J. Hill, William Levason\*, Michael C. Popham, Gillian Reid, Michael Webster

Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK

Received 31 October 2001; accepted 20 February 2002

#### Abstract

The reactions of ScCl<sub>3</sub>·6H<sub>2</sub>O, ScBr<sub>3</sub>·6H<sub>2</sub>O and ScI<sub>3</sub>·8H<sub>2</sub>O with Ph<sub>3</sub>PO, Ph<sub>3</sub>AsO, Ph<sub>2</sub>MePO, Me<sub>3</sub>PO and Me<sub>3</sub>AsO have been examined in EtOH or Me<sub>2</sub>CO solution. The new complexes [ScCl(Me<sub>3</sub>PO)<sub>5</sub>]Cl<sub>2</sub>, [Sc(Me<sub>3</sub>PO)<sub>6</sub>]X<sub>3</sub> (X = Br or I), [ScX<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]X, [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]X<sub>3</sub> (X = Cl, Br or I), [ScCl<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>] and [ScBr<sub>2</sub>(Ph<sub>2</sub>MePO)<sub>4</sub>]Br were isolated as solids and were characterised by analysis, IR and multinuclear (<sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>45</sup>Sc) NMR spectroscopy and conductance measurements. The crystal structures of [ScBr<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]Br·1/2Et<sub>2</sub>O, [ScCl<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]Cl and [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Br<sub>3</sub> are also reported. The solution speciation (in CH<sub>2</sub>Cl<sub>2</sub> or MeNO<sub>2</sub>) in the various systems was examined by multinuclear NMR spectroscopy. The <sup>45</sup>Sc NMR chemical shifts and line widths show systematic trends with donor set and symmetry, which are described. No reaction between these ligands and ScF<sub>3</sub>·1/2H<sub>2</sub>O was observed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Scandium; Phosphine oxide; Arsine oxide; X-ray structures; <sup>45</sup>Sc NMR

#### 1. Introduction

The chemistry of scandium is the least studied of any 3d element, although interest in its complexes has increased in recent years with applications for example, in  $\alpha$ -olefin polymerisation catalysis [1,2], various organic functional group transformations [3,4], and sol-gel preparations for oxide materials [5]. The quadrupolar <sup>45</sup>Sc nucleus ( $^{45}$ Sc = 100%, I = 7/2, Q (quadrupole moment) =  $-0.22 \times 10^{-28}$  m), which is one of the most sensitive NMR nuclei ( $D_c = 1700$ ) has been little used [6] but potentially should provide a very suitable probe for studying solution speciation. We have reported [7,8] detailed studies of  $Sc(NO_3)_3$  and  $Y(NO_3)_3$ complexes with R<sub>3</sub>PO and R<sub>3</sub>AsO ligands which exhibit a range of stoichiometries including nine-coordinate  $[Y(R_3PO)_3(NO_3)_3],$ eight-coordinate  $[M(R_3PO)_4 (NO_3)_2$ <sup>+</sup> (M = Sc or Y) and [Sc(Ph<sub>3</sub>PO)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>], and six-coordinate  $[M(Me_3AsO)_6]^{3+}$  (M = Sc or Y). In all these complexes the coordinated nitrate groups are bidentate, so quite different behaviour is to be expected with the monoatomic halide ligands. We have also reported [9] studies of yttrium halide complexes of these ligands, all of which are six-coordinate  $[YX_2(Ph_3PO)_4]Z$  $(X = Cl, Br \text{ or I}; Z = X \text{ or PF}_6), [YX_3(Ph_2MePO)_3],$  $[YCl_2(Ph_2MePO)_4]PF_6, [YCl(Ph_3PO)_5][SbCl_6]_2, [Y(Me_3-PO)_6]X_3, [YX_2(Ph_3AsO)_4]X and [Y(Me_3AsO)_6]Cl_3. No$ complexes of scandium halides with pnictogen oxideligands have been described, and hence we have nowcarried out systematic studies of the reactions of $scandium halides ScX_3 <math>\cdot n$  H<sub>2</sub>O (X = F, Cl, Br or I) with Ph\_3PO, Ph\_3AsO, Me\_3PO, Ph\_2MePO and Me\_3AsO.

#### 2. Results and discussion

#### 2.1. Synthesis

Reactions of the hydrated scandium halides (excluding fluoride) with Ph<sub>3</sub>PO, Ph<sub>3</sub>AsO, Ph<sub>2</sub>MePO, Me<sub>3</sub>PO and Me<sub>3</sub>AsO in ethanol or acetone were carried out using a variety of molar ratios and reaction conditions. Pure solids could be isolated as described in the Section

<sup>\*</sup> Corresponding author. Tel.: +44-2380-595-000; fax: +44-2380-593-781

E-mail address: wxl@southampton.ac.uk (W. Levason).

4, although NMR studies show that often the solutions contain a mixture of species. The isolated complexes were identified by a combination of analysis, IR, <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>45</sup>Sc NMR spectroscopy, which also revealed that many retain lattice solvent even after prolonged drying in vacuum. The very poorly soluble  $ScF_3 \cdot 1/2H_2O$  did not react with Ph<sub>3</sub>PO or Me<sub>3</sub>PO in boiling ethanol or acetone even with extended reaction times.

#### 2.2. $[ScX_2(Ph_3PO)_4]X$

The reaction of  $ScX_3 \cdot nH_2O$  with  $Ph_3PO$  in ethanol in molar ratios 1:3–6 resulted in white  $[ScCl_2(Ph_3PO)_4]Cl$ ,  $[ScBr_2(Ph_3PO)_4]Br$  and yellow  $[ScI_2(Ph_3PO)_4]I$  (Table 1). Attempts to isolate  $[ScX_3(Ph_3PO)_3]$  using low  $ScX_3:Ph_3PO$  ratios or other solvents were unsuccessful. The presence of six-coordinate cations with  $O_4X_2$  donor sets was confirmed by an X-ray crystal structure of  $[ScBr_2(Ph_3PO)_4]Br \cdot 1/2Et_2O$ , which (Fig. 1, Table 2)

