Tin(II) Cations Stabilized by Non-symmetric *N*,*N´*,*O*-chelating Ligands: Synthesis and Stability

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A series of novel non-symmetric neutral *N*,*N′*,*O*-chelating ligands derived from the α-iminopyridine 2-(C(R^1)=N(C_6H_3-2,6-iPr_2))-6-(R^2R^3P=O)C_5H_3N (**L^1**: R^1 = H, R^2 = R^3 = Ph; **L^2**: R^1 = Me, R^2 = R^3 = Ph; **L^3**: R^1 = H; R^2 = Ph, R^3 = EtO; **L^4**: R^1 = Me, R^2 = Ph, R^3 = EtO**;** **L^5**: R^1 = H. R^2 = R^3 = iPrO; **L^6**: R1 = Me, R^2 = R^3 = iPrO) were synthesized. Ligands **L$^{1\text{-}6}$** were reacted with $SnCl_2$ and $Sn(OTf)_2$ with the aim to study the influnce of different R^2R^3P=O functional groups on the Lewis base mediated ionization of $SnCl_2$ and $Sn(OTf)_2$. While all ligands **L$^{1\text{-}6}$** provided the corresponding ionic tin(II) complexes [**L$^{1\text{-}6}$**→SnCl]$^+$[$SnCl_3$]$^-$ (**1** – **6**), only ligands **L^1**, **L^4** and **L^6** were able to stabilize tin(II) dications [**L^{1,4,6}**→Sn(H_2O)][OTf]$_2$ (**7** – **9**). The auto-ionized compounds [**L$^{3\text{-}6}$**→SnCl]$^+$[$SnCl_3$]$^-$ possessing ethylphenyl phosphinate and diisopropylphosphite substituents undergo elimination of EtCl and iPrCl, respectively, yielding compounds **10** – **13**. These can either be interpreted as neutral tin(II)phosphinate chloride (**10**, **11**) and tin(II)phosphonate chloride (**12**, **13**), respectively, containing Sn–O and Sn–Cl bonds, and a P=O→$SnCl_2$ interaction, or as zwitterionic compounds, where the positive charge of the central tin atom is compensated by a [O$SnCl_2$]$^-$ anion. Finally, DFT studies were performed to better understand the steric and electronic properties of the ligands **L$^{1–6}$** as well as the nature of the bonds in the resulting products, with a particular focus on complexes **10** – **13**.

Introduction

The search for heavier group 14 element cations in their low oxidation state, such as tin(II) cations and dications, is far from being complete and thus it is a subject of ongoing interest. The first tin(II) cationic complex was reported by Jutzi et al., who utilized permethylated-cyclopentadienyl (Cp*) affording [Cp*Sn]$^+$,[1] which represents a [LSn]$^+$ class of cations (L = monoanionic ligand). The following studies then reported a series of [LSn]$^+$ tin cations stabilized by other monoanionic ligands such as N-isopropyl-2-(isopropylamino)troponimine,[2] β-diketiminate CH(CMeNAr)$_2$- (Ar = 2,6-iPr_2-C_6H_3),[3] bulky amido-ligand {N(Ar*)($SiMe_3$)}$^-$ (Ar* = 2,6-CHPh^2-4-Me-C_6H_2),[4] amino-ether phenolate LO^{NO4} (LO^{NO4} = 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl]-4,6-di-tert-butylphenolate)[5] and bis(oxazoline) ligand.[6]

In an effort to verify the possibility of stabilizing the dications of heavier group 14 elements in the oxidation state +II, neutral ligands came into play instead of formally anionic ligands. Roesky et al. observed a Lewis base mediated ionization of $SnCl_2$ and reported the synthesis of [(DIMPY)SnCl]$^+$[$SnCl_3$]$^-$, where DIMPY is 2,6-[(Me)C=N(C_6H_3-2,6-iPr_2)]$_2C_5H_3N$.[7] This approach has become universal for obtaining a wide range of tin(II) cations with a general formula [D→SnX]$^+$ (D = Lewis base, X = halide or pseudohalide) (Chart 1, **A** – **G**)).[8-15]

Many N-donor ligands such as α-iminopyridines,[8] bis(imino)pyridines,[9] bis(α-iminopyridines)[10] and N-heterocyclic imines[11] were then used as Lewis bases for the ionization of $SnCl_2$. In addition to the N-donor ligands, also O-donor ligands have been used for this concept. One such example is the phosphonyl-substituted ferrocene derivative {Fe(η^5-Cp)(η5-C_5H_3-1,2-((iPrO)$_2$P=O)$_2$}.[13] A rare example of a chlorostannyliumylidene, in which the tin cation is not donated by the traditional donor atoms such as nitrogen or oxygen, is [(1,2-(Me_2As)$_2$-C_6H_4)SnCl]$^+$[$SnCl_3$]$^-$ stabilized by the chelating arsine ligand.[14]

After Müller et al. obtained [(tol)$_3$Sn]$^{2+}$ in an attempt to recrystallize a stannylium cation in toluene (Chart 1, **H**),[15] a significant progress has recently been made in the field of tin(II) dications [D→Sn]$^{2+}$. This field is represented by the synthesis of bipy[16], bis(α-iminopyridine)[10,17] and crown-ether[12] stabilized tin(II) dications (Chart 1, **I** – **K**).

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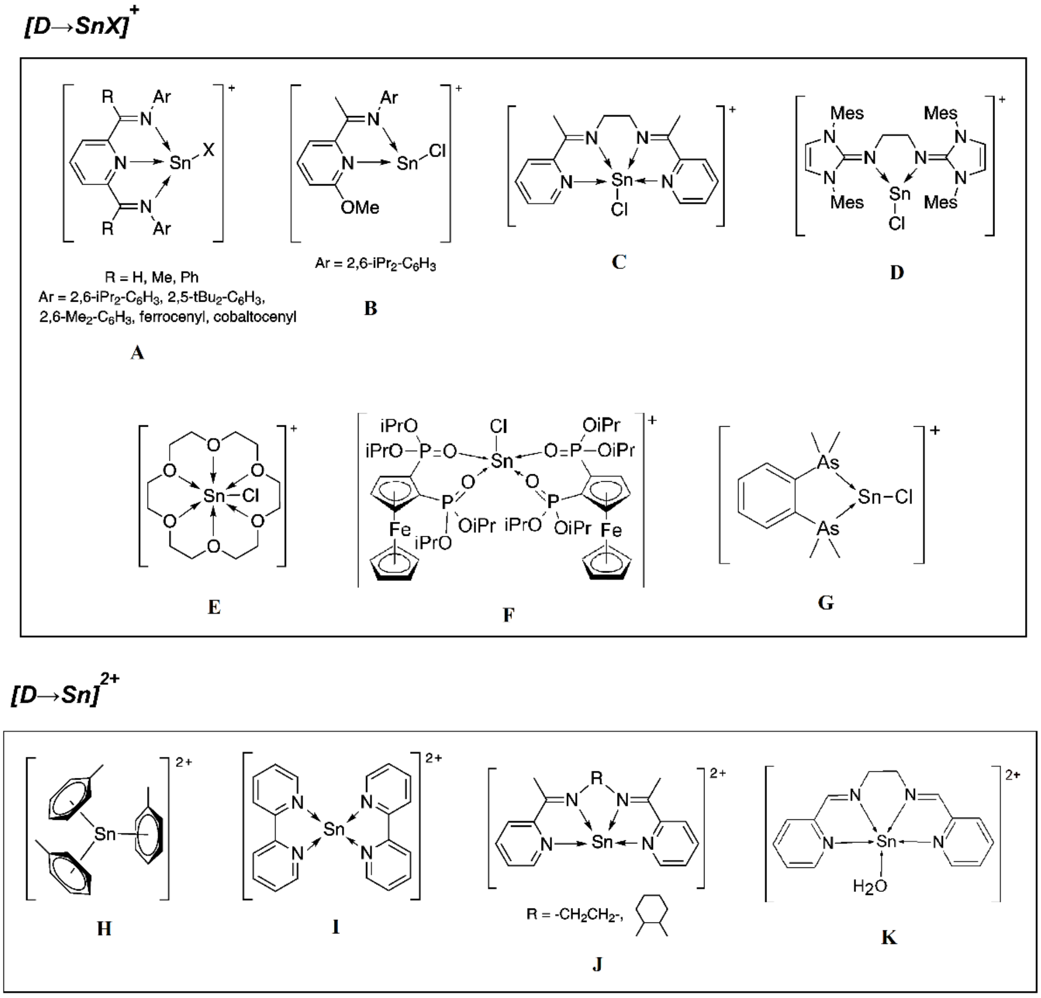


Chart 1. Selected examples of donor-stabilized [D→Sn]+ and [D→Sn]2+ tin(II) cations

Recent studies have shown that heavier carbenes are able to activate small molecules and could be an alternative to commonly used transition metal complexes.[18] From this point of view, the utilization of tin(II) cations in various catalytic cycles and small molecule activations seems to be attractive and promising due to their Lewis acidic character and thus easier interaction of the active center with the substrate.

Several examples of the use of tin(II) cations have been reported so far. The complex $[4\text{-tBu-2,6-}\{\text{P(O)(OiPr)}_2\}_2\text{C}_6\text{H}_2\text{Sn(DMAP)}]^+[\text{BPh}_4]^-$ activated the elemental sulfur providing four-membered ring species $[4\text{-tBu-2,6-}\{\text{P(O)(OiPr)}_2\}_2\text{C}_6\text{H}_2\text{SnS(DMAP)}]_2[\text{BPh}_4]_2$.[19] Hadlington et al. used a phosphine-functionalised cationic tin(II) nickel(0) complex as a catalyst in the hydrosilylation of alkenes and alkynes.[20] Tin(II) cationic complexes have also found use as catalysts in polymerization. $[(\eta^5\text{-C}_5\text{Me}_5)\text{Sn}]^+[\text{B(C}_6\text{F}_5)_4]^-$ in combination with various Zr complexes was found to be an efficient catalytic system in the polymerization of ethylene and propylene.[21]

For a successful catalyst, it is desirable that the ligand must be bound to the active site strong enough to prevent catalyst decomposition. On the other hand, the ligand must not block the active center for the incoming substrate. This concept can be achieved by employing two different donor atoms within the ligand. The synthesis of the non-symmetric *Y,Y´*-chelating ligands, where *Y* and *Y´* are different donor atoms, is thus an attractive field.

To date, only a few examples of tin(II) cations stabilized by *Y,Y´*-chelating ligands containing two different donor atoms have been described in the literature. Stalke et al. isolated $[(\text{N,P})\text{SnCl}]^+[\text{SnCl}_3]^-$,[22] where (N,P) is diphenyl(2-picolyl)phosphane, from the reaction of the lithium derivative of (N,P) with SnCl_2, while Baines et al. reported the synthesis of cryptand-stabilized *N,O*-chelated halostannyliumylidenes $[\text{cryptand[2.2.2]SnX}]^+[\text{SnX}_3]^-$[23] (X = Cl, I) and $[\text{cryptand[2.2.2]Sn}]^{2+}\,2[\text{OTf}]^-$[23] (Chart 2).

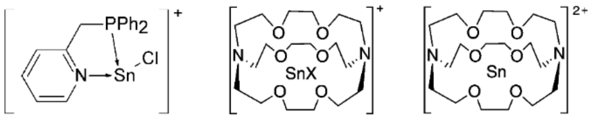


Chart 2. Examples of [D→Sn]+ and [D→Sn]2+ tin(II) cations stabilized by *Y,Y´*-chelating ligands containing two different donor atoms.

