Vibrational Spectra of Anhydrous Scandium(III) Chloride and Bromide and their Complexes

By **N. N. Greenwood*** and **R. L. Tranter,** Department of Inorganic Chemistry, University of Newcastle upon Tyne, NE1 7RU

The far-i.r. spectra of anhydrous $ScCl_3$ and $ScBr_3$ (and the Raman spectrum of the former) are reported. Four well defined pyridine complexes having 1 : 4 and 1 : 3 stoicheiometry were characterized. $ScCl_3$,4py and $ScBr_3$,4py have one loosely bound, non-co-ordinated pyridine molecule, $[py_3ScX_3]py$. The 1 : 3 complex py_3,$ScCl_3$ appears to be a *cis*(facial)-octahedral complex which is only weakly ionized in nitromethane solutions, whereas the corresponding bromo-complex behaves as a strongly ionized tetrahedral complex $[py_3ScBr]^{2+}(Br^-)_2$. The first phosphine complexes of scandium are also reported: $ScCl_3$,dppe and $ScBr_3$,1·5dppe [dppe = 1,2-bis(diphenylphosphino)ethane]. Their far-i.r. spectra are presented and possible structures are discussed.

STRUCTURAL and spectroscopic investigations on scandium compounds are rare and until recently the few i.r. studies which had been made were confined to the region 2000—600 cm.$^{-1}$ Changes in the positions of ligand absorptions were used to determine the nature of co-ordination to scandium in complexes with β-diketones,[1–3] ethers, alcohols, esters,[4] and ammines.[5] More recent investigations at lower frequencies have led to some assignments of scandium–ligand vibrations. Thus, ν(Sc–O) for co-ordinated nitrate and sulphate occurs in the region 278—287 cm.$^{-1}$ in the simple

---

[1] C. Duval, R. Freymann, and J. Lecomte, *Bull. Soc. chim. France*, 1952, 106.

[2] R. D. Hancock and D. A. Thornton, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 419, 423.

[3] A. I. Byrke, N. N. Magdesieva, L. I. Martynenko, and V. I. Spitsyn, *Zhur. neorg. Khim.*, 1967, **12**, 666.

[4] A. Finke and E. M. Kirmse, *Z. Chem.*, 1965, **5**, 193.

[5] Yu. Ya. Kharitonov, V. P. Orlovskii, and I. V. Tananaev, *Zhur. neorg. Khim.*, 1963, **8**, 1093.

hydrated salts[6] but at 348 cm.$^{-1}$ in Sc(NO_3)$_3$,3tbp (tbp = tributylphosphate);[7] ν(Sc–OH_2) in these compounds is at 415—430 cm.$^{-1}$ (ref. 6) while ν(Sc–O) for more firmly bound oxygen and ν(Sc–OH) occur in the region 520—630 cm.$^{-1}$ (ref. 8). Similarly, the β-diketone complexes have ν(Sc–O) in the region 430—445 cm.$^{-1}$.

Few ligands with nitrogen donor atoms have been studied, but the complexes [Sc bipy$_2$]Cl_3,H_2O and [Sc *o*-phen$_2$]Cl_3,4H_2O have absorptions at 287 cm.$^{-1}$ and at 283 and 275 cm.$^{-1}$ respectively; these have been assigned to ν(Sc–N).[9] Bands in the region 300—325 cm.$^{-1}$ have been assigned to ν(Sc–NCS) in *cis*- and *trans*-isomers of [Sc bipy$_2$(NCS)$_2$]CNS and [Sc phen$_2$(NCS)$_2$]-CNS.[10]

Of the Sc–halide vibrations ν(Sc–F) has been reported: in the solid phase a broad absorption at 530—540 cm.$^{-1}$ is observed for ScF_3 [11] whereas the gaseous fluoride has absorptions at 726, 482, and 446 cm.$^{-1}$. The gaseous lower fluorides also have absorptions in this region, *i.e.* 709, 661 cm.$^{-1}$ for ScF_2 and 700 cm.$^{-1}$ for ScF.[12] Very recently[10] ν(Sc–Cl) has been assigned to bands at 342 and 320 cm.$^{-1}$ in [Sc bipy$_2$$Cl_2$]Cl and at 336 and 318 cm.$^{-1}$ in [Sc phen$_2$$Cl_2$]Cl.