Table 1  ${}^{45}Sc$  and  ${}^{31}P\{^1H\}$  NMR data  $^a$ 

	$^{45}$ Sc( $w_{1/2}$ (Hz))	$^{31}P\{^{1}H\}$	Solvent
[ScCl <sub>2</sub> (Ph <sub>3</sub> PO) <sub>4</sub> ]Cl	75(850)	34.5	CH <sub>2</sub> Cl <sub>2</sub> -
			CDCl <sub>3</sub>
[ScCl <sub>3</sub> (Ph <sub>3</sub> PO) <sub>3</sub> ] <sup>b</sup>	121(1400)	34.0, 33.0	$CH_2Cl_2-$
			CDCl <sub>3</sub>
[ScBr <sub>2</sub> (Ph <sub>3</sub> PO) <sub>4</sub> ]Br	108(4500)	35.8	$CH_2Cl_2-$
			CDCl <sub>3</sub>
[ScCl(Me <sub>3</sub> PO) <sub>5</sub> ]Cl <sub>2</sub>	47.0(250)	56.0, 54.5	MeNO <sub>2</sub> -
			CDCl <sub>3</sub>
[ScCl <sub>2</sub> (Me <sub>3</sub> PO) <sub>4</sub> ]Cl <sup>b</sup>	85.0(360)	54.0(?)	MeNO <sub>2</sub> -
			CDCl <sub>3</sub>
[Sc(Me <sub>3</sub> PO) <sub>6</sub> ]Br <sub>3</sub> <sup>c</sup>	4.4(sept)	57.0(eight	MeNO <sub>2</sub> -
L.		lines)	CDCl <sub>3</sub>
[ScBr(Me <sub>3</sub> PO) <sub>5</sub> ]Br <sub>2</sub> <sup>b</sup>	51.5(850)	56.5, 55.0	MeNO <sub>2</sub> -
			CDCl <sub>3</sub>
$[Sc(Me_3PO)_6]I_3$	4.2(sept)	57.0 (eight	MeNO <sub>2</sub> -
		lines)	CDCl <sub>3</sub>
[Sc(Ph <sub>3</sub> AsO) <sub>4</sub> Cl <sub>2</sub> ]Cl	96(4000)		CH <sub>2</sub> Cl <sub>2</sub> -
	1.40(20.000)		CDCl <sub>3</sub>
$[Sc(Ph_3AsO)_4Br_2]Br$	140(20 000)		$CH_2Cl_2-$
	56(00)		CDCl <sub>3</sub>
$[Sc(Me_3AsO)_6]Cl_3$	56(80)		MeNO <sub>2</sub> -
$[\mathbf{C}_{\mathbf{r}}(\mathbf{M}_{\mathbf{r}}, \mathbf{A}_{\mathbf{r}}\mathbf{O})]\mathbf{D}_{\mathbf{r}}$	5((70)		CDCl <sub>3</sub>
$[Sc(Me_3AsO)_6]Br_3$	30(70)		$MeNO_2 - CDC1$
ISe(Ma AsO) II	56(70)		MaNO
[SC(10103ASO)6]13	30(70)		CDC1
[ScCl.(Ph.MePO).]	123(1100)	40 5 42 5	CH-Cl-
	125(1100)	40.5, 42.5	
[ScCl <sub>2</sub> (Ph <sub>2</sub> MePO) <sub>4</sub> ]Cl <sup>b</sup>	80(2000)	42.4	CH <sub>2</sub> Cl <sub>2</sub> -
	2000)		CDCl
[ScBr2(Ph2MePO)4]Br	100(8000)	41.0	CH <sub>2</sub> Cl <sub>2</sub> -
[30312(1 112:100 0)4]BI	100(0000)		
			,

<sup>a</sup> All spectra obtained at 295 K in solvent specified.

<sup>b</sup> Species obtained only in solution.

 $^{c}{}^{2}J(^{45}\text{Sc}-^{31}\text{P}) = 19$  Hz.



Fig. 1. View of the cation in  $[ScBr_2(Ph_3PO)_4]Br \cdot 1/2Et_2O$  showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity.

reveals a trans octahedral cation with Br-Sc-Br very close to linear  $179.04(5)^{\circ}$  and Br-Sc-O  $88.6(3)^{\circ}$ - $91.3(3)^{\circ}$ . The angles Sc-O-P are variable approximately  $154-166^{\circ}$ . The Sc-O(P) distances, approximately 2.07 are very similar to the values [7] in Å.  $[Sc(Ph_3PO)_2(NO_3)_3]$  or  $[Sc(Ph_2MePO)_4(NO_3)_2]^+$ , whilst the Sc-Br distances 2.652(1), 2.661(1) Å appear to be the first reported. The IR spectrum of each complex contains one very strong broad feature in the range 1150–1130 cm<sup>-1</sup> assignable as v(PO), which may be compared with 1195  $\text{cm}^{-1}$  in the 'free' ligand [7]. In CH<sub>2</sub>Cl<sub>2</sub> solution [ScCl<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]Cl approximates to a 1:1 electrolyte<sup>1</sup> and in the  ${}^{31}P{}^{1}H$  NMR spectrum there is a main feature at  $\delta$  34.5 attributed to the tetrakis(Ph<sub>3</sub>PO) complex, and weaker features at 26.0 (Ph<sub>3</sub>PO), 34.0, 33.0. The corresponding <sup>45</sup>Sc NMR spectrum has a broad resonance at  $\delta$  75 and a weaker broader resonance at  $\delta$  121. Addition of excess Ph<sub>3</sub>PO to these solutions results in the loss of the weaker

Table 2

Selected bond lengths (Å) and angles (°) for  $[ScBr_2(Ph_3PO)_4]Br\cdot 1/2Et_2O$ 

Bond lengths			
Sc(1)-Br(1)	2.652(1)	Sc(1)-Br(2)	2.661(1)
Sc(1) - O(1)	2.090(4)	Sc(1) - O(3)	2.059(4)
Sc(1) - O(2)	2.057(4)	Sc(1) - O(4)	2.074(4)
P-O	1.504(4) -		
	1.512(4)		
Bond angles			
Br(1)-Sc(1)-Br(2)	179.04(5)	Br-Sc(1)-O	88.6(3)-91.3(3)
Sc(1) - O(1) - P(1)	153.6(2)	Sc(1) - O(3) - P(3)	163.0(2)
Sc(1) - O(2) - P(2)	159.1(3)	Sc(1) - O(4) - P(4)	166.5(2)

<sup>31</sup>P{<sup>1</sup>H} NMR features at 34.0 and 33.0 and the <sup>45</sup>Sc NMR resonance at 121 which are attributed to mer-[ScCl<sub>3</sub>(Ph<sub>3</sub>PO)<sub>3</sub>]. In the presence of excess Ph<sub>3</sub>PO, [ScCl<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]Cl is the only complex present in significant amounts, but in its absence some decomposition into mer-[ScCl<sub>3</sub>(Ph<sub>3</sub>PO)<sub>3</sub>] occurs. Even a large excess of Ph<sub>3</sub>PO fails to produce substitution of further chloride ligands, in contrast to the corresponding yttrium systems [10]. The  ${}^{31}P{}^{1}H{}$  NMR spectra of  $[ScX_2(Ph_3PO)_4]X$  (X = Br or I) in CH<sub>2</sub>Cl<sub>2</sub> solution show only a single resonance in each and the conductances do not change significantly on addition of Ph<sub>3</sub>PO, consistent with  $[ScX_2(Ph_3PO)_4]X$  as the only species present. The <sup>45</sup>Sc NMR spectrum of the bromide confirms this with a broad feature at  $\delta$  108, but the <sup>45</sup>Sc resonance of the iodo-complex is extremely broad ( $\delta$  ca. 200,  $w_{1/2}$  ca. 20000 Hz) and whilst the  $\delta$  value is reasonable for a O<sub>4</sub>I<sub>2</sub> set, the line-width could clearly obscure any other species present.

