Journal of Organometallic Chemistry 718 (2012) 38–42

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Phosphinimine complex of organotin(IV) compounds stabilized by O,C,O-chelating ligand

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form
31 July 2012
Accepted 2 August 2012

Keywords:
Organotin
Phosphinimine
Intramolecular coordination
NMR
X-ray diffraction

ABSTRACT

Oxidation of an intramolecularly coordinated phosphine ligand {2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}PPh$_2$ (**1**) by Me$_3$SiN$_3$ provided novel silyl-phosphinimine {2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NSiMe$_3$ (**2**), that can be easily hydrolysed to give stable phosphiniminium azide [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH$_2$]$^+$ N$_3^-$ (**3**). Compound **3** was used for the synthesis of novel intramolecularly coordinated phosphinimine compound L^{1}Ph$_2$P=NH, that can be trapped by triorganotin(IV) compounds R$_3$SnCl (R = Me, Cy) as organotin(IV)-phosphinimine complexes [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH]SnR$_3$Cl (R = Me(**4**), Cy(**5**)). Compounds **2**–**5** were characterized by means of elemental analyses, ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR spectroscopy, and compounds **3** and **4** by single crystal X-ray diffraction analysis.

1. Introduction

The use of phosphinimine ligands (R$_3$P=NSiMe$_3$) as suitable ligands for the stabilization of organometallic complexes has been studied over the past few decades and applications of variety of these compounds have been reported [1]. The chemistry of transition metal phosphinimine complexes has led to the development of highly effective olefin polymerization catalysts [2,3]. The corresponding main group phosphinimines complexes have drawn some attention since 1970s, when Wolfsberger synthesized variety of complexes of the formula *t*-Bu$_3$PNMMe$_3$ (M = Si, Ge, Sn) [4]. Further studies of Stephan et al. have probed the structural and chemical behaviour of Li [5], Mg [6], Si, Sn, and Ge [7] phosphinimine derivatives. Dehnicke and co-workers reported several boron-phosphinimines derivatives of group 13-15 species [8]. In general, the synthesis of phosphinimine ligands is based on easy oxidation of phosphine ligands by Me$_3$SiN$_3$ and all given examples are limited to study the effects of sterical demanding phosphinimine ligands, while the synthesis of an intramolecularly coordinated phosphinimine ligands is still unknown. Previously we have reported synthesis of an ether functionalized phosphine ligand {2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}PPh$_2$ (**1**) and its coordination ability towards MCl$_2$ (M is Pd, Pt) (Chart 1) [9].

Here we report an oxidation reaction of **1** by Me$_3$SiN$_3$ that provided novel silyl-phosphinimine ligand {2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NSiMe$_3$ (**2**), that can be easily hydrolysed to give phosphiniminium azide [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH$_2$]$^+$ N$_3^-$ (**3**). Compound **3**, stabilized by the N–H···O hydrogen bonding with an oxygen atom of the O,C,O-chelating ligand, was further used for the synthesis of novel ether functionalized phosphinimine compound [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH. The latter compound was trapped by triorganotin(IV) compounds R$_3$SnCl (R = Me, Cy) to provide the organotin(IV)-phosphinimine complexes [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH]SnR$_3$Cl (R = Me(**4**), Cy(**5**)). Compounds **2**–**5** were characterized by means of elemental analyses, ^{1}H, ^{13}C, ^{31}P, ^{119}Sn NMR spectroscopy, and compounds **3** and **4** by single crystal X-ray diffraction analysis.

2. Results and discussion

Reaction of L^{1}PPh$_2$ (**1**) (L^1 is an abbreviation for 2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3^-$ ligand) with Me$_3$SiN$_3$ provided oxygen stabilized silyl-phosphinimine ligand L^{1}Ph$_2$P=NSiMe$_3$ (**2**) in high yield (Scheme 1). Compound **2** was characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The ^{31}P{^{1}H} NMR spectrum showed a signal at δ −7.4 with ^2J(^{31}P, ^{29}Si) = 104 Hz, that is shifted downfield compare with **1** (δ −20.3) [9]. The ^{1}H NMR spectrum showed a singlet resonance at δ 4.36 for C*H*$_2$O methylene groups and at δ 0.35 ppm for Si(C*H*$_3$)$_3$ groups. Compound **2** is sensitive to water and the treatment of **2** with 2 equivalents of H$_2$O in the presence of Me$_3$SiN$_3$ provided