Here we report the vibrational spectra of scandium trichloride and tribromide and their complexes with pyridine and 1,2-bis(diphenylphosphino)ethane. The structure of these compounds is discussed and the various metal-ligand vibrations are assigned.

Scandium Trihalides.—The far i.r. spectra of anhydrous scandium trichloride and tribromide, and the Raman spectra (R) of solid scandium trichloride are recorded in Table 1. No absorptions were found above 400 cm.$^{-1}$.

TABLE 1

The vibration spectra of scandium trihalides (cm.$^{-1}$)

$ScCl_3$	$ScBr_3$	Suggested assignment
395w		137 + 272 = 409
	349w,sh	138 + 219 = 357
	336w	138 + 190 = 328
	312w	91 + 219 = 310
282s	229s	ν(Sc–X)
272s	219s	ν(Sc–X)
265s(R)		ν(Sc–Cl)
220m	190m,sh	δ(X–Sc–X)
190w		2 × 98 = 196
165b,mw(R)		δ(Cl–Sc–Cl)
137m	138m	δ(X–Sc–X)
98w	91w	δ(X–Sc–X)

Crystal-structure determinations[13] of the two compounds have shown them to be isomorphous with ferric chloride, which has a hexagonal close-packed arrangement of chloride ions with the metal ions occupying two-thirds of the octahedral holes in alternate layers.[14] Such a structure has a point symmetry of D_{3d} at each MX_6^{3-} unit and symmetry arguments predict five i.r.-active modes of vibration ($2A_u + 3E_u$) and two Raman-active modes ($2E_g$), with no coincidences between the i.r. and Raman spectra. These are precisely the patterns found in the spectra and the assignments given in Table 1 were made on this basis, the deformation modes being placed at lower wave numbers than the stretching modes.

Scandium Trihalide–Pyridine Complexes.—Four pyridine complexes of scandium were prepared, ScX_3,4py and ScX_3,3py (X = Cl or Br), but compounds of the type ScX_3,2py reported by Petrů and Jŏst[15] could not be isolated. Kirmse and Schilbach[16] reported the preparation of MX_3,2py (M = Y and Ln) but were unable to obtain reproducible results for scandium. Evidence for their formation during the thermal decomposition of the present compounds was obtained by thermogravimetric analysis at high heating rates, but at lower heating rates decomposition proceeded smoothly to give the halide and under conditions similar to, but more rigorous than, those given for the preparation of ScX_3,2py, compounds with less than three molecules of pyridine could not be obtained.

The near and middle i.r. spectra of the ScX_3,4py compounds were interesting in that besides the spectrum characteristic of co-ordinated pyridine,[17] a number of other bands were seen which could be assigned to free pyridine, *e.g.* 400, 605, 993, and 1214 cm.$^{-1}$. Exposure of the compounds to a vacuum for some time caused the loss of one molecule of pyridine and also the removal of the free pyridine bands from the spectra. This suggests that the tetra-pyridine compounds should be formulated as [py$_3$$ScX_3$]py.

The far-i.r. spectra of the solid compounds are recorded in Table 2 and it can be seen that the tetra- and tri-pyridine compounds of each halide have very similar spectra. Solution measurements were restricted by the low solubility of the compounds in most solvents, but spectra were obtained from pyridine and nitromethane solutions. These are also recorded in Table 2 and it can be seen that they are very similar to those of the solids, thus removing the possibility of some bands being due to lattice or site-symmetry effects.

In the chloride three groups of bands are seen: 320—350, 260—280, and 130—180 cm.$^{-1}$. As the majority of M–Cl stretching frequencies in transition-metal complexes have been found in the range 300—350 cm.$^{-1}$ we have assigned the bands in this region to the Sc–Cl

---

[6] B. Strauch and L. N. Komissarova, *Coll. Czech. Chem. Comm.*, 1967, **32**, 1484.

