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Syntheses, structures and multinuclear NMR (^{45}Sc, ^{89}Y, ^{31}P) studies of Ph_3PO, Ph_2MePO and Me_3PO complexes of scandium and yttrium nitrates

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The reactions of the tertiary phosphine oxides Ph_3PO, Ph_2MePO or Me_3PO with hydrated yttrium(III) nitrate in ethanol gave the complexes $[Y(R_3PO)_2(EtOH)(NO_3)_3]$ ($R_3PO = Ph_3PO$ or Ph_2MePO), $[Y(Me_3PO)_2(H_2O)(NO_3)_3]$, $[Y(R_3PO)_3(NO_3)_3]$ ($R_3PO = Ph_3PO$, Ph_2MePO or Me_3PO), and $[Y(Ph_3PO)_4(NO_3)_2]NO_3$. The species $[Y(R_3PO)_4(NO_3)_2]NO_3$ ($R_3PO = Ph_2MePO$ or Me_3PO) were formed from $[Y(R_3PO)_3(NO_3)_3]$ and an excess of R_3PO in CH_2Cl_2 solution and identified spectroscopically, but have not been isolated as solids. Corresponding reactions of hydrated scandium(III) nitrate produced $[Sc(Ph_3PO)_2(NO_3)_3]$, $[Sc(Ph_2MePO)_3(NO_3)_3]$, $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$, $[Sc(Me_3PO)_2(EtOH)(NO_3)_3]$, and $[Sc(Me_3PO)_6][NO_3]_3$. All complexes were characterised by elemental analysis, IR and ^{1}H NMR spectroscopy and conductance measurements. Variable temperature ^{89}Y, ^{45}Sc and ^{31}P-{^{1}H} NMR spectroscopies have been used to identify species present in solution, and probe the interconversions. ^{31}P-{^{1}H} NMR studies show that exchange with added R_3PO in solution is slow on the NMR timescale. Crystal structures were determined for $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$ and $[Y(R_3PO)_3(NO_3)_3]$ ($R_3PO = Ph_3PO$, Ph_2MePO or Me_3PO): all contain 9-co-ordinate Y with symmetrically co-ordinated bidentate nitrate groups. Structures of the 8-co-ordinate $[Sc(Ph_3PO)_2(NO_3)_3]$ and $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$ are also described.

The co-ordination chemistries of scandium and yttrium have received much less study than that of most d-block elements, in part because the only accessible oxidation state in solution, the d^0 M^{III}, lacks both magnetic and d–d UV-visible spectroscopic probes. However both metals are suitable for NMR studies, being monoisotopic (^{45}Sc and ^{89}Y) and diamagnetic in the metal(III) oxidation state. Scandium-45 is quadrupolar ($I = 7/2$) but with only a moderate quadrupole moment -0.22×10^{-28} m^2, and is one of the most sensitive nuclei in the periodic table (D_c (receptivity relative to ^{13}C) = 1700), whilst ^{89}Y has $I = 1/2$ and moderate sensitivity ($D_c = 0.67$), but has a low absolute frequency ($\Xi = 4.92$ MHz) and very long relaxation times.[1] Here we report the synthesis and multinuclear NMR studies of some phosphine oxide complexes of scandium and yttrium nitrates, and crystal structures of representative examples. Since the first detailed study by Cousins and Hart[2] in the late 1960s, phosphine oxides have been popular ligands for complexing with trivalent lanthanide metals,[3] although much less is known about yttrium or scandium complexes, and none of the latter has been structurally characterised.[2,4–6]

Experimental

Physical measurements were made as described previously.[7] Conductivities were measured in anhydrous CH_2Cl_2 or $MeNO_2$ from 10^{-3} mol dm^{-3} solutions of the complexes on a Pye 1700 Conductance bridge. NMR spectra were recorded on a Bruker AM360 in 10 mm o.d. tubes from CH_2Cl_2–10% $CDCl_3$ solutions. ^{31}P-{^{1}H} NMR spectra at 145.5 MHz were referenced to external 85% H_3PO_4. ^{89}Y NMR spectra were recorded at 17.65 MHz with a sweep width of 25 kHz from solutions containing TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) as a relaxation agent and with a 2 s pulse delay. A 2 mol dm^{-3} solution of YCl_3 at pH 1 (added HCl) was used as zero reference.[8] ^{45}Sc NMR spectra were recorded at 87.5 MHz using a solution of 0.1 mol dm^{-3} $Sc(NO_3)_3$ at pH 1 as zero reference.[1,8] Ph_3PO and Ph_2MePO (Aldrich), Me_3PO (ALFA), $Sc(NO_3)_3\cdot5H_2O$ (Strem) and $Y(NO_3)_3\cdot6H_2O$ (Aldrich) were used as received.

Synthesis

The syntheses generally followed similar methods, with the ratio of reagents and the temperature the main variants. Representative preparations are given below, and for the other complexes only differences are noted.

$[Y(Ph_3PO)_3(NO_3)_3]$. Yttrium nitrate hexahydrate (0.38 g, 1.0 mmol) and Ph_3PO (1.11 g, 4.0 mmol) were dissolved separately in warm (60 °C) ethanol (10 cm^3), the solutions mixed and stirred for 1 h. The solution was evaporated to *ca.* 10 cm^3 and refrigerated overnight. The white solid was filtered off and dried *in vacuo*. Yield 0.93 g, 91% (Found: C, 58.1; H, 3.7; N, 3.7. Calc. for $C_{54}H_{45}N_3O_{12}P_3Y$: C, 58.4; H, 4.1; N, 3.8%). IR (cm^{-1}) (Nujol mull): 1500w, 1437m, 1311w, 1187w, 1168s (PO), 1154s (PO), 1121m, 1092m, 1031w, 815m, 745s, 725m and 690w. ^{31}P-{^{1}H} NMR (300 K, CH_2Cl_2): δ 36.5 and 33.9. ^{89}Y NMR (300 K): not observed. Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 13 ohm^{-1} cm^2 mol^{-1}.

$[Y(Ph_2MePO)_3(NO_3)_3]$. Made similarly 74% (Found: C, 50.2; H, 4.1; N, 4.5. Calc. for $C_{39}H_{39}N_3O_{12}P_3Y$: C, 50.7; H, 4.3; N, 4.6%). IR (cm^{-1}) (Nujol mull): 1500w (sh), 1450m, 1306w, 1300w (sh), 1172w (sh), 1150s (PO), 1126s, 1105m, 1035m, 895w, 883w, 781m, 745m, 716w, 696w and 668m. ^{31}P-{^{1}H} NMR (300 K, CH_2Cl_2): δ 36.6. ^{89}Y NMR (300 K): δ −22br. ^{1}H NMR (300 K, $CDCl_3$): δ 7.2–7.7m, 1.95d, $^2J_{PH}$ 13.5 Hz. Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 4.5 ohm^{-1} cm^2 mol^{-1}.

$[Y(Me_3PO)_3(NO_3)_3]$. Made similarly 33% (Found: C, 19.1; H, 4.8; N, 7.5. Calc. for $C_9H_{27}N_3O_{12}P_3Y$: C, 19.6; H, 4.9; N, 7.6%). IR (cm^{-1}) (Nujol mull): 1308m, 1171 (sh), 1146s (PO), 1120 (sh), 1036m, 949s, 863m, 819w, 390m and 365w. ^{31}P-{^{1}H}

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NMR (300 K, CH_2Cl_2): δ 48.3. ^{89}Y NMR (300 K): δ −17.0s. ^1H NMR (300 K, $CDCl_3$): δ 1.65d, $^2J_{PH}$ 13.6 Hz.

[Y(Ph$_3$PO)$_2$(EtOH)(NO$_3$)$_3$]. Yttrium nitrate hexahydrate (0.38 g, 1.0 mmol) and Ph_3PO (0.28 g, 1.0 mmol) were dissolved in boiling ethanol (15 cm^3). After 15 min the solution was cooled and refrigerated overnight to give a white solid, which was filtered off and dried *in vacuo*. Yield 0.46 g, 53% (Found: C, 52.3; H, 4.1; N, 4.5. Calc. for $C_{38}H_{36}N_3O_{12}P_2Y$: C, 52.0; H, 4.1; N, 4.8%). IR (cm^{-1}) (Nujol mull): 3300 (br) s, 1500w, 1314m, 1171s (PO), 1155s (PO), 1120m, 1039m, 1032 (sh), 816w, 692m and 539s. ^{31}P-{^1H} NMR (300 K, CH_2Cl_2): δ 37.0. ^{89}Y NMR (300 K): not observed. ^1H NMR (d_6-acetone, 300 K): δ 7.1–7.6m, 3.56 (q, $J = 7$) and 1.11 (t, $J = 7$ Hz). Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 10.0 ohm^{-1} cm^2 mol^{-1}.