In continuing research on neutral ligands and their application for the stabilization of tin(II) cations, we report herein the synthesis of novel non-symmetric *N,N´,O*-chelating ligands derived from α-iminopyridine 2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-(R_1R_2P=O)C_5H_3N (**L¹**: $R^1 = R^2$ = Ph; **L³**: R^1 = Ph, R^2 = EtO; **L⁵**: $R^1 = R^2$ = iPrO) and α-ketiminopyridine 2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(R^1R^2P=O)C_5H_3N (**L²**: $R^1 = R^2$ = Ph; **L⁴**: R^1 = Ph, R^2 = EtO; **L⁶**: $R^1 = R^2$ = iPrO) (Chart 3). Following Lewis base mediated ionization of $SnCl_2$ and $Sn(OTf)_2$ as a powerful method for the synthesis of $[D\rightarrow SnX]^+$ and $[D\rightarrow Sn]^{2+}$ cations, ligands $\mathbf{L^{1-6}}$ differing by R^1R^2P=O were used for the synthesis of a series of tin(II) ionic compounds. The influence of the R^1R^2P=O group on the stability of the tin(II) cations will also be discussed.

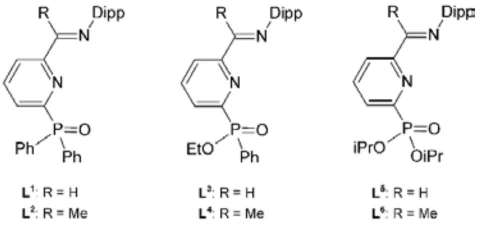
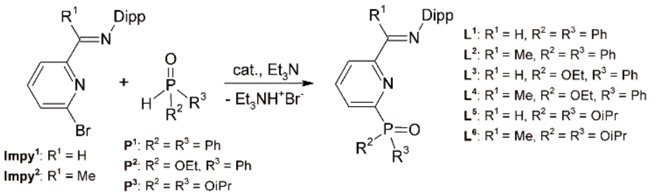


Chart 3. Non-symmetric *N,N´,O*-chelating ligands used in this study.

Results and discussion

Synthesis and Coordination Ability of Ligands $\mathbf{L^{1-6}}$

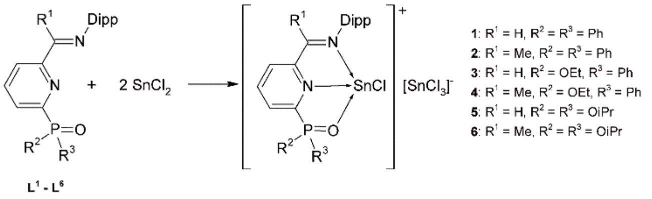
Ligands $\mathbf{L^{1-6}}$ were synthesized via carbon-phosphorus cross-coupling of N-[(6-bromo-2-pyridinyl)methylene]-2,6-diisopropylbenzenamine (**Impy¹**) and N-[(6-bromo-2-pyridinyl)ethylidene]-2,6-diisopropylbenzenamine (**Impy²**) with diphenylphosphine oxide (**P¹**), ethylphenyl phosphinate (**P²**) or diisopropylphosphite (**P³**) using 1,1´-bis(diphenylphosphinoferrocene)palladium acetate as catalyst (Scheme 1).



Scheme 1. Synthesis of non-symmetric *N,N´,O*-chelating ligands ($\mathbf{L^{1-6}}$)

Ligands $\mathbf{L^{1-6}}$ were isolated as yellowish crystalline materials and were characterized by NMR spectroscopy. The expected sets of signals were found in the ^{1}H and ^{13}C NMR spectra of $\mathbf{L^{1-6}}$. The ^{31}P{H} NMR spectra revealed one singlet for each compound whose chemical shift varies depending on the identity of the R^2R^3P=O group (the ^{31}P{H} chemical shifts are listed in Table 1 for clarity). A singlet at δ = 19.0 ppm was observed in the ^{31}P{H} NMR spectrum of ligand **L¹** (δ = 20.0 ppm for **L²**). Similar ^{31}P{H} NMR shifts were also found for the ethylphenyl phosphinate-substituted ligands **L³** (δ = 24.9 ppm) and **L⁴** (δ = 25.4 ppm). On the other hand, the ^{31}P nucleus of the diisopropylphosphite group resonates upfield-shifted at δ = 7.2 ppm for both **L⁵** and **L⁶**. The signals are consistent with the chemical shifts reported for diphenylphosphine oxide- (δ = 21.4 ppm)[24], ethylphenyl phosphinate- (δ = 27.0 ppm)[25] and diisopropylphosphite- (δ = 9.9 ppm)[26] substituted pyridines.

The treatment of $\mathbf{L^{1-6}}$ with 2 molar equivalents of $SnCl_2$ provided the corresponding ionic complexes $[L^{1-6}SnCl]^+[SnCl_3]^-$ (**1 – 6**) (Scheme 2), confirming that $\mathbf{L^{1-6}}$ are indeed suitable Lewis bases for the auto-ionization of $SnCl_2$.



Scheme 2. Synthesis of ionic compounds $[L^{1-6}\rightarrow SnCl]^+[SnCl_3]^-$ (**1** - **6**).

Compounds **1** – **6** are soluble in polar organic solvents such as THF or CH_2Cl_2, but almost insoluble in toluene and hexane. All compounds were characterized by NMR spectroscopy. Table 1 contains the ^{31}P{H} and ^{119}Sn NMR chemical shifts. The ^{31}P{H} NMR spectra of **1** – **6** revealed singlet resonances at δ = 40.8 ppm for **1**, 41.0 ppm for **2**, 36.2 ppm for **3**, 36.1 ppm for **4**, 16.7 ppm for **5** and 16.4 ppm for **6**, which, as a result of P=O→Sn interaction, are shifted downfield as compared with the chemical shift of the ligands $\mathbf{L^{1-6}}$. The ^{119}Sn NMR spectra of **1** – **6** showed each two resonances. While the signals ranging from –523.2 to –469.0 ppm were assigned to the $[L^{1-6}SnCl]^+$ cations, the signals ranging between δ = –101.1 and –57.7 ppm correspond to the related $[SnCl_3]^-$ anions.[8-15] The chemical shifts of the $[L^{1-6}SnCl]^+$ cations are in accordance with those of related bis(imino)pyridine-stabilized chlorostannyliumylidenes (range of –482.4 to –411.7 ppm), containing tetra-coordinated tin centers.[7,9] This clearly indicates the coordination of both nitrogen and also oxygen donor atoms in solutions of **1** – **6**.

Table 1. ^{31}P and ^{119}Sn NMR chemical shifts (in ppm) of ligands $\mathbf{L^{1-6}}$, **1** – **6** and **10** – **13**.

ligand	δ(^{31}P{H})	compound	δ(^{31}P{H})	δ(^{119}Sn) of $[LSnCl]^+$	δ(^{119}Sn) of $[SnCl_3]^-$
L¹	19.0	**1**	40.8	–485.6	–95.4
L²	20.0	**2**	41.0	–469.0	–62.0
L³	24.9	**3**	36.2	–510.3	–101.1
L⁴	25.4	**4**	36.1	–495.5	–64.5
L⁵	7.2	**5**	16.7	–523.2	–64.2
L⁶	7.2	**6**	16.4	–508.4	–57.7

compound	δ(^{31}P{H})	δ(^{119}Sn) of N→Sn	δ(^{119}Sn) of O→Sn
10	25.3	–215.8	–497.4
11	23.7	–212.6	–497.8
12	9.9	–215.1	–518.3
13	9.5	–219.1	–524.1

Given the Sn and P being stereogenic centers, two diastereomers are possible. In solutions of the corresponding bulk materials of **1** - **6**, only one set of signals was observed in the ^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR spectra. Apparently, only one diastereomer was formed or more likely, the epimerization between two diastereomers is fast on the corresponding NMR time scales at room temperature. However, this was not investigated further.

Table 2. Selected interatomic distances [Å] and angles [°] for **1**, **2**·CH_2Cl_2, **3**, **4**·CH_2Cl_2, **10**·$0.5C_7H_8$ and **12**·CH_2Cl_2.

interatomic distances (Å) and angles (°)	**1**	**2**·CH_2Cl_2	**3**	**4**·CH_2Cl_2	**10**·$0.5C_7H_8$	**12**·CH_2Cl_2
N1–Sn1	2.420(2)	2.351(2)	2.397(7)	2.370(4)	2.362(2)	2.409(5)
N2–Sn1	2.574(2)	2.459(2)	2.544(8)	2.476(4)	2.519(2)	2.592(5)
O1–Sn1	2.259(2)	2.281(2)	2.277(8)	2.318(3)	2.230(2)	2.224(4)
P1–O1	1.512(2)	1.507(2)	1.496(8)	1.491(4)	1.507(2)	1.497(5)
P1–O2	-	-	1.570(1)	1.578(4)	1.515(2)	1.512(4)
O2-Sn2	-	-	-	-	2.1439(17)	2.060(9)
Sn1–Cl1	2.4583(6)	2.4574(7)	2.479(2)	2.461(1)	2.4574(8)	2.4816(15)
N1-Sn1-Cl1	83.95(5)	89.01(5)	82.0(2)	83.28(9)	85.68(5)	82.15(12)
N2-Sn1-Cl1	86.86(5)	88.94(5)	81.9(2)	86.26(9)	88.98(5)	81.91(11)
O1-Sn1-Cl1	93.44(5)	84.61(5)	88.9(2)	90.63(9)	88.60(5)	90.91(13)
N1-Sn1-N2	65.66(6)	66.96(7)	66.4(2)	66.7(1)	66.57(7)	65.24(15)
O1-Sn1-N1	73.79(6)	74.97(7)	73.8(3)	74.5(1)	75.03(6)	74.33(17)

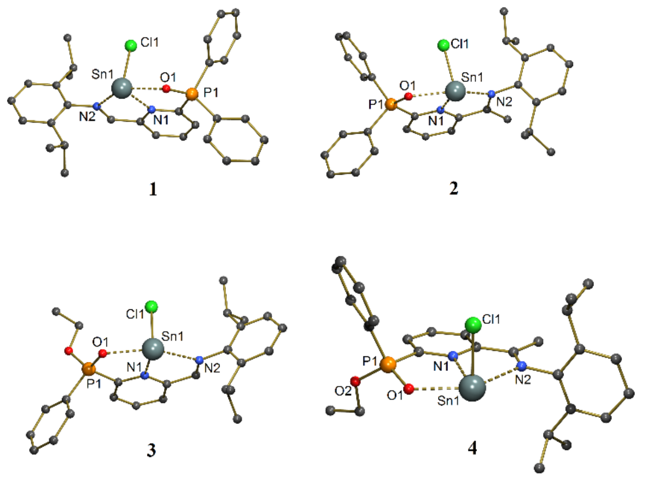


Fig. 1 Povray schematic representation of cationic parts of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2. Hydrogen atoms, $SnCl_3^-$ anions and CH_2Cl_2 solvate molecules are omitted for clarity.

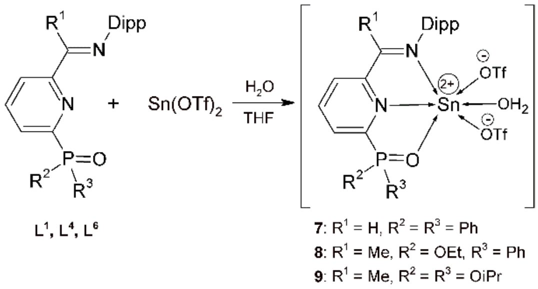
Charge-separated ion pair character of compounds **1** – **4** in the solid state was unambiguously established by single-crystal X-ray diffraction analysis. Suitable single crystals of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 were obtained from the saturated dichloromethane-hexane solution at –20 °C. The molecular structures of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 are depicted in Figure 1 and the most important structural data are summarized in Table 2 (For crystallographic data of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 see Tables S1 – S4, ESI).