# 2.3. $[ScCl(Me_3PO)_5]Cl_2$ and $[Sc(Me_3PO)_6]X_3$ $(X_3 = Br \text{ or } I)$

The reaction of  $ScX_3 \cdot nH_2O$  with Me<sub>3</sub>PO in a 1:6 molar ratio in ethanol gave  $[Sc(Me_3PO)_6]X_3$  (X = Br or I), but only  $[ScCl(Me_3PO)_5]Cl_2$  for the lightest halide. The complexes are insoluble or poorly soluble in chlorocarbons, alcohols or acetone, but dissolve in nitromethane. In nitromethane solution, the <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H} and <sup>45</sup>Sc NMR spectra of [ScCl(Me<sub>3</sub>PO)<sub>5</sub>]Cl<sub>2</sub> show a mixture of species present, which can be identified as [ScCl(Me<sub>3</sub>PO)<sub>5</sub>]Cl<sub>2</sub>, [ScCl<sub>2</sub>(Me<sub>3</sub>PO)<sub>4</sub>]Cl (in ca. equal amounts), Me<sub>3</sub>PO and some unassigned minor species. In the presence of excess Me<sub>3</sub>PO, only  $[ScCl(Me_3PO)_5]Cl_2$  ( $\delta^{-45}Sc = 47$ ) is present in large amounts, but two weak resonances at  $\delta$  <sup>45</sup>Sc 11 and 4 are also seen, the latter due to a small amount of  $[Sc(Me_3PO)_6]^{3+}$  (see below). The molar conductivity of a  $10^{-3}$  mol dm<sup>-3</sup> solution in MeNO<sub>2</sub> is 117  $\Omega^{-1}$  cm<sup>2</sup>  $mol^{-1}$ , intermediate between 1:1 and 1:2 electrolytes and this increases with addition of Me<sub>3</sub>PO to 180  $\Omega^{-1}$  $cm^2 mol^{-1}$ , showing that excess phosphine oxide shifts the equilibrium in favour of the pentakis complex. An attempt to extract the chloride ligand from [ScCl(Me3-PO)<sub>5</sub>|Cl<sub>2</sub> with SbCl<sub>5</sub> in the presence of Me<sub>3</sub>PO was unsuccessful. Dissolution of [Sc(Me<sub>3</sub>PO)<sub>6</sub>]Br<sub>3</sub> in MeNO<sub>2</sub> also produces a mixture of complexes which can be identified by the NMR spectra as  $[Sc(Me_3PO)_6]^{3+}$  ( $\delta$ 

<sup>45</sup>Sc 4.5,  $\delta^{-31}P\{^{1}H\}$  56.5), [ScBr(Me<sub>3</sub>PO)<sub>5</sub>]<sup>2+</sup> ( $\delta^{-45}$ Sc 51.5,  $\delta^{-31}P\{^{1}H\}$  56.0, 55.0), Me<sub>3</sub>PO, and a minor species at  $\delta$  11 in the <sup>45</sup>Sc NMR spectrum. Addition of excess Me<sub>3</sub>PO shifts the equilibria in favour of  $[Sc(Me_3PO)_6]^{3+}$ , although very small amounts of the other complexes remain evident. In contrast to the initial solution where the resonances of  $[Sc(Me_3PO)_6]^{3+}$  in both <sup>45</sup>Sc and <sup>31</sup>P{<sup>1</sup>H} NMR spectra are broad with illdefined coupling, in the presence of excess Me<sub>3</sub>PO well resolved couplings are seen (Fig. 2) confirming the presence of the quadrupolar scandium in a cubic symmetry environment where relaxation is slow. The trends are continued in [Sc(Me<sub>3</sub>PO)<sub>6</sub>]I<sub>3</sub> in that the  $[Sc(Me_3PO)_6]^{3+}$  cation is the only major species in solution even in the absence of added Me<sub>3</sub>PO (there is also a feature at  $\delta$  11 in the <sup>45</sup>Sc spectrum). The weak feature in the <sup>45</sup>Sc NMR spectra of all three complexes at  $\delta$  approximately 11 is attributed to a solventocomplex  $[Sc(Me_3PO)_{6-n}(MeNO_2)_n]^{3+}$  since the resonance is suppressed by addition of Me<sub>3</sub>PO, and moreover is absent if the spectra are recorded in Me<sub>2</sub>CO solution (although solubility in acetone is very poor).

#### 2.4. $[ScX_2(Ph_3AsO)_4]X$

The reaction of  $ScX_3 \cdot nH_2O$  with Ph<sub>3</sub>AsO in 1:4 molar ratio in ethanol gave the *trans*-[ScX<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]X (X = Cl or Br) complexes. The iodide complex failed to give reproducible analytical data, it would appear to be obtained with a mixture of polyiodide–iodide counteranions, although spectroscopically the cation seems analogous to those with the lighter halides (cf. [YI<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]I<sub>5</sub>) [9]. The identity as *trans* octahedral



Fig. 2.  ${}^{45}$ Sc NMR spectrum of  $[Sc(Me_3PO)_6]^{3+}$  in MeNO<sub>2</sub> at 295 K in the presence of excess Me<sub>3</sub>PO.

 $<sup>^{1}</sup>$  CH<sub>2</sub>Cl<sub>2</sub> has rarely been used as a solvent for conductivity measurements and in the standard review (W.J. Geary, Coord. Chem. Rev., 7 (1971) 81), some doubts were raised about its value for this purpose. We have used it here and in previous papers (refs [7–9]) to correlate with the NMR data obtained in CH<sub>2</sub>Cl<sub>2</sub> solution, and with the typical conductances for the electrolyte types established using appropriate tetra-alkylammonium salts.

Table 3 Selected bond lengths (Å) and angles (°) for [ScCl<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]Cl

-			
Bond lengths			
Sc(1)-Cl(1)	2.562(4)	Sc(1)-Cl(2)	2.545(4)
Sc(1) - O(1)	2.079(7)	Sc(1) - O(3)	2.059(7)
Sc(1) - O(2)	2.089(7)	Sc(1) - O(4)	2.063(7)
As-O	1.651(7) -		
	1.668(7)		
Bond angles			
Cl(1)-Sc(1)-Cl(2)	179.8(1)	Cl-Sc(1)-O	88.6(3)-91.3(3)
Sc(1) - O(1) - As(1)	146.6(4)	Sc(1) - O(3) - As(3)	147.3(5)
Sc(1)-O(2)-As(2)	145.4(5)	Sc(1)-O(4)-As(4)	147.5(5)

cations was established by the X-ray structure of  $[ScCl_2(Ph_3AsO)_4]Cl$  (Table 3, Fig. 3). Like the Ph<sub>3</sub>PO complex (above) the scandium cation is *trans* octahedral with bond angles at scandium very close to those of a regular octahedron. The Sc–Cl distances 2.562(4), 2.545(4) Å are approximately 0.15 Å longer than observed in  $[ScCl_3(thf)_3]$  [10] or scandium chloride complexes of crown ethers [11]. The Sc–O(As) distances are very similar to those [8] in the eight-coordinate  $[Sc(Ph_3AsO)_4(NO_3)_2]^+$ , but the Sc–O–As angles (Table 3) are rather more acute than the Sc–O–P angles in  $[ScBr_2(Ph_3PO)_4]^+$ . In CH<sub>2</sub>Cl<sub>2</sub> solution the complexes are litle

in the presence of added ligand. For  $[ScCl_2(Ph_3AsO)_4]Cl$ the <sup>45</sup>Sc NMR spectrum is a broad ( $w_{1/2}$  4000 Hz) resonance at  $\delta$  96 and there was no evidence for any dissociation into a tris(Ph\_3AsO) complex (compare  $[ScCl_2(Ph_3PO)_4]Cl$  above). The <sup>45</sup>Sc NMR spectrum of  $[ScBr_2(Ph_3AsO)_4]Br$  has a very broad resonance ( $w_{1/2}$ 18 000 Hz) centred at approximately  $\delta$  140 ( $\pm$ 20), whilst we have been unable to observe a <sup>45</sup>Sc resonance from the iodocomplex.

