Synthesis and characterization of Sn(II), Pb(II) and Yb(II) complexes supported by $[C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{2-}$ or $[CH(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{-}$ (R = 3,5-dimethyl-1-pyrazolyl or iminophosphoranyl) ligands†

Zuo-Yun Chai and Zhong-Xia Wang*

Received 30th March 2009, Accepted 7th July 2009
First published as an Advance Article on the web 10th August 2009
DOI: 10.1039/b906266a

The synthesis and characterization of several tin(II), lead(II) and ytterbium(II) complexes supported by $[C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{2-}$ or $[CH(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{-}$ (R = 3,5-dimethyl-1-pyrazolyl or iminophosphoranyl) ligands are reported. Reaction of 2-R-6-$\{CH_2P(Ph_2){=}NSiMe_3\}$-$C_5H_3N$ with $M[N(SiMe_3)_2]_2$ (M = Sn, Pb) generated tin(II) and lead(II) complexes $[M\{C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}\}]_2$ [**3**, M = Sn, R = 3,5-dimethyl-1-pyrazolyl; **4**, M = Pb, R = 3,5-dimethyl-1-pyrazolyl; **9**, M = Sn, R = $Me_3SiN{=}P(Ph_2)$; **10**, M = Pb, R = $Me_3SiN{=}P(Ph_2)$]. When R = p-$MeC_6H_4N{=}P(Ph_2)$, a N,N-chelate tin(II) complex, $[Sn\{2\text{-}\{N(p\text{-}MeC_6H_4){=}PPh_2\}\text{-}6\text{-}\{CHP(Ph_2){=}NSiMe_3\}\}\{N(SiMe_3)_2\}]$ (**11**), was isolated. Treatment of 2-$(Ph_2P{=}NSiMe_3)$-6-$\{CH_2P(Ph_2){=}NSiMe_3\}$-$C_5H_3N$ with $Yb[N(SiMe_3)_2]_2(DME)$ afforded N,N,N-chelate ytterbium(II) complex $[Yb\{2\text{-}\{N(SiMe_3){=}PPh_2\}\text{-}6\text{-}\{CHP(Ph_2){=}NSiMe_3\}\}\{N(SiMe_3)_2\}]$ (**12**). The complexes were characterized by elemental analyses and multinuclear NMR spectroscopy. Complexes **3**, **4** and **10–12** were further characterized by single crystal X-ray diffraction techniques.

Introduction

Iminophosphoranes can act as neutral,[1] monoanionic[2] and dianionic ligands[3] and have been proved to be able to stabilize main group, transition and lanthanide metal ions.[4] Some of the metal complexes bearing iminophosphorane ligands exhibit catalytic activity and interesting reactivity.[5,6] Examples include the catalysis of magnesium and zinc complexes in the ring-opening polymerization of ε-caprolactone or lactides,[5a–5d] the catalysis of vanadium, iron, cobalt and nickel complexes bearing neutral or monoanionic iminophosphorane ligands in the polymerization or oligomerization of ethylene[5e–5g] and catalysis of nickel complexes in the carbon-carbon coupling.[5h–5j] Iminophosphorane metal complexes also attracted considerable attention due to their diverse structural patterns.[7] For example, complexes of the dianionic ligand $[C(Ph_2P{=}NSiMe_3)_2]^{2-}$ with Ti(IV), Zr(IV), Hf(IV), Mo(II), Sm(III) or Ge(II) afforded carbon-metal double bond complexes (**I** and **II** in Chart 1),[3e,6c,7e–7h] but the germanium complex showed different coordination mode from the others.[7e] The same ligand with Cr(II), Mn(II), iron(II), tin(II) or lead(II) gave 1,3-dimetallacyclobutanes (**III** in Chart 1).[3d,6h,7a] One of authors with collaborators reported synthesis of tin(II) and lead(II) complexes supported by $[C(Ph_2P{=}NSiMe_3)(2\text{-}Py)]^{2-}$ ligand, which exhibit homo- or hetero-1,3-dimetallacyclobutane structures (**IV** in Chart 1).[8] In this paper, we wish to report the synthesis and characterization of tin(II) and lead(II) complexes supported by $[C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{2-}$ (R = 3,5-Me_2-1-C_3HN_2 or $Me_3SiN{=}PPh_2$) ligands and tin(II) and ytterbium(II) complexes supported by $[CH(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}RC_5H_3N)\}]^{-}$ (R = p-$MeC_6H_4N{=}PPh_2$ or $Me_3SiN{=}PPh_2$) ligands.

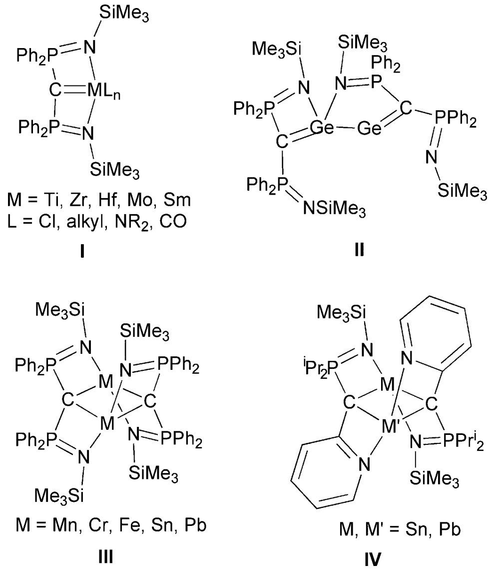


Chart 1

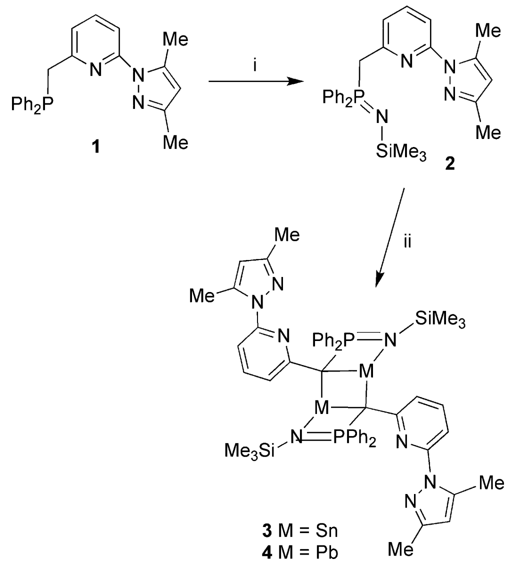
Results and discussion

Syntheses of compounds **2–4** are shown in Scheme 1. Iminophosphorane **2** was obtained by the reaction of **1** with Me_3SiN_3 at 140–160 °C, and the product was purified by recrystallizing from

---

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China. E-mail: zxwang@ustc.edu.cn; Fax: +86-551-3601592; Tel: +86-551-3603043

† CCDC reference numbers 725691–725695. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b906266a



Scheme 1 Synthesis of complexes **3** and **4**. *Reagents and conditions:* i, Me_3SiN_3, 140–160 °C, 12 h; ii, $M[N(SiMe_3)_2]_2$ (M = Sn, Pb), toluene, r.t., 24 h, then 60 °C, 12 h (for Sn compound) or r.t., 72 h (for Pb compound).

