Supporting Information

Table S1. Crystallographic data for compounds **6Ph**, **C_{1OPh}**,**C_{2Ph}**, **C_{4NOPh}**, **C_{5OPh}** and **C_{6Ph}**.

Compound	**6Ph**	**C_{1OPh}**	**C_{2Ph}**	**C_{4NOPh}**	**C_{5OPh}**	**C_{6Ph}**
Empirical formula	$C_{28}H28N2O2P2$, H2O	$C_{66}H_{54}Cl_2O_8P_2Sn_2$	$C_{66}H_{55}Cl_2NO_3P_2Sn_2$	$C_{68}H_{62}Cl_2N_4O_4P_2Sn_2$	$C_{68}H_{60}Cl_2N_2O_6P_2Sn_2$	$C_{64}H_{58}Cl_2N_2O_2P_2Sn_2$
Formula weight	504.48	1345.42	1280.33	1369.44	1371.40	1257.34
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	100	90	100	100	292	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P21/n*	*P21/c*	*P21/n*	*P2/c*	*P2/c*	$P\bar{1}$
a [Å]	9.6969(6)	16.9373(7)	18.1178(8)	20.193(3)	19.1057(8)	10.5009(4)
b [Å]	12.8371(7)	9.79356(24)	9.1500(4)	9.5523(16)	10.0612(4)	11.9976(5)
c [Å]	10.8482(6)	18.1950(7)	18.8435(8)	16.433(3)	16.6443(6)	12.6149(5)
α [°]	90.00	90.00	90.00	90.00	90.00	65.7630(10)
β [°]	111.7380(10)	105.673(3)	114.1380(10)	104.235(3)	99.540(3)	83.3280(10)
γ [°]	90.00	90.00	90.00	90.00	90.00	74.3130(10)
V [Å^3]	1254.35(12)	2905.91(18)	2850.7(2)	3072.4(9)	3155.2(2)	1395.21(10)
Z	2	2	2	2	2	1
Density [g/cm^3]	1.336	1.538	1.492	1.480	1.443	1.496
μ [mm^{-1}]	0.207	1.063	1.074	1.004	0.979	1.095
F(000)	532	1356	1292	1388	1388	636
θ [°]	2.4 to 27	2.3 to 29.4	2.0 to 30	2.1 to 25	2.0 to 29.4	2.0 to 32
Crystal Size [mm]	0.15 x 0.2 x 0.2	0.18 x 0.45 x 0.57	0.05 x 0.35 x 0.35	0.18 x 0.32 x 0.43	0.14 x 0.36 x 0.59	0.15 x 0.18 x 0.23
Index ranges	–12≤h≤12, –16≤k≤16, –13≤l≤13	–23≤h≤23, –12≤k≤12, –24≤l≤24	–25≤h≤25, –12≤k≤12, –26≤l≤26	–24≤h≤24, –11≤k≤11, –19≤l≤19	–26≤h≤26, –13≤k≤13, –21≤l≤22	–15≤h≤15, –17≤k≤17, –18≤l≤18
Reflections collected	10048	26834	36601	25602	28755	48407
R_{int} [%]	0.028	0.0345	0.0340	0.1015	0.0242	0.0224
Absorption correction	Semi-empirical from equivalents	Integration	Semi-empirical from equivalents	Semi-empirical from equivalents	Integration	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	2735 [R(int) = 0.028]	7823 [R(int) = 0.0345]	8320 [R(int) = 0.0340]	5347 [R(int) = 0.1015]	8519 [R(int) = 0.0242]	9670 [R(int) = 0.0224]
Max. and min. transmission	0.966 and 0.958	0.822 and 0.595	0.943 and 0.700	0.840 and 0.672	0.873 and 0.656	0.849 and 0.728
Data/restraints/parameters	2735/0/163	7823/0/362	8320/0/346	5347/0/310	8519/1/377	9670/0/334
Goodness-of-fit on F^2	1.28	1.083	1.007	1.059	1.000	1.038
Final R indices [I>2sigma(I)]	*R1* = 0.0702, *wR2* = 0.2248	*R1* = 0.0199, *wR2* = 0.0482	*R1* = 0.0247, *wR2* = 0.0571	*R1* = 0.0556, *wR2* = 0.1128	*R1* = 0.0262, *wR2* = 0.0560	*R1* = 0.0171, *wR2* = 0.0432
R indices (all data)	*R1* = 0.0740, *wR2* = 0.2276	*R1* = 0.0248, *wR2* = 0.0533	*R1* = 0.0321, *wR2* = 0.0608	*R1* = 0.0883, *wR2* = 0.1241	*R1* = 0.0436, *wR2* = 0.0618	*R1* = 0.0191, *wR2* = 0.0445
Largest diff. peak/hole [e/Å^3]	0.46 and –0.58	0.54 and –0.55	0.45 and –0.52	1.39 and –0.70	0.41 and –0.36	0.60 and –0.40