The molecular structures of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 consist of well-separated $[L^{1\text{-}4}SnCl]^+$ cations and the $SnCl_3^-$ anions. The Sn1 centres are tetra-coordinated by N1, N2, O1 and Cl1 in a distored square pyramidal environment, where two nitrogen atoms N1 and N2 and one oxygen atom O1 together with the lone electron pair of the Sn1 atom define a basal plane. The chlorine atom Cl1 occupies the apical position. The O1–Sn1 interatomic distances, which vary between 2.259(2) and 2.318(3) Å (see Table 2), show a negligible effect of different $R^2R^3P{=}O$ groups on the strength of the O→Sn interaction. The O1–Sn1 interatomic distances are similar to those found in the related chlorostannyliumylidene $[\{Fe(\eta^5\text{-}Cp)(\eta^5\text{-}C_5H_3\text{-}1,2\text{-}((iPrO)_2P{=}O)_2\}_2SnCl]^+[SnCl_3]^-$ (2.263(2) – 2.603(2) Å)[13], but shorter than in $[cryptand[2.2.2]SnCl]^+[SnCl_3]^-$ (2.745(6) – 3.076(6) Å)[23]. The (pyridine)nitrogen-tin N1–Sn1 interatomic distances with the range of 2.351(2) – 2.420(2) Å are shorter than the (imino)nitrogen-tin N2-Sn1 interatomic distances (range of 2.459(2) – 2.574(2) Å). This agrees with the N-Sn distances reported for the chlorostannyliumylidenes stabilized by bis(imino)pyridine ligands, where the (pyridine)nitrogen-tin distances = 2.267 – 2.314 Å, while the range of 2.3839 – 2.516 Å was established for the (imino)nitrogen-tin distances.[7-9]

Accordingly, it can be stated that ligands **L$^{1-6}$** behave in the same manner as the related DIMPY ligands in the auto-ionization of $SnCl_2$, yielding tin(II) ionic complexes $[L^{1-6}SnCl]^+[SnCl_3]^-$ (**1** – **6**) without any influence of the $R^2R^3P=O$ group on this process. Furthermore, the structural characterization of **1** – **6** showed the coordination of both nitrogen atoms as well as the oxygen atom to the central tin atom in the cationic part of **1** – **6**.

To better understand the steric and electronic properties of ligands **L$^{1–6}$** and their bonding in the tin(II) cationic complexes, a DFT study was performed at the M06-2X[27]/cc-pVDZ(-PP)[28] level of theory. The formation of all ionic complexes **1** – **6** is exergonic (ΔG = –29.8 to –31.5 kcal mol$^{–1}$; Table 8, ESI), again demonstrating the robustness and straightforward nature of the Lewis base mediated ionization reaction in the formation of cations of the heavier group 14 elements in a low oxidation state. As indicated by the experimental data, the substitution pattern of the $R^2R^3P=O$ group has a negligible effect on the formation and structure of the formed complexes. This was further confirmed by calculating the percentage buried volume descriptor ($\%V_{Bur}$),[29] which showed very similar steric properties for all six ligands with $\%V_{Bur}$ values between 41.5 and 44.1 % (Table S9, ESI). The somewhat higher $\%V_{Bur}$ values found for ligands **L^2**, **L^4** and **L^6** are due to the increased torsion of the Dipp substituent as a result of its steric clash with the methyl substituent of the imine group. Similarly, the interaction energies (ΔE_{int}) between the ligand and the metal centre, evaluated and decomposed using Ziegler-Rauk energy decomposition analysis (EDA),[30] fall in the narrow interval of –116.2 to –125.9 kcal mol$^{–1}$. The highest ΔE_{int} values were revealed for the phenyl substituted ligands **L^1** and **L^2**, whereas the lowest values were observed for ligands **L^5** and **L^6** with two iPrO groups (Table S10, ESI). As expected for the chelating ligands, electrostatic interactions (59 %) are preferred over orbital interactions (41%). In line with the experimental data, the structures of compounds **1** – **6** are very similar, with each tin centre stabilized by three strong donor-acceptor bonds with the ligand. (Figure S1, ESI) Similarly, the natural bond orbital (NBO)[31] analysis revealed a very similar bonding pattern in **1** – **6** with four NBOs involving the tin centre. These include Sn-Cl σ bond and σ-type lone pair orbital NBOs together with two NBOs corresponding to the empty π orbitals on Sn (Figure S4, ESI). The Wiberg bond index (WBI)[32] values for all complexes suggest that the (pyridine)nitrogen-tin bond (N^{Py}-Sn) is stronger than the (imine)nitrogen-tin bond (N^{Im}-Sn) (average $WBI_{N–Sn}$ = 0.15 for N^{Im}-Sn and 0.16 for N^{Py}-Sn; Table S11, ESI). While the O–Sn bond is clearly the strongest in **1** – **4** ($WBI_{O–Sn}$ = 0.172 – 0.194), in **5** and **6** it has equal strength to the N–Sn bond with the pyridine group. However, according to NBO analysis,[31] in all of the six compounds studied, the stabilizing second-order perturbation energy $E^{(2)}$ corresponding to the $n_O \rightarrow \pi^*_{Sn}$ interaction is about 11 to 24 kcal mol$^{–1}$ stronger as compared with the $n_{N(Pyridine)} \rightarrow \pi^*_{Sn}$ interaction (Table S12, ESI). As the increased Lewis acidity is expected to play a role in the possible catalytic activity, the electrophilic nature of the Sn centres in **1** – **6** was quantified using the computed fluoride ion affinity (FIA). The FIA values are in a narrow range of 535 – 563 kJ mol^{-1} (Table S13, ESI), comparable with the value found for the related $[(1,2\text{-}(C_5H_4N\text{-}2\text{-}CH=N)_2CH_2CH_2)SnCl]^+[SnCl_3]^-$.[10b]

Following the synthesis of tin(II) dications by the ionization of $Sn(OTf)_2$ mediated by crown-ethers, cryptands or bis(α-iminopyridine), analogous reactions were conducted also with ligands **L$^{1-6}$**. The equimolar reactions of **L$^{1-6}$** with $Sn(OTf)_2$ provided tin(II) dications only in the case of **L^1**, **L^4** and **L^6** and aqua complexes $[L^1Sn(H_2O)][OTf]_2$ (**7**), $[L^4Sn(H_2O)][OTf]_2$ (**8**) and $[L^6Sn(H_2O)][OTf]_2$ (**9**) were isolated as yellow solid materials (Scheme 3). Traces of water in the starting $Sn(OTf)_2$ are most likely the cause of the isolation of aqua complexes **7** – **9**.



Scheme 3. Synthesis of ionic compounds $[L^{1,4,6} \rightarrow Sn(H_2O)][OTf]_2$ (**7** – **9**).

Compounds **7** – **9** were characterized by NMR spectroscopy. The $^{31}P\{H\}$ NMR spectra of **7** – **9** revealed singlet resonances at δ = 42.8 ppm for **7**, 38.0 ppm for **8** and 16.2 ppm for **9**, which are shifted downfield as compared with the starting ligand as a result of the P=O→Sn interaction.

The ^{119}Sn NMR signals at δ = –918.2 ppm for **7**, –859.9 ppm for **8** and –900.9 ppm for **9** are shifted upfield in comparison with signals found in $[\{1,2\text{-}(C_5H_4N\text{-}2\text{-}C(CH_3)=N)_2CH_2CH_2\}Sn]^{2+}$ $2[OTf]^-$ (δ = –637 ppm)[10a], $[\{1,2\text{-}(C_5H_4N\text{-}2\text{-}CH=N)_2CH_2CH_2\}Sn(H_2O)]^{2+}$ $2[Otf]^-$ (δ = –658 ppm)[10b] and $[\{1,2\text{-}(C_5H_4N\text{-}2\text{-}C(CH_3)=N)_2C_6H_{10}\}Sn]^{2+}$ $2[Otf]^-$ (δ = –596 ppm)[17]. The presence of the triflate anions in **7** – **9** was confirmed by the ^{19}F NMR spectra showing resonances at δ = –79.1 ppm for **7**, –79.3 ppm for **8** and –78.7 ppm for **9**. The IR spectra of **7** – **9** showing absorptions at 2963 cm^{-1} for **7**, 2960 cm^{-1} for **8** and 2967 cm^{-1} for **9**) reveal the presence of the Sn-coordinated water molecules.

The molecular structure of **9** in the solid state was unambiguously established by single-crystal X-ray diffraction analysis. Suitable single crystals of **9** were obtained from the saturated THF-hexane solution at –20 °C. The molecular structure of **9** is depicted in Figure 2 (For crystallographic data of **9** see Table S5, ESI).

The Sn1 center is hexa-coordinated by N1, N2 and O1 of the ligand **L^6**, by O2 originating from H_2O and by O5 and O6 of the triflate anion. The coordination environment of the Sn1 center can be described as distorted octahedral. The N1–Sn1 and N2–Sn1 interatomic distances (2.380(3) Å and 2.509(3) Å) as well as the O2–Sn1 interatomic distance (2.280(3) Å) are shorter than the nitrogen-tin and oxygen-tin bonds found in related $[cryptand[2.2.2]Sn]^{2+}$ $2[OTf]^-$ similarly possessing N→Sn (range of 2.707 – 2.862 Å)[23] and O→Sn (range of 2.456 – 2.783 Å)[23] coordination. The O1–Sn1 interatomic distance (2.250(3) Å) is slightly elongated as compared with the related distance in the aqua complex [{1,2-(C_5H_4N-2-CH=N)$_2CH_2CH_2$}Sn(H_2O)]$^{2+}$ 2[OTf]$^-$ (2.195 Å)[10b]. The O6–Sn1 and O9–Sn1 interatomic distances (2.952(3) Å and 2.609(3) Å) indicate that both OTf moieties are in closer interaction with the tin cation than the OTf anions are in bis(α-iminopyridine)-stabilized dicationic tin(II) triflates containing completely non-coordinating OTf.[10,17] A similar situation has been found for the DIMPY-coordinated tin(II) triflate, where triflate groups are bound at Sn–O distances of 2.350 Å and 2.554 Å.[33]

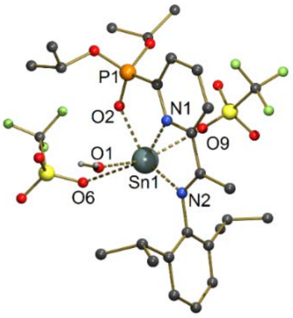


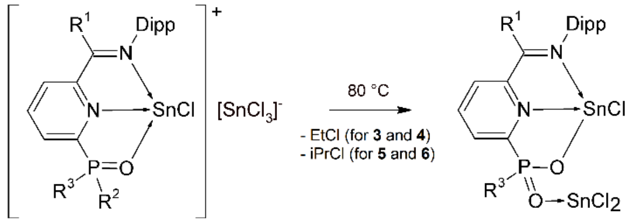
Fig. 2. Povray schematic representation of **9**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): N1-Sn1 2.380(3), N2-Sn1 2.509(3), O1-Sn1 2.250(3), P1-O2 1.492(3), O2-Sn1 2.280(3), O9-Sn1 2.609(3), O6-Sn1 2.952(3), N1-Sn1-O1 81.0(1), N2-Sn1-O1 83.17(9), O2-Sn1-O1 84.05(9), N1-Sn1-N2 66-0(1), O2-Sn1-N1 74.24(9).