[Y(Ph$_2$MePO)$_2$(EtOH)(NO$_3$)$_3$]. Made similarly 33% (Found: C, 46.4; H, 4.0; N, 4.8. Calc. for $C_{28}H_{32}N_3O_{12}P_2Y$: C, 44.6; H, 4.3; N, 5.6%) see text. IR (cm^{-1}) (Nujol mull): 3300 (br), 1591w, 1300 (br) s, 1181 (sh), 1155s (PO), 1126m, 1109m, 1073w, 998w, 969w, 893m, 881m, 816m, 779w, 741s, 693s, 513m, 504s and 398w. ^{31}P{^1H} NMR (300 K, CH_2Cl_2): δ 37.7. ^{89}Y NMR (300 K) not observed. ^1H NMR (d_6-acetone, 300 K): δ 7.6–7.9m, 3.60 (q, $J = 7$), 2.05 (d, $^2J_{PH} = 14$) and 1.15 (t, $J = 7$ Hz). Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 7.5 ohm^{-1} cm^2 mol^{-1}.

[Y(Me$_3$PO)$_2$(H$_2$O)(NO$_3$)$_3$]. Prepared by boiling $Y(NO_3)_3\cdot 6H_2O$ and Me_3PO in a 1 : 1 mol ratio in ethanol, similar to the preparation of the ethanol complexes, 36% (Found: C, 14.5; H, 3.9; N, 8.7. Calc. for $C_6H_{20}N_3O_{12}P_2Y$: C, 15.1; H, 4.2; N, 8.7%). IR (cm^{-1}) (Nujol mull): 3400 (br) s, 1650m, 1297s, 1160 (sh) (PO), 1140s (PO), 1083m, 1034m, 951s, 866m, 816m, 745m, 605 (br), 391m, 371m and 333w. ^{31}P{^1H} NMR (300 K, CH_2Cl_2): δ 50.5. ^{89}Y NMR (300 K) not observed. ^1H NMR (d_6-acetone, 300 K): δ 1.45d, $^2J_{PH} = 13.6$ Hz.

[Y(Ph$_3$PO)$_4$(NO$_3$)$_2$]NO$_3$. A solution of Ph_3PO (0.84 g, 3.0 mmol) in ice-cold ethanol (15 cm^3) was added to yttrium nitrate hexahydrate (0.175 g, 0.50 mmol) in ethanol (5 cm^3) at 0 °C. The white product was filtered off after 1 h and dried *in vacuo*. Yield 0.35 g, 51% (Found: C, 62.0; H, 4.0; N, 3.2. Calc. for $C_{72}H_{60}N_3O_{13}P_4Y$: C, 62.3; H, 4.3; N, 3.0%). IR (cm^{-1}) (Nujol mull): 1520w, 1298m, 1154s (PO), 1121s, 1091m, 1031w, 997w, 971w, 830w, 816w, 742m, 692m, 542s, 416w and 308w. ^{31}P-{^1H} NMR (300 K, CH_2Cl_2): δ 36.5, 33.3 and 26.0. ^{89}Y NMR (300 K): not observed. Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 14.5 ohm^{-1} cm^2 mol^{-1}.

[Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$]. A boiling solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.23 g, 1.0 mmol) in absolute ethanol (20 cm^3) was treated with a solution of Ph_3PO (0.83 g, 3.0 mmol) in absolute ethanol (10 cm^3). The solution was concentrated to *ca.* 15 cm^3, cooled and refrigerated for 24 h. White crystals separated and were filtered off, rinsed with cold ethanol (5 cm^3), and dried *in vacuo*. Yield 0.26 g, 33% (Found: C, 54.5; H, 4.0; N, 5.1. Calc. for $C_{36}H_{30}N_3O_{11}P_2Sc$: C, 54.9; H, 3.8; N, 5.3%). IR (cm^{-1}) (Nujol mull): 1562, 1437, 1299, 1282, 1167 (PO), 1140, 1123, 1009, 808, 747, 725, 692 and 542. ^{31}P-{^1H} NMR (300 K, CH_2Cl_2): δ 37.7. ^{45}Sc NMR (300 K, CH_2Cl_2): δ −7.5 ($W_{1/2} = 900$ Hz). Λ_m (CH_2Cl_2, 10^{-3} mol dm^{-3}) = 2 ohm^{-1} cm^2 mol^{-1}.

[Sc(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$. Prepared similarly from $Sc(NO_3)_3\cdot 5H_2O$ (1 mmol) and Ph_2MePO (4 mmol) in absolute ethanol, 60% (Found: C, 56.9; H, 5.0; N, 3.7. Calc. for $C_{52}H_{52}N_3O_{13}P_4Sc$: C, 57.0; H, 4.7; N, 3.8%). IR (cm^{-1}) (Nujol mull): 1591w, 1299m, 1153s (PO), 1125m, 1108m, 1073m, 1037w, 996w, 889s, 831w, 818w, 811s, 744s, 694s, 507s, 479m, 453m, 425w, 400w and 277m. ^{31}P-{^1H} NMR (CH_2Cl_2): (300 K) δ 38.5 ($W_{1/2} = 700$ Hz); (220 K) δ 39.6vw, 38.7s and 29.2vw. ^{45}Sc NMR (300 K, CH_2Cl_2): δ −3.5 ($W_{1/2} = 500$) and −33 ($W_{1/2}$ 10000 Hz). ^1H NMR (300 K, $CDCl_3$): δ 2.10d, $^2J_{PH} = 12$ Hz. Λ_m (10^{-3} mol dm^{-3} CH_2Cl_2) = 8 ohm^{-1} cm^2 mol^{-1}.

[Sc(Ph$_2$MePO)$_3$(NO$_3$)$_3$]. A boiling solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.23 g, 1.0 mmol) in absolute ethanol (20 cm^3) was treated with a solution of Ph_2MePO (0.43 g, 2.0 mmol) in absolute ethanol (10 cm^3). The solution was concentrated to *ca.* 5 cm^3, cooled and refrigerated for 24 h. A sticky solid deposited, the supernatent liquid was decanted off, the solid washed with ice-cold diethyl ether (5 cm^3), and dried *in vacuo*. Yield 0.25 g, 28% (Found: C, 53.2; H, 4.4; N, 4.6. Calc. for $C_{39}H_{39}N_3O_{12}P_3Sc$: C, 53.3; H, 4.5; N, 4.8%). IR (cm^{-1}) (Nujol mull): 1590w, 1302s, 1153s (PO), 1090w, 1025w, 971w, 890m, 814w, 777m, 692m, 502s, 422w, 400w and 287m. ^{31}P-{^1H} NMR (300 K, CH_2Cl_2): δ 39.5. ^{45}Sc NMR (300 K, CH_2Cl_2): δ −4.0 ($W_{1/2} = 350$ Hz). ^1H NMR ($CDCl_3$): δ 2.10d, $^2J_{PH} = 12$ Hz.

[Sc(Me$_3$PO)$_2$(EtOH)(NO$_3$)$_3$]. A boiling solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.346 g, 1.5 mmol) in ethanol (20 cm^3) was added to a boiling ethanol (10 cm^3) solution of Me_3PO (0.139 g, 1.5 mmol). The solution was evaporated *in vacuo* to dryness, redissolved in the minimum volume of alcohol and refrigerated overnight. A sticky solid formed which was discarded and the mother liquor allowed to evaporate to produce colourless crystals, which were filtered off and dried *in vacuo*. Yield 0.05 g, 10% (Found: C, 20.4; H, 5.1; N, 9.6. Calc. for $C_8H_{24}N_3O_{12}P_2Sc$: C, 20.8; H, 5.6; N, 9.1%). IR (cm^{-1}) (Nujol mull): 3200 (br), 1312m, 1152s (PO), 1112m, 1026w, 956m, 866w, 815w, 534w, 485w, 430w, 372w and 327w. ^{31}P-{^1H} NMR (300 K, CH_2Cl_2): δ 54.8. ^{45}Sc NMR (300 K, CH_2Cl_2): δ −2.5 ($W_{1/2} = 600$ Hz). ^1H NMR (300 K, $CDCl_3$): δ 0.9 (t, $J = 7$), 1.6 (d, $^2J_{PH} = 10$) and 3.6 (q, $J = 7$ Hz).