Table S2. Hydrogen bond lengths (Å) and angles (°) for ligand 6Ph

D–H...A	*d*(D–H)	*d*(H…A)	*d*(D…A)	<DHA	Symmetry codes
O1W–H1WA...O1	0.78	2.03	2.762(8)	157	
O1W -- H1WA .. O1W	0.78	1.80	2.181(9)	110	
O1W–H1WB...O1	0.95	1.91	2.773(7)	159	[-x,-y,1-z]
O1W -- H1WB .. O1W	0.91	1.79	2.181(9)	103	
C3–H3A...O1	0.95	2.45	3.381(4)	165	[-1/2+x,1/2-y,-1/2+z]
C9–H9A...O1W	0.95	2.48	3.381(8)	157	[-1/2+x,1/2-y,-1/2+z]
C12–H12A...O1	0.95	2.60	3.007(5)	107	

Table S3. Calculated bond lengths (Å) at B3LYP/6-311G*/LANL2DZ level for the optimized geometries[a]

Compound	P-(C/N/O)$_R$		P-(N/O)$_X$		P=O		Sn-O	Sn-Cl	Sn-C
	Ligand	Complex	Ligand	Complex	Ligand	Complex			
***C*$_{1OPh}$**	1.603	1.597	1.606	1.601	1.473	1.479	2.658	2.443	2.136-7
***C*$_{2OPh}$**[b]	1.616	1.607	1.662	1.664	1.475	1.487	2.589	2.452	2.138
	1.604	1.597	1.604	1.600	1.474	1.479	2.652	2.443	2.138
***C*$_{2Ph}$**[b]	1.826	1.818	1.698	1.680	1.494	1.519	2.456	2.480	2.148
	1.818	1.810	1.643	1.631	1.488	1.502	2.508	2.467	2.141
***C*$_{3OPh}$**	1.618	1.611	1.660	1.662	1.476	1.482	2.698	2.445	2.134-8
***C*$_{4OPh}$**	1.623	1.611	1.644	1.640	1.478	1.487	2.663	2.449	2.137-50
***C*$_{4NOPh}$**	1.678 (P-N)	1.671	1.647	1.645	1.481	1.489	2.641	2.454	2.139
	1.642 (P-O)	1.633							
***C*$_{5OPh}$**	1.623	1.615	1.650	1.642	1.477	1.486	2.674	2.447	2.136-49
***C*$_{5NOPh}$**	1.677 (P-N)	1.684	1.653	1.659	1.480	1.496	2.637	2.438	2.134-46
	1.640 (P-O)	1.624							
***C*$_{5Ph}$**	1.827	1.818	1.692	1.677	1.498	1.520	2.416	2.487	2.143-56
***C*$_{6Ph}$**	1.820	1.820	1.703	1.688	1.498	1.515	2.407	2.480	2.141

[a] The mean values are represented for two sites of molecules which have similar phosphorous substituent.
[b] the first row is related to the moiety containing P-N and the latter refers to the other part.