As in the case of **1** – **6**, the formation of dications **7** – **9** is exergonic (Table S8, ESI). Although it is quite common that the gas phase optimized geometries tend to slightly underestimate the donor-acceptor bond distances compared to XRD data, for compound **9**, solid-state effects and tight packing in the unit cell may play a bigger role. The optimized geometries of **7** – **9** show very similar structures (Figure S2, ESI), where both N–Sn bonds are significantly elongated, and the main stabilization of the metal centre comes from the O–Sn donor-acceptor bond with the ligand along with the additional interactions with the water molecule and OTf groups. This is clearly reflected in the WBIs of the respective bonds, showing that all four O–Sn interactions are associated with higher values than the N–Sn bonds ($WBI_{O–Sn}$ = 0.099 – 0.163, $WBI_{N–Sn}$ = 0.065 – 0.082; Table S11, ESI). As expected, NBO[31] analysis showed four NBOs corresponding to the Sn lone pair and three empty π orbitals on Sn (Figure S4, ESI). The ligand-metal interaction energies (ΔE_{int} = –93.0, –94.3 3 and –91.2 kcal mol^{-1} for **7**, **8** and **9**, respectively; Table S10, ESI) are also strikingly different from the value found for the bis(α-iminopyridine)-stabilized dicationic tin(II) triflate with completely separated OTf anions (–216.3 kcal mol^{-1}).[10a] Despite the relatively strong interactions with the counter anion, the $WBI_{O–Sn}$ values and the natural population analysis (NPA) charge of the Sn atom (q_{Sn} = 1.64 e) in **7** – **9** agree well with those calculated for analogous tin(II) dications stabilized by crown-ethers.[12]

Stability of studied compounds

The stability of the compounds **1** – **9** in solution was further monitored by $^{31}P\{H\}$ NMR spectroscopy. While all tin(II) triflates **7** – **9** and chlorostannyliumylidenes **1** and **2** containing a $Ph_2P=O$ group are stable, the $^{31}P\{H\}$ NMR spectra of **3** – **6** in $CDCl_3$ revealed, after the samples had been stored at ambient temperature for 24 hours, new signals at δ = 25.6 ppm for **3**, 23.7 ppm for **4**, 9.9 ppm for **5** and 9.5 ppm for **6**. The quantitative conversion of **3** – **6** was observed by heating of their toluene/THF solutions for 7 days affording compounds **10** – **13** as an orange solid materials.

The ^1H NMR spectra of **10** and **11** showed the absence of any signals for the EtO group. Additionally, signals of C*H*(iPr) and C*H*(iPrO) in a 2:1 ratio were found in the ^1H NMR spectra of **12** and **13**. This fact clearly indicates the presence of only one iPrO group in **12** and **13** as compared with two iPrO groups in **5** and **6**. These data suggest the cleavage of Et-O and iPr-O bonds accompanied by the formation of EtCl, iPrCl and Sn-O bonds to give five-membered rings (Scheme 4), in analogy with the reported formation of benzoxaphosphasiloles,[34] benzoxaphosphastannoles,[35] benzoxaphosphaplumbole,[36] and benzoxaphosphaphosphole sulfide[37]. The source of the chloride anion acting as a nucleophile in the course of the formation of **10** – **13** is the $SnCl_3^-$ anion, which in turn gives $SnCl_2$ being complexed by a phosphorus-bound oxygen center (Scheme 4). The $^{31}P\{H\}$ NMR spectra of **10 – 13** revealed single resonances at δ = 25.6 ppm for **10**, 23.7 ppm for **11**, 9.9 ppm for **12** and 9.5 ppm for **13**. These signals are significantly upfield-shifted compared to the complexes **3** – **6**. The ^{119}Sn NMR spectra of **10** – **13** showed two signals at δ = –215.8 and –497.4 ppm for **10**, –212.6 and –497.8 ppm for **11**, –215.1 and –518.3 ppm for **12** and –219.1 and –524.1 ppm for **13**. While the downfield-shifted signals are similar to that found in $SnCl_2$·THF (δ = –236 ppm)[38], the upfield-shifted signals correspond to those of the tin centres in the [$L^{1-6}SnCl$]$^+$ cations (ranging from –523.2 to –469.0 ppm) and to those found in the tin(II) aryloxide derivatives (ranging from –526.5 to –501.4 ppm).[39]

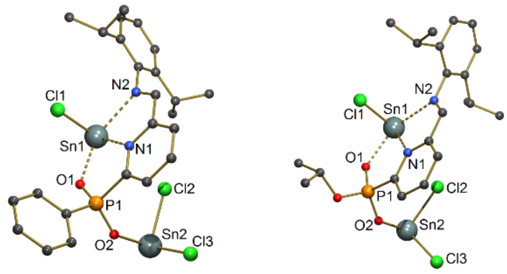


3: R^1 = H, R^2 = OEt, R^3 = Ph
4: R^1 = Me, R^2 = OEt, R^3 = Ph
5: R^1 = H, R^2 = R^3 = OiPr
6: R^1 = Me, R^2 = R^3 = OiPr

10: R^1 = H, R^3 = Ph
11: R^1 = Me, R^3 = Ph
12: R^1 = H, R^3 = OiPr
13: R^1 = Me, R^3 = OiPr

Scheme 4. Formation of compounds **10** – **13**.

The molecular structures of **10** and **12** were unambiguously established by single-crystal X-ray diffraction analysis. The structures of **10** and **12** are depicted in Figure 3 (For crystallographic data of **10** and **12** see Tables S6 and S7, ESI).



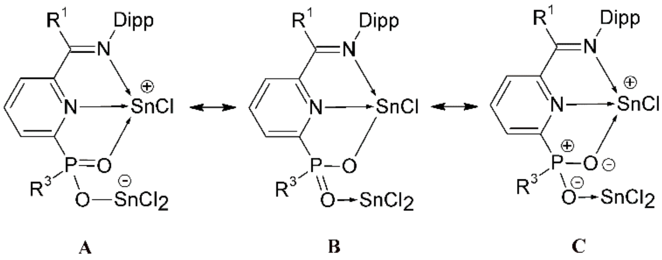
10 **12**

Fig. 3. Povray schematic representation of **10** and **12**. Hydrogen atoms are omitted for clarity.

In both **10** and **12** the Sn1 centre is tetra-coordinated by N1, N2, O1 and Cl1. The coordination arrangement of the Sn1 atom can be described as a distorted square pyramid, where N1, N2, O1 and the lone electron pair of Sn1 define a basal plane. The chlorine Cl1 atom then occupies the top of this square pyramid. The (pyridine)nitrogen-tin N1–Sn1 interatomic distances (2.362(2) Å for **10** and 2.409(5) Å for **12**) are shorter than the (imino)nitrogen-tin N2-Sn1 interatomic distances (2.519(2) Å for **10** and 2.592(5) Å for **12**). While the P1-O1 interatomic distance (1.507(2) Å) in **10** is comparable with those found in **3** (1.496(8) Å) and **4** (1.491(4) Å), the P1-O2 distance (1.515(2) Å) is quite shorter compared to **3** (1.570(1) Å) and **4** (1.578(4). Similar values were also found for the P1-O1 ((1.497(5) Å) and P1-O2 (1.512(4) Å) interatomic distances in **12**. The O1–Sn1 bond distances are 2.230(2) Å for **10** and 2.224(4) Å for **12**. The former is slightly shortened compared with **3** (2.277(8) Å), but is longer than the O–Sn single bond ($\Sigma_{cov,SB}$O,Sn = 2.05 Å).[40] In contrast, the O2–Sn2 interatomic distances (2.1439(17) Å for **10** and 2.060(9) Å for **12**) are closer to the O–Sn single bond and indicate a strong O–Sn interaction. Moreover, the O2–Sn2 distances are comparable with the O–Sn bond found in tin(II) aryloxide derivatives (2.107–2.124 Å).[39]

Based on these findings and according to the ^{119}Sn NMR data revealing almost the same δ for the N,N´,O→Sn fragment as in **1** – **6**, compounds **10** – **13** can be seen as zwitterionic compounds containing each a [Sn–Cl]$^+$ moiety. The positive charge is compensated by a newly formed [O-SnCl$_2$]$^-$ anion (Scheme 5A). The negative charge is then delocalized within the [O-P-O-SnCl$_2$]$^-$ fragment, which is reflected by almost the same P1-O1 and P1-O2 interatomic distances in **10** and **12**. The second possible explanation for the structure of **10** – **13** is the presence of Sn–O and Sn–Cl single bonds and the P=O→SnCl$_2$ Lewis base – Lewis acid interactions (Scheme 5B). This view gets support from the ^{119}Sn NMR chemical shift of the P=O→*Sn*Cl$_2$, which is comparable with the chemical shift of SnCl$_2$·THF (δ = –236 ppm)[38].

The unusual reactivity of compounds **3** – **6** and the bonding in the newly formed neutral complexes **10** – **13** were the subject of the final part of the DFT investigation. The calculated Δ*G* value of –19 kcal mol^{-1} for the formation of **10** – **13** correlates well with the spontaneous nature of the reaction (Table S8). As with all the other compounds studied, the nature of the substituent on both the P atom and N atom of the imine group has a negligible effect on the structure of the complex formed (Figure S3, ESI). Based on the NBO analysis[31], the bonding around the Sn centre of the SnCl moiety is identical to that in **3** – **6**, while two Sn-Cl σ bonds, a σ-type lone pair orbital and an empty π orbital on Sn were found for the Sn atom of SnCl$_2$ (Figure S4, ESI). Analogous to **1**–**6**, the WBI values in the central N,N´,O→Sn fragment are highest for the O–Sn bond (WBI$_{O–Sn}$ = 0.188 – 0.202), followed by the WBI values for the N–Sn bonds with pyridine (WBI$_{N–Sn}$ = 0.163 – 0.166) and imine groups (WBI$_{N–Sn}$ = 0.118 – 0.120; Table S11, ESI). These values, together with the NPA charge on the central Sn atom (q_{Sn} = 1.40 *e*), which has a nearly identical value to that in **3**–**6**, suggest the presence of the [SnCl]$^+$ moiety. Moreover, the NPA charge of the Sn atom of the SnCl$_2$ group (q_{Sn} = 1.29 *e*) is very close to that in free SnCl$_2$ (q_{Sn} = 1.26 *e*), even though the interaction with the O atom of the ligand is stronger than with the [SnCl]$^+$ fragment (WBI$_{O–Sn}$ = 0.241 – 0.245). Based on all these facts, the bonding in **10** – **13** would be best described as a negatively charged ligand **L**$^{\mathbf{3–6}}$ coordinating [SnCl]$^+$ and SnCl$_2$ via strong O→Sn and N→Sn donor-acceptor interactions (Scheme 5C). The negative charge on the ligand can be explained on the basis of the well-known discussion of bonding in phosphine oxides, where the R$_3$P=O double bond can be represented as R$_3$P$^+$–O$^-$ with one σ bond and two π bonds formed by back-bonding from the lone pair orbitals on oxygen into the antibonding orbitals of the phosphine moiety.[41] This idea is further supported by the highly positive NPA charge of the P atom (q_P = 2.23 – 2.47 *e*) and the negative NPA charge on both O atoms (q_O = –1.20 to –1.21 *e*; Table S11, ESI).



Scheme 5. Possible mesomeric forms of **10** – **13**.

Lewis acidity was also assessed experimentally by the Gutmann-Beckett test[42]. For this test, complexes **4**, **8** and **11** were selected, to represent the individual types of complexes prepared. The difference in the chemical shift (Δδ in ^{31}P NMR) after the reaction with Ph$_3$P=O increases in the order **11** (Δδ = 1.3 ppm) < **4** (Δδ = 2.1 ppm) < **8** (Δδ = 10.6 ppm). Thus, the weakest interaction with Ph$_3$P=O is observed for **11**, while **8** shows the strongest Lewis acidity.

Conclusions

In conclusion, we have reported the synthesis of a series of novel non-symmetric neutral *N,N´,O*-chelating ligands 2-(C(R^1)=N(C$_6$H$_3$-2,6-iPr$_2$))-6-(R^{2}R^{3}P=O)C$_5$H$_3$N containing variety of different substituents R^1-R^3. Upon reaction with SnCl$_2$, these novel ligands gave, via donor-assisted autoionization, the corresponding complexes [**L**$^{\mathbf{1-6}}$SnCl]$^+$[SnCl$_3$]$^-$. Notably, the phosphane oxide-, phosphinate-, and phosphonate-substituted ligands **L^1**, **L^4** and **L^6** are even able to stabilize tin(II) dications in the complexes [**L^{1,4,6}**Sn(H_2O)][OTf]$_2$. Complexes [**L$^{3-6}$**SnCl]$^+$[SnCl$_3$]$^-$ containing OR substituents (R = Et, i-Pr) in the ligand backbone show limited thermal stability and undergo chloride anion-induced O-R bond cleavage (ester cleavage) accompanied by elimination of RCl and five-membered ring closure upon Sn-O bond formation. These compounds can be seen as composed of tin(II)phosphinate chloride (**10**, **11**) and tin(II)phosphonate chloride (**12**, **13**), respectively, being both intramolecularly doubly N-coordinated and themselves intramolecularly coordinating SnCl$_2$ by P=O (P$^+$–O$^-$). DFT calculations revealed high ionic character of the Sn-N and Sn-O bonds in these compounds.