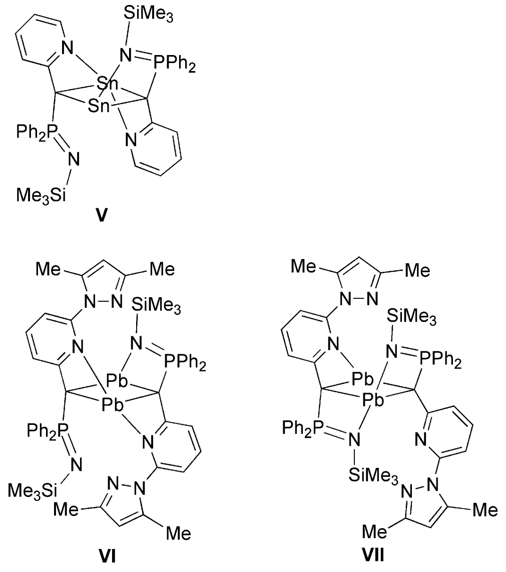


Chart 2

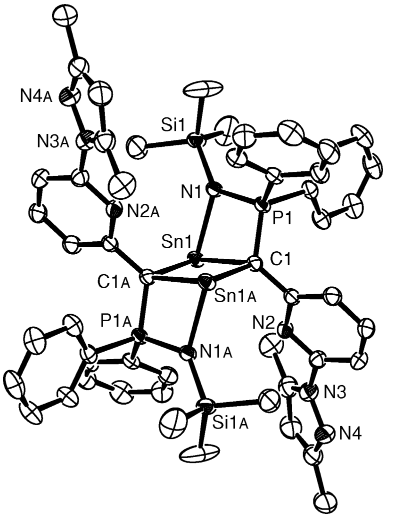


Fig. 1 ORTEP drawing of complex **3** shown with 30% thermal ellipsoids. Symmetry operations for generating equivalent positions are: −x + 1, −y + 2, −z + 2. Selected bond distances (Å) and angles (°): Sn1-C1 2.278(3), Sn1-N1 2.283(3), Sn1-C1A 2.342(3), P1-C1 1.735(3), P1-N1 1.611(3), C1-Sn1-N1 68.86(10), C1-Sn1-C1A 86.36(11), N1-Sn1-C1A 94.29(10), Sn1-C1-Sn1A 93.64(11), P1-C1-Sn1 91.56(13), P1-N1-Sn1 94.77(12), N1-P1-C1 100.75(14).

hexane. Treatment of **2** with an equivalent of $Sn[N(SiMe_3)_2]_2$ in toluene afforded complex **3** in 49% yield. Similar reaction between **2** and $Pb[N(SiMe_3)_2]_2$ generated complex **4** in 57% yield. Reaction between **2** and $M[N(SiMe_3)_2]_2$ (M = Sn or Pb) might first form an unstable intermediate metallavinylidene, :M = $C(Ph_2P{=}NSiMe_3)(Ar)$, which then underwent a "head-to-tail" cycloaddition to give 1,3-dimetallacyclobutanes, **3** and **4**.[7e,8b] Both **3** and **4** are air-sensitive crystalline solids, soluble in pyridine and THF and slightly soluble in toluene. Each of the compounds **2–4** was characterized by elemental analysis and ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^1H NMR spectrum of complex **3** exhibited a set of signals, showing the two ligands to adopt the same coordination mode to the central metals. This is consistent with its solid structure determined by single X-ray diffraction (see below). However, each of ^1H, ^{13}C and ^{31}P NMR spectra of complex **4** gave two sets of ligand signals. For example, its ^{31}P NMR spectrum exhibited resonance signals at δ 3.17 and 12.32 ppm, respectively. This observation supports that the two lead atoms have different coordination modes, being different from its solid structure identified by the single crystal X-ray diffraction. Unfortunately, and as seen before,[7e,8b] the ^{13}C NMR signals of the quarternary methandiide carbon in complexes **3** and **4** could not be detected, and hence could not provide clues to the solution structures. However, based on the coordination mode of a related tin(II) complex (**V** in Chart 2)[8b] we conjecture that the solution structure of **4** may be **VI** or **VII** (Chart 2).

The ORTEP drawing of complex **3** is displayed in Fig. 1, along with selected bond lengths and angles. In the molecule the tin atoms are bridged by the methandiide carbons, the skeletal structure being ladder-shaped. The central Sn_2C_2 ring is planar with the angle at carbon [93.64(11)°] wider than that at tin, 86.36(11)°. The two imino nitrogen atoms rather than the pyridyl nitrogen atoms of the ligand coordinate to the Sn(II) centers, forming two SnCPN four-membered rings. This coordination pattern is different from that of 1,3-$[Sn\{C(Pr^i_2P{=}NSiMe_3)(2\text{-}Py)\}_2]_2$, in which one tin center is bonded to the methandiide carbons and coordinated to two imino nitrogens and the other tin atom is bonded to the methandiide carbons and coordinated to two pyridyl nitrogens.[8b] This difference does not appear to be caused by the steric hindrance of the 2-substituents of the pyridyls in complex **3** because a related complex with a sterically hindered ligand (**VIII** in Chart 3) adopts a completely different coordination pattern.[7k] The Sn-C bond distances in complex **3** [2.278(3) and 2.342(3) Å, respectively] are comparable to those corresponding in **VIII** [2.287(6) and 2.362(7) Å, respectively]. The Sn1-N1 distance of 2.283(3) Å in complex **3** is shorter than the Sn-N(pyridyl) distance in **VIII** [2.316(5) Å], and the Sn-N(iminophosphoranyl) distances in **III** (Chart 1, M = Sn)

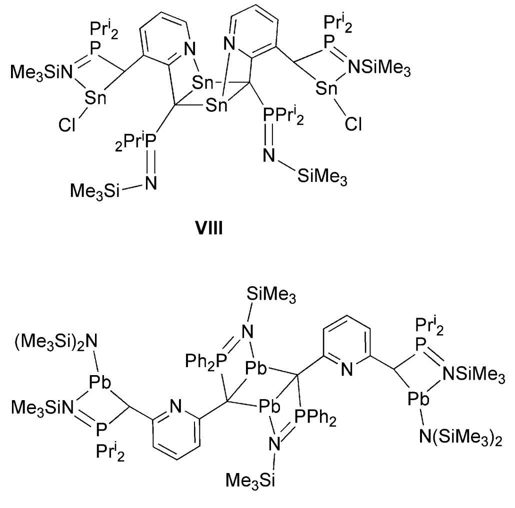


Chart 3

[2.542(6) and 2.550(5) Å, respectively], but within the normal range of the Sn-N(iminophosphoranyl) distances.[7j,7k,8]

The ORTEP drawing of complex **4** is displayed in Fig. 2, along with selected bond lengths and angles. Crystalline complex **4** exhibits a similar structure to **3**. Thus, the lead atoms are bridged by the methandiide carbons and the imino nitrogen atoms coordinate to the Pb(II) centers to form a fused tricyclic ladder-shaped skeleton. The molecule is centro-symmetric and the central Pb_2C_2 ring is planar with the angle at carbon [93.72(8)°] wider than that at lead [86.28(8)°]. This coordination mode is different from that of **III** (Chart 1, M = Pb),[7e] but similar to that of **IX** (Chart 3).[7k] The endocyclic angles of the central rhomboidal Pb_2C_2 ring in complex **4** are almost same as the corresponding ones in **IX**. However, the Pb-C distances in complex **4** [2.442(2) and 2.345(2) Å, respectively] are different from the corresponding ones of **VI** [2.426(2) and 2.363(2) Å, respectively]. The Pb-N distance of complex **4** [2.428(2) Å] is longer than that of **VI** [2.406(2) Å], and both are much shorter than those in **III** (Chart 1, R = Pb) [2.625(4) and 2.631(4) Å].[7e,7k]