Table S4. QTAIM parameters (in au) at B3LYP/6-311+G*/LANL2DZ for optimized structures[a]

Compounds	P=O			Sn-O			Sn-Cl		
	ρ	$\nabla^2\rho$	*H* (r)	ρ	$\nabla^2\rho$	*H* (r)	ρ	$\nabla^2\rho$	*H* (r)
Ligands									
1OPh	0.238	1.497	-0.183	-	-	-	-	-	-
2OPh[b]	0.237	1.483	-0.180	-	-	-	-	-	-
	0.238	1.493	-0.182						
2Ph[b]	0.226	1.353	-0.168	-	-	-	-	-	-
	0.228	1.399	-0.170						
3OPh	0.236	1.479	-0.180	-	-	-	-	-	-
4OPh	0.236	1.466	-0.180	-	-	-	-	-	-
4NOPh	0.234	1.442	-0.178	-	-	-	-	-	-
5OPh	0.236	1.473	-0.180	-	-	-	-	-	-
5NOPh	0.234	1.445	-0.178	-	-	-	-	-	-
5Ph	0.224	1.318	-0.167	-	-	-	-	-	-
6Ph	0.224	1.330	-0.167	-	-	-	-	-	-
Complexes									
***C*$_{1OPh}$**	0.233	1.456	-0.175	0.022	0.084	0.001	0.066	0.154	-0.018
***C*$_{2OPh}$**[b]	0.228	1.402	-0.171	0.026	0.098	0.000	0.065	0.150	-0.018
	0.233	1.457	-0.175	0.022	0.086	0.001	0.066	0.154	-0.018
***C*$_{2Ph}$**[b]	0.212	1.190	-0.155	0.036	0.132	-0.002	0.062	0.140	-0.017
	0.219	1.302	-0.159	0.030	0.118	-0.001	0.064	0.144	-0.017
***C*$_{3OPh}$**	0.231	1.438	-0.173	0.020	0.077	0.001	0.066	0.153	-0.018
***C*$_{4OPh}$**	0.228	1.401	-0.171	0.022	0.083	0.001	0.066	0.152	-0.018
***C*$_{4NOPh}$**	0.226	1.372	-0.167	0.023	0.086	0.001	0.065	0.149	-0.018
***C*$_{5OPh}$**	0.224	1.334	-0.167	0.023	0.088	0.001	0.067	0.157	-0.019
***C*$_{5NOPh}$**	0.224	1.334	-0.167	0.023	0.088	0.001	0.067	0.157	-0.019
***C*$_{5Ph}$**	0.211	1.182	-0.153	0.038	0.146	-0.003	0.062	0.137	-0.016
***C*$_{6Ph}$**	0.212	1.219	-0.153	0.038	0.151	-0.002	0.062	0.140	-0.017

[a] The mean values are represented for two sites of molecules which have similar phosphorous substituent.
[b] the first row is related to the moiety containing P-N and the latter refers to the other part.