Experimental part

General Consideration

All moisture and air sensitive reactions were carried out under an argon atmosphere using standard Schlenk tube techniques. All solvents were dried using Pure Solv–Innovative Technology equipment. Diphenylphosphine oxide, ethylphenyl phosphinate, diisopropylphosphite, Pd(OAc)$_2$, 1,1'-bis(diphenylphosphino)ferrocene, Et$_3$N, SnCl$_2$ and Sn(OTf)$_2$ were purchased from Sigma Aldrich and used as received. **Impy1** and **Impy2** were prepared according to the literature.[43] Elemental analyses were performed on an LECO-CHNS-932 analyser. The ^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on a Bruker 500 NMR spectrometer at 298 K. The ^{1}H and ^{13}C NMR spectra were referenced internally to the residual protio-solvent. The ^{31}P NMR spectra were referenced externally to 85% H_3PO_4 in an aqueous solution and the ^{119}Sn NMR spectra to Me$_4$Sn. Solid state IR spectra were recorded on Nicolet 6700 FTIR spectrometer using a single-bounce silicon ATR crystal (resolution 2 cm^{-1}).

Synthesis of 2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-(Ph$_2$P=O)C_5H_3N (L^1)

Impy^1 (2.30 g, 6.66 mmol) was placed in a three-neck round-bottom flask and dissolved in acetonitrile (30 mL). Pd(OAc)$_2$ (15 mg, 0.067 mmol) along with 1,1'-bis(diphenylphosphino)ferrocene (37 mg, 0.067 mmol) were added to the solution as a catalytic system. After that, 1.2 eq. of Ph$_2$PH=O (1.62 g, 8.04 mmol) and 3 eq. of Et$_3$N (2.79 mL, 20.1 mmol) were added to the flask. The reaction mixture was heated to reflux for 3 days. After completion of the reaction, the solvent was evaporated and the residue was extracted with hexane (30 ml) followed by recrystallization with Carborafin. The hexane solution was placed in a freezer at -20 °C yielding a pale-yellow crystalline material. Yield: 1.90 g (61 %), mp = 136 – 139 °C. Anal.Calcd.for $C_{30}H_{31}ON_2P$ (MW 466.55): C, 77.2; H, 6.7. Found: C, 77.4; H, 6.8. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.11 (d, 12H, C*H*$_3$(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.5 Hz), 2.87 (sept, 2H, C*H*(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.5 Hz), 7.07-7.10 (m, 3H, Ar-*H*), 7.36-7.43 (m, 8H, Ar-*H*), 7.90-7.94 (m, 4H, Ar-*H*), 8.29 (s, 1H, C*H*=N), 8.33 (d, 1H, Ar-*H*, ^{3}*J*(^{1}H, ^{1}H) = 4.5 Hz). ^{13}C{^{1}H} NMR (125.72 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 23.3 (*C*H$_3$(iPr)), 27.9 (*C*H(iPr)), 122.4 (d, ^{n}*J*(^{31}P, ^{13}C) = 3.0 Hz), 123.0, 124.6, 128.2 (d, ^{n}*J*(^{31}P, ^{13}C) = 12.0 Hz), 129.4 (d, ^{n}*J*(^{31}P, ^{13}C) = 20.0 Hz), 131.9 (d, ^{n}*J*(^{31}P, ^{13}C) = 105.0 Hz), 131.8 (d, ^{n}*J*(^{31}P, ^{13}C) = 3.0 Hz), 132.0 (d, ^{n}*J*(^{31}P, ^{13}C) = 10.0 Hz), 136.9 (d, ^{n}*J*(^{31}P, ^{13}C) = 9.0 Hz), 137.1, 148.3, 154.5 (d, ^{n}*J*(^{31}P, ^{13}C) = 20.0 Hz), 156.4 (d, ^{n}*J*(^{31}P, ^{13}C) = 130.0 Hz) (Ar-*C*), 162.7 (*C*H=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 19.0. IR: ν(P=O) 1203 cm^{-1}.

Synthesis of 2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(Ph$_2$P=O)C_5H_3N (L^2)

The synthetic protocol is the same as for **L^1**. **Impy^2** (2.20 g, 6.12 mmol), Ph$_2$PH=O (1.48 g, 7.34 mmol) and Et$_3$N (2.51 mL, 18.36 mmol) provided ligand **L^2**. Yield: 2.09 g (71 %). mp = 117 – 119 °C. Anal.Calcd.for $C_{31}H_{33}ON_2P$ (MW 480.58): C, 77.5; H, 6.9. Found: C, 77.8; H, 7.0. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.05 (t, 12H, C*H*$_3$(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.4 Hz), 2.03 (s, 3H, (C*H*$_3$)C=N), 2.60 (sept, 2H, C*H*(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.7 Hz), 7.03 (d, 1H, Ar-H, ^{3}*J*(^{1}H, ^{1}H) = 7.0 Hz), 7.09-7.11 (m, 2H, Ar-*H*), 7.38-7.41 (m, 4H, Ar-*H*), 7.45-7.48 (m, 2H, Ar-*H*), 7.88-7.92 (m, 5H, Ar-*H*), 8.33 (t, 1H, Ar-*H*, ^{3}*J*(^{1}H, ^{1}H) = 6.4 Hz), 8.38 (d, 1H, Ar-*H*, ^{3}*J*(^{1}H, ^{1}H) = 7.9 Hz). ^{13}C{^{1}H} NMR (125.72 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 17.0 ((*C*H$_3$)C=N), 22.6 (*C*H$_3$(iPr)), 23.0 (*C*H$_3$(iPr)), 28.1 (*C*H(iPr)), 122.6, 123.9, 123.7, 128.1 (d, ^{n}J(^{31}P, ^{13}C) = 11.7 Hz), 129.1 (d, ^{n}J(^{31}P, ^{13}C) = 19.6 Hz), 131.7, 131.9 (d, ^{n}J(^{31}P, ^{13}C) = 8.8 Hz), 132.6, 135.4, 136.7 (d, ^{n}J(^{31}P, ^{13}C) = 9.0 Hz), 146.0, 155.0 (d, ^{n}J(^{31}P, ^{13}C) = 132.2 Hz), 156.2 (d, ^{n}J(^{31}P, ^{13}C) = 18.2 Hz) (Ar-*C*), 166.1 ((CH$_3$)*C*=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 20.0. IR: ν(P=O) 1201 cm^{-1}.

Synthesis of 2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-(Ph(EtO)P=O)C_5H_3N (L^3)

The synthetic protocol is the same as for **L^1**. **Impy^1** (2.30 g, 6.66 mmol), Ph(EtO)PH=O (1.20 mL, 8.00 mmol) and Et$_3$N (2.79 mL, 20.00 mmol) provided ligand **L^3**. Yield: 2.01 g (69 %). mp = 98 – 102 °C. Anal.Calcd.for $C_{26}H_{31}O_2N_2P$ (MW 434.51): C, 71.9; H, 7.2. Found: C, 71.6; H, 7.0. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.09 (d, 12H, C*H*$_3$(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.5 Hz), 1.32 (t, 3H, C*H*$_3$(Et), ^{3}*J*(^{1}H, ^{1}H) = 7.3 Hz), 2.84 (sept, 2H, C*H*(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.5 Hz), 4.11 (m, 2H, C*H*$_2$(Et)), 7.06-7.11 (m, 3H, Ar-*H*), 7.39-7.41 (m, 2H, Ar-*H*), 7.46-7.48 (m, 1H, Ar-*H*), 7.86-7.90 (m, 1H, Ar-*H*), 7.96-8.00 (m, 2H, Ar-*H*), 8.10-8.13 (m, 1H, Ar-*H*), 8.27 (s, 1H, C*H*=N), 8.29 (d, 1H, Ar-*H*, ^{3}*J*(^{1}H, ^{1}H) = 8.5 Hz). ^{13}C{^{1}H} NMR (125.72 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 16.5 (d, *C*H$_3$(OEt), ^{3}*J*(^{31}P, ^{13}C) = 5.9 Hz), 23.3 (*C*H$_3$(iPr)), 27.9 (*C*H(iPr)), 61.9 (d, *C*H$_2$(OEt), ^{2}*J*(^{31}P, ^{13}C) = 6.6 Hz), 122.8, 123.0, 124.6, 128.2 (d, ^{n}*J*(^{31}P, ^{13}C) = 13.2 Hz), 129.3, 129.5 (d, ^{n}*J*(^{31}P, ^{13}C) = 22.5 Hz), 132.5, 132.5 (d, ^{n}*J*(^{31}P, ^{13}C) = 9.5 Hz), 136.8 (d, ^{n}*J*(^{31}P, ^{13}C) = 10.3 Hz), 137.1, 148.2, 154.5 (d, ^{n}*J*(^{31}P, ^{13}C) = 101.2 Hz), 155.2 (Ar-*C*), 162.8 (*C*H=N). ^{31}P{1H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 24.9. IR: ν(P=O) 1232 cm^{-1}.

Synthesis of 2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(Ph(EtO)P=O)C_5H_3N (L^4)

The synthetic protocol is the same as for **L^1**. **Impy^2** (2.20 g, 6.12 mmol), Ph(EtO)PH=O (1.11 mL, 7.34 mmol) and Et$_3$N (2.51 mL, 18.36 mmol) provided ligand **L^4**. Yield: 2.42 g (88 %). mp = 98 – 102 °C. Anal.Calcd.for $C_{27}H_{33}O_2N_2P$ (MW 448.54): C, 72.3; H, 7.4. Found: C, 72.6; H, 7.6. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.03 (d, 6H, C*H*$_3$(iPr), ^{3}*J*(^{1}H, ^{1}H) = 6.7 Hz), 1.07-1.09 (m, 6H,

CH_3(iPr)), 1.33 (t, 3H, CH_3(OEt), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 2.09 (s, 3H, (CH_3)C=N), 2.56 (sept, 1H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 2.64 (sept, 1H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 4.12 (m, 2H, CH_2(OEt)), 7.02-7.05 (m, 1H, Ar-*H*), 7.08-7.11 (m, 2H, Ar-*H*), 7.40-7.44 (m, 2H, Ar-*H*), 7.48-7.51 (m, 1H, Ar-*H*), 7.82-7.86 (m, 1H, Ar-*H*), 8.01-8.05 (m, 2H, Ar-*H*), 8.13 (t, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 6.1 Hz), 8.38 (d, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 8.2 Hz). $^{13}C\{^{1}H\}$ NMR (125.72 MHz, $CDCl_3$, 25 °C): δ (ppm) 16.4 (d, CH_3(OEt), $^{3}J(^{31}P, ^{13}C)$ = 7.0 Hz), 16.9 ((CH_3)C=N), 22.6, 22.7, 23.0, 23.1 (CH_3(iPr)), 28.1, 28.2 (CH(iPr)), 61.6 (d, CH_2(OEt)), $^{1}J(^{31}P, ^{13}C)$ = 7.0 Hz), 122.6, 122.9, 123.0 (d, $^{n}J(^{31}P, ^{13}C)$ = 3.0 Hz), 123.7, 128.1 (d, $^{n}J(^{31}P, ^{13}C)$ = 13.0 Hz), 128.8 (d, $^{n}J(^{31}P, ^{13}C)$ = 23.1 Hz), 129.9 (d, $^{n}J(^{31}P, ^{13}C)$ = 139 Hz), 132.3 (d, $^{n}J(^{31}P, ^{13}C)$ = 3.0 Hz), 132.5, 132.6, 135.5, 136.4 (d, $^{n}J(^{31}P, ^{13}C)$ = 10.0 Hz), 146.1, 153.6 (d, $^{n}J(^{31}P, ^{13}C)$ = 169.6 Hz), 156.5 (d, $^{n}J(^{31}P, ^{13}C)$ = 20.0 Hz) (Ar-*C*), 166.3 ((CH_3)*C*=N). $^{31}P\{^{1}H\}$ NMR (202.40 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 25.4. IR: ν(P=O) 1229 cm^{-1}.