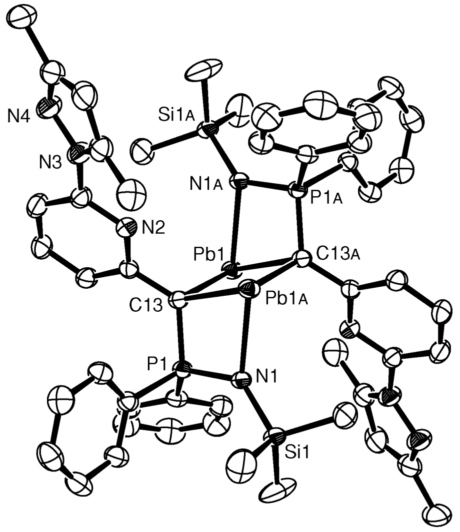
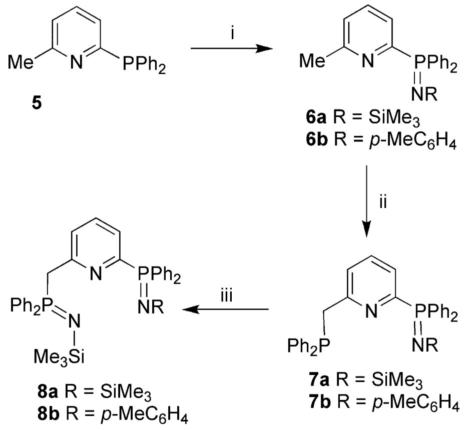
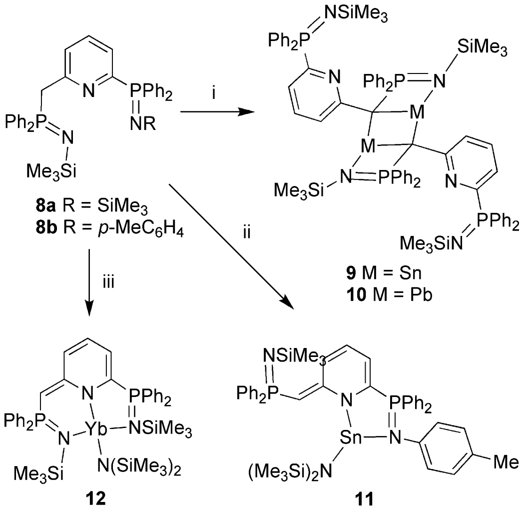


Fig. 2 ORTEP drawing of complex **4** shown with 30% thermal ellipsoids. Symmetry operations for generating equivalent positions are: −x, −y + 1, −z. Selected bond distances (Å) and angles (°): Pb1-C13 2.442(2), Pb1-C13A 2.345(2), Pb1-N1A 2.428(2), P1-N1 1.604(2), P1-C13 1.741(2), C13-Pb1-C13A 86.28(8), C13A-Pb1-N1A 66.25(8), N1A-Pb1-C13 92.85(7), Pb1-C13-Pb1A 93.72(8), P1-C13-Pb1 107.36(11), N1-P1-C13 102.42(11), P1-N1-Pb1A 93.84(9).

Synthesis of compounds **5**, **6a**, **7a** and **8a** followed the same methods we reported previously.[5c] Pre-ligand **8b** was synthesized according to similar procedures to **8a** as shown in Scheme 2. Thus, reaction of **5** with p-$MeC_6H_4N_3$ in THF at room temperature gave iminophosphorane **6b** in 73% yield. Lithiation of **6b** with LDA and then treatment with Ph_2PCl afforded **7b** in 54% yield. Treatment of **7b** with Me_3SiN_3 at 140–160 °C yielded **8b** in 63% yield. The Sn(II), Pb(II) and Yb(II) complexes were synthesized from **8a** and **8b** as shown in Scheme 3. Thus, reaction of **8a** with $M[N(SiMe_3)_2]_2$ (M = Sn, Pb) in toluene under reflux conditions produced complexes **9** and **10**, respectively. Reaction of **8b** with $Sn[N(SiMe_3)_2]_2$ at room temperature for 72 h afforded complex **11** as red crystals in 61% yield. It was expected that complex



Scheme 2 Synthesis of compounds **6b-8b**. *Reagents and conditions for **6b**, **7b** and **8b**:* i, p-$MeC_6H_4N_3$, THF, r.t., 3 h; ii, LDA, THF, −60 °C to −20 °C, 20 min., then Ph_2PCl, −80 °C, 15 min. and r.t., overnight; iii, Me_3SiN_3, 140–1600 °C, 12 h.



Scheme 3 Synthesis of complexes **9–12**. *Reagents and conditions:* i, $M[N(SiMe_3)_2]_2$ (M = Sn, Pb), toluene, r.t., 24 h, then reflux, 6h; ii, $Sn[N(SiMe_3)_2]_2$, toluene, r.t., 72 h; iii, $Yb[N(SiMe_3)_2]_2(DME)$, hexane, r.t., 24 h.

11 further lost a proton under intenser conditions to form a methandiide complex similar to complex **9**. For this purpose the solution of **11** in toluene was heated at 80 °C for 24 h to give yellow precipitates. The species was insoluble in most organic solvents such as Et_2O, THF, toluene, CH_2Cl_2 and pyridine, and hence was not characterized by NMR spectroscopy. In this case we can not judge if a methandiide complex has been formed although its elemental analytical data matched the formula of the supposed methandiide complex. Attempts to isolate an analogue of **11** through reaction of **8a** with $Sn[N(SiMe_3)_2]_2$ at room temperature were unsuccessful, a mixture was always obtained. Reaction of **8a** with $Yb[N(SiMe_3)_2]_2(DME)$ in hexane at room temperature afforded complex **12** as brown crystals. Attempts to prepare ytterbium methandiide complex from **12** by prolonging reaction time or heating the toluene solution of **12** were unsuccessful. No reactions occurred under these conditions.

Compound **6b** was crystallized from Et_2O. However, the crystalline solid is only slightly soluble in Et_2O, but soluble in THF and CH_2Cl_2. Compound **7b** is slightly soluble in hexane and soluble in toluene, THF and CH_2Cl_2. Compound **8b** was crystallized from a mixed solvent of CH_2Cl_2 and hexane, and is soluble in Et_2O, toluene and CH_2Cl_2. Each of **6b**, **7b** and **8b** gave satisfactory elemental analysis. The ^1H, ^{13}C and ^{31}P NMR spectra match their respective structure.

Complexes **9–12** are air-sensitive crystalline solids. Both complexes **9** and **10** were crystallized from toluene, and are soluble in THF, slightly soluble in toluene and insoluble in Et_2O and hexane. Complex **11** was crystallized from a mixture of Et_2O and hexane, and is soluble in Et_2O and toluene and slightly soluble in hexane. Complex **12** was crystallized from Et_2O, and is soluble in Et_2O and toluene and slightly soluble in hexane. Each of the complexes **9–12** was characterized by elemental analysis, ^1H, ^{13}C and ^{31}P NMR spectroscopy. It is worth indicating that the solution NMR spectra of complex **10** gave a set of ligand signals, while those of complex **4** displayed two sets of ligand signals, showing different coordination patterns of the complexes in solution. In addition, the signals due to the quarternary methandiide carbons could not be detected in the ^{13}C NMR spectra of **9** and **10**, being same as the situation in complexes **3** and **4**.