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http://dx.doi.org/10.1016/j.jorganchem.2012.08.003

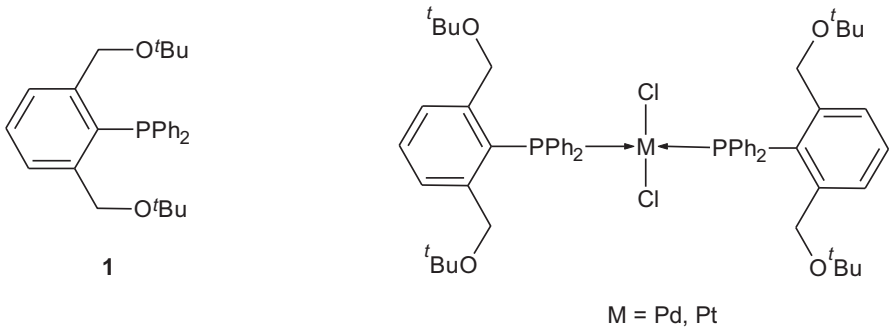
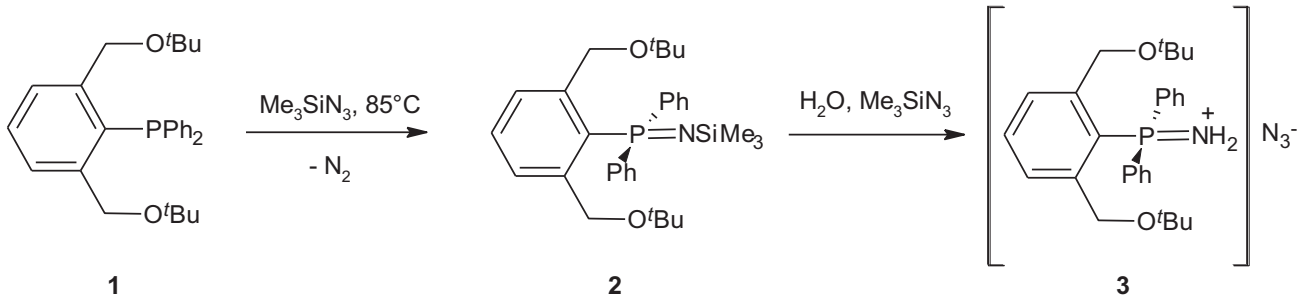


Chart 1.



Scheme 1. Synthesis of oxygen stabilized silyl-phosphinimine ligand **2** and its hydrolytic product **3**.

phosphiniminium azide $[L^1Ph_2P{=}NH_2]^+ N_3^-$ (**3**), as the controlled hydrolytic product of **2**, in quantitative yield.

Compound **3** was characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, mass spectrometry and molecular structure was determined by X-ray diffraction analysis. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet resonance at δ +30.5 shifted downfield compare with **2** (δ −7.4 ppm). The ^1H NMR spectrum revealed a singlet resonance at δ 4.35 for C*H*$_2$O methylene groups together with a resonance at δ 8.00 assigned to N*H*$_2$ groups. The ESI/MS spectrum showed a specific ion at *m*/*z* 450 corresponding to $[M - N_3]^+$ fragment.