[Sc(Me$_3$PO)$_6$][NO$_3$]$_3$. A solution of $Sc(NO_3)_3\cdot 5H_2O$ (0.23 g, 1.0 mmol) in ice-cold ethanol (20 cm^3) was added to a solution of Me_3PO (0.53 g, 6.0 mmol) in ethanol (10 cm^3) and the mixture shaken. A white precipitate formed immediately, the solution was refrigerated for 24 h, filtered and the solid dried *in vacuo*. Yield 0.43 g, 57% (Found: C, 26.9; H, 6.6; N, 5.2. Calc. for $C_{18}H_{54}N_3O_{15}P_6Sc$: C, 27.6; H, 6.9; N, 5.4%). IR (cm^{-1}) (Nujol mull): 1361m, 1298m, 1156 (sh), 1104vs (PO), 958s, 891w, 870s, 834s, 760m, 681w, 423m, 371m, 363m and 350w. ^{31}P-{^1H} NMR (300 K, $MeNO_2$): δ 64.7, 62.0 (sh) and 43.0. ^{45}Sc NMR (300 K, $MeNO_2$): δ 11.4 ($W_{1/2} = 450$) and 5.0 ($W_{1/2} = 180$ Hz). ^1H NMR (300 K, CD_3NO_2): δ 2.6 (d, $^2J_{PH} = 13$) and 2.4 (d, $^2J_{PH} = 13$ Hz). Λ_M (10^{-3} mol dm^{-3} $MeNO_2$) = 157 ohm^{-1} cm^2 mol^{-1}.

Crystallography

Diffraction data were recorded using either a Rigaku AFC7S or a Nonius CCD diffractometer both fitted with Mo-Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Unless stated otherwise data were collected on the former diffractometer with the sample at 150 K. The crystals studied scattered weakly as judged by $I/\sigma(I)$ and the area detector diffractometer was used for the smaller crystals. Data processing was performed using the TEXSAN package[9] for AFC7S data and structure refinement was carried out using either TEXSAN or SHELXL 97.[10] Trial structures were obtained from SHELXS 86[11] unless stated otherwise. Crystallographic data are reported in Table 1 and brief comments about each structure determination are given below. A number of the crystals appeared of high quality by microscopic examination but disappointingly gave structures of moderate quality.

[Y(Ph$_3$PO)$_2$(EtOH)(NO$_3$)$_3$]. Crystals were grown by slow evaporation of an EtOH solution of complex and data collected on the CCD diffractometer at 150 K. The structure was solved using DIRDIF[12] and the data refined[9] on F with isotropic atomic displacement parameters (adps) for C and N atoms due to the small amount of 'observed' data. Hydrogen atoms were placed in calculated positions for phenyl groups only.

$[Y(Ph_3PO)_3(NO_3)_3]\cdot x CH_2Cl_2$ and $[Y(Ph_3PO)_3(NO_3)_3]$. Colourless plate-like crystals of the dichloromethane solvate were grown by vapour diffusion of Et_2O into a CH_2Cl_2 solution of the compound with the crystallising cell held in a freezer. At a later stage of refinement, solvate CH_2Cl_2 molecules were apparent and included in the model with a refined population. Although correlation was not a problem between the atom population parameters and the isotropic adp values of the solvate atoms, refinement tended to drift and the adps were eventually fixed for the final refinement. The H atoms were included in the model in calculated positions (d(C–H) = 0.95 Å) and significantly improved the fit to the data. Refinement on F^2 was carried out using SHELXL 97[10] with anisotropic (Y, P, O, N) and isotropic (C, H, Cl) atoms. A non-solvated form of the crystals was obtained in later experiments using the same crystallising solvents. During refinement one phenyl ring became an odd shape and was treated as a rigid group. The weaker data, poorer R value and refinement difficulty led us to concentrate on the structure of the solvated crystal.

$[Y(Ph_2MePO)_3(NO_3)_3]$. Small colourless needle crystals were grown as above. Nonius CCD data recorded at 150 K, with SORTAV[13] absorption correction applied. Full-matrix least-squares refinement on F was carried out in TEXSAN. A number of plausible H atoms appeared in the Fourier difference synthesis and all were introduced in calculated positions (d(C–H) = 0.95 Å). All the non-H atoms were treated as anisotropic and there was no evidence for solvate molecules.

$[Y(Me_3PO)_3(NO_3)_3]$. A few large crystals were grown as above and in view of the rather weak data noted for other samples a larger than usual crystal was selected. During refinement some C atoms went non-positive definite on anisotropic refinement and all C atoms were retained with isotropic adp values in the model and no H atoms were included. The space group $P\bar{1}$ (no. 2) with $Z = 4$ caused some concern but the Niggli cell did not indicate any missed symmetry and although the coordinates of the two Y atoms of the asymmmetric unit look to be related this did not appear to extend to the other atoms and thus no smaller cell with $Z = 2$ was identified.

$[Sc(Ph_3PO)_2(NO_3)_3]$. The crystal used was isolated from the preparation of the compound. Attempts were also made to grow crystals by vapour diffusion using the procedure in the preceding section, but these experiments tended to give clusters of very small crystals. From the trial Sc and P atoms, subsequent structure factor-Fourier calculations identified the remaining non-H atoms. There was no evidence for solvate molecules and later electron-density maps showed evidence for some of the phenyl H atoms. All H atoms were introduced into the model in calculated positions (d(C–H) = 0.95 Å) and full-matrix least-squares refinement[10] was carried out on F^2. The absolute configuration of the selected crystal was established (Flack parameter[14] 0.01(9)).

$[Sc(Ph_2MePO)_4(NO_3)_2]NO_3\cdot x CH_2Cl_2$. Crystals were grown from CH_2Cl_2 solution by vapour diffusion of light petroleum (bp 40–60 °C). The solvate CH_2Cl_2 became apparent in later electron-density maps but gave rather large U values. Accordingly the population of CH_2Cl_2 was adjusted to get Cl atom adp values similar to those of Sc and P atoms. Phenyl H atoms were added in calculated positions (d(C–H) = 0.95 Å) and full-matrix least-squares refinement[10] was carried out on F^2. The largest peaks in the residual electron density are close to Cl atoms.

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See http://www.rsc.org/suppdata/dt/b0/b001669l/ for crystallographic files in .cif format.

Results and discussion

Yttrium complexes

The complexes were made straightforwardly by reaction of hydrated yttrium(III) nitrate with the phosphine oxide in ethanol. Although, as shown by the ^{31}P NMR studies described below, many solutions contain a mixture of complexes, pure samples of a single complex usually crystallise from the solutions with the reagents in the ratios described. The reaction of $Y(NO_3)_3\cdot 6H_2O$ with Ph_3PO in a 1 : 1 or 1 : 2 mole ratio in boiling ethanol produced $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$, whilst from a 1 : 4 ratio the product was the tris(phosphine oxide) complex $[Y(Ph_3PO)_3(NO_3)_3]$. Finally, reaction of a 1 : 6 ratio in ice-cold ethanol produced $Y(Ph_3PO)_4(NO_3)_3$. For Ph_2MePO, reaction with $Y(NO_3)_3\cdot 6H_2O$ in boiling ethanol in a 3 : 1 ratio gave $[Y(Ph_2MePO)_3(NO_3)_3]$, whilst a 1 : 1 ratio gave poor yields of $[Y(Ph_2MePO)_2(EtOH)(NO_3)_3]$. The latter always seems to be contaminated with some (<10%) $[Y(Ph_2MePO)_3(NO_3)_3]$, and an analytically pure sample has not been obtained despite many attempts, although the spectroscopic identification of the ethanol complex is clear (Experimental section). The ^{89}Y NMR data (below) show that solutions of $[Y(Ph_2MePO)_3(NO_3)_3]$ in CH_2Cl_2 containing an excess of Ph_2MePO are essentially completely converted into $Y(Ph_2MePO)_4(NO_3)_3$, but concentration of such solutions, or reaction of $Y(NO_3)_3\cdot 6H_2O$ with Ph_2MePO in a 1 : 6 ratio in ethanol, resulted only in isolation of the tris(phosphine oxide) complex. The $[Y(Me_3PO)_3(NO_3)_3]$ was easily formed from the constituents in a 3 : 1 ratio in hot ethanol, but from a 1 : 1 ratio in boiling ethanol the product was $[Y(Me_3PO)_2(H_2O)(NO_3)_3]$ rather than the expected ethanol complex. Although NMR studies showed that mixtures of $Y(NO_3)_3\cdot 6H_2O$ and Me_3PO with 1 : ≥6 in ethanol or CH_2Cl_2 contained a tetrakis(phosphine oxide) complex (*cf.* the Ph_2MePO system), on concentration these solutions deposited crystals of $[Y(Me_3PO)_3(NO_3)_3]$. Treatment of Ph_3PS with yttrium nitrate under similar conditions in EtOH gave no evidence for complex formation.