Complexes **10**, **11** and **12** were further characterized by single crystal X-ray diffraction. The ORTEP drawing of **10** is presented in Fig. 3, along with selected bond lengths and angles. The molecule has a similar structure skeleton to **4**. Thus, the lead atoms are bridged by the methandiide carbon atoms and the nitrogen atoms of the iminophosphoranyl attached on methandiide carbons coordinate to the Pb(II) centers to form a centro-symmetric fused tricyclic ladder-shaped skeleton. The central rhomboidal Pb_2C_2 ring has the endocyclic angles subtended at the carbon atoms *ca.* 10° wider than those at lead. The C-Pb-C angles [84.9(4) °] are close to those in complex **4** [86.28(8)°]. The angles of N2-Pb1-C1A and P1-C1-Pb1A [93.9(3) and 105.7(5)°, respectively] are also close to those corresponding in complex **4** [92.85(7) and 107.36(11)°, respectively]. The Pb1-C1 distance [2.380(10) Å] is longer than that of complex **4** [2.345(2) Å], while Pb1-C1A distance [2.431(11) Å] is comparable to that corresponding in **4** [2.442(2) Å].

The ORTEP drawing of **11** is presented in Fig. 4, along with selected bond lengths and angles. The structure consists of a tin atom bonded to the ligand in an N,N-chelate fashion. The geometry around the tin center is a distorted trigonal pyramid with one vertex occupied by a lone pair of electrons. The geometry around the N2 atom is approximately planar, supporting a sp^2 hybrid N atom. C16 and P1 atoms are approximately coplanar with the pyridyl ring, which shows C16 to be a sp^2 hybrid atom. The C16-C17 distance of 1.375(6) Å is also indicative of a C-C double bond. The Sn1-N2 distance [2.209(4) Å] is shorter than that of Sn1-N3 [2.239(4) Å], and both are comparable to those in $[ClSn\{CH(Pr^i{}_2P{=}NSiMe_3)(2\text{-}Py)\}]$ [2.201 Å][8a] and in $[(Me_3Si)_2NSn\{(NBu^t)_2P(Ph)(CH_2Ph)\}]$ [2.206(3) and 2.238(3) Å, respectively].[9] The Sn1-N4 distance of 2.108(4) Å is comparable to those of Sn(II) amides {*cf.*, 2.09(1) Å in $Sn[N(SiMe_3)_2]_2$}[10] or eneamides {*cf.*, 2.130(3) Å in $Sn[N(SiMe_3)C(Bu^t){=}CH(C_6H_3Me_2\text{-}2,5)]_2$}.[11]

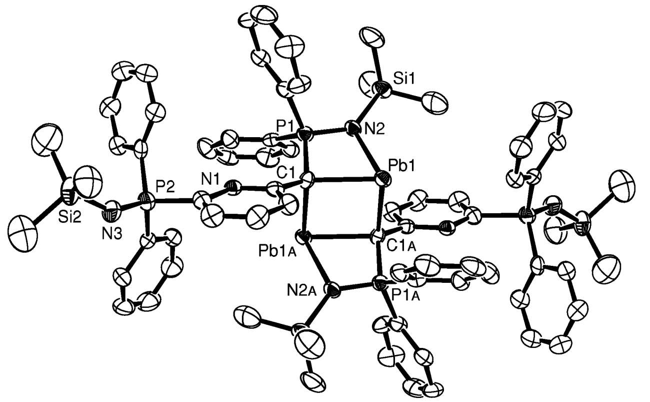


Fig. 3 ORTEP drawing of complex **10** shown with 30% thermal ellipsoids. Symmetry operations for generating equivalent positions are: −x + 1, −y + 1, −z + 1. Selected bond distances (Å) and angles (°): Pb1-C1 2.380(10), Pb1-C1A 2.431(11), Pb1-N2 2.404(8), P1-C1 1.743(11), P1-N2 1.616(9), C1-Pb1-C1A 84.9(4), N2-Pb1-C1A 93.9(3), C1-Pb1-N2 66.7(3), Pb1-C1-Pb1A 95.1(4), P1-C1-Pb1A 105.7(5).

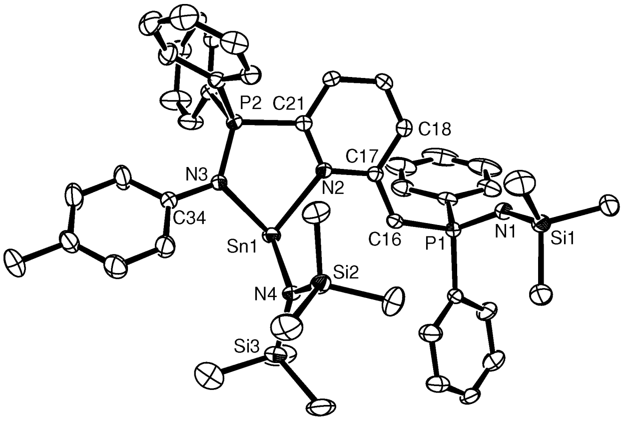


Fig. 4 ORTEP drawing of complex **11** shown with 20% thermal ellipsoids. Selected bond distances (Å) and angles (°): Sn1-N2 2.209(4), Sn1-N3 2.239(4), Sn1-N4 2.109(4), P1-N1 1.539(4), P1-C16 1.733(5), P2-N3 1.597(4), P2-C21 1.787(5), N2-C21 1.356(5), N2-C17 1.378(5), C16-C17 1.375(6), N2-Sn1-N4 102.79(14), N2-Sn1-N3 77.77(13), N3-Sn1-N4 101.45(14), C17-N2-Sn1 119.4(3), C21-N2-Sn1 119.4(3), C17-N2-C21 119.6(4), N3-P2-C21 103.8(2), C17-C16-P1 124.8(4).

The ORTEP drawing of **12** is presented in Fig. 5, along with selected bond lengths and angles. The complex is monomeric in the solid state. The ligand adopts an N,N,N-tridentate coordination mode and the ytterbium atom exhibits a distorted

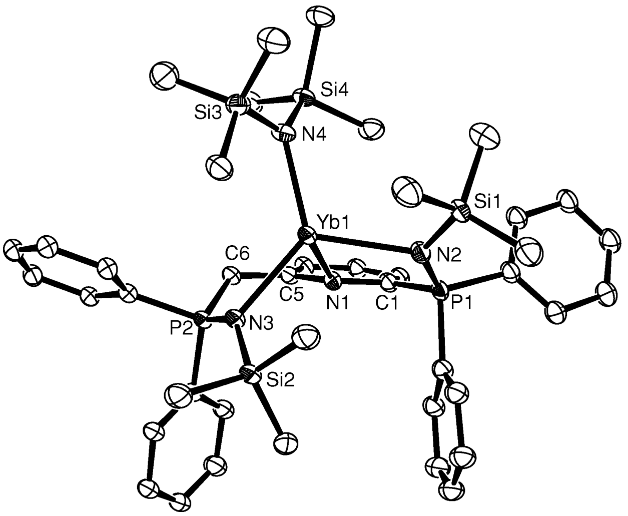


Fig. 5 ORTEP drawing of complex **12** shown with 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): Yb1-N1 2.352(9), Yb1-N2 2.529(9), Yb1-N3 2.446(8), Yb1-N4 2.338(10), P1-C1 1.777(12), P1-N2 1.544(10), P2-C6 1.741(12), P2-N3 1.549(9), N1-C1 1.368(13), N1-C5 1.364(13), C5-C6 1.415(15), N1-Yb1-N2 73.8(3), N1-Yb1-N3 83.3(3), N1-Yb1-N4 115.2(3), N2-Yb(1)-N3 121.9(3), N2-Yb1-N4 111.8(3), N3-Yb1-N4 126.3(4), C1-N1-Yb1 121.3(7), C5-N1-Yb1 111.3(7), P1-N2-Yb1 112.1(5), P2-N3-Yb1 107.4(4), N2-P1-C1 109.6(5), N3-P2-C6 116.9(5), N1-C1-P1 111.0(9), C5-C6-P2 124.9(10).