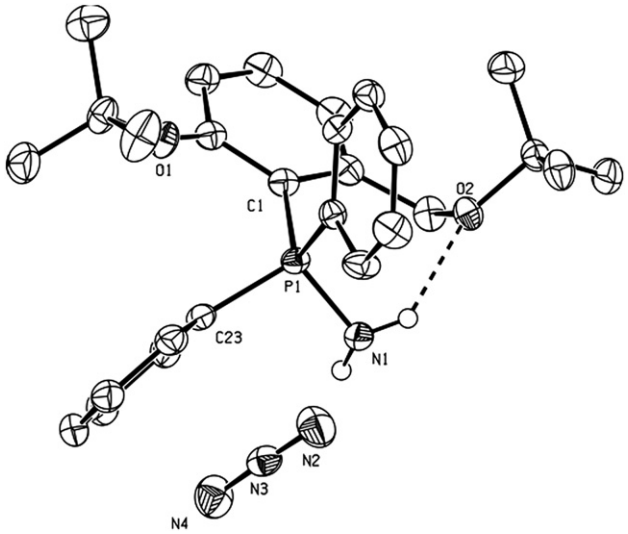


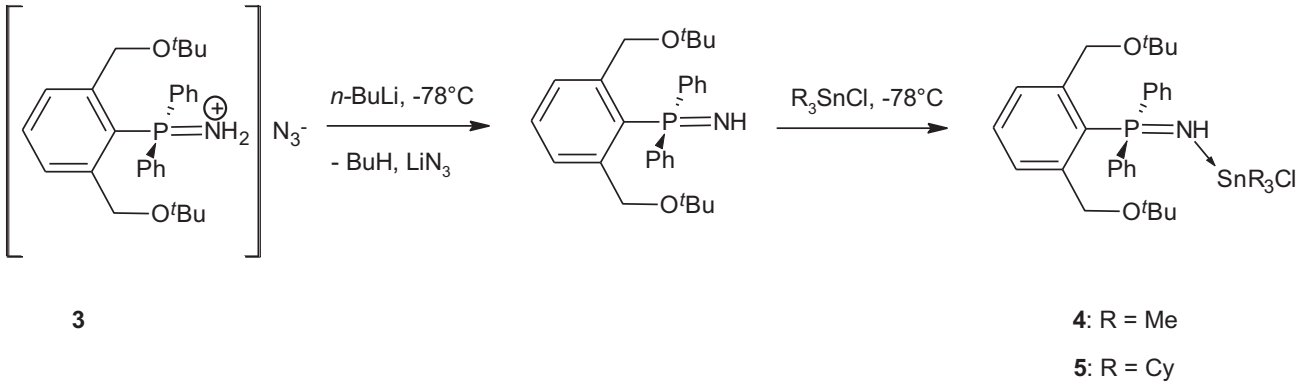
Fig. 1. ORTEP view of **3**. The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–N1 1.6314(14), P1–N3 4.6221(16), C1–P1–N1 117.24(8), C17–P1–C23 115.08(8), O2···N1 2.7387(19) Å.

Single crystals of **3** suitable for X-ray diffraction analysis were obtained by crystallization from toluene/hexane solution at + 4 °C. The molecular structure of **3**, selected bond lengths, and angles are shown in Fig. 1, the crystallographic data are given in Table S1.

The central phosphorus atom is four coordinated with distorted tetrahedral geometry as defined from bonding angles C1–P1–N1 (117.24(8)°), C1–P1–C17 (109.87(8)°) and C1–P1–C23 (109.42(8)°). Compound **3** can be described as aminophosphonium salt with P–N single bond and positive charge on phosphorus atom (see supporting information, Scheme S1A) or as phosphiniminium salt where P=N double bond contains positive charge on nitrogen atom (Scheme S1B). The P1–N1 (1.6314(14) Å) bond length is shorter that P–N single bond predicted by Pyykkö (Σ_{cov}(P,N) = 1.82 Å) [10] and proved the existence of P=N double bond in **3** (for double bond covalent radii Σ_{cov}(P,N) = 1.62 Å) [10]. The phosphiniminium form P=N*H*$_2$ in **3** is further stabilized by the O,C,O-chelating ligand L^1, due to the existence an N–H···O hydrogen bonding [O2···N1 2.7387(19) Å] with one of the oxygen atom of ligand L^1.

Treatment of **3** with equivalent of n-BuLi allowed an *in situ* preparation of phosphinimine $L^1Ph_2P{=}NH$ (Scheme 2). Subsequent reaction of $L^1Ph_2P{=}NH$ with triorganotin(IV) compounds R_3SnCl (R = Me, Cy) provided organotin(IV)phosphinimine complexes ($L^1Ph_2P{=}NH)SnR_3Cl$ (R = Me(**4**), Cy(**5**)) (Scheme 2).