[7] J. R. Ferraro, C. Cristallini, and I. Fox, *J. Inorg. Nuclear Chem.*, 1967, **29**, 139.

[8] L. N. Komissarova, G. Ya. Pushkina, and E. G. Teterin, *Zhur. neorg. Khim.*, 1967, **12**, 2586.

[9] J. R. Ferraro, L. J. Basile, and D. L. Kovacic, *Inorg. Chem.*, 1966, **5**, 391.

[10] N. P. Crawford and G. A. Melson, *J. Chem. Soc.* (*A*), 1969, 427.

[11] F. Kutek, *Zhur. neorg. Khim.*, 1964, **9**, 2784.

[12] D. McLeod and W. Weltner, *J. Phys. Chem.*, 1966, **70**, 3293.

[13] W. Klemm and E. Krose, *Z. anorg. Chem.*, 1947, **253**, 218; A. A. Men'kov and L. N. Komissarova, *Zhur. neorg. Khim.*, 1964, **9**, 1759.

[14] R. W. G. Wyckoff, 'Crystal Structures,' Interscience, New York, 1964, pp. 45—51.

[15] F. Petrů and F. Jŏst, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2041.

[16] E. M. Kirmse and U. Schilbach, *Z. Chem.*, 1967, **7**, 238.

[17] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1960, 1130.

formulations $[\cdot CH_2PPh_2ScCl_2Ph_2PCH_2\cdot]^{n+}{}_n$ nCl$^-$ and $[\cdot CH_2PPh_2ScBr(Ph_2PCH_2\cdot)_2]^{2n+}{}_n$ $2n$Br$^-$ for the two compounds respectively. In such polymers each scandium would be tetrahedrally co-ordinated and the resulting local C_{2v} and C_{3v} symmetries would imply far-i.r. spectra consistent with those observed. These structures would also explain the difference in molecular-weights, as the chloro-complex could readily form cyclic polymers with no terminal phosphine groups, whereas it would be difficult for the bromo-complex to do this.

EXPERIMENTAL

All preparations were carried out in a dry, nitrogen-filled glove box or in a closed apparatus, evacuated or filled with dry nitrogen. Solvents were dried before use by heating them under reflux over powdered calcium hydride; they were then distilled and saturated with dry oxygen-free nitrogen. Unless specifically mentioned, all were of reagent grade.

Scandium Trichloride.—The method of Bourion [26] was slightly modified. Disulphur dichloride (250 ml.) was distilled back and forth through a silica tube containing scandium(III) oxide (Johnson, Matthey and Son Ltd., Pure Grade) (1·0 g.) at 800°. After 3 hr. the distillation was stopped, chlorine was blown through for several minutes to remove any sulphur which may have deposited, and the tube was then cooled in a stream of dry nitrogen. The product was resublimed *in vacuo* at 800—900° in a silica tube (yield 85%) (Found: Cl, 70·2; Sc, 29·5. Calc. for $ScCl_3$: Cl, 70·3; Sc, 29·7%).

Scandium Tribromide.—The preparation was similar to that described by Men'kov and Komissarova.[13] Dry nitrogen, saturated with dry bromine at 25°, was passed over a 3 : 1 mixture of sugar carbon and scandium(III) oxide contained in a silica tube at 1000°. After 1 hr. the tube was cooled in a stream of dry nitrogen and the product was resublimed *in vacuo* at 800° (yield 85%) (Found: Br, 83·2; Sc, 15·9. Calc. for $ScBr_3$: Br, 84·2; Sc, 15·8%).

Tetrapyridine–Scandium(III) *Halides*.—Scandium trihalide (1·0 g.) was dissolved in boiling pyridine (50 ml.) and the hot solution was rapidly filtered. The filtrate was rapidly reduced in volume to 10 ml. by evaporation under reduced pressure and the white crystalline products were collected and washed with portions (3 × 5 ml.) of freshly distilled carbon tetrachloride (Found: C_5H_5N, 67·7; Cl, 23·2; Sc, 9·6. $ScCl_3,4C_5H_5N$ requires C_5H_5N, 67·7; Cl, 22·8; Sc, 9·6%. Found: C_5H_5N, 48·0; Br, 40·4; Sc, 7·5. $ScBr_3,4C_5H_5N$ requires C_5H_5N, 52·6; Br, 39·9; Sc, 7·5%).