Table S5. NBO parameters at B3LYP/6-311+G*/LANL2DZ for optimized structures

Compounds	Atomic Charge of $O_{P=O}$ $q(O_{P=O})$	NEC[b] of $O_{P=O}$	Hybridization of $Lp(O_{P=O})$	$E^{(2)}$ (kcal mol^{-1})[c]	
				(Sn-O)	(Sn-Cl)
Ligands				-	-
1OPh	-1.055	[core] $2s^{1.82}$ $2p^{5.23}$	$sp^{0.47}$	-	-
2OPh[a]	-1.059	[core] $2s^{1.81}$ $2p^{5.24}$	$sp^{0.49}$	-	-
	-1.057	[core] $2s^{1.82}$ $2p^{5.23}$	$sp^{0.47}$		
2Ph[a]	-1.073	[core] $2s^{1.80}$ $2p^{5.26}$	$sp^{0.52}$	-	-
	-1.066	[core] $2s^{1.81}$ $2p^{5.25}$	$sp^{0.52}$		
3OPh	-1.061	[core] $2s^{1.81}$ $2p^{5.24}$	$sp^{0.49}$	-	-
4OPh	-1.064	[core] $2s^{1.81}$ $2p^{5.24}$	$sp^{0.49}$	-	-
4NOPh	-1.065	[core] $2s^{1.81}$ $2p^{5.25}$	$sp^{0.51}$	-	-
5OPh	-1.060	[core] $2s^{1.81}$ $2p^{5.24}$	$sp^{0.49}$	-	-
5NOPh	-1.065	[core] $2s^{1.81}$ $2p^{5.25}$	$sp^{0.51}$	-	-
5Ph	-1.090	[core] $2s^{1.80}$ $2p^{5.27}$	$sp^{0.54}$	-	-
6Ph	-1.080	[core] $2s^{1.80}$ $2p^{5.27}$	$sp^{0.53}$	-	-
Complexes					
$\mathbf{C_{1OPh}}$	-1.091	[core]$2s^{1.79}$ $2p^{5.29}$ $3p^{0.01}$	$sp^{0.52}$	19.68	154.47
$\mathbf{C_{2OPh}}$[a]	-1.100	[core]$2s^{1.78}$ $2p^{5.30}$ $3p^{0.01}$	$sp^{0.54}$	23.47	154.40
	-1.091	[core]$2s^{1.79}$ $2p^{5.29}$ $3p^{0.01}$	$sp^{0.52}$	19.84	152.26
$\mathbf{C_{2Ph}}$[a]	-1.143	[core]$2s^{1.77}$ $2p^{5.36}$ $3p^{0.01}$	$sp^{0.64}$	28.65	142.80
	-1.124	[core]$2s^{1.77}$ $2p^{5.34}$ $3p^{0.01}$	$sp^{0.58}$	26.74	147.62
$\mathbf{C_{3OPh}}$	-1.091	[core]$2s^{1.79}$ $2p^{5.29}$ $3p^{0.01}$	$sp^{0.53}$	18.64	155.29
$\mathbf{C_{4OPh}}$	-1.106	[core]$2s^{1.78}$ $2p^{5.31}$ $3p^{0.01}$	$sp^{0.54}$	20.02	154.30
$\mathbf{C_{4NOPh}}$	-1.110	[core]$2s^{1.78}$ $2p^{5.32}$ $3p^{0.01}$	$sp^{0.56}$	22.14	154.23
$\mathbf{C_{5OPh}}$	-1.094	[core]$2s^{1.78}$ $2p^{5.30}$	$sp^{0.55}$	20.07	161.08
$\mathbf{C_{5NOPh}}$	-1.117	[core]$2s^{1.78}$ $2p^{5.33}$ $3p^{0.01}$	$sp^{0.57}$	25.00	150.98
$\mathbf{C_{5Ph}}$	-1.150	[core]$2s^{1.77}$ $2p^{5.37}$ $3p^{0.01}$	$sp^{0.67}$	32.98	141.00
$\mathbf{C_{6Ph}}$	-1.150	[core]$2s^{1.76}$ $2p^{5.37}$ $3p^{0.01}$	$sp^{0.61}$	32.38	141.68

[a] The first row is related to the moiety containing P-N and the latter refers to the other part.
[b] Natural electron configuration
[c] The term $E^{(2)}$ refers to stabilizing energy of the LP(O) → LP*(Sn) and LP(Cl) → LP*(Sn), respectively.

Table S6. Experimental and calculated stretching frequencies (cm^{-1})

Compounds	υ(N-H)				υ(P=O)				υ(P-N/O)			
	Ligand		Complex		Ligand		Complex		Ligand		Complex	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.[a]	Exp.	Cal.[a]
C1OPh	-	-	-	-	1307	1289	1288	1268	960	951	963	962
C2OPh	3155	3591	3176	3522	1289	1284	1275	1269	962	952 931	967	925 963
C2Ph	3248	3599	3369	3545	1205	1231	1177	1150	926	899	938	930 910
C3OPh	3175	3591	3247	3568	1258	1279	1251	1262	946	950 931	937	953 940
C4OPh	3218	3602	3351	3584	1251	1284	1238	1233	936	863 924	953	868 942
C4NOPh	3390 3202	3610	3362 3277	3591	1211	1266	1197	1212	930	939 900	946	955 917
C5OPh	3185	3591	3343 3305	3583	1240	1286	1235	1234	926	843 935	951	929 943
C5NOPh	3387 3203	3606	3366 3289	3530	1208	1268	1201	1201	928	877 901	940	932 929
C5Ph	3134	3562	3341	3525	1193	1211	1132	1149	1065	1093	996	858
C6Ph	-	-	-	-	1179	1207	1127	1160	952	931	963	946

[a] The first row is related to υ(P-N) vibrational mode and the latter refers to υ(P-O).