Compounds **4** and **5** were characterized by the ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectroscopy, ESI-MS and molecular structure of **4** was determined by diffraction analysis. The $^{31}P\{^1H\}$ NMR spectrum of **4** showed a resonance at δ +28.9 ppm (δ +28.0 ppm for **5**) flanked by ^{119}Sn satellites with coupling constant $^2J(^{31}P, ^{119}Sn) = 113$ Hz ($^2J(^{31}P, ^{119}Sn) = 100$ Hz for **5**). The ^1H NMR spectrum of **4** revealed a resonance at δ 4.48 ppm of methylene C*H*$_2$O groups (δ 4.50 ppm for **5**) and singlet at δ 0.60 ppm of Sn*Me* groups. The ^1H NMR spectrum of **4** also showed a doublet of N*H* group at δ 4.19 ppm with coupling constant $^2J(^1H,^{31}P) = 101$ Hz suggesting the presence of P=N*H*



Scheme 2. Synthesis of oxygen stabilized phosphinimine and its organotin(IV) complexes **4** and **5**.

fragment (δ 4.28 ppm, $^2J(^1H,^{31}P) = 100$ Hz for **5**). The $^{119}Sn\{^1H\}$ NMR spectrum of **4** revealed a resonance at δ 24.7 ppm (δ 35.5 ppm for **5**). This value is shifted upfield compare with the value found for Me_3SnCl (+160 ppm) [11] but is similar to $Me_3SnCl\cdot py$ (−9 ppm) [11] and indicates the presence of five coordinated tin atom in solution of **4**. This was further corroborate from ^{13}C NMR spectrum of **4**, where the value of C–Sn–C bond angle 121° was calculated from the $^1J(^{119}Sn,^{13}C) = 558$ Hz [12] (for comparison the value of $^1J(^{119}Sn,^{13}C)$ for Me_3SnCl is 379.7 Hz) [13]. An interestingly, the fact that the $^{31}P\{^1H\}$ NMR spectrum of compounds **4** and **5** revealed $^2J(^{31}P,^{119}Sn)$ at room temperature suggests that both complexes are kinetically inert and it contrasts with organotin(IV) complexes of HMPA. The later complexes are kinetically more labile and similar $^2J(^{31}P,^{119}Sn)$ couplings were observed at low temperature only [14] suggesting that the $R_3P{=}NH$ group is a stronger ligand towards R_3SnCl moiety in comparison to HMPA.

Single crystals of **4** suitable for X-ray diffraction analysis were obtained by crystallization from toluene/hexane solution at +4 °C. The molecular structure of **4**, selected bond lengths, and angles are shown in Fig. 2 (for the crystallographic data see Table S1).

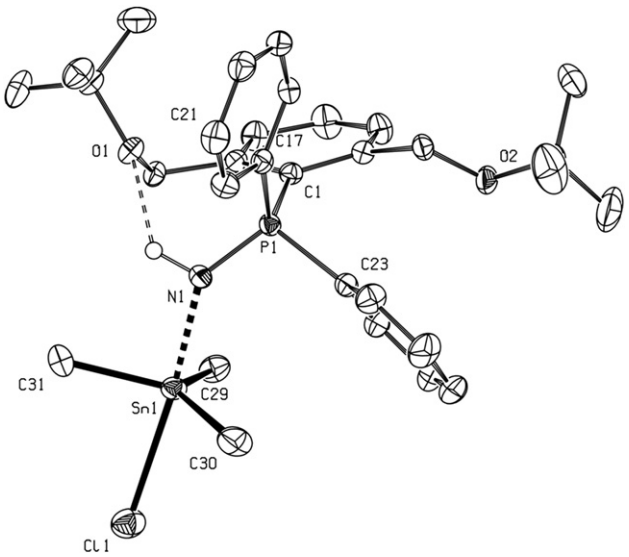


Fig. 2. ORTEP view of **4**. The thermal ellipsoids are drawn with 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): P1–N1 1.594(2), N1–Sn1 2.258(3), Sn1–Cl1 2.7093(10), P1–N1–Sn1 136.77(18), N1–Sn1–Cl1 172.27(8), C29–Sn1–C31 110.64(13), C30–Sn1–C29 123.73(14), C29–Sn1–Cl1 90.95(9), O1···N1 2.789(3) Å.