tetrahedral geometry. The pyridyl ring is approximately planar, and coplanar with P1 and C6 atoms. The Yb atom is out of the plane, the torsion angle of P1C1N1Yb1 being 34.4°. The distances of the ytterbium atom to the iminophosphorano-nitrogen atoms [2.529(9) and 2.5446(8) Å, respectively] is longer than that to the formally negatively charged pyridyl-nitrogen atom [2.352(9) Å]. The former is longer than those of ytterbium atom to the iminophosphorano-nitrogen atoms in [$\{(Me_3SiN{=}PPh_2)_2CH\}YbI(THF)_2$] [2.491(4) and 2.475(3) Å, respectively],[12a] but within the range of the coordinated Yb-N bond distances [2.50(3) to 2.61(3) Å] in [$Yb\{N(SiMe_3)_2\}\{\mu\text{-DAC}\}]_2Yb$ (DAC = 4,13-diaza-18-crown-6).[12b] The latter is comparable to those of Yb(II) bis(trimethylsilyl)amides (2.33–2.44 Å).[12b–12e] The C5-C6 bond distance of 1.415(15) Å is between a single bond and a double bond, which suggests C6 to be conjugate with the pyridyl ring.

Conclusions

We have synthesized tin(II) and lead(II) complexes containing 1,3-dimetallobutanes through reaction of 2-R-6-$\{Me_3SiN{=}P(Ph_2)CH_2\}C_5H_4N$ (R = 3,5-dimethyl-1-pyrazolyl or iminophosphoranyl) with $M[N(SiMe_3)_2]_2$ (M = Sn or Pb). In these complexes, the nitrogen atoms of the iminophosphoranyl attached on the methandiide carbons coordinate to the central tin(II) or lead(II) atoms. We also obtained [$M\{2\text{-}\{N(R'){=}P(Ph_2)\}\text{-}6\text{-}\{Me_3SiN{=}P(Ph_2)CH\}C_5H_4N\}\{N(SiMe_3)_2\}$] (**11**, M = Sn, R′ = *p*-MeC_6H_4; **12**, M = Yb, R′ = $SiMe_3$) by reaction of 2-$\{N(R'){=}P(Ph_2)\}$-6-$\{Me_3SiN{=}P(Ph_2)CH_2\}C_5H_4N$ with $M[N(SiMe_3)_2]_2(L)$ (M = Sn, L = nothing; M = Yb, L = DME). The tin(II) complex **11** has an N,N-chelate coordination mode and can be further transformed by heating to a new complex which was not fully characterized, while the ytterbium(II) complex **12** adopts an N,N,N-tridentate coordination mode and can not be further converted by heating or prolonging reaction time.

Experimental

General remarks

All air or moisture sensitive manipulations were performed under dry nitrogen using standard Schlenk techniques. Solvents were distilled under nitrogen over sodium (toluene), sodium/benzophenone (n-hexane, THF and diethyl ether) or CaH_2 (CH_2Cl_2) and degassed prior to use. $LiBu^n$, Me_3SiN_3 and $(Me_3Si)_2NH$ were purchased from Acros Organics and used as received. C_6D_6, $CDCl_3$ and C_5D_5N were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over Na/K alloy (C_6D_6) or 4A molecular sieves ($CDCl_3$ and C_5D_5N). $Sn[N(SiMe_3)_2]_2$,[13] $Pb[N(SiMe_3)_2]_2$[13] and [$Yb\{N(SiMe_3)_2\}_2(DME)$][14] were prepared according to the reported methods. All other chemicals were obtained from commercial vendors and used as received. NMR spectra were recorded on a Bruker av300 spectrometer at ambient temperature. The chemical shifts of the ^1H and ^{13}C NMR spectra were referenced to TMS or internal solvent resonances; the ^{31}P NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China.

Preparations

2-(3,5-$Me_2C_3HN_2$)-6-($CH_2PPh_2{=}NSiMe_3$)C_5H_3N (2). A stirred mixture of 2-(PPh_2CH_2)-6-(3,5-$Me_2C_3HN_2$)C_5H_3N (**1**) (2.62 g, 7.05 mmol) and Me_3SiN_3 (1.1 cm^3, 8.1 mmol) was heated at 140–160 °C for 12 h. The unreacted Me_3SiN_3 was removed *in vacuo* and the residue was dissolved in hexane. The solution was filtered and the filtrate was concentrated to afford colorless crystals of **2** (2.62 g, 81%) (found: C, 67.75; H, 6.74; N, 11.97. $C_{26}H_{31}N_4PSi$ requires C, 68.09; H, 6.81; N, 12.22%), mp 70–71 °C. ^1H NMR ($CDCl_3$): δ −0.08 (s, 9H, $SiMe_3$), 2.23 (s, 3H, Me), 2.27 (s, 3H, Me), 3.83 (d, 2H, *J* = 14.1 Hz, CH_2), 5.89 (s, 1H, pyrazolyl), 7.16–7.18 (m, 2H, Py), 7.36–7.46 (m, 5H, Ar + Py), 7.60–7.68 (m, 6H, Ar). ^{13}C NMR ($CDCl_3$): δ 4.01, 13.71, 14.35, 42.68 (d, *J* = 66.9 Hz), 106.77, 113.42 (d, *J* = 2.9 Hz), 122.24 (d, *J* = 3.9 Hz), 128.17, 128.33, 130.89 (d, *J* = 2.8 Hz), 131.25, 131.38, 134.65, 135.94, 138.05 (d, *J* = 2.5 Hz), 141.53, 149.61, 151.98 (d, *J* = 7.4 Hz), 153.02. ^{31}P NMR ($CDCl_3$): δ −4.12.