Synthesis of 2-(CH=N(C_6H_3-2,6-iPr_2))-6-((iPrO)$_2$P=O)C_5H_3N (L^5)

The synthetic protocol is the same as for **L^1**. **Impy^1** (2.30 g, 6.66 mmol), (iPrO)$_2$PH=O (1.34 mL, 8.00 mmol) and Et_3N (2.79 mL, 20.00 mmol) provided ligand **L^5**. Yield: 2.26 g (79 %). mp = 97 – 99 °C. Anal.Calcd.for $C_{24}H_{35}O_3N_2P$ (MW 430.52): C, 67.0; H, 8.2. Found: C, 67.3; H, 8.4. ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 1.11 (d, 12H, CH_3(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 1.15 (d, 6H, CH_3(OiPr), $^{3}J(^{1}H, ^{1}H)$ = 6.1 Hz), 1.22 (d, 6H, CH_3(OiPr), $^{3}J(^{1}H, ^{1}H)$ = 6.1 Hz), 3.05 (sept, 2H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 4.83-4.90 (m, 2H, CH(OiPr)), 7.06-7.08 (m, 1H, Ar-*H*), 7.11-7.13 (m, 2H, Ar-*H*), 7.14 (bs, 1H, Ar-*H*), 7.98 (t, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 6.4 Hz), 8.16-8.19 (m, 1H, Ar-*H*), 8.44 (s, 1H, C*H*=N). $^{13}C\{^{1}H\}$ NMR (125.72 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 23.3 (CH_3(iPr)), 23.7 (d, CH_3(OiPr)), $^{3}J(^{31}P, ^{13}C)$ = 5.5 Hz), 24.0 (d, CH_3(OiPr)), $^{3}J(^{31}P, ^{13}C)$ = 3.6 Hz), 27.9 (*C*H(iPr)), 72.0 (*C*H(OiPr), $^{2}J(^{31}P,^{13}C)$ = 5,5 Hz)), 122.7, 122.8 (d, $^{n}J(^{31}P,^{13}C)$ = 3.6 Hz), 123.0, 124.6, 129.0 ($^{n}J(^{31}P,^{13}C)$ = 24.5 Hz), 136.6 ($^{3}J(^{31}P,^{13}C)$ = 11.8 Hz), 137.0, 148.1, 153.2 (d, $^{n}J(^{31}P,^{13}C)$ = 229.0 Hz), 154.7, 154.9 (Ar-*C*), 162.7 (*C*H=N). $^{31}P\{^{1}H\}$ NMR (202.40 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 7.2. IR: ν(P=O) 1251 cm^{-1}.

Synthesis of 2-(C(Me)=N(C_6H_3-2,6-iPr_2))-6-((iPrO)$_2$P=O)C_5H_3N (L^6)

The synthetic protocol is the same as for **L^1**. **Impy^2** (2.20 g, 6.12 mmol), (iPrO)$_2$PH=O (1.23 mL, 7.34 mmol) and Et_3N (2.51 mL, 18.36 mmol) provided ligand **L^6**. Yield: 2.26 g (79 %). mp = 95 – 96 °C. Anal.Calcd.for $C_{25}H_{37}O_3N_2P$ (MW 444.54): C, 67.5; H, 8.4. Found: C, 67.6; H, 8.5. ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 1.08 (d, 6H, CH_3(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 1.13-1.15 (m, 12H, CH_3(iPr) + CH_3(OiPr)), 1.23 (d, 6H, CH_3(OiPr), $^{3}J(^{1}H, ^{1}H)$ = 6.1 Hz), 2.25 (s, 3H, (CH_3)C=N), 2.80 (sept, 2H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 4.84-4.91 (m, 2H, CH(OiPr)), 7.10-7.17 (m, 4H, Ar-*H*), 7.99 (t, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 7.3 Hz), 8.40 (d, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 8.6 Hz). $^{13}C\{^{1}H\}$ NMR (125.72 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 17.2 ((CH_3)C=N), 22.6 (CH_3(iPr)), 23.2 (CH_3(iPr)), 23.9 (d, CH_3(OiPr)), $^{3}J(^{31}P, ^{13}C)$ = 4.5 Hz), 24.1 (d, CH_3(OiPr)), $^{3}J(^{31}P, ^{13}C)$ = 3.6 Hz), 28.2 (*C*H(iPr), 71.9 (d, *C*H(O-iPr), $^{2}J(^{31}P,^{13}C)$ = 6.4 Hz), 122.8, 123.0, 123.2 (d, $^{n}J(^{31}P, ^{13}C)$ = 3.6 Hz), 123.7, 128.7 (d, $^{n}J(^{31}P,^{13}C)$ = 24.5 Hz), 135.7, 136.4 (d, $^{n}J(^{31}P,^{13}C)$ = 11.8 Hz), 146.2, 152.1 (d, $^{n}J(^{31}P,^{13}C)$ = 229.0 Hz), 156.7 (d, $^{n}J(^{31}P,^{13}C)$ = 21.8 Hz) (Ar-*C*), 166.7 ((CH_3)*C*=N). $^{31}P\{^{1}H\}$ NMR (202.40 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 7.2. IR: ν(P=O) 1239 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr_2))-6-(Ph_2P=O)C_5H_3N}SnCl]$^+$[$SnCl_3$]$^-$ (1)

$SnCl_2$ (0.24 g, 1.26 mmol) was added to a solution of **L^1** (0.29 g, 0.63 mmol) in THF (15 mL). The reaction mixture was stirred for 24 h at room temperature. The organic solvent was evaporated under reduced pressure. The residue was washed with a small amount of hexane (10 mL) yielding **1** as a bright yellow powder material. Yield: 0.49 g (92 %). mp = 225 – 228 °C. Anal.Calcd.for $C_{30}H_{31}Cl_4ON_2PSn_2$ (MW 845.79): C, 42.6; H, 3.7. Found: C, 42.8; H, 3.8. ^{1}H NMR (500.13 MHz, THF-d8, 25 °C): *δ (ppm)* 1.23 (d, 12H, CH_3(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 3.18 (sept, 2H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 7.25-7.31 (m, 3H, Ar-*H*), 7.65-7.68 (m, 4H, Ar-*H*), 7.75-7.78 (m, 2H, Ar-*H*), 8.08-8.13 (m, 4H, Ar-*H*), 8.59-8.62 (m, 1H, Ar-*H*), 8.73 (bs, 1H, Ar-*H*), 8.78-8.79 (m, 1H, Ar-*H*), 8.99 (s, 1H, C*H*=N). $^{13}C\{^{1}H\}$ NMR (125.78 MHz, THF-d8, 25 °C): *δ (ppm)* representative ^{13}C NMR spectrum could not be recorded due to low solubility of **1**. $^{31}P\{^{1}H\}$ NMR (202.40 MHz, THF-d8, 25 °C): *δ (ppm)* 35.7. $^{119}Sn\{^{1}H\}$ NMR (186.49 MHz, THF-d8, 25 °C): *δ (ppm)* –95.4, –485.6. IR: ν(P=O) 1131 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr_2))-6-(Ph_2P=O)C_5H_3N}SnCl]$^+$[$SnCl_3$]$^-$ (2)

The synthetic protocol is the same as for **1**. $SnCl_2$ (0.24 g, 1.26 mmol) and **L^2** (0.30 g, 0.63 mmol) provided **2** as a bright yellow powder material. Yield: 0.50 g (97 %). mp = 194 – 199 °C. Anal.Calcd.for $C_{31}H_{33}Cl_4ON_2PSn_2$ (MW 859.81): C, 43.3; H, 3.9. Found: C, 43.5; H, 4.1. ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 1.15 (d, 6H, CH_3(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 1.28 (d, 6H, CH_3(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 2.65 (s, 3H, (CH_3)C=N), 2.97 (sept, 2H, CH(iPr), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz), 7.32-7.37 (m, 3H, Ar-*H*), 7.64-7.67 (m, 4H, Ar-*H*), 7.74-7.77 (m, 2H, Ar-*H*), 7.97-8.02 (m, 4H, Ar-*H*), 8.20-8.22 (m, 1H, Ar-*H*), 8.68-8.70 (m, 1H, Ar-*H*), 8.77-8.81 (m, 1H, Ar-*H*). $^{13}C\{^{1}H\}$ NMR (125.78 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 19.7 ((CH_3)C=N), 25.0, 25.0 (CH_3(iPr)), 28.5 (*C*H(iPr)), 124.6, 124.8, 125.5, 127.9, 128.3, 129.6, 129.7, 131.7 (d, $^{n}J(^{31}P, ^{13}C)$ = 2.7 Hz), 132.5 (d, $^{n}J(^{31}P, ^{13}C)$ = 19.1 Hz), 133.5 (d, $^{n}J(^{31}P, ^{13}C)$ = 12.7 Hz), 134.8 (d, $^{n}J(^{31}P, ^{13}C)$ = 2.7 Hz), 137.3, 139.9, 144.3 (d, $^{n}J(^{31}P, ^{13}C)$ = 9.1 Hz), 149.3, 150.2, 151.4 (d, $^{n}J(^{31}P, ^{13}C)$ = 13.6 Hz) (Ar-*C*), 169.2 ((CH_3)*C*=N). $^{31}P\{^{1}H\}$ NMR (202.40 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 41.0. $^{119}Sn\{^{1}H\}$ NMR (186.49 MHz, $CDCl_3$, 25 °C): *δ (ppm)* –62.0, –469.0. IR: ν(P=O) 1068 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr_2))-6-(Ph(EtO)P=O)C_5H_3N}SnCl]$^+$[$SnCl_3$]$^-$ (3)

The synthetic protocol is the same as for **1**. $SnCl_2$ (0.24 g, 1.26 mmol) and **L^3** (0.27 g, 0.63 mmol) provided **3** as a bright yellow powder material. Yield: 0.49 g (97 %). mp = 184 – 186 °C. Anal.Calcd.for $C_{26}H_{31}Cl_4O_2N_2PSn_2$ (MW 813.74): C, 38.4; H, 3.8. Found: C, 38.6; H, 4.0. ^{1}H NMR (500.13 MHz, THF-d8, 25 °C): *δ (ppm)* 1.15 (bs, 12H, CH_3(iPr)), 1.39 (t, 3H, CH_3(OEt), $^{3}J(^{1}H, ^{1}H)$ = 7.0 Hz)), 3.02-3.19 (m, 2H, CH(iPr)), 4.33 (m, 1H, CH_2(OEt)), 4.52 (m, 1H, CH_2(OEt)), 7.19-7.25 (m, 3H, Ar-*H*), 7.50-7.54 (m, 2H, Ar-*H*), 7.61 (t, 1H, Ar-*H*, $^{3}J(^{1}H, ^{1}H)$ = 7.3 Hz)), 8.06-8.13 (m, 3H, Ar-*H*), 8.51 (bs, 2H, Ar-*H*), 8.76 (s, 1H, C*H*=N). $^{13}C\{^{1}H\}$ NMR (125.78 MHz, $CDCl_3$, 25 °C): *δ (ppm)* 16.4 (d, CH_3(OEt), $^{3}J(^{31}P, ^{13}C)$ = 6.4 Hz), 23.6 (CH_3(iPr)), 28.5 (*C*H(iPr)), 67.3 (d, CH_2(OEt), $^{2}J(^{31}P, ^{13}C)$ = 7.3 Hz), 123.3, 124.4, 124.5, 127.9, 129.6 (d, $^{n}J(^{31}P, ^{13}C)$ = 14.5