All the complexes are poorly soluble in alcohols, the 3 : 1 and 4 : 1 complexes are easily soluble in CH_2Cl_2, the 2 : 1 complexes less so, which made it difficult to obtain ^{89}Y NMR spectra of the latter. The mull IR spectra are complex (Experimental section), but the ν(PO) vibrations are easily identified by their high intensities, and in all cases are 20–50 cm^{-1} to lower wavenumbers of the vibrations of the "free" ligand (Me_3PO 1161, Ph_2MePO 1172, Ph_3PO 1195 cm^{-1}) showing that all the phosphine oxides are co-ordinated to the yttrium. The IR spectrum of $Y(Ph_3PO)_4(NO_3)_3$ is very similar to that[15] of $[Lu(Ph_3PO)_4(NO_3)_2]NO_3$ (which contains 8-co-ordinate lutetium and bidentate nitrato-groups) and in particular shows a weak band at 830 cm^{-1}, absent for the other yttrium complexes, which may be assigned as ν_2 of an ionic NO_3^-, indicating a $[Y(Ph_3PO)_4(NO_3)_2]NO_3$ constitution. Distinction of mono- and bi-dentate co-ordinated nitrate groups by IR spectroscopy is notoriously difficult[16] and has not been attempted. However crystal structures have been determined for $[Y(R_3PO)_3(NO_3)_3]$ ($R_3 = Me_3$, Ph_2Me or Ph_3) and $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$. Unfortunately all attempts to grow crystals of $Y(Ph_3PO)_4(NO_3)_3$ failed; it separates as a powder from the synthesis, and attempts to grow crystals using the pre-isolated complex from a variety of solvents produced crystals of $[Y(Ph_3PO)_3(NO_3)_3]$.

The crystal structure of $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$ is shown in Fig. 1 and selected bond lengths and angles are given in Table 2. As with all the structures reported here, the co-ordinated

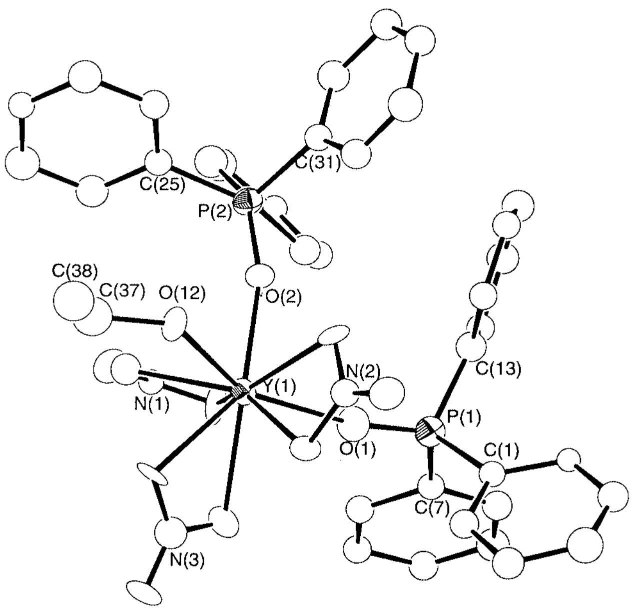

Fig. 1 The structure of [Y(Ph$_3$PO)$_2$(EtOH)(NO$_3$)$_3$] showing the atom labelling scheme. Thermal ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity.

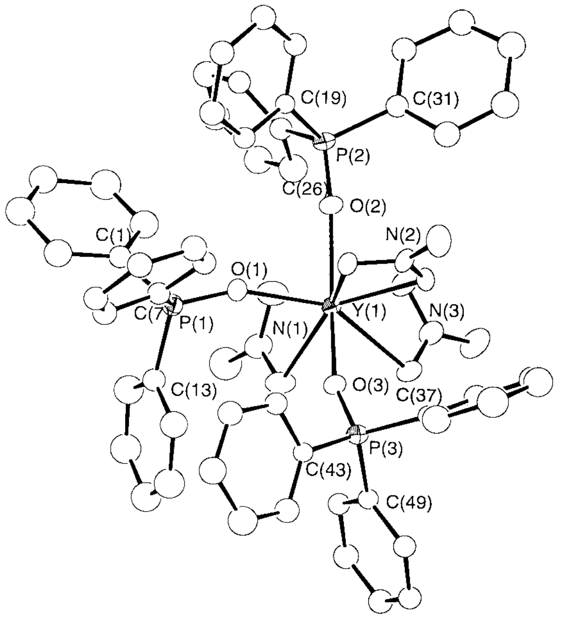

Fig. 2 The co-ordination polyhedron around Y in [Y(Ph$_3$PO)$_3$(NO$_3$)$_3$]·xCH$_2$Cl$_2$. Details as in Fig. 1.

nitrate groups bond in the bidentate symmetrical mode, one of the several modes of co-ordination of this anion.[17] As has been recognised before,[18] the geometry shows that the co-ordinated O atoms (O$_c$) have longer N–O distances than the unco-ordinated or "free" N–O and the O$_c$–N–O$_c$ angles to be smaller than the idealised 120° of the isolated NO$_3^-$ anion. The Y atom is nine-co-ordinate, but if the NO$_3$ group is conceptually replaced by a monatomic ligand the molecule can be described as *mer*-(pseudo)-octahedral with *cis* Ph$_3$PO ligands. The corresponding compounds of Ce,[15] Eu,[18] Nd[19] and Sm[20] are probably isomorphous judged by cell dimensions and space group. The structures of [Y(R$_3$PO)$_3$(NO$_3$)$_3$] (R$_3$ = Ph$_3$, Ph$_2$Me or Me$_3$) have also been determined, the first as both the dichloromethane solvate and non-solvated forms (see Figs. 2, 3 and 4 and Table 2). All are based on nine-co-ordinate Y with the symmetrical bidentate NO$_3$ ligand. They are based on a (pseudo-)octahedral metal atom when regarding NO$_3$ as a monatomic ligand with the *mer* arrangement for Ph$_3$PO and Ph$_2$MePO and, unexpectedly, the *fac* arrangement for the Me$_3$PO adduct (both molecules). This is most easily seen from the figures and the (P)O–Y–O(P) angles (Table 2). The Y–O(P) and Y–O(N) distances are insensitive to the compound with the latter *ca.* 0.2 Å longer. The M–O–P angle in complexes of R$_3$PO is very variable and the values in these four compounds range from 140 to 170° with the hint in the data that the larger angles correlate with more phenyl substituents (Y–O–P (av.): Me$_3$PO, 146; Ph$_2$MePO, 156; Ph$_3$PO, 166°). The non-solvated form of [Y(Ph$_3$PO)$_3$(NO$_3$)$_3$] has the same stereochemistry as that of the CH$_2$Cl$_2$ solvate with similar bond lengths and angles.

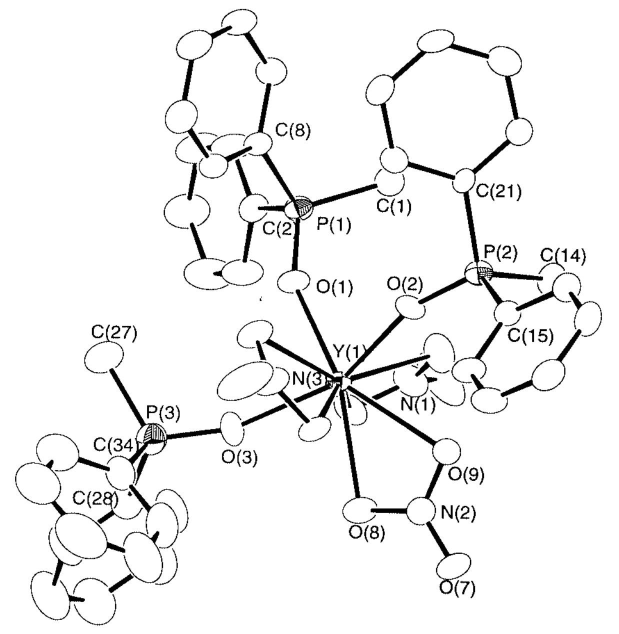

Fig. 3 The co-ordination polyhedron around Y in [Y(Ph$_2$MePO)$_3$-(NO$_3$)$_3$]. Details as in Fig. 1.