[$Sn_2\{C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}(3,5\text{-}Me_2C_3HN_2)C_5H_3N)\}\}_2$] (3). To a solution of **2** (0.36 g, 0.79 mmol) in toluene (20 cm^3) was added a solution of $Sn[N(SiMe_3)_2]_2$ (0.36 g, 0.82 mmol) in toluene (5 cm^3) at room temperature with stirring. The mixture was stirred at room temperature for 24 h, and then at 60 °C for 12 h. The mixture was cooled to room temperature and filtered. The filtrate was concentrated to form yellow crystals of **3** (0.22 g, 49%) (found: C, 53.98; H, 5.22; N, 9.42. $C_{52}H_{58}N_8P_2Si_2Sn_2$ requires C, 54.28; H, 5.08; N, 9.74%), mp 257–258 °C. ^1H NMR (C_6D_6+C_5D_5N): δ −0.10 (s, 18H, $SiMe_3$), 2.51 (s, 6H, Me), 2.74 (s, 6H, Me), 6.17 (s, 2H, pyrazolyl), 7.18 (d, *J* = 7.5 Hz, 2H, Py), 7.31–7.47 (m, 14H, Ph + Py), 7.68 (d, *J* = 7.8 Hz, 2H, Ph), 8.11–8.20 (m, 8H, Ph). ^{13}C NMR (C_6D_6+C_5D_5N): δ 2.64, 13.95, 14.76, 108.20, 109.19, 110.71, 125.69, 128.56, 129.33, 131.21 (d, J = 1.8 Hz), 131.41, 131.54, 132.28, 132.42, 136.04, 137.08, 137.76, 137.90, 140.74, 149.00, 154.00, 161.39. ^{31}P NMR ($\mathrm{C_6D_6}$+$\mathrm{C_5D_5N}$): δ 26.94.

$[\mathrm{Pb_2\{C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}(3,5\text{-}Me_2C_3HN_2)C_5H_3N)\}\}_2}]$ (4). To a slolution of **2** (0.36 g, 0.79 mmol) in toluene (20 cm^3) was added a solution of $\mathrm{Pb[N(SiMe_3)_2]_2}$ (0.44 g, 0.83 mmol) in toluene (5 cm^3) at room temperature with stirring. The mixture was stirred at room temperature for 72 h and then filtered. Concentration of the filtrate afforded red crystals identified as **4**·0.8PhMe (0.32 g, 58%) (found: C, 49.40; H, 4.56; N, 8.13. $\mathrm{C_{52}H_{58}N_8P_2Pb_2Si_2\cdot 0.8C_7H_8}$ requires C, 49.30; H, 4.63; N, 7.99%), mp 178–180 °C (dec). ^{1}H NMR ($\mathrm{C_5D_5N}$): δ −0.11 (s, 9H, $\mathrm{SiMe_3}$), 0.28 (s, 9H, $\mathrm{SiMe_3}$), 1.93 (s, 3H, Me), 2.20 (s, 3H, Me), 2.26 (s, PhMe), 2.35 (s, 3H, Me), 2.40 (s, 3H, Me), 5.64 (s, 1H, pyrazolyl), 5.80 (d, J = 7.8 Hz, 1H, Py), 5.86 (d, J = 7.8 Hz, 1H, Py), 5.93 (s, 1H, pyrazolyl), 6.50 (d, J = 7.5 Hz, 1H, Ar), 6.83 (t, J = 8 Hz, 1H, Ar), 7.09–7.32 (m, 18H, Ar), 7.87–7.97(m, 8H, Ar). ^{13}C NMR ($\mathrm{C_5D_5N}$): δ 1.42, 3.66 (d, J = 3.1 Hz), 13.37, 13.98, 14.24, 14.51, 21.42, 104.07, 107.99, 108.26, 109.07, 109.45, 109.72, 125.70, 127.91, 128.57, 128.66, 129.34, 130.24 (d, J = 4.7 Hz), 130.58, 130.84, 130.98, 131.19, 131.32, 134.90, 136.88, 137.90, 138.78, 140.04, 141.06, 144.56, 145.43, 145.62, 146.53, 148.74, 149.03, 149.17, 151.89, 158.75, 161.82. ^{31}P NMR ($\mathrm{C_5D_5N}$): δ 3.17, 12.32.

2-(*p*-$\mathrm{MeC_6H_4N{=}PPh_2}$)-6-$\mathrm{MeC_5H_3N}$ (6b). To a stirred solution of **5** (0.40 g, 1.44 mmol) in THF (10 cm^3) was added dropwise *p*-$\mathrm{MeC_6H_4N_3}$ (0.23 g, 1.73 mmol) at room temperature. The solution color changed to pale yellow. The mixture continued to stir for 3 h. Solvent was removed *in vacuo* and the residue was dissolved in $\mathrm{Et_2O}$. The ether solution was filtered and the filtrate was concentrated to give pale yellow powder (0.40 g, 73%) (found: C, 78.50; H, 6.09; N, 7.20. $\mathrm{C_{25}H_{23}N_2P}$ requires C, 78.51; H, 6.06; N, 7.32%), mp 149–150 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): 2.12 (s, 3H, Me), 2.50 (s, 3H, Me), 6.65–6.77 (m, 3H, Ar), 7.11–7.14 (m, 1H, Ar), 7.30–7.43 (m, 7H, Ar), 7.83–8.02 (m, 6H, Ar). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 20.62, 24.72, 123.19, 123.43, 124.81, 126.18, 126.38, 126.65, 128.33 (d, J = 11.8 Hz), 129.34, 130.38, 131.47, 131.67, 133.07 (d, J = 9.1 Hz), 136.19 (d, J = 9.7 Hz), 148.62, 153.54, 155.24, 159.00, 159.25. ^{31}P NMR ($\mathrm{CDCl_3}$): δ −7.78.

2-(*p*-$\mathrm{MeC_6H_4N{=}PPh_2}$)-6-($\mathrm{CH_2PPh_2}$)$\mathrm{C_5H_3N}$ (7b). A solution of **6b** (0.55 g, 1.44 mmol) in THF (30 cm^3) was cooled to about −60 °C. To the solution was added LDA (1.8 mmol) prepared from $\mathrm{Pr^i{}_2NH}$ (0.37 cm^3, 1.85 mmol) and $\mathrm{Bu^nLi}$ (0.72 cm^3, 2.5 M, 1.8 mmol). The mixture was stirred at −20 °C for 20 min and recooled to about −80 °C. To the cooled solution $\mathrm{Ph_2PCl}$ (0.32 cm^3, 1.8 mmol) in THF (5 cm^3) was added. The solution was stirred at −80 °C for 15 min and at room temperature overnight. Solvent was removed *in vacuo* and the residue was extracted with diethyl ether. The extract was filtered and the filtrate was concentrated to afford yellow crystals of **7b** (0.44 g, 54%) (found: C, 78.06; H, 5.83; N, 4.75. $\mathrm{C_{37}H_{32}N_2P}$ requires C, 78.43; H, 5.69; N, 4.94%), mp 78–80 °C. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.11 (s, 3H, Me), 3.58 (s, 2H, $\mathrm{CH_2}$), 6.63 (d, J = 8.1 Hz, 1H, Py), 6.74 (d, J = 8.1 Hz, 1H, Py), 7.06–7.54 (m, 20H, Ar), 7.67–7.83 (m, 4H, Ar), 7.98 (t, J = 6.6 Hz, 1H, Py). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 20.65, 38.74 (d, J = 16.7 Hz), 123.21 (d, J = 18.3 Hz), 125.22 (d, J = 3.5 Hz), 125.29 (d, J = 3.5 Hz), 126.27, 126.74, 127.00, 128.28, 128.44, 128.53, 128.78, 129.35, 131.47 (d, J = 2.6 Hz), 132.69, 132.95, 133.05, 133.17, 136.36 (d, J = 9.6 Hz), 138.08, 138.28, 159.00, 159.12, 159.26, 159.37. ^{31}P NMR ($\mathrm{CDCl_3}$): δ −14.99 (m), −7.57.

