

Supplementary Data

Table S1 Principle infrared bands (cm⁻¹) for Ln(NO₃)₃(^tBu₃PO)₂(H₂O)_x(EtOH)_y

			ν_{OH}	ν_{NO}			ν_{PO}
	x	y		ν_5	ν_1	ν_2	
L							1107
La	1	2	3481 3282	1459 1444	1298 1280	1028	1065
Nd	1	2	3502 3278	1460 1447	1303 1281	1030	1067
Sm	0	0.5	3392	1511 1458	1305 1278	1031	1063
Eu	0	1	3407	1508 1456	1305 1277	1021	1066
Dy	0	0		1507 1470	1274	1021	1073
Er	0	0		1512 1472	1283	1024	1070
Lu	0	0		1512 1471	1280	1022	1085

Table S2 ESMS data for the principle metal containing ions from Ln(NO₃)₃L₂ in CH₂Cl₂ /MeCN
Observed (calculated)

	La	Nd	Sm	Eu	Dy	Er	Lu
Ln(NO ₃) ₂ L ₃ ⁺	917.4209 (917.4213)	922.4265 (922.4227)	930.4348 (930.4347)	931.4364 (931.4362)	942.4451 (942.4694)	944.4475 (944.4452)	953.4552 (953.4557)
Ln(NO ₃) (OH)L ₃ ⁺	872.4368 (872.4362)	877.4422 (877.4376)	885.4503 (885.4496)	886.4521 (886.4511)	897.4605 (897.4590)	901.4627 (901.4602)	908.4701 (908.4706)
Ln(NO ₃) ₂ L ₂ ⁺	699.2403 (699.2414)	704.2459 (704.2456)	712.2545 (712.2547)	713.2560 (713.2562)	724.2644 (724.2642)	726.2643 (726.2653)	735.2747 (735.2758)
Ln(NO ₃)L ₄ ²⁺	Not obs	(547.3127)	552.3183 (522.3187)	552.8192 (552.8195)	558.3234 (558.3234)	560.3244 (560.3240)	563.8282 (563.8292)
	426.2291	428.7319		433.2367	437.3673		444.7472
Ln(OH)L ₃ ²⁺	405.2241 (405.2242)	407.7219 (407.7249)	411.7308 (411.7309)	412.2315 (412.2317)	417.7358 (417.7356)	419.7370 (419.7362)	423.2411 (423.2414)

Table S3 NMR data for $\text{Ln}(\text{NO}_3)_3(\text{tBu}_3\text{PO})_2$ in CD_2Cl_2

			Temperature /°C				
	nucleus		20	-30	-60	-90	
La	^{31}P		78.69	77.34	76.97	76.93(4) ^c 76.29(1) 73.56(1)	
	$^{13}\text{C}^{\text{a}}$	C	39.58(d)	39.19(d)	38.84(d)	38.50(d)	
		CH_3	28.80	28.45	28.06	28.84(2) ^c 25.33(1)	
	$^1\text{H}^{\text{b}}$		1.389(d)	1.341(d)	1.309(d)	1.282(s)	
Nd	^{31}P		194.50	229.50	251.85	277.64(8) ^c 287.99(1)	
	^{13}C	C	42.45(d)	44.17(br,s)	45.10(br,s)	44.78(br,s)	
		CH_3	31.47	32.93	33.75	34.97	
	^1H		3.742	4.7463	5.211	6.606 5.864 4.908	
Sm	^{31}P		72.26	73.54	75.66	78.56(10) ^c 81.77(1) 79.61(1) 72.60(1)	
	$^{13}\text{C}^{\text{a}}$	C	39.84(d)	39.90(d)	39.72 (d)	39.48(d)	
		CH_3	28.37	28.59	28.53	29.75 25.72	
	$^1\text{H}^{\text{b}}$		1.570(d)	1.486(d)	1.438(d)	1.329(s)	
Eu	^{31}P		-57.66	-85.54	-107.46	-133.57	
	$^{13}\text{C}^{\text{a}}$	C	37.77(d)	34.0	30.9	26.5	
		CH_3	25.52	22.93	20.79	19.59	
	$^1\text{H}^{\text{b}}$		1.338(d)	-3.17(s)	-4.74(s)	-6.67(s)	
Dy	^{31}P		620.2	1033.5	1429.0	2052.1	
	^{13}C	C	388.8	605.4	Not obs	Not obs	
		CH_3	207.2	324.5	Not obs	Not obs	
	^1H			-0.55	-1.1	-1.2	
Er	^{31}P		-267.4	-391.8	-498.4	-657.1	
	^{13}C	C	-32.5	-65.9	-97.2	Not obs	
		CH_3	-14.9	-35.0	-53.4	-68.6	
	^1H		19.98	6.04	-6.78	-23.11	
Lu	^{31}P		80.21	79.50	79.07	78.66	
	$^{13}\text{C}^{\text{a}}$	C	39.82(d)	39.47(d)	39.46(d)	39.45(d)	
		CH_3	28.65	28.26	28.29	29.47,	

						25.58	
	¹ H ^b		1.393(d)	1.334(d)	1.307(d)	1.271(s)	

a. $^1J_{PC} \sim 49$ Hz b. $^3J_{PH} \sim 13.5$ Hz c. Relative intensities

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Lanthanide nitrate complexes with $t\text{Bu}_3\text{PO}$ ($=\text{L}$) form 1:2 complexes $\text{Ln}(\text{NO}_3)_3\text{L}_2$ rather than the more common $\text{Ln}(\text{NO}_3)_3\text{L}_3$ found with other trialkylphosphine oxides. The complexes of the heavier lanthanides ($\text{Ln} = \text{Dy}, \text{Er}$ and Lu) crystallise with two isomers in the solid state. These are not observable as separate species in solution and show no evidence of interconversion in the solid state. Attempts to prepare pure 1:3 complexes $[\text{Ln}(\text{NO}_3)_2\text{L}_3]^+$ were not successful.