#### 2.5. $[Sc(Me_3AsO)_6]X_3$

The reaction of  $ScX_3 \cdot nH_2O$  with Me<sub>3</sub>AsO in boiling ethanol readily affords the hexakis(Me<sub>3</sub>AsO) complexes; the contrast with [ScCl(Me<sub>3</sub>PO)<sub>5</sub>]Cl<sub>2</sub> is notable. The complexes are characterised by a sharp singlet in the <sup>1</sup>H NMR spectra at approximately  $\delta$  2.1, and a sharp <sup>45</sup>Sc NMR signal at  $\delta$  56. The IR spectra show three strong bands in the region 925–840 cm<sup>-1</sup> attributable to v(As-O) and methyl rocking modes. These data compare well with those reported [7] for [Sc(Me<sub>3</sub>-AsO)<sub>6</sub>](NO<sub>3</sub>)<sub>3</sub>, and the presence of [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]<sup>3+</sup> cations was confirmed by an X-ray crystal structure of [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Br<sub>3</sub> (Fig. 4, Table 4). As expected the dimensions of the cation are very similar to those reported previously for the corresponding nitrate salt



Fig. 3. View of the cation in  $[ScCl_2(Ph_3AsO)_4]Cl$  showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity.



Fig. 4. View of the cation in  $[Sc(Me_3AsO)_6]Br_3$  showing the atom numbering scheme. Ellipsoids are drawn at the 40% probability level. The Sc(1) is located on a centre of symmetry.

Table 4 Selected bond lengths (Å) and angles (°) for [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Br<sub>3</sub>

2.08(2)	Sc(1) - O(3)	2.11(2)
2.11(2)		
1.65(2)-1.69(2)		
89.5(6)	Sc(1) - O(1) - As(1)	133.8(9)
90.5(7)	Sc(1) - O(2) - As(2)	132.6(10)
88.3(6)	Sc(1) - O(3) - As(3)	146.3(10)
	2.08(2) 2.11(2) 1.65(2)-1.69(2) 89.5(6) 90.5(7) 88.3(6)	2.08(2) 2.11(2) 1.65(2)-1.69(2) 89.5(6) 90.5(7) 88.3(6) Sc(1)-O(1)-As(1) Sc(1)-O(2)-As(2) Sc(1)-O(3)-As(3)

[8], but the structure serves to confirm the ScO<sub>6</sub> environment with uncoordinated bromide ions. All three complexes are 3:1 electrolytes in  $10^{-3}$  mol dm<sup>-3</sup> MeNO<sub>2</sub> solution, although the conductivities increase a little on addition of Me<sub>3</sub>AsO, possibly indicating some small amounts of coordination of halide, which is suppressed by excess ligand. However, only for [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Cl<sub>3</sub> is there any NMR evidence for a second complex in MeNO<sub>2</sub> solution, with a very weak singlet at  $\delta$  2.05 in the <sup>1</sup>H, and a broad weak feature at  $\delta$  84 in the <sup>45</sup>Sc spectrum, which we propose are due to small amounts of [ScCl(Me<sub>3</sub>AsO)<sub>5</sub>]<sup>2+</sup>, although this is ~ 5% of the concentration of the hexakis-complex.

#### 2.6. $[ScCl_3(Ph_2MePO)_3]$ and $[ScBr_2(Ph_2MePO)_4]Br$

Isolation of pure complexes containing Ph2MePO proved difficult and attempts to obtain reproducible products from the ScI<sub>3</sub>·8H<sub>2</sub>O-Ph<sub>2</sub>MePO system in either ethanol or acetone were unsuccessful. The white solid isolated from the reaction of hydrated ScCl<sub>3</sub> with Ph<sub>2</sub>MePO in ethanol or acetone was identified as the [ScCl<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>] complex by analysis. In CH<sub>2</sub>Cl<sub>2</sub> solution this complex partially rearranges into  $[ScCl_2(Ph_2MePO)_4]^+$  readily identified by a combination of  ${}^{45}Sc$  and  ${}^{31}P{}^{1}H$  NMR spectroscopy. A small amount of Ph2MePO is also present and there are weak features in the <sup>45</sup>Sc NMR spectrum which have no corresponding resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. From the NMR spectra the two scandium species are tentatively assigned as mer-[ScCl<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>] and *trans*- $[ScCl_2(Ph_2MePO)_4]^+$  isomers. Addition of excess Ph<sub>2</sub>MePO to the solution converts the scandium to the  $[ScCl_2(Ph_2MePO)_4]^+$  and this is accompanied by the expected increase in conductance. In contrast the bromide complex isolated was [ScBr<sub>2</sub>(Ph<sub>2</sub>MePO)<sub>4</sub>]Br, and in solution in CH<sub>2</sub>Cl<sub>2</sub> this appears to be the only significant species present and the conductance is that of a 1:1 electrolyte, showing that [ScBr<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>] does not form.

### 2.7. <sup>45</sup>Sc NMR data

The use of <sup>45</sup>Sc and <sup>31</sup>P NMR spectroscopy to identify solution species has been discussed in previous sections. There are advantages and disadvantages to both nuclei in these systems. The  $I = 1/2^{31}$ P nucleus is very sensitive, but the chemical shifts vary little between complexes in each ScX<sub>3</sub>-R<sub>3</sub>PO system, and coincidence or only partial resolution of resonances is a concern when identifying minor species or isomers present. The <sup>45</sup>Sc nucleus is also inherently very sensitive, but the line widths (Table 1) vary greatly and in some systems this also causes problems. The <sup>45</sup>Sc NMR spectra often show a number of weak and usually sharp resonances in addition to those of the major species, which we tentatively assign to hydrolysis/solvolysis impurities in solution, although there remains the possibility that some are due to other isomers of the phosphine oxide complexes. In situ <sup>45</sup>Sc NMR studies by Kirakosyan et al. [12,13], on ScCl<sub>3</sub>–(RO)<sub>3</sub>PO (L) systems (R = Me, Et or Bu) identified a range of complexes including  $[ScClL_5]^{2+}$ , cis- and trans- $[ScCl_2L_4]^{2+}$ , fac- and mer- $[ScCl_3L_3]$ , *cis*- and *trans*- $[ScCl_4L_2]^-$ . In these phosphate systems the line-widths are much smaller than in the present phosphine oxides and often partial resolution of  ${}^{45}Sc - {}^{31}P$  couplings were seen. The line widths in the present complexes increase Cl < Br « I and in several cases we were unable to observe resonances from the iodo-complexes. There is also a significant increase in line-width  $R_3PO < R_3AsO$  in the halide systems. The broad lines indicate that the electric field gradient is substantial, promoting fast quadrupolar relaxation of the <sup>45</sup>Sc nucleus. The increasing line width  $Cl \rightarrow Br \rightarrow I$  is predictable as the disparity in electron density increases between the hard O (of Ph<sub>3</sub>AsO) and the increasingly soft halide, but clearly the effect is much greater than in the Ph<sub>3</sub>PO analogues. We have shown elsewhere [8] that the donor power towards oxophilic metals is  $R_3AsO >$ R<sub>3</sub>PO and this is manifested here in increased electric field asymmetry. The <sup>45</sup>Sc NMR chemical shifts show systematic trends with donor set (Table 1, Scheme 1) the  $\delta$  (<sup>45</sup>Sc) shifting to high frequency with halide Cl  $\rightarrow$  Br  $\rightarrow$ I and  $R_3PO \rightarrow R_3AsO$ . This pattern is also seen in the <sup>89</sup>Y NMR shifts of the yttrium analogues [9]. As discussed above, only for  $[Sc(Me_3PO)_6]^{3+}$  were  ${}^{31}P-{}^{45}Sc$  couplings resolved (Fig. 2). We also note that intermolecular exchange with added R<sub>3</sub>PO or R<sub>3</sub>AsO is slow on the NMR time-scales in these systems.