The central tin atom is five coordinated. The geometry of tin atom is best described as trigonal bipyramidal, with the methyl groups occupying the equatorial plane and the phosphinimine and the chlorine atom occupying the axial sites as defined from bonding angles C29–Sn1–C31 (110.64(13)°), C31–Sn1–C30 (125.14(14)°), C30–Sn1–C29 (123.73(14)°) and N1–Sn–Cl1 (172.27(8)°). The P1–N1 (1.594(2) Å) bond length proved the existence of P=N double bond in the phosphinimine $L^1Ph_2P{=}NH$ (for double bond covalent radii Σ_{cov}(P,N) = 1.62 Å) [10]. The N1–Sn1 (2.258(3) Å) bond length is longer than the sum of covalent radii of both atoms ($\sum_{cov}$(N,Sn) = 2.11 Å) [10] and suggests the presence of strong N → Sn intermolecular interaction of phosphinimine $L^1PPh_2P{=}NH$ to Me_3SnCl. This interaction also resulted to a substantive elongation of Sn–Cl bond in Me_3SnCl, as indicated from the Sn1–Cl1 bond length (2.7093(10) Å) being longer than the sum of covalent radii of both atoms ($\sum_{cov}$(Sn,Cl) = 2.39 Å) [10]. Compound **4** is related to the adduct (i-$Pr_3P{=}NH$)$SnMe_3Cl$, where the similar arrangement of central tin atom was found [15] and is similar to the related plutonyl(VI) chloride complex of triphenyl phosphinimine [16]. It is noteworthy, that related reaction of t-Bu_3PNH with Me_3SnCl does not result in the Lewis base adduct [15]. Stabilization of monomeric form of **4** is supported by the presence of ligand L^1, since the ammonium P=N*H* group is involved in a N–H···O hydrogen bonding with one of the oxygen atom of ligand L^1[O1···N1 2.789(3) Å]. This contrasts with a molecular structure of (i-$Pr_3P{=}NH$)$SnMe_3Cl$, where an extended polymeric chain was observed in the solid state due the presence of NH–Cl hydrogen bonding [15].

3. Conclusion

We have demonstrated that compound **1** is useful starting material for synthesis silyl-phosphinimine ligand {2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NSiMe$_3$ (**2**). Thy hydrolysis of **2** provided an oxygen stabilized phosphiniminium azide [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH$_2$]$^+$ N_3^- (**3**) and phosphinimine compound $L^1Ph_2P{=}NH$. The later compound can be trapped by triorganotin(IV) compounds R_3SnCl (R = Me, Cy) as organotin(IV)-phosphinimine complexes [{2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$}Ph$_2$P=NH]SnR_3Cl (R = Me(**4**), Cy(**5**)).

4. Experimental

4.1. General methods

The starting compound [2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]PPh$_2$ (**1**) was prepared according to literature [9], Me_3SiN_3, Me_3SnCl and Cy_3SnCl were purchased by Sigma Aldrich. All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried

by standard methods, distilled prior to use. The ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ and $^{119}Sn\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 spectrometer at 300 K in C_6D_6 or $CDCl_3$. The ^{1}H, ^{13}C, ^{31}P and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to internal Me_4Si (^{1}H and ^{13}C) and external H_3PO_4 (^{31}P) and Me_4Sn (^{119}Sn). Elemental analyses were performed on an LECO-CHNS-932 analyzer.

4.2. Synthesis of [2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]Ph$_2$PNSiMe$_3$ (**2**)

0.11 mL of Me_3SiN_3 (0.85 mmol) was added to toluene solution (10 mL) of **1** (0.24 g; 0.56 mmol) and reaction mixture was heated to 85 °C. The reaction was monitored by ^{31}P NMR spectroscopy and the reaction was complete in 7 days. The solvent was evaporated in reduced pressure to form orange viscous oil of **2** (yield 0.61 g; 97%). For **2**: Anal. Calcd for $C_{31}H_{44}NO_2PSi$ (521.74 g/mol): C, 71.36; H, 8.50. Found: C, 71.29; H, 8.39. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.35 (s, 9H, SiMe$_3$); 1.04 (s, 18H, O^{t}Bu); 4.36 (s, 4H, CH_2O); 7.07–8.01 (m, 13H, ArH); ^{13}C NMR (C_6D_6, 100 MHz) δ (ppm): 2.1 (SiMe$_3$); 27.9 (CH_3); 63.5 (CH_2O, $^{3}J(^{13}C,^{31}P)$ = 27 Hz); 73.3 (OCMe$_3$); 127.8 (C(3′,5′), $^{3}J(^{13}C,^{31}P)$ = 11 Hz); 128.9 (C(3,5), $^{3}J(^{13}C,^{31}P)$ = 23 Hz); 129.6 C(4′); 130.7 C(4); 131.3 (C(2′,6′), $^{2}J(^{13}C,^{31}P)$ = 22 Hz); 136.2 (C(1′), $^{1}J(^{13}C,^{31}P)$ = 32 Hz); 140.5 (C(1), $^{1}J(^{13}C,^{31}P)$ = 100 Hz); 144.5 (C(2,6), $^{2}J(^{13}C,^{31}P)$ = 13 Hz); ^{31}P NMR (C_6D_6, 162 MHz): δ −7.4 ($^{2}J(^{31}P,^{29}Si)$ = 104 Hz).