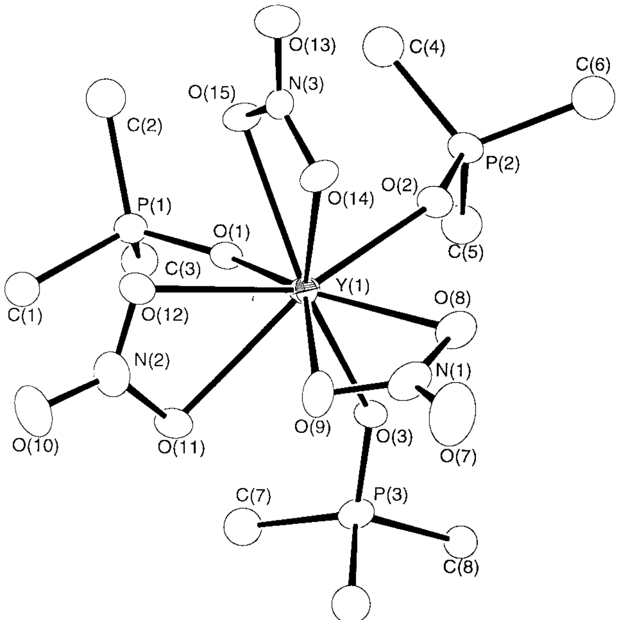

Fig. 4 The structure of [Y(Me$_3$PO)$_3$(NO$_3$)$_3$] showing the atom labelling scheme for the molecule centred on Y(1). Thermal ellipsoids are drawn at the 40% probability level. The second molecule in the asymmetric unit is very similar.

^{31}P-{^{1}H} and ^{89}Y NMR studies. ^{89}Y is among the more difficult nuclei to observe,[1,21] a consequence of its low resonance frequency (Ξ = 4.92 MHz) and very long T_1 values. Our spectra were obtained from CH$_2$Cl$_2$ solutions containing 1–2 mg of

Table 1 Crystallographic data

	$[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$	$[Y(Ph_3PO)_3(NO_3)_3]\cdot xCH_2Cl_2$ ($x = 1.78$)	$[Y(Ph_3PO)_3(NO_3)_3]$	$[Y(Ph_2MePO)_3(NO_3)_3]$	$[Y(Me_3PO)_3(NO_3)_3]$	$[Sc(Ph_3PO)_2(NO_3)_3]$	$[Sc(Ph_2MePO)_4(NO_3)_2]$-$NO_3\cdot xCH_2Cl_2$
Molecular formula	$C_{38}H_{36}N_3O_{12}P_2Y$	$C_{54}H_{45}N_3O_{12}P_3Y + xCH_2Cl_2$ ($x = 1.78$)	$C_{54}H_{45}N_3O_{12}P_3Y$	$C_{39}H_{39}N_3O_{12}P_3Y$	$C_9H_{27}N_3O_{12}P_3Y$	$C_{36}H_{30}N_3O_{11}P_2Sc$	$C_{52}H_{52}N_3O_{13}P_4Sc\cdot xCH_2Cl_2$ (x *ca.* 1.3)
M_r	877.57	1109.79 + x84.93	1109.79	923.58	551.15	787.53	1095.85 + x84.93
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	Pn (no. 7)	$P2_1/n$ (no. 14)
a/Å	16.975(2)	11.118(2)	11.170(6)	20.111(1)	14.578(10)	10.249(5)	13.712(5)
b/Å	10.745(2)	19.342(3)	11.411(4)	10.8636(4)	15.394(23)	10.628(4)	23.412(4)
c/Å	22.024(3)	27.244(3)	41.504(6)	20.648(1)	10.567(22)	17.289(5)	18.650(4)
α/°					99.99(14)		
β/°	105.877(8)	94.57(2)	93.48(3)	106.830(2)	93.03(11)	100.76(3)	98.40(2)
γ/°					96.91(9)		
U/Å	3863.8(9)	5839.8(16)	5280.3(3.5)	4318.0(4)	2312.0(6.2)	1850.0(12)	5922.9(2.9)
Z	4	4	4	4	4	2	4
Total no. observations	19560	10823	10349	68129	8495	2706	11172
No. unique observations	6286 ($R_{int} = 0.252$)	10255 ($R_{int} = 0.059$)	9809 ($R_{int} = 0.078$)	8832 ($R_{int} = 0.228$)	8145 ($R_{int} = 0.093$)	2704 ($R_{int} = 0.200$)	10398 ($R_{int} = 0.088$)
No. data in refinement	1765 ($I > 2\sigma(I)$)	10255	2941 ($I > n\sigma(I)$, $n = 2$)	4609 ($I > n\sigma(I)$, $n = 2$)	5513 ($I > n\sigma(I)$, $n = 2$)	2704	10398
No. parameters/restraints	300/0	409/0	356/0	523/0	415/0	284/2	428/0
μ/cm^{-1}	16.61	13.1 ($x = 1.78$)	12.61	15.26	27.94	3.49	4.1 ($x = 1.3$)
R ($F_o > n\sigma(F_o)$)	0.097 ($n = 4$, 1765)	0.0656 ($n = 4$, 4523)	0.087 ($n = 4$, 2941)	0.0623 ($n = 4$)	0.060 ($n = 4$, 5513)	0.0515 ($n = 4$, 1707)	0.0846 ($n = 4$, 4535)
(all data)	—	0.1926	—	—	—	0.1084	0.2183
$wR2$ (all data)	—	0.2206	—	—	—	0.1546	0.3322
wR ($F_o > n\sigma(F_o)$)	0.095 ($n = 4$)	—	0.095 ($n = 4$)	0.0422 ($n = 4$, 4609)	0.062 ($n = 4$)	—	—

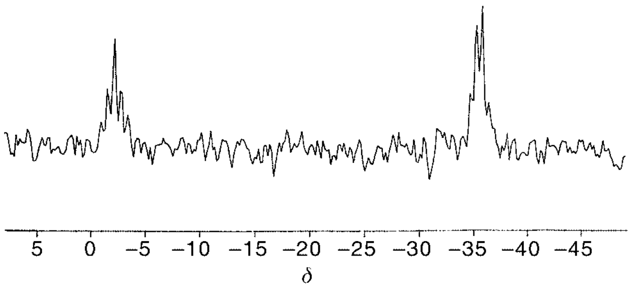

Fig. 5 The ^{89}Y NMR spectrum at 200 K of $[Y(Ph_3PO)_3(NO_3)_3]$ in CH_2Cl_2–10%$CDCl_3$ with 2 mg TEMPO. 2000 scans, 25 kHz sweep width and 2 s pulse delay.

TEMPO as a relaxation agent and with a pulse delay of 2 s. From concentrated solutions ^{89}Y resonances were typically observed after 2000–3000 scans. The NMR data obtained at 300 K are given in the Experimental section, but in a number of cases ^{89}Y resonances were observed only from cooled solutions, and low temperatures were necessary to resolve spin–spin couplings. The high resolution data are listed in Table 3, the temperatures quoted being those at which couplings were well resolved.