#### 3. Conclusions

All the scandium halide complexes isolated are based upon six-coordinate metal centres. The results also suggest that the affinity of scandium for chloride is much greater than for the heavier halides; compare [ScCl(Me<sub>3</sub>PO)<sub>5</sub>]Cl<sub>2</sub> and [Sc(Me<sub>3</sub>PO)<sub>6</sub>]X<sub>3</sub> (X = Br or I), and that [ScX<sub>3</sub>(R<sub>3</sub>PO)<sub>3</sub>] form only with X = Cl. Comparison with the yttrium halide systems [9] shows that whilst both metals form [MX<sub>2</sub>(Ph<sub>3</sub>EO)<sub>4</sub>]X (E = As or P), in the presence of excess Ph<sub>3</sub>PO, the yttrium systems also form [YX(Ph<sub>3</sub>EO)<sub>5</sub>]<sup>2+</sup>, whereas we have no evidence for pentakis complexes in the scandium systems. This is probably due to the smaller radius of scandium (r = 83 vs. 106 pm for Y) which may be unable to accommodate more than four bulky Ph<sub>3</sub>EO ligands. For both metals the affinity for R<sub>3</sub>AsO is greater than for R<sub>3</sub>PO.

#### 4. Experimental

Multinuclear NMR spectra were obtained on a Bruker DPX400 at 161.9 MHz  $({}^{31}P{}^{1}H{})$  and referenced to external 85% H<sub>3</sub>PO<sub>4</sub>, 97.2 MHz (<sup>45</sup>Sc) and referenced to 1 mol dm<sup>-3</sup>  $Sc(NO_3)_3$  in water at pH 1. Other physical measurements were made as before [7]. Ph<sub>3</sub>PO, Ph<sub>2</sub>MePO, Ph<sub>3</sub>AsO (Aldrich) and Me<sub>3</sub>PO (ALFA) were used as received. Me<sub>3</sub>AsO was made by H<sub>2</sub>O<sub>2</sub> oxidation of Me<sub>3</sub>As in diethyl ether and purified by sublimation in vacuo [8]. ScF<sub>3</sub> $\cdot$ 1/2H<sub>2</sub>O was made by precipitation from aqueous solutions of Sc<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and NaF, washed with water and dried in vacuo. ScBr<sub>3</sub>·6H<sub>2</sub>O was prepared by evaporating  $Sc_2O_3$  with 48% HBr, and recrystallising the product from H<sub>2</sub>O. Yield 79% (Found: Br, 60.8. Calc. for ScBr<sub>3</sub>·6H<sub>2</sub>O: Br, 61.0%). ScCl<sub>3</sub>·6H<sub>2</sub>O and ScI<sub>3</sub>· 8H<sub>2</sub>O were made by metathesis of aqueous solutions of scandium sulfate and the appropriate barium halide, removal of the precipitated BaSO<sub>4</sub>, and evaporation to dryness in vacuo. ScCl<sub>3</sub>·6H<sub>2</sub>O yield 90% (Found: Cl, 40.8. Calc. for ScCl<sub>3</sub>·6H<sub>2</sub>O: Cl, 41.0%). ScI<sub>3</sub>·8H<sub>2</sub>O yield 86% (Found: I, 66.7. Calc. for ScI<sub>3</sub>·8H<sub>2</sub>O: I, 66.8%).

#### 4.1. $[ScCl(Me_3PO)_5]Cl_2$

Ice-cold ethanol solutions (10 cm<sup>3</sup>) of  $ScCl_3 \cdot 6H_2O$ (0.13 g, 0.5 mmol) and Me<sub>3</sub>PO (0.28 g, 3.0 mmol) were mixed, stirred for 1 h and then concentrated to approximately 5 cm<sup>3</sup> and refrigerated overnight. The white solid was filtered off and dried in vacuo. Yield 0.24 g, 63%. (Found: C, 29.7; H, 8.1. Calc. for  $C_{15}H_{45}Cl_{3}O_{5}P_{5}Sc: C, 29.4; H, 7.4\%$ ). IR (cm<sup>-1</sup>) (CsI disc): 2964w, 2896w, 1421w, 1360w, 1299m, 1182w, 1109br,vs (PO), 959s, 872s, 845m, 762s, 682m, 559w, 427s. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 1.5(d)  ${}^{2}J({}^{31}P-{}^{1}H) =$ 14 Hz (Me<sub>3</sub>PO); 1.90(d)  $^{2}J(^{31}P-^{1}H) = 14$  Hz  $([ScCl_2(Me_3PO)_4]^+);$ 1.8(d) [4H] 1.70(d) [H]  ${}^{2}J({}^{31}P-{}^{1}H) = 14$  Hz ([ScCl(Me<sub>3</sub>PO)<sub>5</sub>]<sup>2+</sup>).  ${}^{31}P\{{}^{1}H\}$ NMR (MeNO<sub>2</sub>) 36.5 (Me<sub>3</sub>PO), 54.0 ([ScCl<sub>2</sub>- $(Me_3PO)_4]^+$ ), 54.5 [P], 56.0 [4P] [ScCl $(Me_3PO)_5]^{2+}$ ). <sup>45</sup>Sc NMR (MeNO<sub>2</sub>) 47.0 ([ScCl(Me<sub>3</sub>PO)<sub>5</sub>]<sup>2+</sup>), 84.5



Scheme 1. Systematic trends in the  ${}^{45}$ Sc NMR chemical shifts. The values under formulae are the chemical shift, values over arrows the chemical shift differences. Data for the hexahaloscandate ions are taken from Ref. [6].

 $([ScCl_2(Me_3PO)_4]^+)$ .  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 117  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>PO 180.

4.2.  $[Sc(Me_3PO)_6]Br_3$ 

A solution of ScBr<sub>3</sub>·6H<sub>2</sub>O (0.20 g, 0.50 mmol) in icecold ethanol (10 cm<sup>3</sup>) was treated with Me<sub>3</sub>PO (0.28 g, 3.0 mmol) in ethanol (5 cm<sup>3</sup>), resulting in an immediate white precipitate. After stirring for 1 h, the solid was filtered off and dried in vacuo. Yield 0.29 g, 54%. (Found: C, 25.2; H, 6.6. Calc. for C<sub>18</sub>H<sub>54</sub>Br<sub>3</sub>O<sub>6</sub>P<sub>6</sub>Sc: C, 25.8; H, 6.5%). IR (cm<sup>-1</sup>) (CsI disc): 2964w, 2897w, 1422m, 1361w, 1312m, 1299m, 1183w, 1110vbr s (PO), 960s, 872s, 762m, 682m, 428s, 418s. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 1.5(d)  ${}^{2}J({}^{31}P^{-1}H) = 14$  Hz ([Scfr(Me<sub>3</sub>PO); 1.85(d)  ${}^{2}J({}^{31}P^{-1}H) = 14$  Hz ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>); 1.70(d) [H], 1.85(d) [4H]  ${}^{2}J({}^{31}P^{-1}H) = 14$  Hz ([ScBr(Me<sub>3</sub>PO)<sub>5</sub>]<sup>2+</sup>).  ${}^{31}P{}^{1}H{}$  NMR (MeNO<sub>2</sub>) 36.5 (Me<sub>3</sub>PO), 56.5(m) ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>), 56.0 [4P], 55.0 [P] ([ScBr(Me<sub>3</sub>-PO)<sub>5</sub>]<sup>2+</sup>).  ${}^{45}Sc$  NMR (MeNO<sub>2</sub>) 51.5 ([ScBr(Me<sub>3</sub>-PO)<sub>5</sub>]<sup>2+</sup>), 4.5 ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>).  ${}^{A}_{M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 179  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>PO 221.