4.3. Synthesis of {[2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]Ph$_2$PNH$_2$}$^{+}$N$_3^{-}$ (3)

0.52 g (1.05 mmol) of **2** was dissolved in toluene (10 mL), Me_3SiN_3 (0.27 mL, 2.10 mmol) and distilled water (0.04 mL, 2.1 mmol) were added via syringe. Reaction mixture was stirred for 3 days. The solvent was evaporated and resulting orange oil was washed with hexane (6 mL) to give light orange solid of **3** (yield 0.49 g, 95%). For **3**: mp 127.8–129.7 °C; Anal. Calcd for $C_{28}H_{37}N_4O_2P$ (492.59 g/mol): C, 68.12; H, 7.76. Found: C, 68.08; H, 7.70. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.97 (s, 18H, O^{t}Bu); 4.35 (s, 4H, CH_2O); 7.10–7.85 (m, 13H, ArH); 8.00 (bs, 2H, NH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ 27.0 (CH_3); 59.6 (CH_2O, $^{3}J(^{13}C,^{31}P)$ = 5 Hz); 73.2 (OCMe$_3$); 120.6 (C(1′); $^{1}J(^{13}C,^{31}P)$ = 90 Hz]; 125.4 C(4′); 126.5 C(4); 129.4 (C(3′,5′), $^{3}J(^{13}C,^{31}P)$ = 14 Hz); 129.8 (C(2′,6′), $^{2}J(^{13}C,^{31}P)$ = 11 Hz); 132.5 (C(3,5), $^{3}J(^{13}C,^{31}P)$ = 12 Hz); 135.3 (C(1), $^{1}J(^{13}C,^{31}P)$ = 99 Hz); 145.5 (C(2,6); $^{2}J(^{13}C,^{31}P)$ = 11 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.5; MS: ESI+: m/z 450 [M − N$_3$]$^{+}$ (100%).

4.4. Synthesis of {[2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]Ph$_2$PNH}Me$_3$SnCl (4)

0.29 mL (0.46 mmol) of n-BuLi was added drop-wise to the toluene solution (10 mL) of **3** (0.22 g, 0.46 mmol) at −78 °C and resulting dark red solution was stirred for 30 min at −78 °C. The Me_3SnCl (0.09 g, 0.46 mmol) was added at one portion and reaction mixture was stirred for additional 17 h at r.t. Solid was filtered off and solvent was evaporated and resulting light yellow oil was washed with hexane (6 mL) to give colourless solid of **4** (yield 0.49 g, 90%). For **4**: mp 125–127 °C; Anal. Calcd for $C_{31}H_{45}ClNO_2PSn$ (648.83 g/mol): C, 57.39; H, 6.99. Found: C, 58.08; H, 7.15. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.60 (s, 9H, Me$_3$Sn, $^{2}J(^{119}Sn,^{1}H)$ = 68.5 Hz); 0.94 (s, 18H, O^{t}Bu); 4.19 (d, 1H, PN*H*, $^{2}J(^{1}H,^{31}P)$ = 101 Hz); 4.48 (s, 4H, CH_2O); 6.94–7.65 (m, 13H, ArH); ^{13}C NMR (C_6D_6, 125 MHz): δ 1.1 (SnCH_3; $^{1}J(^{13}C,^{119}Sn)$ = 558 Hz); 27.4 (CH_3); 63.5 (CH_2O; $^{3}J(^{13}C,^{31}P)$ = 5 Hz); 73.0 (OCMe$_3$); 126.1 (C(1′), $^{1}J(^{13}C,^{31}P)$ = 100 Hz); 127.2 (C(3′,5′), $^{3}J(^{13}C,^{31}P)$ = 11 Hz); 128.4 C(4′); 128.7 (C(3,5), $^{3}J(^{13}C,^{31}P)$ = 11 Hz); 131.4 C(4); 131.4 (C(2′,6′), $^{2}J(^{13}C,^{31}P)$ = 20 Hz); 135.6 (C(1); $^{1}J(^{13}C,^{31}P)$ = 100 Hz); 145.3 (C(2,6); $^{2}J(^{13}C,^{31}P)$ = 21 Hz); ^{31}P NMR (C_6D_6, 162 MHz): δ 28.9 ($^{2}J(^{31}P,^{119}Sn)$ = 113 Hz); ^{119}Sn NMR (C_6D_6, 186 MHz): δ 24.7 (bs); MS: ESI+: m/z 450 [M-Me$_3$SnCl + H]$^{+}$ (100%).