Tripyridine–Scandium(III) *Halides*.—Tetrapyridine–scandium(III) halide (0·5 g.) set aside over phosphorus pentoxide *in vacuo* for 3 weeks. During the last week the loss of weight was very slow and the total losses were 19·5% for the chloride and 15·2% for the bromide corresponding to slightly more than 1 mol. of pyridine in each case. This was confirmed by analysis (Found: Cl, 27·4; Sc, 11·9. $ScCl_3,3C_5H_5N$ requires Cl, 27·5; Sc, 11·6%. Found Br, 47·1; Sc, 8·6. $ScBr_3,3C_5H_5N$ requires Br, 46·8; Sc, 8·6%).

A sample of tetrapyridine–scandium(III) bromide (0·25 g.) was also exposed to continuous pumping at 10^{-3} mm. Hg. for 1 week and was thereby converted into tripyridine–scandium(III) bromide (Found: Br, 44·7; Sc, 9·0%).

The pyridine complexes were all extremely hygroscopic and tended to give pyridinium halides in the presence of traces of moisture. The compounds were insoluble in carbon tetrachloride, methylene chloride, chloroform, benzene, nitrobenzene, and tetrahydrofuran, but were soluble in pyridine and nitromethane. However, solutions in these two solvents slowly darkened at room temperature thus restricting solution measurements to freshly prepared solutions.

1,2-*Bis*(*diphenylphosphino*)*ethane*.— The triphenylphosphine–lithium–ethylenedichloride method, described by Chatt and Hart,[27] was used; the product was recrystallized from boiling light petroleum (80—100°) and had m.p. 141° (lit.,[27] 143°).

1,2-*Bis*(*diphenylphosphinyl*)*ethane*.— 1,2-Bis(diphenylphosphino)ethane was dissolved in hot ethanol (50 ml.) and hydrogen peroxide (20 vol.; 10 ml.) was added in portions during 1 hr. The solution was evaporated to a volume of 25 ml., after which water was added until the solution was slightly turbid; it was then cooled. The white crystalline product was filtered off and recrystallised from a small volume of ethanol. Its melting point was above 200° and its i.r. spectrum showed strong absorption in the region assigned to the P=O stretching frequency.

1,2-*Bis*(*diphenylphosphino*)*ethane–Scandium*(III) *Chloride*.—Scandium trichloride (1·0 g., 7 mmoles) and dppe (5·5 g., 14 mmoles) were shaken together for 3 days in a sealed flask containing dry chloroform (200 ml.) and dry tetrahydrofuran (2 ml.). The solution was filtered, evaporated to dryness, and the excess of ligand removed from the finely ground product with boiling light petroleum (b.p. 100—120°) or with freshly distilled carbon tetrachloride (yield 80%) (Found: C, 55·5; H, 4·9; Cl, 18·7; P, 10·7; Sc, 6·5. $ScCl_3,C_{26}H_{24}P_2$ requires C, 56·8; H, 4·4; Cl, 19·4; P, 11·3; Sc, 8·2%).

Alternative preparations were also tried. In one, scandium trichloride (0·25 g.) was fused with a large excess of dppe at 200—250° *in vacuo* for 24 hr. The product, after removal of the excess of ligand, was found to be contaminated with unchanged scandium trichloride. For this reason the preceding method was preferred. Attempts were also made to prepare the complex in other solvents, *e.g.* dimethylformamide, tetrahydrofuran, and pyridine, but these led to the formation of complexes with the solvents.

$ScCl_3$,dppe was obtained as a white powder; it was apparently stable towards moist air but its solutions in nitromethane or pyridine reacted rapidly with air. It was insoluble in water and most organic solvents but was soluble in pyridine, nitromethane, and ethanol. The solid decomposed at *ca.* 300° in air before melting.