#### 4.3. $[Sc(Me_3PO)_6]I_3 \cdot EtOH$

Me<sub>3</sub>PO (0.14 g, 1.5 mmol) and ScI<sub>3</sub>·8H<sub>2</sub>O (0.11 g, 0.25 mmol) were dissolved separately in boiling ethanol  $(2 \times 5 \text{ cm}^3)$  and the solutions mixed to yield a pale yellow precipitate. After stirring for 1 h this was filtered off and dried in vacuo. Yield 0.14 g, 67%. (Found: C, 24.2; H, 6.1. Calc. for C<sub>20</sub>H<sub>60</sub>I<sub>3</sub>O<sub>7</sub>P<sub>6</sub>Sc: C, 23.6; H, 5.9%). IR (cm<sup>-1</sup>) (CsI disc): 3480br, 2964w, 2898w,

1421m, 1360w, 1312m, 1299m, 1184w, 1108vbr s (PO), 957s, 871s, 761m, 681m, 427s. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 1.1(t) [3H], 3.4(q) [2H] (EtOH), 1.88(d) [54H] <sup>2</sup>J(<sup>31</sup>P<sup>-1</sup>H) = 13 Hz ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>); 1.82– 1.78(br). <sup>31</sup>P{<sup>1</sup>H} NMR (MeNO<sub>2</sub>) approximately 57.5(s) ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>). <sup>45</sup>Sc NMR (MeNO<sub>2</sub>) 4.0 ([Sc(Me<sub>3</sub>PO)<sub>6</sub>]<sup>3+</sup>), 9.0.  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 189  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>PO 242.

4.4.  $[ScCl_2(Ph_3PO)_4]Cl$ 

Warm (60 °C) ethanol solutions (10 cm<sup>3</sup>) of ScCl<sub>3</sub>. 6H<sub>2</sub>O (0.13 g, 0.5 mmol) and Ph<sub>3</sub>PO (0.55 g, 2.0 mmol) were mixed, concentrated to approximately 10 cm<sup>3</sup> and then refrigerated for 1 h. The white solid was filtered off and dried in vacuo. Yield 0.35 g, 50%. (Found: C, 68.4; H, 4.7. Calc. for  $C_{72}H_{60}Cl_3O_4P_4Sc$ : C, 68.4; H, 4.8%). IR (cm<sup>-1</sup>) (CsI disc): 3055w, 1624w, 1591w, 1439m, 1358w, 1191w, 1152s (PO), 1122s, 1091s, 1046w, 1029w, 999m, 751m, 726s, 697s, 544s, 473m, 460m, 445m, 430m. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.0–7.9(m). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $([ScCl_2(Ph_3PO)_4]^+), 34.0 [2P],$ 33.0 [P] 34.5 ([ScCl<sub>3</sub>(Ph<sub>3</sub>PO)<sub>3</sub>]), 26.0 (Ph<sub>3</sub>PO). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) 76 ( $[ScCl_2(Ph_3PO)_4]^+$ ), 121 ( $[ScCl_3(Ph_3PO)_3]$ ).  $\Lambda_M$  $(10^{-3} \text{ mol } \text{dm}^{-3} \text{ CH}_2\text{Cl}_2) = 17 \ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}, +XS$ Ph<sub>3</sub>PO 22.

#### 4.5. $[ScBr_2(Ph_3PO)_4]Br \cdot CH_2Cl_2$

A solution of  $\text{ScBr}_3 \cdot 6\text{H}_2\text{O}$  (0.39 g, 1.0 mmol) in icecold ethanol (10 cm<sup>3</sup>) was added to  $\text{Ph}_3\text{PO}$  (1.11 g, 4.0 mmol) in ethanol (5 cm<sup>3</sup>) and stirred for 1 h. The solution was refrigerated and the white solid filtered off and dried in vacuo. It was recrystallised by dissolving in CH<sub>2</sub>Cl<sub>2</sub> and diffusion of diethyl ether. Yield 0.84 g, 60%. (Found: C, 59.0; H, 4.5. Calc. for C<sub>73</sub>H<sub>62</sub>Br<sub>3</sub>Cl<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Sc: C, 59.1; H, 4.2%). IR (cm<sup>-1</sup>) (CsI disc): 3056w, 1620w, 1591w, 1438m, 1358w, 1188w, 1137s(PO), 1120s, 1084s, 1028m, 1000m, 750m, 725s, 692s, 547s, 465m, 454m, 426w, 317m, 306m, 269m, 255m. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.0–7.6(m) [30H], 5.2 [H] (CH<sub>2</sub>Cl<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) 35.8. <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) 108. *Λ*<sub>M</sub> (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 21 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, +XS Ph<sub>3</sub>PO 23.

#### 4.6. $[ScI_2(Ph_3PO)_4]I \cdot 2H_2O$

This was made similarly to the chloride analogue, as a pale yellow solid. Yield 44%. (Found: C, 54.7; H, 3.7. Calc. for  $C_{72}H_{64}I_3O_6P_4Sc: C, 54.9; H, 4.1\%$ ). IR (cm<sup>-1</sup>) (CsI disc): 3466br, 3054w, 1624w, 1590w, 1438m, 1359w, 1187w, 1132s(PO), 1122s, 1073s, 1027m, 999m, 750m, 725s, 693s, 543s, 464m, 452m, 425w. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.0–7.7(m) [60H], 1.7 [4H] (H<sub>2</sub>O). <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) 38.0. <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) approximately 200 vbr.  $\Lambda_M$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 22  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 4.7. $[ScCl_2(Ph_3AsO)_4]Cl \cdot 2EtOH$

An ethanol solution (5 cm<sup>3</sup>) of Ph<sub>3</sub>AsO (0.32 g, 1.0 mmol) was added to a solution of ScCl<sub>3</sub>·6H<sub>2</sub>O (0.06 g, 0.25 mmol) in boiling ethanol (10 cm<sup>3</sup>). The mixture was concentrated to 5 cm<sup>3</sup> and refrigerated overnight. The white solid was separated and dried in vacuo. Yield 0.24 g, 64%. (Found: C, 58.9; H, 4.5. Calc. for C<sub>76</sub>H<sub>72</sub>-As<sub>4</sub>Cl<sub>3</sub>O<sub>6</sub>Sc: C, 59.5; H, 4.7%). IR (cm<sup>-1</sup>) (CsI disc): 3407br, 3055w, 1583w, 1485m, 1440m, 1358w, 1187w, 1162w, 1089s, 1070w, 1027m, 999m, 908vs (AsO), 883m, 745s, 692s, 480s, 458m. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.0–7.7(m) [60H], 1.2(t) [6H], 3.4(q) [4H] (EtOH). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) 96.  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 20  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Ph<sub>3</sub>AsO 24.