4.5. Synthesis of {[2,6-(^{t}BuOCH$_2$)$_2$C$_6$H$_3$]Ph$_2$PNH}Cy$_3$SnCl (5)

0.36 mL (0.57 mmol) of n-BuLi was added drop-wise to the toluene solution (10 mL) of **3** (0.28 g, 0.57 mmol) at −78 °C and resulting dark red solution was stirred for 30 min at −78 °C. The Cy_3SnCl (0.23 g, 0.57 mmol) was added in one portion and reaction mixture was stirred for additional 17 h at r.t. Solid was filtered off and solvent was evaporated and resulting light yellow oil was washed with hexane (6 mL) to give colourless solid of **5** (yield 0.44 g, 92%). For **5**: mp 125–127 °C; Anal. Calcd for $C_{31}H_{45}ClNO_2PSn$ (853.18 g/mol): C, 64.59; H, 8.22. Found: C, 64.68; H, 8.26. ^{1}H NMR (C_6D_6, 400 MHz): δ 0.97 (s, 18H, O^{t}Bu); 1.32 (bs, 4H, CyH); 1.69 (bs, 2H, CyH); 1.85 (bs, 4H, CyH); 2.05 (bs, 1H, CyH); 4.28 (d, 1H, PN*H*) ($^{2}J(^{1}H,^{31}P)$ = 100 Hz); 4.50 (s, 4H, CH_2O); 7.04–7.91 (m, 13H, ArH); ^{13}C NMR (C_6D_6, 100 MHz): δ 27.2 (CH_3); 28.9 (C(1)-Cy; $^{1}J(^{13}C,^{119}Sn)$ = 560 Hz); 31.2 (C(2,6)-Cy; $^{2}J(^{13}C,^{119}Sn)$ = 17.0 Hz); 32.4 C(3,5)-Cy; 34.8 C(4)-Cy; 63.4 (CH_2O, $^{3}J(^{13}C,^{31}P)$ = 5 Hz); 72.9 (OCMe$_3$); 126.5 (C(1′), $^{1}J(^{13}C,^{31}P)$ = 95 Hz); 127.0 (C(2′,6′), $^{2}J(^{13}C,^{31}P)$ = 10 Hz); 128.1 C(4′); 128.3 (C(3′,5′), $^{3}J(^{13}C,^{31}P)$ = 12 Hz); 128.9 C(4); 131.5 (C(3,5), $^{3}J(^{13}C,^{31}P)$ = 10 Hz); 135.8 (C(1), $^{1}J(^{13}C,^{31}P)$ = 100 Hz); 145.1 (C(2,6), $^{2}J(^{13}C,^{31}P)$ = 13 Hz); ^{31}P NMR (C_6D_6, 162 MHz): δ 28.0 ($^{2}J(^{31}P,^{119}Sn)$ = 100 Hz); ^{119}Sn NMR (C_6D_6, 186 MHz): δ 35.5 (bs).

4.6. Crystallography

Compounds **3** and **4** were dissolved in toluene/hexane solution, put to the freezer and let to crystallize at 4 °C. The obtained materials were suitable for X-ray analysis and characterized as compounds **3** and **4**.

The X-ray data (Table S1) for colourless crystals of **3** and **4** were obtained at 150 K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN [17]. The absorption was corrected by integration methods [18]. Structures were solved by direct methods (Sir92) [19] and refined by full matrix least-square based on F^2 (SHELXL97) [20]. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H)$ = 1.2 U_{eq}(pivot atom) or of 1.5 U_{eq} for the methyl moiety with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings, respectively, and 0.97 Å for N–H groups.

Acknowledgement

The authors wish to thank the Grant Agency of the Czech Republic (project no. P207/10/0215) and The Ministry of Education of the Czech Republic for financial support.

Appendix A. Supplementary material

CCDC 882967 and 882968 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.08.003.

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