2-(*p*-$\mathrm{MeC_6H_4N{=}PPh_2}$)-6-($\mathrm{Me_3SiN{=}PPh_2CH_2}$)$\mathrm{C_5H_3N}$ (8b). A mixture of **7b** (0.44 g, 0.78 mmol) and $\mathrm{Me_3SiN_3}$ (0.20 cm^3, 1.5 mmol) was heated at 140–160 °C for 12 h with stirring. Excess $\mathrm{Me_3SiN_3}$ was removed *in vacuo* and the residue was dissolved in $\mathrm{CH_2Cl_2}$. The solution was filtered and the filtrate was concentrated to about 2 cm^3. Hexane (10 cm^3) was added and set aside overnight to give yellow crystals of **8b** (0.32 g, 63%) (found: C, 70.30; H, 6.07; N, 6.39. $\mathrm{C_{40}H_{41}N_3P_2Si\cdot 0.4CH_2Cl_2}$ requires C, 70.55; H, 6.13; N, 6.11%), mp 92–94 °C.^{1}H NMR ($\mathrm{CDCl_3}$): −0.21 (s, 9H, $\mathrm{SiMe_3}$), 2.09 (s, 3H, Me), 3.79 (d, J = 14.1 Hz, 2H, $\mathrm{CH_2}$), 6.60 (d, J = 8.2 Hz, 2H, Ar), 6.73 (d, J = 8.1 Hz, 2H, Ar), 7.09–7.15 (m, 4H, Ar), 7.23–7.28 (m, 6H, Ar), 7.35–7.40 (m, 3H, Ar), 7.44–7.58 (m, 5H, Ar), 7.63–7.70 (m, 4H, Ar), 8.01–8.06 (m, 1H, Py). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 3.97 (d, J = 3.3 Hz), 20.63, 42.76 (d, J = 66.6 Hz), 120.08, 123.14, 123.38, 126.29, 127.00 (d, J = 3.3 Hz), 127.04 (d, J = 3 Hz), 127.25 (d, J = 2.3 Hz), 127.51 (d, J = 2.6 Hz), 128.21 (d, J = 9.6 Hz), 128.36 (d, J = 9.6 Hz), 129.35 (d, J = 1.7 Hz), 130.09, 130.86 (d, J = 2.8 Hz), 131.11, 131.24, 131.38, 131.44 (d, J = 2.8 Hz), 133.08 (d, J = 9.4 Hz), 134.76, 135.93, 136.06, 148.46 (d, J = 2.6 Hz), 155.19, 155.29. ^{31}P NMR ($\mathrm{CDCl_3}$): −6.77, −3.96 (m).

$[\mathrm{Sn_2\{C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}(PPh_2{=}NSiMe_3)C_5H_3N)\}\}_2}]$ (9). To a solution of **8a** (0.18 g, 0.28 mmol) in toluene (10 cm^3) was added a solution of $\mathrm{Sn[N(SiMe_3)_2]_2}$ (0.14 g, 0.31 mmol) in toluene (5 cm^3) at room temperature with stirring. The mixture was kept stirring at room temperature for 24 h and then refluxed for 6 h. The hot solution was filtered and the filtrate was cooled to room temperature to afford yellow crystals of **9** (0.14 g, 66%) (found: C, 57.34; H, 5.55; N, 5.39. $\mathrm{C_{72}H_{82}N_6P_4Si_4Sn_2}$ requires C, 57.46; H, 5.49; N, 5.58%), mp 220–222 °C. ^{1}H NMR ($\mathrm{C_6D_6}$+THF): δ −0.86 (s, 9H, $\mathrm{SiMe_3}$), 0.06 (d, J = 1.8 Hz, 9H, $\mathrm{SiMe_3}$), 6.95–6.99 (m, 1H, Py), 7.05–7.31 (m, 14H, Ar), 7.35–7.42 (m, 2H, Ar), 7.62–7.68 (m, 2H, Ar), 7.83–8.02 (m, 2H, Ar), 8.15–8.21 (m, 2H, Ar). ^{13}C NMR($\mathrm{C_6D_6}$+THF): 1.77, 3.99 (d, J = 3.4 Hz), 120.49, 121.73, 122.04, 125.64, 126.40, 126.67, 127.93, 128.16, 128.22, 128.51, 128.59, 129.28, 130.11 (d, J = 1.9 Hz), 130.83 (d, J = 2.9 Hz), 131.35, 131.47, 133.60, 133.72, 134.36, 135.11, 135.20, 135.85, 136.53, 137.15, 138.83, 139.22, 157.43, 159.08. ^{31}P NMR ($\mathrm{C_6D_6}$+THF):δ −7.91 (m), 30.24 (m).

$[\mathrm{Pb_2\{C(Ph_2P{=}NSiMe_3)\{6\text{-}(2\text{-}(PPh_2{=}NSiMe_3)C_5H_3N)\}\}_2}]$ (10). A similar procedure to **9** was followed. Thus, to a solution of **8a** (0.14 g, 0.22 mmol) in toluene (10 cm^3) was added a solution of $\mathrm{Pb[N(SiMe_3)_2]_2}$ (0.14 g, 0.27 mmol) in toluene (5 cm^3) at room temperature with stirring. The mixture was kept stirring at room temperature for 24 h and then refluxed for 6 h. The hot solution was filtered and the filtrate was cooled to room temperature to precipitate red crystals of **10** (0.08 g, 43%) (found: C, 51.19; H, 4.91; N, 5.00. $\mathrm{C_{72}H_{82}N_6P_4Pb_2Si_4}$ requires C, 51.41; H, 4.91; N, 5.00%), mp 103–105 °C. ^{1}H NMR ($\mathrm{C_6D_6}$+THF): δ −0.04 (d, J = 3 Hz, 9H, $\mathrm{SiMe_3}$), −0.05 (d, J = 3.3 Hz, 9H, $\mathrm{SiMe_3}$), 6.81–6.87 (m, 1H, Ar), 6.95–7.23 (m, 16H, Ar), 7.42–7.76 (m, 4H, Ar), 8.12 (t, J = 7.5 Hz, 2H, Ar). ^{13}C NMR($\mathrm{C_6D_6}$+THF): 1.17, 4.11, 126.39, 126.73, 126.89, 128.22, 128.65, 126.82, 129.28, 130.46 (d, J = 11.8 Hz), 130.84 (d, J = 2.8 Hz), 131.12, 131.35, 131.49, 131.84, 131.98, 132.63, 132.76, 133.02, 134.53, 135.20, 135.86, 136.53,

Table 1 Details of the X-ray structure determinations of complexes **3**, **4**, **10**, **11** and **12**†