#### 4.8. $[ScBr_2(Ph_3AsO)_4]Br \cdot 5H_2O$

[ScBr<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]Br·5H<sub>2</sub>O was made similarly (54%) (Found: C, 51.4; H, 3.6. Calc. for C<sub>72</sub>H<sub>70</sub>As<sub>4</sub>Br<sub>3</sub>O<sub>9</sub>Sc: C, 51.9; H, 4.3%). IR (cm<sup>-1</sup>) (CsI disc): 3400br, 3051w, 1654m, 1582w, 1485m, 1440s, 1354w, 1185m, 1162w, 1088s, 1027w, 999m, 883s (AsO), 762s, 744s, 691s, 482s, 473s, 457m, 413m. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.1–6.6(m) [60H], 1.8(br) [11H] (H<sub>2</sub>O). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) approximately 140.  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 19 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, +XS Ph<sub>3</sub>AsO 23.

#### 4.9. $[ScI_2(Ph_3AsO)_4]I$

[ScI<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]I was made similarly as a mustard coloured solid (46%). Not obtained analytically pure see text. IR (cm<sup>-1</sup>) (CsI disc): 3300m, 1636w, 1439m, 1359w, 1185w, 1161w, 1088s, 1027w, 998m, 883s,br (AsO), 739s, 690s, 477m, 457m, 419m. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.15–7.7(m). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) not observed.  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 20 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, +XS Ph<sub>3</sub>AsO 23.

#### 4.10. $[Sc(Me_3AsO)_6]Cl_3$

Scandium chloride hydrate (0.05 g, 0.19 mmol) was dissolved in boiling ethanol (10 cm<sup>3</sup>) and added to a solution of Me<sub>3</sub>AsO (0.21 g, 1.5 mmol) in ethanol (10 cm<sup>3</sup>), resulting in a white suspension. The solution was concentrated to approximately 10 cm<sup>3</sup> and the white solid filtered off and dried in vacuo. Yield 0.13 g, 71%. (Found: C, 22.1; H, 5.6. Calc. For C<sub>18</sub>H<sub>54</sub>As<sub>6</sub>Cl<sub>3</sub>O<sub>6</sub>Sc: C, 22.3; H, 5.6%). IR (cm<sup>-1</sup>) (CsI disc): 2981w, 2904w, 1418m, 1359w, 1295w, 1269m, 1114w, 924s, 874s, 844s, 647s, 420m. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 2.1(s), 2.05(w). <sup>45</sup>Sc NMR (MeNO<sub>2</sub>) 56.0 ([Sc(Me<sub>3</sub>AsO)<sub>6</sub>]<sup>3+</sup>), 84(vw) ([ScCl(Me<sub>3</sub>AsO)<sub>5</sub>]Cl<sub>2</sub>).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 214  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>AsO 251.

#### 4.11. $[Sc(Me_3AsO)_6]Br_3$

[Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Br<sub>3</sub> was made similarly. Yield 62%. (Found: C, 19.0; H, 5.0. Calc. for C<sub>18</sub>H<sub>54</sub>As<sub>6</sub>Br<sub>3</sub>O<sub>6</sub>Sc: C, 19.6; H, 5.0%). IR (cm<sup>-1</sup>) (CsI disc): 2982w, 2920w, 1653w, 1418m, 1359m, 1268m, 1088m, 926s, 874s, 846s, 648s, 420m. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 2.05(s). <sup>45</sup>Sc NMR (MeNO<sub>2</sub>) 56.0 ([Sc(Me<sub>3</sub>AsO)<sub>6</sub>]<sup>3+</sup>).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 239 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>AsO 281.

#### 4.12. $[Sc(Me_3AsO)_6]I_3 \cdot 3H_2O$

A solution of ScI<sub>3</sub>·8H<sub>2</sub>O (0.10 g, 0.17 mmol) in warm (60 °C) ethanol (10 cm<sup>3</sup>) was added to a solution of Me<sub>3</sub>AsO (0.14 g, 1.0 mmol) resulting in immediate precipitation of a yellowish solid. After stirring for 1 h this was filtered off and dried in vacuo. Yield 0.11 g, 53%. (Found: C, 15.8; H, 3.9. Calc. for C<sub>18</sub>H<sub>60</sub>-As<sub>6</sub>I<sub>3</sub>O<sub>9</sub>Sc: C, 16.7; H, 4.6%). IR (cm<sup>-1</sup>) (CsI disc): 3440br, 2978w, 2902w, 1647w, 1417m, 1359w, 1265m, 1088w, 921s, 872s, 844s, 646s, 420m. <sup>1</sup>H NMR (300 K, CD<sub>3</sub>NO<sub>2</sub>): 2.1(s) [10H], 2.05(vw) 1.7 [H] (H<sub>2</sub>O). <sup>45</sup>Sc NMR (MeNO<sub>2</sub>) 56.0 ([Sc(Me<sub>3</sub>AsO)<sub>6</sub>]<sup>3+</sup>).  $\Lambda_{\rm M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> MeNO<sub>2</sub>) = 253  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, +XS Me<sub>3</sub>AsO 280.

#### 1587

#### 4.13. $[ScCl_3(Ph_2MePO)_3] \cdot H_2O$

Solutions of ScCl<sub>3</sub>·6H<sub>2</sub>O (0.06 g, 0.25 mmol) and  $Ph_2MePO$  (0.16 g, 0.75 mmol) in boiling acetone (2 × 10  $cm^{3}$ ) were mixed resulting in a white suspension. Hexane  $(10 \text{ cm}^3)$  was added and the white sticky solid separated and stirred with diethyl ether for 24 h. The white powder was dried in vacuo. Yield 0.17 g, 59%. (Found: C, 56.8; H, 5.1. Calc. for C<sub>39</sub>H<sub>41</sub>Cl<sub>3</sub>O<sub>4</sub>P<sub>3</sub>Sc: C, 57.2; H, 5.0%). IR (cm<sup>-1</sup>) (CsI disc): 3420br, 3056w, 2913w, 1643m, 1439s, 1359w, 1143s(PO), 1127sh, 1099m, 1028w, 998w, 901s, 783m, 746s, 720m, 696s, 517s, 507sh, 429w. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.7br (H<sub>2</sub>O), 1.9(d)  ${}^{2}J_{PH} = 13$  Hz, 2.03(d)  ${}^{2}J_{PH} = 13$  Hz, 2.5(d)  ${}^{2}J_{PH} = 13$  Hz, 7.3–7.9(m). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) 123 ([ScCl<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>]), 80(w)  $([ScCl_2(Ph_2MePO)_4]^+)$ . <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>) 29.0 (Ph<sub>2</sub>MePO), 40.5 [P], 42.5 [2P] [ScCl<sub>3</sub>(Ph<sub>2</sub>MePO)<sub>3</sub>)], 42.4  $[ScCl_2(Ph_2MePO)_4)]^+$ .  $\Lambda_M (10^{-3} \text{ mol } dm^{-3} CH_2Cl_2) =$  $8 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ , +XS Ph<sub>2</sub>MePO 23.

#### 4.14. $[ScBr_2(Ph_2MePO)_4]Br$

To a solution of Ph<sub>2</sub>MePO (0.22 g, 1.0 mmol) in icecold acetone (10 cm<sup>3</sup>) was added a solution of ScBr<sub>3</sub>.  $6H_2O$  (0.09 g, 0.25 mmol) in acetone (5 cm<sup>3</sup>). After stirring for 1 h, the solution was concentrated to approximately 5 cm<sup>3</sup> and refrigerated overnight. The white precipitate was filtered off and dried in vacuo.