Hz), 132.1 (d, ^{n}J(^{31}P, ^{13}C) = 20.0 Hz), 133.1 (d, ^{n}J(^{31}P, ^{13}C) = 11.8 Hz), 134.5 (d, ^{n}J(^{31}P, ^{13}C) = 1.8 Hz), 135.1 (d, ^{n}J(^{31}P, ^{13}C) = 2.7 Hz), 140.7, 144.2 (d, ^{n}J(^{31}P, ^{13}C) = 9.1 Hz), 148.8 (^{n}J(^{31}P, ^{13}C) = 126.3 Hz), 149.5 (Ar-*C*), 162.6 (*C*H=N). ^{31}P{^{1}H} NMR (202.40 MHz, THF-d8, 25 °C): *δ (ppm)* 36.2. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –101.1, –510.3. IR: ν(P=O) 1151 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(Ph(EtO)P=O)C_5H_3N}SnCl]$^+$[SnCl$_3$]$^-$ (4)

The synthetic protocol is the same as for **1**. SnCl$_2$ (0.24 g, 1.26 mmol) and **L^4** (0.28 g, 0.63 mmol) provided **4** as a bright yellow powder material. Yield: 0.50 g (96 %). mp = 175 – 177 °C. Anal.Calcd.for $C_{27}H_{33}Cl_4O_2N_2PSn_2$ (MW 827.77): C, 39.2; H, 4.0. Found: C, 39.3; H, 4.1. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.05 (d, 3H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 1.10 (d, 3H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 1.23 (t, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.4 Hz), 1.44 (t, 3H, C*H*$_3$(OEt), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 2.56 (s, 3H, (C*H*$_3$)C=N), 2.88 (sept, 1H, C*H*(iPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 3.01 (sept, 1H, C*H*(iPr), ^{3}J(^{1}H, ^{1}H) = 6.4 Hz), 4.37-4.44 (m, 1H, C*H*$_2$(OEt)), 4.54-4.59 (m, 1H, C*H*$_2$(OEt)), 7.25-7.31 (m, 3H, Ar-*H*), 7.53-7.57 (m, 2H, Ar-*H*), 7.64-7.67 (m, 1H, Ar-*H*), 8.08-8.16 (m, 3H, Ar-*H*), 8.52-8.53 (m, 1H, Ar-*H*), 8.59-8.63 (m, 1H, Ar-*H*). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 16.4 (*C*H$_3$(OEt), ^{3}J(^{31}P, ^{13}C) = 6.4 Hz), 19.7 ((*C*H$_3$)C=N), 24.9, 25.0, 25.1, 25.2 (*C*H$_3$(iPr)), 28.4, 28.6 (*C*H(iPr)), 67.3 (*C*H$_2$(OEt), ^{2}J(^{31}P, ^{13}C) = 7.3 Hz), 124.8, 124.9, 128.0, 129.4, 129.6, 131.8 (^{n}J(^{31}P, ^{13}C) = 2.7 Hz), 132.2 (^{n}J(^{31}P, ^{13}C) = 19.1 Hz) 133.0, 133.1, 135.0 (^{n}J(^{31}P, ^{13}C) = 2.7 Hz), 137.2, 140.0, 140.1, 144.4 (^{n}J(^{31}P, ^{13}C) = 10.0 Hz), 148.8 (^{n}J(^{31}P, ^{13}C) = 144.4 Hz), 150.6 (^{n}J(^{31}P, ^{13}C) = 15.4 Hz) (Ar-*C*), 169.9 ((CH$_3$)*C*=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 36.1. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –64.5, –495.5. IR: ν(P=O) 1148 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-((iPrO)$_2$P=O)C_5H_3N}SnCl]$^+$[SnCl$_3$]$^-$ (5)

The synthetic protocol is the same as for **1**. SnCl$_2$ (0.24 g, 1.26 mmol) and **L^5** (0.27 g, 0.63 mmol) provided **5** as a bright yellow powder material. Yield: 0.46 g (91 %). mp = 172 – 174 °C. Anal.Calcd.for $C_{24}H_{35}Cl_4O_3N_2PSn_2$ (MW 809.75): C, 35.6; H, 4.4. Found: C, 35.7; H, 4.5. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.17 (d, 12H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 1.30 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 1.43 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.4 Hz), 3.12 (bs, 1H, C*H*(iPr)), 5.04-5.09 (m, 2H, C*H*(OiPr)), 7.20-7.25 (m, 3H, Ar-*H*), 8.11 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 8.0 Hz), 8.53-8.62 (m, 2H, Ar-*H*), 8.81 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 23.6 (*C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 6.4 Hz), 23.8 (*C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 3.0 Hz), 24.7, 25.3 (*C*H$_3$(iPr)), 28.2 (*C*H(iPr)), 77.1 (*C*H(OiPr), ^{2}J(^{31}P, ^{13}C) = 7.3 Hz), 124.2, 127.3, 131.0 (^{n}J(^{31}P, ^{13}C) = 18.9 Hz), 134.5 (^{n}J(^{31}P, ^{13}C) = 2.0 Hz), 140.3 (^{n}J(^{31}P, ^{13}C) = 25.2 Hz), 143.6 (^{n}J(^{31}P, ^{13}C) = 10.0 Hz), 145.4, 147.1, 148.4 (^{n}J(^{31}P, ^{13}C) = 20.2 Hz) (Ar-*C*), 163.0 (*C*H=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 16.7. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –64.2, –532.2. IR: ν(P=O) 1171 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-((iPrO)$_2$P=O)C_5H_3N}SnCl]$^+$[SnCl$_3$]$^-$ (6)

The synthetic protocol is the same as for **1**. SnCl$_2$ (0.24 g, 1.26 mmol) and **L^6** (0.28 g, 0.63 mmol) provided **6** as a bright yellow powder material. Yield: 0.48 g (93 %). mp = 167 – 169 °C. Anal.Calcd.for $C_{25}H_{37}Cl_4O_3N_2PSn_2$ (MW 823.78): C, 36.5; H, 4.5. Found: C, 36.7; H, 4.7. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.08 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 1.21 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 1.30 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 1.43 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.4 Hz), 2.57 (s, 3H, (C*H*$_3$)C=N), 2.92 (sept, 2H, C*H*(iPr), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 5.02-5.010 (m, 2H, C*H*(OiPr)), 7.20-7.29 (m, 3H, Ar-*H*), 8.17 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 8.0 Hz), 8.61 (d, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 8.0 Hz), 8.67-8.72 (m, 1H, Ar-*H*). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 19.8 ((*C*H$_3$)C=N), 23.5 (*C*H$_3$(iPr)), 23.8 (*C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 7.0 Hz), 24.1 (*C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 3.0 Hz), 25.0 (*C*H$_3$(iPr)), 28.4 (*C*H(iPr)), 68.0 (*C*H(OiPr)), 124.7 (^{n}J(^{31}P, ^{13}C) = 22.6 Hz), 127.9, 131.4 (^{n}J(^{31}P, ^{13}C) = 22.6 Hz), 131.9 (^{n}J(^{31}P, ^{13}C) = 3.8 Hz), 136.9, 140.0, 141.5, 144.4 (^{n}J(^{31}P, ^{13}C) = 12.6 Hz), 145.4, 147.6, 149.6 (^{n}J(^{31}P, ^{13}C) = 25.2 Hz) (Ar-*C*), 170.6 (*C*(CH$_3$)=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 16.4. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –57.7, –508.4. IR: ν(P=O) 1177 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-(Ph$_2$P=O)C_5H_3N}Sn(H$_2$O)][OTf]$_2$ (7)

A solution of Sn(OTf)$_2$ (0.18 g, 0.43 mmol) in THF (20 mL) was added to a stirred solution of **L^1** (0.20 g, 0.43 mmol) in THF (20 mL). The reaction mixture was stirred for 24 h at room temperature. After that, all volatiles were removed under reduced pressure and the residue was washed with benzene (10 ml) yielding **7** as a yellow powder material. Yield: 0.33 g (85 %). For **7**: mp = 172-175 °C. Anal.Calcd.for $C_{32}H_{33}O_8F_6N_2S_2PSn$ (MW 901.42): C, 42.6; H, 3.7. Found: C, 42.7; H, 3.8. ^{1}H NMR (500.13 MHz, THF-d8, 25 °C): *δ (ppm)* 1.26 (d, 12H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 3.19 (sept, 2H, C*H*(iPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 7.31-7.34 (m, 4H, Ar-*H*), 7.61-7.65 (m, 4H, Ar-*H*), 7.75-7.78 (m, 2H, Ar-*H*), 8.02-8.06 (m, 4H, Ar-*H*), 8.58-8.63 (m, 3H, Ar-*H*), 9.03 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (125.78 MHz, THF-d8, 25 °C): *δ (ppm)* representative ^{13}C NMR spectrum could not be recorded due to low solubility of **7**. ^{31}P{^{1}H} NMR (202.40 MHz, THF-d8, 25 °C): *δ (ppm)* 42.8. ^{119}Sn{^{1}H} NMR (186.49 MHz, THF-d8, 25 °C): *δ (ppm)* –918.2. ^{19}F NMR (470.59 MHz, THF-d8, 25 °C) *δ (ppm)* -79.1. IR: ν(P=O) 1169 cm^{-1}, ν(O-H) 2963 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(Ph(EtO)P=O)C_5H_3N}Sn(H$_2$O)][OTf]$_2$ (8)

The synthetic protocol is the same as for **7**. Sn(OTf)$_2$ (0.25 g, 0.60 mmol) and **L^4** (0.27 g, 0.60 mmol) provided **8** as a bright yellow powder material. Yield: 0.47 g (91 %). mp = 260 – 262 °C. Anal.Calcd.for $C_{28}H_{33}O_9F_6N_2S_2PSn$ (MW 869.37): C, 38.7; H, 3.8. Found: C, 38.5; H, 3.7. ^{1}H NMR (500.13 MHz, THF-d8, 25 °C): *δ (ppm)* 1.18 (t, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.5 Hz), 1.27-1.29 (m, 6H, C*H*$_3$(iPr)), 1.47 (t, 3H, C*H*$_3$(OEt), ^{3}J(^{1}H, ^{1}H) = 7.0 Hz), 3.16 (m, 2H, C*H*(iPr)), 4.50 (m, 2H, C*H*$_2$(OEt)), 7.36-7.38 (m, 3H, Ar-*H*), 7.60-7.65 (m, 2H, Ar-*H*), 7.74-7.76 (m, 1H, Ar-*H*), 8.17-8.22 (m, 2H, Ar-*H*), 8.40-8.44 (m, 1H, Ar-*H*), 8.57-8.60 (m, 1H, Ar-*H*), 8.69-8.71 (m, 1H, Ar-*H*). ^{13}C{^{1}H} NMR (125.78 MHz, THF-d8, 25 °C): *δ (ppm)* representative ^{13}C NMR spectrum could not be recorded due to low solubility of **8**. ^{31}P{^{1}H} NMR (202.40 MHz, THF-d8, 25 °C): *δ (ppm)* 38.0. ^{119}Sn{^{1}H} NMR (186.49 MHz, THF-d8, 25 °C): *δ (ppm)* –859.9. ^{19}F NMR (470.59 MHz, THF-d8, 25 °C) *δ (ppm)* -79.3. IR: ν(P=O) 1158 cm^{-1}, ν(O-H) 2960 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-((iPrO)$_2$P=O)C_5H_3N}Sn(H_2O)][OTf]$_2$ (9)