The ^{31}P-{^1H} NMR spectrum of $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$ at 300 K is a singlet at δ 37.0, and we did not observe an ^{89}Y resonance from this solution. On cooling to 200 K the phosphorus resonance was a poorly resolved doublet, but more importantly an ^{89}Y resonance at δ −35.8 showed a clear triplet structure with $^2J(^{31}P–^{89}Y) = 11$ Hz. Solutions of $[Y(Ph_3PO)_3(NO_3)_3]$ at 300 K consistently showed two phosphorus resonances at δ 36.5 and 33.9. The possibility that these reflected inequivalent phosphine oxides (a "T" shaped arrangement of the ligands is present in the solid) was ruled out by their relative intensities which were nearer 1.5 : 1 than the expected 2 : 1, moreover the relative intensities varied slightly with dilution of the solution. Addition of Ph_3PO to the solution at 300 K showed three resonances δ 26.0 (Ph_3PO), 33.9, and 36.5, showing slow exchange with "free" ligand on the ^{31}P NMR timescale, but notably with the δ 36.5 resonance now relatively much more intense than that at δ 33.9. On cooling the solution to 200 K both resonances of the co-ordinated phosphine oxides exhibited doublet couplings (Table 3). At 200 K an ^{89}Y NMR spectrum was obtained from the initial solution which revealed two resonances of approximately equal intensity, a quartet at δ −35.7 and a quintet at δ −2.0 (Fig. 5), demonstrating that in solution $[Y(Ph_3PO)_3(NO_3)_3]$ exists as a mixture of $[Y(Ph_3PO)_3(NO_3)_3]$ and $[Y(Ph_3PO)_4(NO_3)_2]NO_3$.† Addition of an excess of Ph_3PO (>10 fold) to this solution results in the disappearance of the $\delta(^{31}P)$ of 33.9 and $\delta(^{89}Y)$ of −35.7 resonances showing that the equilibrium is easily shifted in favour of the tetrakis(phosphine oxide) complex. As would be expected, NMR studies of solutions of $[Y(Ph_3PO)_4(NO_3)_2]NO_3$ reveal very similar data to those of the tris(phosphine oxide) complex with an extra resonance in the ^{31}P-{^1H} spectrum due to free Ph_3PO at δ 26.0. Support for the presence of $[Y(Ph_3PO)_4(NO_3)_2]NO_3$ in CH_2Cl_2 solutions of both the 3 : 1 and 4 : 1 complexes comes from the molar conductances which are significantly higher (Λ_m *ca.* 13–14 ohm^{-1} cm^2 mol^{-1}) than those expected for non-electrolytes, and which increase on addition of Ph_3PO, approaching that of 1 : 1 electrolytes with an excess of Ph_3PO (Λ_m *ca.* 22 ohm^{-1} cm^2 mol^{-1}).[22]

In contrast to the Ph_3PO complex, the 300 K ^{31}P-{^1H} NMR spectrum of $[Y(Ph_2MePO)_3(NO_3)_3]$ in CH_2Cl_2 shows only a single resonance, and at 200 K this resolves into a doublet, whilst a quartet ^{89}Y resonance is observed (Table 3). Thus we conclude that unlike the Ph_3PO complex, the Ph_2MePO

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† Mass balance requires at least one other yttrium species is formed, but none was detected in the ^{89}Y spectrum.

Table 2 Selected bond lengths (Å) and angles (°) for $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$ and $[Y(R_3PO)_3(NO_3)_3]$ ($R_3 = Ph_3$, Me_3 or Ph_2Me)

(a) $[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$			
Y(1)–O(1)	2.25(2)	O(1)–P(1)	1.50(2)
Y(1)–O(2)	2.27(1)	O(2)–P(2)	1.50(1)
Y(1)–O(N)	2.39(2)–2.47(1)	Y(1)–O(12)	2.40(2)
N–O_c[a]	1.22(2)–1.33(2)	N–O_f[a]	1.25(2), 1.20(2), 1.21(2)
O(1)–Y(1)–O(2)	89.2(6)	Y(1)–O(1)–P(1)	170(1)
O(1)–Y(1)–O(12)	149.8(6)	Y(1)–O(2)–P(2)	164(1)
O(2)–Y(1)–O(12)	79.8(5)	O_c–N–O_c	113(2)–115(2)
O_c–Y(1)–O_c[b]	52.1(5)–52.9(6)		
(b) $[Y(Ph_3PO)_3(NO_3)_3]\cdot xCH_2Cl_2$			
Y(1)–O(1)	2.269(5)	O(1)–P(1)	1.503(5)
Y(1)–O(2)	2.284(5)	O(2)–P(2)	1.484(5)
Y(1)–O(3)	2.283(5)	O(3)–P(3)	1.498(5)
Y(1)–O(N)	2.403(5)–2.506(5)	P–C	1.789(7)–1.807(8)
N–O_c[a]	1.254(8)–1.271(8)	N–O_f[a]	1.215(8), 1.235(8), 1.220(8)
O(1)–Y(1)–O(2)	83.4(2)	Y(1)–O(1)–P(1)	156.8(3)
O(1)–Y(1)–O(3)	86.2(2)	Y(1)–O(2)–P(2)	173.7(3)
O(2)–Y(1)–O(3)	149.5(2)	Y(1)–O(3)–P(3)	162.6(3)
O_c–N–O_c	116.0(7)–116.7(6)	O_c–Y(1)–O_c[b]	51.5(2)–52.1(2)
(c) $[Y(Ph_2MePO)_3(NO_3)_3]$			
Y(1)–O(1)	2.258(3)	O(1)–P(1)	1.510(3)
Y(1)–O(2)	2.248(4)	O(2)–P(2)	1.513(4)
Y(1)–O(3)	2.252(4)	O(3)–P(3)	1.494(4)
Y(1)–O(N)	2.413(4)–2.491(4)	P–C	1.773(6)–1.815(7)
N–O_c[a]	1.255(6)–1.279(5)	N–O_f[a]	1.221(6), 1.232(5), 1.209(6)
O(1)–Y(1)–O(2)	84.1(1)	Y(1)–O(1)–P(1)	154.3(3)
O(1)–Y(1)–O(3)	84.2(1)	Y(1)–O(2)–P(2)	157.9(2)
O(2)–Y(1)–O(3)	153.5(1)	Y(1)–O(3)–P(3)	157.3(3)
O_c–N–O_c	115.8(5)–116.4(6)	O_c–Y(1)–O_c[b]	50.9(1)–52.4(1)
(d) $[Y(Me_3PO)_3(NO_3)_3]$			
Y(1)–O(1)	2.281(7)	Y(2)–O(4)	2.270(6)
Y(1)–O(2)	2.279(7)	Y(2)–O(5)	2.251(7)
Y(1)–O(3)	2.262(7)	Y(2)–O(6)	2.258(7)
Y(1)–O(N)	2.441(7)–2.520(8)	Y(2)–O(N)	2.463(8)–2.525(7)
P(*n*)–O(*n*) (n = 1–6)	1.495(7)–1.521(7)		
N–O_c[a]	1.26(1)–1.30(1)	N–O_f[a]	1.21(1)–1.25(1)
O(1)–Y(1)–O(2)	86.0(2)	O(4)–Y(2)–O(5)	82.5(2)
O(1)–Y(1)–O(3)	82.9(2)	O(4)–Y(2)–O(6)	86.8(3)
O(2)–Y(1)–O(3)	84.3(2)	O(5)–Y(2)–O(6)	86.1(2)
Y(1)–O(1)–P(1)	149.9(4)	Y(2)–O(4)–P(4)	149.3(4)
Y(1)–O(2)–P(2)	140.2(4)	Y(2)–O(5)–P(5)	147.8(4)
Y(1)–O(3)–P(3)	147.0(4)	Y(2)–O(6)–P(6)	144.5(4)
O_c–N–O_c	115(1)–119(1)	O_c–Y–O_c[b]	51.2(2)–52.5(2)

[a] O_c and O_f refer to co-ordinated and 'free' O respectively of NO_3. [b] The O_c–Y–O_c angle refers to co-ordination by one NO_3 group.

Table 3 Multinuclear NMR data[a]

Complex	δ (^{31}P-{^1H})	δ(^{89}Y/^{45}Sc)	^2J(^{31}P–^{89}Y)/Hz	T/K
$[Y(Ph_3PO)_3(NO_3)_3]$	33.3 (d)	−35.7 (quartet)	9	240
$[Y(Ph_3PO)_4(NO_3)_2]NO_3$	35.7 (d)	−2.0 (quintet)	12	240
$[Y(Ph_3PO)_2(EtOH)(NO_3)_3]$	37.0 (d)	−35.8 (triplet)	11	200
$[Y(Ph_2MePO)_3(NO_3)_3]$	36.6 (d)	−26.2 (quartet)	10	220
$[Y(Ph_2MePO)_2(EtOH)(NO_3)_3]$	37.7 (d)	−37.6 (triplet)	8	200
"$Y(Ph_2MePO)_4(NO_3)_3$"[b]	38.3 (d)	+6.0 (quintet)	10	200
$[Y(Me_3PO)_3(NO_3)_3]$	48.3 (d)	−17.7 (quartet)	6	200
"$Y(Me_3PO)_4(NO_3)_3$"[c]	52.0[d]	−0.3 (quintet)	8	200
$[Y(Me_3PO)_2(H_2O)(NO_3)_3]$	51.0[d]	−12.0 (triplet)	≈12	200
$[Sc(Ph_3PO)_2(NO_3)_3]$	37.7	−7.5	—	300
$[Sc(Ph_2MePO)_3(NO_3)_3]$	39.5	−4.0	—	300
$[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$	38.7	−36.0 (br)	—	240
$[Sc(MePO)_2(EtOH)(NO_3)_3]$	54.8	−2.5	—	300
$[Sc(Me_3PO)_6][NO_3]_3$[e]	62.0 (octet)	+5.0	20[f]	300
"$[Sc(Me_3PO)_5(NO_3)][NO_3]_2$"[g]	64.7	+11.5	—	300

[a] At temperature stated in CH_2Cl_2–$CDCl_3$ solutions resonances are singlets unless indicated otherwise, d = doublet. [b] *In situ* from $[Y(Ph_2MePO)_3(NO_3)_3]$ and an excess of Ph_2MePO (see text). [c] *In situ* from $[Y(Me_3PO)_3(NO_3)_3]$ and an excess of Me_3PO. [d] Ill defined coupling. [e] In $MeNO_2$–CD_3NO_2 solution containing an excess of Me_3PO. [f] ^2J(^{45}Sc–^{31}P). [g] *In situ* from $[Sc(Me_3PO)_6][NO_3]_3$ in $MeNO_2$–CD_3NO_2 (see text).