#### Table 5 Crystallographic data <sup>a</sup>

Yield 0.14 g, 49%. (Found: C, 55.3; H, 4.8. Calc. for  $C_{52}H_{52}Br_{3}O_{4}P_{4}Sc:$  C, 54.3; H, 4.6%). IR (cm<sup>-1</sup>) (CsI disc): 3420br, 3050w, 2908w, 1638m, 1486m, 1438s, 1363w, 1138s (PO), 1094m, 1073w, 1028m, 998w, 894s, 787m, 746s, 719m, 695s, 515s. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.92(d)  ${}^{2}J_{PH} = 13$  Hz, 7.3–7.9(m). <sup>45</sup>Sc NMR (CH<sub>2</sub>Cl<sub>2</sub>) 100,  $w_{1/2} = 5000$  Hz.  ${}^{31}P{}^{1}H{}$  NMR (CH<sub>2</sub>Cl<sub>2</sub>) 41.0, 40.3(w).  $\Lambda_{M}$  (10<sup>-3</sup> mol dm<sup>-3</sup> CH<sub>2</sub>Cl<sub>2</sub>) = 22  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

#### 4.15. X-ray crystallographic studies

Crystallographic details together with data collection and refinement parameters are given in Table 5. Crystals were obtained by vapour diffusion from MeNO<sub>2</sub>-Et<sub>2</sub>O systems (with excess Me<sub>3</sub>AsO added for that complex), or from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O. Data were recorded from small, modest quality crystals at low temperature using a Nonius Kappa CCD diffractometer. The structure solutions and refinements (on F or  $F^2$  (Cl compound)) were carried out using standard methods [14-17] except for [ScCl<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]Cl which was initially solved and refined in the triclinic space group  $P\bar{1}$  (no. 2) (with Z =4). The value of Z caused concern [18]; subsequent reexamination of the data showed systematic absences consistent with a monoclinic space group and the structure was re-solved and refined in this higher symmetry space group. Anisotropic refinement of

	$[ScBr_2(Ph_3PO)_4]Br\cdot 1/2Et_2O$	[ScCl <sub>2</sub> (Ph <sub>3</sub> AsO) <sub>4</sub> ]Cl	[Sc(Me <sub>3</sub> AsO) <sub>6</sub> ]Br <sub>3</sub>
Formula	$C_{72}H_{60}Br_{3}O_{4}P_{4}Sc + 1/2(C_{4}H_{10}O)$	C <sub>72</sub> H <sub>60</sub> As <sub>4</sub> Cl <sub>3</sub> O <sub>4</sub> Sc	C <sub>18</sub> H <sub>54</sub> As <sub>6</sub> Br <sub>3</sub> O <sub>6</sub> Sc
M	1434.89	1440.19	1100.82
Crystal system	triclinic	Monoclinic	monoclinic
Space group	<i>P</i> 1 (no. 2)	$P2_1/n$ (no. 14)	C2/c (no. 15)
a (Å)	14.2119(4)	18.436(2)	17.7475(5)
b (Å)	14.7923(4)	18.946(3)	16.9358(5)
c (Å)	17.6032(5)	18.393(3)	12.5771(4)
α (°)	66.695(2)	90.0	90.0
β(°)	80.919(1)	90.04(1)	96.643(1)
γ (°)	89.302(1)	90.0	90.0
U (Å <sup>3</sup> )	3351.0(2)	6424.5(18)	3754.9(2)
$T(\mathbf{K})$	150	120	120
Z	2	4	4
<i>F</i> (000) (e)	1462	2912	2136
Total number of observations	46 706	31 012	14 955
Number of unique observations $(R_{int})$	15012 (0.054)	9826 (0.16)	4371 (0.093)
Max/min transmission	0.668/0.581	0.269/0.240	0.314/0.288
Number of data in refinement	8868 $(I > 3\sigma(I))$	9826	1581 $(I > 3\sigma(I))$
Number of parameters/restraints	777/0	758/0	96/0
$\mu  (\rm cm^{-1})$	20.5	23.33	86.7
S	2.13	0.92	1.80
$R (I > n\sigma(I))$	$0.059 \ (n=3)$	$0.081 \ (n = 2, 4002 \ \text{reflections})$	0.065 (n = 3)
R (all data)		0.217	
$wR_2$ (all data)		0.265	
$wR \ (I > n\sigma(I))$	$0.073 \ (n=3)$		$0.114 \ (n = 3)$

 $R = \Sigma ||F_{o}| - |F_{c}|| \Sigma |F_{o}|; wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} \Sigma w F_{o}^{4}]^{1/2}; wR = [\Sigma w (F_{o} - F_{c})^{2} \Sigma w F_{o}^{2}]^{1/2}.$ 

<sup>a</sup> Common data: Mo K $\alpha$  ( $\lambda = 0.71073$  Å).

 $[Sc(Me_3AsO)_6]Br_3$  gave some npd thermal parameters for O and C and all were subsequently refined with an isotropic model.

#### 5. Supplementary data

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and given numbers 173058 [ScBr<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]Br·1/2Et<sub>2</sub>O, 173059 [Sc(Me<sub>3</sub>AsO)<sub>6</sub>]Br<sub>3</sub>, 173060 [ScCl<sub>2</sub>(Ph<sub>3</sub>AsO)<sub>4</sub>]Cl. Copies of the data can be obtained on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers.

#### Acknowledgements

We thank the EPSRC for support and Professor M.B. Hursthouse for access to the Nonius Kappa CCD diffractometer.

#### References

 P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.

- [2] S. Hajela, W.P. Schaefer, J.E. Bercaw, J. Organomet. Chem. 532 (1997) 45.
- [3] S. Kobayashi, Eur. J. Org. Chem. (1999) 15.
- [4] M. Nakajima, Y. Yamaguchi, S. Hashimoto, Chem. Commun. (2001) 1596.
- [5] D. Grosso, P.A. Sermon, J. Mater. Chem. 10 (2000) 359.
- [6] D. Rehder, in: P.S. Pregosin (Ed.), Transition Metal NMR, Elsevier, New York, 1991.
- [7] L. Deakin, W. Levason, M.C. Popham, G. Reid, M. Webster, J. Chem. Soc., Dalton Trans. (2000) 2439.
- [8] W. Levason, B. Patel, M.C. Popham, G. Reid, M. Webster, Polyhedron 20 (2001) 2711.
- [9] N.J. Hill, W. Levason, M.C. Popham, G. Reid, M. Webster, Polyhedron 21 (2002) 445.
- [10] J.L. Atwood, K.D. Smith, J. Chem. Soc., Dalton Trans. (1974) 921.
- [11] (a) G.R. Willey, M.T. Lakin, N.W. Alcock, J. Chem. Soc., Dalton Trans. (1993) 3407.;
  (b) G.R. Willey, P.R. Meehan, M.D. Rudd, M.G.B. Drew, J. Chem. Soc., Dalton Trans. (1995) 811.
- [12] G.A. Kirakosyan, V.P. Tarasov, Y.A. Buslaev, Mag. Res. Chem. 27 (1989) 103.
- [13] Y.A. Buslaev, G.A. Kirakosyan, V.P. Tarasov, Dokl. Akad. Nauk. SSSR 264 (1982) 1405.
- [14] PATTY, The DIRDIF Program System. P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
- [15] G.M. Sheldrick, SHELXS 97, Program for crystal structure solution, University of Göttingen, 1997.
- [16] TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1997.
- [17] G.M. Sheldrick, SHELXL 97, Program for crystal structure refinement, University of Göttingen, 1997.
- [18] R.E. Marsh, Acta Crystallogr., Sect. B 55 (1999) 931.