The synthetic protocol is the same as for **7**. Sn(OTf)$_2$ (0.22 g, 0.53 mmol) and **L^6** (0.23 g, 0.53 mmol) provided **9** as a bright yellow powder material. Yield: 0.46 g (84 %). mp = 135 – 138 °C. Anal.Calcd.for $C_{26}H_{37}O_{10}F_6N_2S_2PSn$ (MW 865.38): C, 36.1; H, 4.3. Found: C, 36.4; H, 4.5. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.05 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.6 Hz), 1.17 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 7.6 Hz), 1.32 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz), 1.42 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.8 Hz), 2.42 (s, 3H, (C*H*$_3$)C=N), 2.85 (bs, 1H, C*H*(iPr)), 3.04 (sept, 1H, C*H*(iPr), ^{3}J(^{1}H, ^{1}H) = 7.6 Hz), 5.02 (m, 2H, C*H*(OiPr)), 7.25-7.34 (m, 3H, Ar-*H*), 8.11 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 8.0 Hz), 8.36-8.43 (m, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* representative ^{13}C NMR spectrum could not be recorded due to low solubility of **9**. ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 16.2. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –900.9. ^{19}F NMR (470.59 MHz, CDCl$_3$, 25 °C) *δ (ppm)* -78.7. IR: ν(P=O) 1156 cm^{-1}, ν(O-H) 2967 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-(PhP=O(OSnCl$_2$))C_5H_3N}SnCl] (10)

Compound **3** (0.50 g, 0.61 mmol) was dissolved in toluene/THF (1:1, 20 mL) and the solution was heated at 80 °C for 7 days. The progress of the reaction was monitored by ^{31}P NMR spectroscopy until the signal of the starting compound **3** disappeared, replaced by the new signal of the compound **10**. After that, all volatiles were removed under reduced pressure and the residue was washed with hexane (5 mL) yielding **10** as a yellow powder material. Yield: 0.41 g (90 %). mp = 116 – 119 °C. Anal.Calcd.for $C_{24}H_{26}Cl_3O_2N_2PSn_2$ (MW 749.23): C, 38.5; H, 3.5. Found: C, 38.3; H, 3.4. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.11 (bs, 3H, C*H*$_3$(iPr)), 1.15 (bs, 3H, C*H*$_3$(iPr)), 1.28 (d, 6H, CH$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz)), 3.04 (bs, 1H, C*H*(iPr)), 3.19 (sept, 1H, C*H*(iPr)), ^{3}J(^{1}H, ^{1}H) = 6.7 Hz)), 7.10-7.13 (m, 2H, Ar-*H*), 7.18-7.24 (m, 2H, Ar-*H*), 7.38 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 7.9 Hz)), 7.45-7.50 (m, 1H, Ar-*H*), 7.57 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 7.0 Hz)), 8.00- 8.04 (m, 1H, Ar-*H*), 8.08-8.12 (m, 1H, Ar-*H*), 8.18-8.21 (m, 1H, Ar-*H*), 8.54 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 23.6 (*C*H$_3$(iPr)), 28.6 (*C*H(iPr)), 123.2, 124.8, 127.6, 129.1 (d, ^{n}J(^{31}P, ^{13}C) = 14.5 Hz), 130.4, 131.0, 132.9 (d, ^{n}J(^{31}P, ^{13}C) = 11.8 Hz), 133.6 (d, ^{n}J(^{31}P, ^{13}C) = 3.6 Hz), 139.6, 141.8, 141.9, 147.3 (d, ^{n}J(^{31}P, ^{13}C) = 14.5 Hz), 156.3 (d, ^{n}J(^{31}P, ^{13}C) = 142.6 Hz) (Ar-*C*), 160.4 (*C*H=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 25.3. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –215.8, –497.4. IR: ν(P=O) 1130 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-(PhP=O(OSnCl$_2$))C_5H_3N}SnCl] (11)

The synthetic protocol is the same as for **10**. Compound **4** (0.50 g, 0.60 mmol) provided **11** as a yellow powder material. Yield: 0.46 g (94 %). mp = 113 – 116 °C. Anal.Calcd.for $C_{25}H_{28}Cl_3O_2N_2PSn_2$ (MW 763.25): C, 39.3; H, 3.7. Found: C, 39.5; H, 3.8. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.11 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.5 Hz)), 1.27 (d, 6H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.5 Hz)), 2.47 (s, 3H, (C*H*$_3$)C=N), 3.01 (bs, 2H, C*H*(iPr)), 7.28-7.32 (m, 3H, Ar-*H*), 7.51 (bs, 2H, Ar-*H*), 7.58 (d, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 7.3 Hz)), 8.11 (t, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 6.8 Hz)), 8.20-8.25 (m, 2H, Ar-*H*), 8.22-8.24 (m, 1H, Ar-*H*), 8.41 (d, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 7.3 Hz)). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 19.0 ((*C*H$_3$)C=N), 24.5, 25.0 (*C*H$_3$(iPr)), 28.2, 28.9 (*C*H(iPr)), 124.3 , 124.7, 127.4, 128.1, 128.9 (d, ^{n}J(^{31}P, ^{13}C) = 14.7 Hz), 130.3, 132.7, 132.9 (d, ^{n}J(^{31}P, ^{13}C) = 11.7 Hz), 134.4 (d, ^{n}J(^{31}P, ^{13}C) = 2.9 Hz), 137.4, 141.7 (^{n}J(^{31}P, ^{13}C) = 9.5 Hz), 148.3 (^{n}J(^{31}P, ^{13}C) = 13.9 Hz), 155.8 (^{n}J(^{31}P, ^{13}C) = 139.4 Hz) (Ar-*C*), 167.1 (*C*(CH)$_3$=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 23.7. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –212.6, –497.8. IR: ν(P=O) 1156 cm^{-1}.

Synthesis of [{2-(CH=N(C_6H_3-2,6-iPr$_2$))-6-((iPrO)P=O(OSnCl$_2$))C_5H_3N}SnCl] (12)

The synthetic protocol is the same as for **10**. Compound **5** (0.59 g, 0.73 mmol) provided **12** as a yellow powder material. Yield: 0.49 g (93 %). mp = 114 – 116 °C. Anal.Calcd.for $C_{21}H_{28}Cl_3O_3N_2PSn_2$ (MW 731.21): C, 34.5; H, 3.9. Found: C, 34.7; H, 3.8. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.14 (d, 12H, C*H*$_3$(iPr), ^{3}J(^{1}H, ^{1}H) = 6.8 Hz)), 1.21 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.5 Hz)), 2.99 (bs, 2H, C*H*(iPr)), 4.77 (bs, 1H, C*H*(OiPr), 7.19-7.21 (m, 3H, Ar-*H*), 8.07 (d, 1H, Ar-*H*, ^{3}J(^{1}H, ^{1}H) = 6.8 Hz)), 8.30-8.33 (m, 2H, Ar-*H*), 8.56 (s, 1H, C*H*=N). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 23.1 (*C*H$_3$(iPr)), 23.9 (d, *C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 4.0 Hz), 24.7 (*C*H$_3$(iPr)), 28.5 (*C*H(iPr)), 73.5 (d, *C*H(OiPr), ^{3}J(^{31}P, ^{13}C) = 5.0 Hz), 124.1, 127.6, 131.4, 131.9 (d, ^{n}J(^{31}P, ^{13}C) = 19.0 Hz), 139.5, 141.6, 142.1 (d, ^{n}J(^{31}P, ^{13}C) = 10.0 Hz), 146.9 (d, ^{n}J(^{31}P, ^{13}C) = 19.0 Hz), 153.3 (^{n}J(^{31}P, ^{13}C) = 203.0 Hz) (Ar-*C*), 161.1 (*C*H=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 9.9. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –215.1, –518.3. IR: ν(P=O) 1152 cm^{-1}.

Synthesis of [{2-(C(Me)=N(C_6H_3-2,6-iPr$_2$))-6-((iPrO)P=O(OSnCl$_2$))C_5H_3N}SnCl] (13)

The synthetic protocol is the same as for **10**. Compound **6** (0.52 g, 0.63 mmol) provided **13** as a yellow powder material. Yield: 0.46 g (99 %). mp = 117 – 119 °C. Anal.Calcd.for $C_{22}H_{30}Cl_3O_3N_2PSn_2$ (MW 745.24): C, 35.5; H, 4.1. Found: C, 35.7; H, 4.2. ^{1}H NMR (500.13 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 1.15 (bs, 6H, C*H*$_3$(iPr)), 1.30 (d, 6H, C*H*$_3$(OiPr), ^{3}J(^{1}H, ^{1}H) = 6.8 Hz)), 1.44 (bs, 6H, C*H*$_3$(iPr)), 2.78 (bs, 1H, C*H*(iPr)), 2.98 (bs, 1H, C*H*(iPr)), 4.92 (bs, 1H, C*H*(OiPr), 7.26 (bs, 3H, Ar-*H*), 8.22 (bs, 1H, Ar-*H*), 8.45 (bs, 2H, Ar-*H*). ^{13}C{^{1}H} NMR (125.78 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 19.2 ((*C*H$_3$)C=N), 23.9 (d, *C*H$_3$(OiPr), ^{3}J(^{31}P, ^{13}C) = 4.0 Hz), 24.5, 25.0 (*C*H$_3$(iPr)), 28.3, 29.0 (*C*H(iPr)), 73.3 (d, *C*H(OiPr), ^{3}J(^{31}P, ^{13}C) = 5.0 Hz), 124.6, 127.6, 128.4, 132.3 (d, ^{n}J(^{31}P, ^{13}C) = 18.0 Hz), 137.8, 139.0, 139.7, 141.9 (d, ^{n}J(^{31}P, ^{13}C) = 10.0 Hz), 148.0 (d, ^{n}J(^{31}P, ^{13}C) = 18.0 Hz), 153.3 (^{n}J(^{31}P, ^{13}C) = 200.0 Hz) (Ar-*C*), 167.7 (*C*(CH)$_3$=N). ^{31}P{^{1}H} NMR (202.40 MHz, CDCl$_3$, 25 °C): *δ (ppm)* 9.5. ^{119}Sn{^{1}H} NMR (186.49 MHz, CDCl$_3$, 25 °C): *δ (ppm)* –219.1, –524.1. IR: ν(P=O) 1161 cm^{-1}.

Crystallography

Single crystals of **1**, **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 were obtained from saturated CH_2Cl_2/hexane solutions of the parent complexes at –20 °C. Single crystals of **9** was obtained from saturated THF/hexane solutions of the parent complexes at –20 °C. Single crystals of **10**·$0.5C_7H_8$ and **12**·CH_2Cl_2 were obtained from saturated toluene/hexane and CH_2Cl_2/hexane, respectively, solutions of the parent complexes at –20 °C. The X-ray data for crystals of **1**, **2**·CH_2Cl_2, **3**, **4**·CH_2Cl_2, **9**, **10**·$0.5C_7H_8$ and **12**·CH_2Cl_2 were obtained at 150K using Oxford Cryostream low-temperature device with a Bruker D8-Venture diffractometer equipped with Mo (Mo/K_α radiation; $\lambda = 0.71073$ Å) microfocus X-ray (IμS) source, Photon CMOS detector and Oxford Cryosystems cooling device was used for data collection. Obtained data were treated by XT-version 2014/5 and SHELXL-2017/1 software implemented in APEX3 v2016.9-0 (Bruker AXS) system.[44] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$, $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data. Crystallographic data for all structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2182031-2182037. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

The frames for all complexes were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved and refined using the Bruker SHELXTL Software Package.

Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, most of the hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors Hiso(H) = 1.2 Ueq (pivot atom) or of 1.5Ueq (methyl). H atoms in methyl, methylene moieties and C-H in aromatic rings were placed with C-H distances of 0.96, 0.97 and 0.93 Å. Hydrogen atoms in O-H bonds were refined freely. In **12**, the disordered dichlormethane solvent was split into two positions.

Conflicts of interest

There are no conflicts to declare.

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