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Table S1. Hydrogen bonds data of the crystalline compounds

Compound	D–H...A	*d*(D–H) Å	*d*(H…A) Å	*d*(D–A) Å	∠DHA °
FPA	N(1)–H(1)…O(1)[a]	0.806	2.139	2.930(2)	166.8
ClPA	N(1)–H(1)…O(1)[b]	0.897	2.044	2.866(2)	156.2
BrPA	N(1)–H(1)…O(1)[b]	0.900	2.034	2.917(2)	166.3
LaClPA	N(1)–H(1)…Cl(1)[c]	0.900	2.597	3.452(7)	158.6
	O(4)–H(4A)…N(4)[d]	0.881	2.116	2.968(9)	162.6
	O(4)–H(4B)…O(2)[e]	0.880	1.941	2.808(8)	168.0
LaBrPA	N(1)–H(1)…Cl(1)[f]	0.934	2.388	3.318(2)	174.4
	O(1S)–H(1S)…O(2)[e]	0.891	1.964	2.832(2)	164.3
CeHPA	N(1)–H(1)…Cl(1)[g]	0.835	2.568	3.400(2)	174.3
	O(1W)–H(1WA)…O(3)[h]	0.811	2.017	2.798(2)	161.7
	O(1W)–H(1WB)…O(2)[i]	0.812	1.954	2.757(2)	169.4
CeFPA	N(1)–H(1)…Cl(1)[j]	0.880	2.585	3.420(5)	158.8
	O(1W)–H(1W)…O(2)[k]	0.851	1.862	2.712(6)	179.7
	O(1W)–H(2W)…O(3)[l]	0.850	1.982	2.832(6)	179.6
CeClPA	N(1)–H(1)…Cl(1)[m]	0.837	2.495	3.329(2)	174.6
	O(1S)–H(1S)…O(2)[n]	0.876	1.972	2.824(11)	163.9
NdHPA	N(1)–H(1)…Cl(1)[o]	0.740	2.765	3.475(2)	161.4
	O(1W)–H(1W)…O(3)[p]	0.749	2.098	2.840(4)	171.3
	O(1W)–H(2W)…O(2)[q]	0.733	2.066	2.794(4)	171.9

[a]1+x,y,z, [b]1/2-x,-1/2+y,z, [c]-1/2+x,-1/2+y,z, [d]x,y,z, [e]1/2-x,1/2+y,1/2-z, [f]-1/2-x,1/2+y,1/2-z, [g]-1/2-x,-y,1/2+z, [h]1/2-x,y,1/2+z, [i]3/4-x,-1/4+y,1/4+z, [j]1/2+x,y,-1/2+z, [k]-1/2-x,-y,-1/2+z, [l]-x,1/2-y,1/2+z, [m]1/2-x,-1/2+y,1/2-z, [n]-1/2+x,-1/2+y,z, [o]-1/2+x,y,1/2+z, [p]1/2-x,-y,1/2+z, [q]3/4-x,1/4+y,-1/4+z

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Table S2. Calculated bond lengths (d, Å)[a] at DFT/ECP/6–31G* level with B3LYP, B3PW91 and PBE functionals and their errors (ε%) relative to the X-ray values

Compound	B3LYP	B3PW91	PBE
	d(Ln…O_P) / (ε%)		
HPA	–	–	–
FPA	–	–	–
ClPA	–	–	–
BrPA	–	–	–
LaHPA	2.438 / (1.7)	2.433 / (1.5)	2.433 / (1.5)
LaClPA	2.437 / (2.1)	2.433 / (1.9)	2.447 / (2.6)
LaBrPA	2.450 / (2.3)	2.446 / (2.1)	2.450 / (2.3)
CeHPA	2.411 / (1.7)	2.407 / (1.5)	2.409 / (1.6)
CeFPA	2.412 / (1.6)	2.409 / (1.5)	2.408 / (1.5)
CeClPA	2.414 / (1.8)	2.410 / (1.6)	2.414 / (1.8)
NdHPA	2.372 / (1.2)	2.369 / (1.1)	2.482 / (5.9)
	d(P=O) / (ε%)		
HPA	1.491 / (1.2)	1.489 / (1.1)	1.504 / (2.1)
FPA	1.492 / (0.8)	1.490 / (0.7)	1.506 / (1.8)
ClPA	1.491 / (1.3)	1.489 / (1.2)	1.505 / (2.2)
BrPA	1.491 / (1.6)	1.489 / (1.4)	1.505 / (2.5)
LaHPA	1.517 / (1.6)	1.514 / (1.4)	1.529 / (2.4)
LaClPA	1.516 / (0.9)	1.513 / (0.7)	1.528 / (1.7)
LaBrPA	1.517 / (1.6)	1.514 / (1.4)	1.532 / (2.6)
CeHPA	1.516 / (1.5)	1.514 / (1.3)	1.528 / (2.3)
CeFPA	1.516 / (2.2)	1.514 / (2.0)	1.529 / (3.0)
CeClPA	1.514 / (1.5)	1.511 / (1.3)	1.507 / (1.1)
NdHPA	1.516 / (2.2)	1.513 / (2.0)	1.529 / (3.0)
	d(P–$N_{aniline}$) / (ε%)		
HPA	1.692 / (2.6)	1.688 / (2.4)	1.704 / (3.3)
FPA	1.692 / (2.5)	1.687 / (2.2)	1.702 / (3.1)
ClPA	1.695 / (2.4)	1.690 / (2.1)	1.705 / (3.0)
BrPA	1.695 / (3.0)	1.690 / (2.7)	1.706 / (3.6)
LaHPA	1.685 / (2.6)	1.681 / (2.4)	1.697 / (3.3)
LaClPA	1.685 / (2.7)	1.681 / (2.4)	1.700 / (3.6)
LaBrPA	1.686 / (2.4)	1.682 / (2.2)	1.702 / (3.4)
CeHPA	1.681 / (2.6)	1.678 / (1.9)	1.702 / (3.4)
CeFPA	1.681 / (2.5)	1.678 / (2.3)	1.692 / (3.2)
CeClPA	1.683 / (2.1)	1.678 / (1.8)	1.695 / (2.9)
NdHPA	1.681 / (2.5)	1.678 / (2.3)	1.702 / (3.8)