Tris-(1,2-*bis*(*diphenylphosphino*)*ethane*)-*Discandium Hexabromide*.—The preparation and properties of this compound were very similar to those of $ScCl_3$,dppe (Found: C, 53·9; H, 4·9; Br, 27·9; P, 9·9; Sc, 3·8. $ScBr_3,C_{39}H_{36}P_3$ requires C, 53·1; H, 4·1; Br, 27·2; P, 10·5; Sc, 5·1%).

Analyses.—Scandium was determined by titration with EDTA at pH 4 with Xylenol Orange as indicator.[28] With the phosphine complexes, difficulty was found in obtaining aqueous solutions of the uncomplexed scandium. Fusion methods of decomposition of the complex invariably gave intractable scandium phosphates. Hydrolysis with ethanolic sodium hydroxide released most of the scandium but it

---

[26] F. Bourion, *Ann. Chim. Phys.*, [8], 1910, **21**, 49.

[27] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

[28] J. Körbl, R. Pribil, and A. Emv, *Chem. Listy*, 1965, **50**, 1440; *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.

weight determinations were unsuccessful as solutions of sufficient concentration and stability could not be prepared. A definite choice of structure in the solid phase is not possible because of the small number (2) of far-i.r. bands observed and the lack of success which attended attempts to record the Raman spectrum.

It would thus appear that the chloro-complex should be formulated 1,2,3-py$_3$ScCl$_3$ and the bromo-complex either as $[py_3ScBr]^{2+}(Br^-)_2$ or $[1,5\text{-}py_3ScBr_2]^+Br^-$. In view of the probable structures of the phosphine complexes discussed next, the tetrahedral structure of the bromo-complex is preferred.

Scandium–Phosphine Complexes.—There have been no reports of the preparation of phosphine complexes of scandium, and their preparation was of interest here as a possible route to lower-valent complexes of scandium. However, although attempts were made to prepare low-valent scandium complexes by a variety of means, only scandium(III) complexes were, in fact, isolated, *viz.* ScCl$_3$,dppe and ScBr$_3$1·5dppe [dppe is 1,2-bis(diphenylphosphino)ethane].

In the middle region of the spectrum, 2000—600 cm.$^{-1}$ the two compounds had identical spectra; these were very different from the spectrum of the parent ligand, but were rather similar to the spectrum of complexed dppe dioxide, Ph$_2$P(O)CH$_2$·CH$_2$·P(O)Ph$_2$. Thus it has been shown that the P=O (ref. 23—25) stretching frequencies at 1185 and 1173 cm.$^{-1}$ in free phosphine oxides shift to lower frequencies, by *ca.* 50 cm.$^{-1}$ when complexed with transition metals. The strong band at 1147 cm.$^{-1}$ in the scandium complexes of dppe might therefore be thought to indicate the presence of complexed P=O. However, the methods of preparation of the compounds, the recovery of the free unoxidized phosphine ligand from the complexes after hydrolysis, and the very rapid change in the spectra of solutions of the compounds when exposed to air, all indicate that the compounds are, in fact, phosphine complexes and not phosphine oxide complexes.

The far-i.r. spectra of the two compounds are also very similar and Table 4 records the spectra of the solids together with those of their pyridine and nitromethane solutions. Unfortunately, the bands are rather broad and poorly resolved and the determination of structure from them was not possible.

The band at 303 cm.$^{-1}$ occurs in both compounds, and in the solutions and may reasonably be assigned to the ν(Sc–P). Of the remaining bands, that at 317 cm.$^{-1}$ is assigned to ν(Sc–Cl), 275 cm.$^{-1}$ to ν(Sc–Br) and the weak bands in the region 180—130 cm.$^{-1}$ to the various deformation modes.