Table 4 Selected bond lengths (Å) and angles (°) for [Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$] and [Sc(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$·xCH$_2$Cl$_2$

(a) [Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$]			
Sc–O(1)	2.068(7)	O(1)–P(1)	1.497(8)
Sc–O(2)	2.047(7)	O(2)–P(2)	1.513(7)
Sc–O(N)	2.205(8)–2.311(7)	P–C	1.77(1)–1.81(1)
N–O$_c$[a]	1.264(12)–1.280(11)	N–O$_f$[a]	1.208(11)–1.216(12)
O(1)–Sc–O(2)	90.7(3)		
Sc–O(1)–P(1)	165.1(5)	Sc–O(2)–P(2)	178.5(5)
O$_c$–N–O$_c$	112.0(10)–114.4(9)	O$_c$–Sc–O$_c$[b]	55.2(3)–57.1(3)
(b) [Sc(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$·xCH$_2$Cl$_2$			
Sc–O(1)	2.099(6)	O(1)–P(1)	1.493(6)
Sc–O(2)	2.097(6)	O(2)–P(2)	1.505(6)
Sc–O(3)	2.090(6)	O(3)–P(3)	1.502(6)
Sc–O(4)	2.088(6)	O(4)–P(4)	1.504(6)
Sc–O(N)	2.311(6)–2.425(6)	P–C	1.782(9)–1.822(9)
N–O$_c$[a]	1.257(9)–1.277(9)	N–O$_f$[a]	1.214(9), 1.219(9)
O(1)–Sc–O(2)	93.8(2)	Sc–O(1)–P(1)	162.7(4)
O(1)–Sc–O(4)	91.7(2)	Sc–O(2)–P(2)	159.6(4)
O(2)–Sc–O(3)	93.5(2)	Sc–O(3)–P(3)	161.3(4)
O(3)–Sc–O(4)	92.2(2)	Sc–O(4)–P(4)	162.4(4)
O$_c$–N–O$_c$	114.4(7), 116.5(7)	O$_c$–Sc–O$_c$[b]	54.8(2), 53.3(2)

[a] O$_c$ and O$_f$ refer to co-ordinated and 'free' O respectively of NO$_3$. [b] The O$_c$–Sc–O$_c$ angle refers to co-ordination by one NO$_3$ group.

complex does not disproportionate in solution. Moreover, the phosphine oxides are equivalent according to NMR, which contrasts with the "T" shape arrangement in the solid, and presumably indicates fluxionality in solution. Although it was not possible to isolate a [Y(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$ complex, addition of an excess of Ph$_2$MePO to CH$_2$Cl$_2$ solutions of [Y(Ph$_2$MePO)$_3$(NO$_3$)$_3$] produces essentially complete conversion into the tetrakis complex, identified (Table 3) by a quintet at δ 6.0 in the ^{89}Y NMR spectrum. The Me$_3$PO complexes generally behave similarly to the Ph$_2$MePO analogues in solution, including formation of [Y(Me$_3$PO)$_4$(NO$_3$)$_2$]NO$_3$ in the presence of an excess of ligand (Table 3). All the Y–R$_3$PO complexes show slow exchange (on the phosphorus NMR timescale) with added R$_3$PO at ambient temperatures, which contrasts with the lanthanum systems where exchange is fast at 300 K, but slows at <*ca.* 240 K.[15]

Scandium complexes

The scandium nitrate–R$_3$PO systems are simpler than the yttrium ones showing a more limited range of stoichiometries. The reaction of Sc(NO$_3$)$_3$·5H$_2$O with Ph$_3$PO in ethanol, irrespective of the ratio of reagents, gave colourless crystals of [Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$]. In contrast, a ≥4:1 molar ratio of Ph$_2$MePO:Sc(NO$_3$)$_3$·5H$_2$O in ethanol gave [Sc(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$. A 1:1 or 2:1 molar ratio in ethanol produced [Sc(Ph$_2$MePO)$_3$(NO$_3$)$_3$] which was very soluble and difficult to isolate, tending to separate as an oily product on concentration of the solution. The species has not been obtained as a crystalline solid, but in solution in CH$_2$Cl$_2$ it has a conductance well below that of a 1:1 electrolyte, whilst the IR spectrum of the solid shows no evidence for ionic nitrate. It is not possible on the basis of the available data to distinguish between 9-co-ordinate [Sc(Ph$_2$MePO)$_3$(η^2-NO$_3$)$_3$] or 8-co-ordinate [Sc(Ph$_2$MePO)$_3$(η^2-NO$_3$)$_2$(η^1-NO$_3$)] structures, and whereas 9-co-ordination is very rare for the small scandium ion,[23] it may be possible here given the small bite of η^2-NO$_3$ groups. The Me$_3$PO–Sc(NO$_3$)$_3$ system proved to be significantly different, in that reaction of a large excess (6–10 fold) of ligand with Sc(NO$_3$)$_3$·5H$_2$O in cold ethanol gave white [Sc(Me$_3$PO)$_6$][NO$_3$]$_3$. The IR spectrum (CsI disc) is rather simple and, in addition to phosphine oxide bands, shows moderate intensity peaks at 1361, 1298 and 834 cm^{-1} which are assigned to ionic nitrate groups,[16] and there was no evidence of co-ordinated nitrate groups. The complex is insoluble in chlorocarbons, acetone and cold ethanol, but is soluble in nitromethane in which it has a molar conductance of 157 ohm^{-1} cm^2 mol^{-1} which is in the range expected for 2:1 electrolytes, and on addition of Me$_3$PO the conductance rises to 250 ohm^{-1} cm^2 mol^{-1}, typical of a 3:1 electrolyte.[22] It dissolves with some decomposition in cold dmf, and in boiling ethanol it decomposes mainly to [Sc(Me$_3$PO)$_2$(EtOH)(NO$_3$)$_3$] and Me$_3$PO identified by *in situ* ^{31}P and ^{45}Sc NMR studies. The [Sc(Me$_3$PO)$_2$(EtOH)(NO$_3$)$_3$] was isolated with difficulty in very poor yield from solutions of Sc(NO$_3$)$_3$·5H$_2$O and Me$_3$PO in a 1:1 ratio in ethanol.

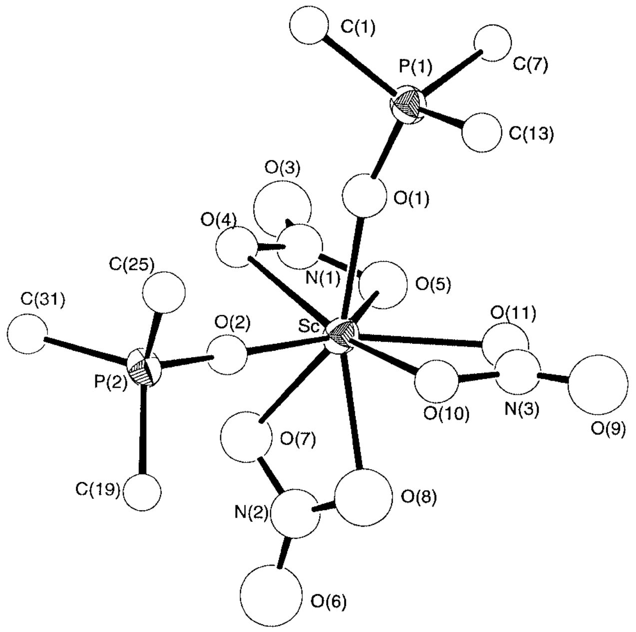

Fig. 6 The co-ordination polyhedron around Sc in [Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$] showing the atom labelling scheme. Phenyl C atoms not bonded to P have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level and H atoms omitted.