[a]The mean values are represented for two coordinated ligands

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Table S3. Selected bond lengths[a] for fully optimized structures at B3PW91/ECP/6–311G* level

Compound	d(Ln…O_P)	d(P=O)	d(P–$N_{aniline}$)	d(Ln…O_S)	d(Ln…Cl)	∠P–O–Ln
HPA	–	1.484	1.686	–	–	–
FPA	–	1.484	1.687	–	–	–
ClPA	–	1.483	1.691	–	–	–
BrPA	–	1.483	1.691	–	–	–
LaHPA	2.413	1.509	1.672	2.583	2.918	175.6
	2.452	1.506	1.687	2.648	2.781	157.9
					2.855	
LaClPA	2.441	1.507	1.684	2.573	2.849	162.6
	2.422	1.508	1.675	2.635	2.850	173.1
					2.855	
LaBrPA	2.430	1.507	1.675	2.645	2.812	173.7
	2.439	1.509	1.678	2.604	2.768	164.9
					3.040	
CeHPA	2.403	1.508	1.674	2.585	2.831	169.9
	2.403	1.508	1.674	2.585	2.831	169.9
					2.840	
CeFPA	2.405	1.509	1.674	2.581	2.831	169.8
	2.405	1.509	1.674	2.581	2.831	169.8
					2.844	
CeClPA	2.412	1.508	1.675	2.588	2.773	173.5
	2.398	1.505	1.675	2.588	2.774	173.4
					3.032	
NdHPA	2.392	1.508	1.685	2.583	2.771	161.8
	2.352	1.506	1.674	2.526	2.799	175.5
					2.837	

[a]The values are given separately for two coordinated ligands XPA, two coordinated solvents, and three chloride counterions.

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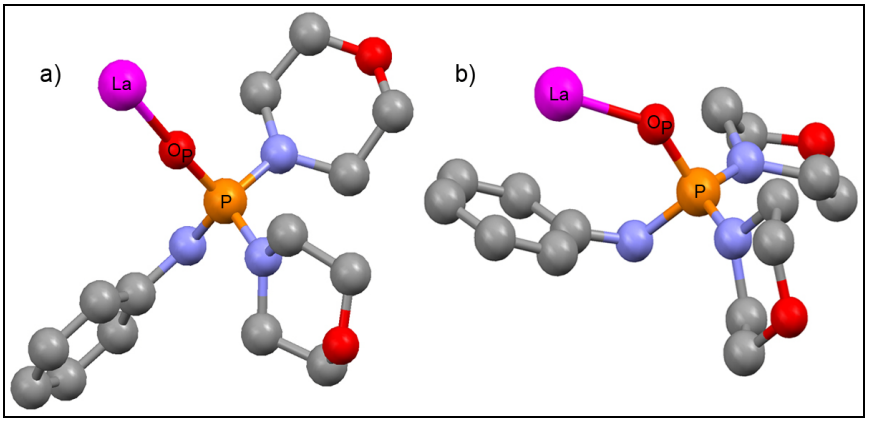

Figure S1. Optimized structure of the model complex HPA–La^{3+} with frozen P–O–La angle (a) and unexpected structure of the organometal complex HPA–La^{3+}