TABLE 4

Spectra of ScCl$_3$,dppe; ScBr$_3$,1·5 dppe; dppe, and dppeO$_2$ in the range 600—100 cm.$^{-1}$

		ScCl$_3$,dppe			ScBr$_3$,1·5dppe		
dppe	dppeO$_2$	Solid	py soln.	MeNO$_2$ soln.	Solid	py soln.	MeNO$_2$ soln.
	555w	550sh	550w	551w	550sh	550w	550w
505vs	532vs	537s	536s	538s	537s	537s	537s
				531w			530w
475vs	511vs	510b,s	510m	522m	510b,s	513 503 b,m	
	499sh						
443m	454m	480b,w	469m	*	480b,w	473sh	*
			420sh			420sh	
397m	409m						
333m	391w						
		317b,s	324b,s	313sh			
		303b,s		304s	303s	317s	301s
	309						
	302m						
					275s	278s	275m
281w	288w						
	269w						
	251w						
	226						
	195m						
	178m						
		180—130w			180—130w		

* Strong solvent absorption obscured these bands.

Conductivity measurements on nitromethane solutions (see Table 3) show that the chloride behaves as a weak 1 : 1-electrolyte whereas the bromide is a strong 1 : 1-electrolyte or an ion-paired 1 : 2 -electrolyte.

Molecular-weight measurements, also in nitromethane, indicated polymer formation; the chloride had an average degree of association of 4·5 monomer units while the bromide had a molecular-weight that continually increased during the time of the measurements (2 weeks). Models were constructed and it was found that only four of the halide and Ph$_2$PCH$_2$ groups could be arranged round each scandium ion and this, together with the conductivity measurements and analyses, suggested the

---

[23] K. W. Bagnall, D. Brown, and J. G. H. du Preez, *J. Chem. Soc.*, 1965, 5217.

[24] F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 1960, 2199.

[25] J. C. Sheldon and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

formulations $[\cdot CH_2PPh_2ScCl_2Ph_2PCH_2\cdot]^{n+}{}_n$ $n\mathrm{Cl}^-$ and $[\cdot CH_2PPh_2ScBr(Ph_2PCH_2\cdot)_2]^{2n+}{}_n$ $2n\mathrm{Br}^-$ for the two compounds respectively. In such polymers each scandium would be tetrahedrally co-ordinated and the resulting local C_{2v} and C_{3v} symmetries would imply far-i.r. spectra consistent with those observed. These structures would also explain the difference in molecular-weights, as the chloro-complex could readily form cyclic polymers with no terminal phosphine groups, whereas it would be difficult for the bromo-complex to do this.

EXPERIMENTAL

All preparations were carried out in a dry, nitrogen-filled glove box or in a closed apparatus, evacuated or filled with dry nitrogen. Solvents were dried before use by heating them under reflux over powdered calcium hydride; they were then distilled and saturated with dry oxygen-free nitrogen. Unless specifically mentioned, all were of reagent grade.

Scandium Trichloride.—The method of Bourion [26] was slightly modified. Disulphur dichloride (250 ml.) was distilled back and forth through a silica tube containing scandium(III) oxide (Johnson, Matthey and Son Ltd., Pure Grade) (1·0 g.) at 800°. After 3 hr. the distillation was stopped, chlorine was blown through for several minutes to remove any sulphur which may have deposited, and the tube was then cooled in a stream of dry nitrogen. The product was resublimed *in vacuo* at 800—900° in a silica tube (yield 85%) (Found: Cl, 70·2; Sc, 29·5. Calc. for $ScCl_3$: Cl, 70·3; Sc, 29·7%).

Scandium Tribromide.—The preparation was similar to that described by Men'kov and Komissarova.[13] Dry nitrogen, saturated with dry bromine at 25°, was passed over a 3 : 1 mixture of sugar carbon and scandium(III) oxide contained in a silica tube at 1000°. After 1 hr. the tube was cooled in a stream of dry nitrogen and the product was resublimed *in vacuo* at 800° (yield 85%) (Found: Br, 83·2; Sc, 15·9. Calc. for $ScBr_3$: Br, 84·2; Sc, 15·8%).