The crystal structures of [Sc(Ph$_3$PO)$_2$(NO$_3$)$_3$] and [Sc(Ph$_2$MePO)$_4$(NO$_3$)$_2$]NO$_3$·xCH$_2$Cl$_2$ have been determined and are shown in Figs. 6 and 7 with selected bond lengths and angles in Table 4. In both structures the Sc atom is eight-co-ordinate with the co-ordinated NO$_3$ group bonded in the symmetrical bidentate mode. With a monodentate group conceptually

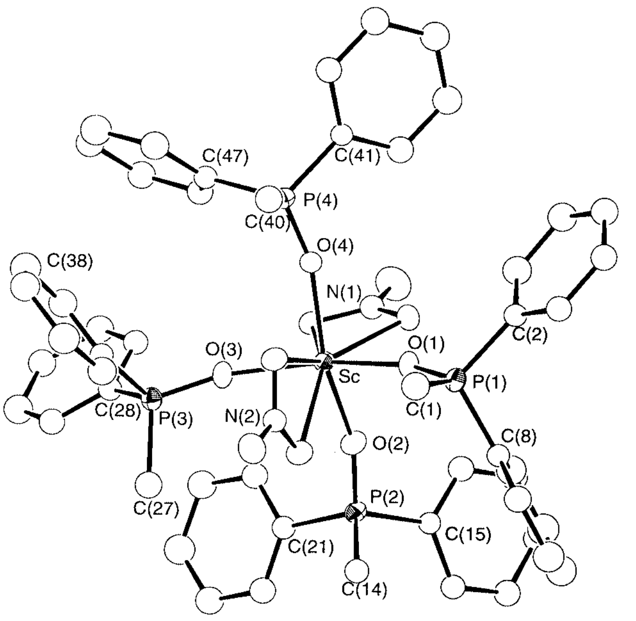

Fig. 7 The structure of the cation in $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3 \cdot xCH_2Cl_2$ showing the atom labelling scheme. Thermal ellipsoids are drawn at the 40% probability level and H atoms omitted for clarity.

replacing NO_3 the two structures are described as a trigonal bipyramid (with axial and equatorial Ph_3PO) and an octahedron (with *trans* NO_3 groups). Similar changes in NO_3 geometry are observed as were seen in the yttrium compounds above and the difference in Sc–O(P) and Sc–O(N) is again similar but with smaller values for both due to the smaller radius of Sc.

^{31}P-{^1H} and ^{45}Sc NMR Studies. In contrast to ^{89}Y, the ^{45}Sc NMR spectra were easily observed even at ambient temperatures, but in only one case ^{31}P–^{45}Sc coupling was resolved, its absence for the other complexes no doubt due to the fast quadrupolar relaxation resulting from the low symmetry environments of the scandium nuclei. The ^{31}P-{^1H} NMR spectrum of $[Sc(Ph_3PO)_2(NO_3)_3]$ in CH_2Cl_2 was a singlet at δ 37.7 and was unchanged on cooling the solution to 200 K. The ^{31}P-{^1H} resonance and the scandium resonance at δ −7.5 ($W_{1/2} = 900$ Hz) were unaffected by the addition of an excess of Ph_3PO showing both that exchange with ligand was slow on the NMR timescales and that no other complex formed. The NMR data on $[Sc(Ph_2MePO)_3(NO_3)_3]$ are also simple; $\delta(^{31}P) = 39.5$, $\delta(^{45}Sc)$ −4.0 ($W_{1/2}$ 350 Hz) (Table 3). In contrast the ^{31}P-{^1H} NMR spectrum of $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$ at 300 K (CH_2Cl_2) is a broad ($W_{1/2}$ 700 Hz) peak at δ 38.5, which on cooling sharpens rapidly to give at 250 K a major peak at δ 38.7 (tetrakis complex) and weaker peaks at δ 39.5 (tris) and 29.2 (Ph_2MePO). The ^{45}Sc NMR spectrum at 300 K shows partially overlapping resonances at *ca.* δ −4 and −33 which broaden into one asymmetric feature on cooling, presumably a result of the scandium quadrupole. Addition of an excess of Ph_2MePO to the solution at 300 K results in an increase in the relative intensity of the lower frequency resonance, but in contrast to the yttrium systems it does not appear to be possible completely to suppress the tris complex by adding an excess of phosphine oxide.

The ^{31}P-{^1H} NMR spectrum obtained from $[Sc(Me_3PO)_6][NO_3]_3$ in $MeNO_2$ solution at 300 K was a broad singlet δ 64.7 with a shoulder at 62.0, and a weaker resonance at 43.0 (Me_3PO) (integration *ca.* 5.3 : 1). The former sharpened a little on cooling to 245 K (lower temperature cannot be reached in $MeNO_2$, mp 244 K). On addition of a 10 fold excess of Me_3PO the co-ordinated phosphine oxide resonance shifted to δ 62.0 and under higher resolution was seen to be an eight line pattern (Fig. 8) due to coupling to ^{45}Sc ($I = 7/2$). The ^{45}Sc NMR of the initial solution contained a broad feature at δ 11.8 ($W_{1/2} = 450$ Hz) and a sharp weaker feature at δ 5.0 ($W_{1/2}$ *ca.* 150 Hz). In the presence of an excess of Me_3PO only a single resonance at δ 5.0 ($W_{1/2}$ 180 Hz) was observed, but unlike the corresponding ^{31}P resonance this showed no resolved ^{45}Sc–^{31}P coupling. The species which shows resolved ^{45}Sc coupling on the ^{31}P NMR resonance (Fig. 8) must be $[Sc(Me_3PO)_6]^{3+}$, where the regular O_h symmetry slows the quadrupolar relaxation rate. This is also supported by the conductance data showing a 3 : 1 electrolyte is present. In the absence of an excess of Me_3PO, the complex partially decomposes to a lower symmetry cation $[Sc(Me_3PO)_5(NO_3)][NO_3]_2$ (which is likely to be fluxional) and Me_3PO, consistent with the lower conductance and the NMR data described above.

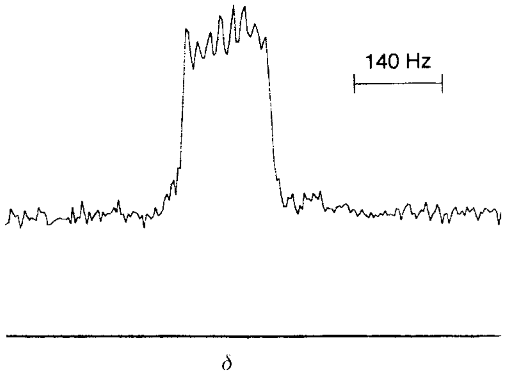

Fig. 8 The ^{31}P-{^1H} NMR resonance of $[Sc(Me_3PO)_6]^{3+}$ in $MeNO_2$ solutions of $[Sc(Me_3PO)_6][NO_3]_3$ containing an excess of Me_3PO.

The $\delta(^{31}P)$ of 54.8 and $\delta(^{45}Sc)$ of −2.5 of $[Sc(Me_3PO)_2(EtOH)(NO_3)_3]$ in CH_2Cl_2 seem unexceptional. As noted above, *in situ* ^{31}P-{^1H} and ^{45}Sc NMR studies of $Sc(NO_3)_3$–Me_3PO mixtures with 1 : 1–1 : 4 ratios in ethanol show $[Sc(Me_3PO)_2(EtOH)(NO_3)_3]$ (and sometimes Me_3PO $\delta(^{31}P)$ 43.0) as the only major constituents, and similar spectra were obtained from solutions of $[Sc(Me_3PO)_6][NO_3]_3$ dissolved in hot ethanol.

Conclusion

The multinuclear NMR studies have revealed a range of complexes are present in $M(NO_3)_3$–R_3PO systems, which show subtle variations with M, R_3PO and the reaction conditions. Although the complexes are not undergoing fast exchange with free R_3PO on the NMR timescale, all are labile and interconvert easily in solution, the fast equilibria probably accounting for the fact that single species crystallise from most solutions. The NMR data do not reflect the inequivalent R_3PO environments identified in the crystalline solids, consistent with fluxionality at the high co-ordination number metal centres in solution.

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