Tetrapyridine–Scandium(III) *Halides*.—Scandium trihalide (1·0 g.) was dissolved in boiling pyridine (50 ml.) and the hot solution was rapidly filtered. The filtrate was rapidly reduced in volume to 10 ml. by evaporation under reduced pressure and the white crystalline products were collected and washed with portions (3 × 5 ml.) of freshly distilled carbon tetrachloride (Found: C_5H_5N, 67·7; Cl, 23·2; Sc, 9·6. $ScCl_3,4C_5H_5N$ requires C_5H_5N, 67·7; Cl, 22·8; Sc, 9·6%. Found: C_5H_5N, 48·0; Br, 40·4; Sc, 7·5. $ScBr_3,4C_5H_5N$ requires C_5H_5N, 52·6; Br, 39·9; Sc, 7·5%).

Tripyridine–Scandium(III) *Halides*.—Tetrapyridine–scandium(III) halide (0·5 g.) set aside over phosphorus pentoxide *in vacuo* for 3 weeks. During the last week the loss of weight was very slow and the total losses were 19·5% for the chloride and 15·2% for the bromide corresponding to slightly more than 1 mol. of pyridine in each case. This was confirmed by analysis (Found: Cl, 27·4; Sc, 11·9. $ScCl_3,3C_5H_5N$ requires Cl, 27·5; Sc, 11·6%. Found Br, 47·1; Sc, 8·6. $ScBr_3,3C_5H_5N$ requires Br, 46·8; Sc, 8·6%).

A sample of tetrapyridine–scandium(III) bromide (0·25 g.) was also exposed to continuous pumping at 10^{-3} mm. Hg. for 1 week and was thereby converted into tripyridine–scandium(III) bromide (Found: Br, 44·7; Sc, 9·0%).

The pyridine complexes were all extremely hygroscopic and tended to give pyridinium halides in the presence of traces of moisture. The compounds were insoluble in carbon tetrachloride, methylene chloride, chloroform, benzene, nitrobenzene, and tetrahydrofuran, but were soluble in pyridine and nitromethane. However, solutions in these two solvents slowly darkened at room temperature thus restricting solution measurements to freshly prepared solutions.

1,2-*Bis*(*diphenylphosphino*)*ethane*.— The triphenylphosphine–lithium–ethylenedichloride method, described by Chatt and Hart,[27] was used; the product was recrystallized from boiling light petroleum (80—100°) and had m.p. 141° (lit.,[27] 143°).

1,2-*Bis*(*diphenylphosphinyl*)*ethane*.— 1,2-Bis(diphenylphosphino)ethane was dissolved in hot ethanol (50 ml.) and hydrogen peroxide (20 vol.; 10 ml.) was added in portions during 1 hr. The solution was evaporated to a volume of 25 ml., after which water was added until the solution was slightly turbid; it was then cooled. The white crystalline product was filtered off and recrystallised from a small volume of ethanol. Its melting point was above 200° and its i.r. spectrum showed strong absorption in the region assigned to the P=O stretching frequency.

1,2-*Bis*(*diphenylphosphino*)*ethane–Scandium*(III) *Chloride*.—Scandium trichloride (1·0 g., 7 mmoles) and dppe (5·5 g., 14 mmoles) were shaken together for 3 days in a sealed flask containing dry chloroform (200 ml.) and dry tetrahydrofuran (2 ml.). The solution was filtered, evaporated to dryness, and the excess of ligand removed from the finely ground product with boiling light petroleum (b.p. 100—120°) or with freshly distilled carbon tetrachloride (yield 80%) (Found: C, 55·5; H, 4·9; Cl, 18·7; P, 10·7; Sc, 6·5. $ScCl_3,C_{26}H_{24}P_2$ requires C, 56·8; H, 4·4; Cl, 19·4; P, 11·3; Sc, 8·2%).

Alternative preparations were also tried. In one, scandium trichloride (0·25 g.) was fused with a large excess of dppe at 200—250° *in vacuo* for 24 hr. The product, after removal of the excess of ligand, was found to be contaminated with unchanged scandium trichloride. For this reason the preceding method was preferred. Attempts were also made to prepare the complex in other solvents, *e.g.* dimethylformamide, tetrahydrofuran, and pyridine, but these led to the formation of complexes with the solvents.

$ScCl_3$,dppe was obtained as a white powder; it was apparently stable towards moist air but its solutions in nitromethane or pyridine reacted rapidly with air. It was insoluble in water and most organic solvents but was soluble in pyridine, nitromethane, and ethanol. The solid decomposed at *ca.* 300° in air before melting.

Tris-(1,2-*bis*(*diphenylphosphino*)*ethane*)–*Discandium Hexabromide*.—The preparation and properties of this compound were very similar to those of $ScCl_3$,dppe (Found: C, 53·9; H, 4·9; Br, 27·9; P, 9·9; Sc, 3·8. $ScBr_3,C_{39}H_{36}P_3$ requires C, 53·1; H, 4·1; Br, 27·2; P, 10·5; Sc, 5·1%).

Analyses.—Scandium was determined by titration with EDTA at pH 4 with Xylenol Orange as indicator.[28] With the phosphine complexes, difficulty was found in obtaining aqueous solutions of the uncomplexed scandium. Fusion methods of decomposition of the complex invariably gave intractable scandium phosphates. Hydrolysis with ethanolic sodium hydroxide released most of the scandium but it

---

[26] F. Bourion, *Ann. Chim. Phys.*, [8], 1910, **21**, 49.

[27] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1960, 1378.

[28] J. Körbl, R. Pribil, and A. Emv, *Chem. Listy*, 1965, **50**, 1440; *Coll. Czech. Chem. Comm.*, 1957, **22**, 961.

was never possible to release it all. The scandium figures quoted for these compounds were obtained by this method.

Halide was determined by the Volhard titration.

Pyridine was removed from the complexes by steam distillation of an alkaline solution. The distillate was trapped in a saturated boric acid solution and titrated to pH 4·0 with standard hydrochloric acid.

C, H, P and some halide determinations were carried out by M. Beller of Göttingen.

I.r and Raman Spectra.—I.r. spectra of solids were obtained from Nujol mulls (the Nujol was dried at 150° with sodium wire). Films between potassium bromide plates were used for the 4000—400 cm.$^{-1}$ region with a Perkin–Elmer 125 Grating Spectrophotometer, and between Polythene discs for the region 400—20 cm^{-1} with a Grubb Parsons DM4 Mark II Spectrophotometer (400—200 cm.$^{-1}$) and an R.I.I.C. FS-520 Fourier Spectrophotometer (400—20 cm.$^{-1}$).

Liquids and solutions were contained in a 0·1-mm. path-length Polythene cell for measurements below 400 cm.$^{-1}$ and in a variable path-length cell fitted with potassium bromide windows for measurements above 400 cm.$^{-1}$.

The Raman spectrum of solid scandium trichloride was obtained from 2 g. of the powdered solid with a Cary 81 Raman Spectrophotometer.

Calibration of these instruments was effected with polystyrene (4000—400 cm.$^{-1}$), water vapour (400—20 cm.$^{-1}$), and carbon tetrachloride (Raman).

Conductivity Measurements.—Conductivity measurements were made in a glass apparatus which could be closed from the atmosphere. The electrodes were of platinized platinum and calibration was effected with standard potassium chloride solution.

Solutions 2×10^{-5}M—10^{-2}M were prepared by weighing the required amount of complex and dissolving it in dry nitromethane at room temperature. The conductivity of the solution was measured at 25·0° with a Wayne Kerr Universal Bridge B221.

Molecular Weight Measurements.—These were made by the isopiestic method in an all-glass apparatus sealed under a high vacuum. Nitromethane was found to be a satisfactory solvent for this method providing the temperature of the external bath was *ca.* 40°. Equilibrium with a standard azobenzene solution was reached in approximately 1 week.

Thermogravimetric Analysis.—This was carried out in a stream of dry nitrogen with a Stanton MF5 Thermobalance. Two rates of heating were used, 2·4°/min. and 0·6°/min.

We thank the S.R.C. for a maintenance grant (to R. L. T.).

[9/957 *Received, June 5th*, 1969]