	3$\cdot C_6H_{14}$	**4**$\cdot C_7H_8$	**10**$\cdot C_4H_8O$	**11**$\cdot 0.5C_6H_{14}$	**12**
empirical formula	$C_{58}H_{72}N_8P_2Si_2Sn_2$	$C_{59}H_{66}N_8P_2Pb_2Si_2$	$C_{76}H_{90}N_6OP_4Pb_2Si_4$	$C_{49}H_{65}N_4P_2Si_3Sn$	$C_{42}H_{60}N_4P_2Si_4Yb$
fw	1236.74	1419.70	1754.16	974.95	968.28
T (K)	294(2)	293(2)	298(2)	294(2)	293(2)
crystal system	triclinic	triclinic	orthorhombic	triclinic	monoclinic
space group	P–1	P–1	$Pbca$	P–1	$P2(1)/n$
a (Å)	9.9696(13)	9.9080(9)	20.789(2)	10.4319(16)	14.9293(17)
b (Å)	12.8011(17)	12.6483(12)	17.829(2))	15.457(3)	13.9411(15)
c (Å)	12.8842(17)	12.8690(12)	22.813(3)	17.668(3)	23.677(2)
α (deg)	100.983(2)	98.515(1)	90	80.404(3)	90
β (deg)	108.444(2)	107.279(1)	90	72.936(3)	105.018(2)
γ (deg)	91.686(2)	98.784(2)	90	71.534(2)	90
V (Å3)	1524.2(3)	1489.6(2)	8455.3(17)	2574.7(7)	4759.6(9)
Z	1	1	4	2	4
D_{calcd} (gcm^{-3})	1.347	1.583	1.378	1.258	1.351
μ (mm^{-1})	0.953	5.781	4.15	0.664	2.165
no. of reflns collected	7769	8465	40850	10880	24375
no. of indep reflns(R_{int})	5337 (R_{int} = 0.0221)	5991 (R_{int} = 0.0169)	7463 (R_{int} = 0.1288)	8408 (R_{int} = 0.0250)	8345 (R_{int} = 0.1532)
goodness of fit on F^2	1.030	1.013	0.999	1.036	0.995
final R indices[a] [$I > 2\sigma(I)$]	$R_1 = 0.0318$ w$R_2 = 0.0735$	$R_1 = 0.0245$ w$R_2 = 0.0552$	$R_1 = 0.0496$ w$R_2 = 0.1214$	$R_1 = 0.0459$ w$R_2 = 0.1068$	$R_1 = 0.0681$ w$R_2 = 0.1337$
R indices (all data)	$R_1 = 0.0451$ w$R_2 = 0.0827$	$R_1 = 0.0333$ w$R_2 = 0.0590$	$R_1 = 0.1473$ w$R_2 = 0.1536$	$R_1 = 0.0768$ w$R_2 = 0.1260$	$R_1 = 0.1679$ w$R_2 = 0.1604$

[a] $R_1 = \Sigma \|Fo| - |Fc\|/\Sigma|Fo|$; w$R_2[\Sigma w(Fo^2 – Fc^2)^2/\Sigma w(Fo^4)]^{1/2}$

137.16, 155.57, 158.91, 159.33. ^{31}P NMR (C_6D_6+THF): δ –8.27, 21.20.

[Sn{2-(N(*p*-MeC$_6$H$_4$)=PPh$_2$)-6-(CHP(Ph$_2$)=NSiMe$_3$)}{N-(SiMe$_3$)$_2$}] (11). To a solution of **8b** (0.18 g, 0.28 mmol) in toluene (10 cm^3) was added a solution of Sn[N(SiMe$_3$)$_2$]$_2$ (0.12 g, 0.27 mmol) in toluene (5 cm^3) at room temperature with stirring. The mixture was kept stirring at room temperature for 72 h. Solvent was removed *in vacuo* and the residue was dissolved in Et$_2$O. The solution was filtered and the filtrate was concentrated to about 5 cm^3. Hexane (10 cm^3) was added and the solution was kept at –20 °C for 24 h to form red crystals of **11** (0.16 g, 61%) (found: C, 59.01; H, 6.11; N, 5.87. $C_{46}H_{58}N_4P_2Si_3Sn$ requires C, 59.29; H, 6.27; N, 6.01%), mp 108–110 °C (dec). ^{1}H NMR (C_6D_6): δ 0.23 (s, 18H, SiMe$_3$), 0.42 (s, 9H, SiMe$_3$), 1.85 (s, 3H, Me), 4.91 (d, J = 11.4 Hz, 1H, CH), 5.98–6.00 (m, 1H, Ar), 6.68–7.05 (m, 17H, Ph), 7.26–7.29 (m, 3H, Ph), 7.48–7.49 (m, 2H, Ph), 8.09–8.13 (m, 4H, Ar). ^{13}C NMR (C_6D_6): 4.83 (d, J = 3.5 Hz), 6.47, 20.62, 31.97, 126.25 (d, J = 9.9 Hz), 128.21, 128.26, 128.84, 129.00, 129.10, 129.27, 130.00 (d, J = 1.8 Hz), 130.11, 131.70, 131.85 (d, J = 2.6 Hz), 132.00, 132.17, 133.31, 133.60, 133.73, 140.58, 141.14, 157.86, 158.80, 159.22, 160.08. ^{31}P NMR (C_6D_6) : δ –5.85, 19.02.

A solution of complex **11** in toluene was heated at 80 °C for 24 h to give yellow precipitates. The precipitates were washed with toluene and dried in vacuo. It was insoluble in toluene, Et$_2$O, THF, pyridine and CH$_2$Cl$_2$. Elemental analysis found: C, 62.55; H, 5.21; N, 5.32. $C_{80}H_{78}N_6P_4Si_2Sn_2$ requires C, 62.35; H, 5.10; N, 5.45%.

[Yb{2-(N(SiMe$_3$)=PPh$_2$)-6-(CHP(Ph$_2$)=NSiMe$_3$)}{N(SiMe$_3$)$_2$}] (12). A solution of **8a** (0.23 g, 0.36 mmol) in hexane (10 cm^3) was cooled to about –80 °C. To the solution was added a solution of Yb[N(SiMe$_3$)$_2$](DME) (0.24 g, 0.41 mmol) in hexane (5 cm^3) with stirring. The mixture was allowed to warm to room temperature and stirred for 24 h. Solvent was removed *in vacuo* and the residue was dissolved in Et$_2$O. The solution was filtered and the filtrate concentrated to afford brown crystals of **12** (0.16 g, 46%) (found: C, 52.01; H, 6.19; N, 5.55. $C_{42}H_{60}N_4P_2Si_4Yb$ requires C, 52.10; H, 6.25; N, 5.79%), m.p. 162–163 °C. ^{1}H NMR (C_6D_6): δ 0.04 (s, 9H, SiMe$_3$), 0.37 (s, 9H, SiMe$_3$), 0.57 (s, 18H, SiMe$_3$), 3.54 (d, J = 15.9 Hz, 1H, CH), 5.94 (t, J = 6.8 Hz, 1H, Py), 6.55–6.66 (m, 2H, Ar), 6.89–7.25 (m, 10H, Ar), 7.33–7.35 (m, 2H, Ar), 7.44–7.50 (m, 2H, Ar), 7.58–7.68 (m, 2H, Ar), 7.79–7.82 (m, 2H, Ar), 7.99–8.05 (m, 2H, Ar). ^{13}C NMR (C_6D_6): 3.83 (d, J = 4.3 Hz), 4.15 (d, J = 4.2 Hz), 5.96, 57.48 (d, J = 130.4 Hz), 112.52 (d, J = 24.4 Hz), 123.01 (d, J = 3.2 Hz), 123.20 (d, J = 3.2 Hz), 127.91, 128.16, 128.23, 128.65, 128.81, 131.14, 131.29, 131.43, 131.49, 131.61, 132.67, 132.80, 133.63 (d, J = 2.3 Hz), 133.80 (d, J = 2.1 Hz), 150.69, 152.53, 166.69 (d, J = 1.3 Hz), 166.92 (d, J = 1.5 Hz). ^{31}P NMR (C_6D_6): δ 11.74 (m), 14.31.

X-Ray crystal structure determination of complexes 3, 4, 10, 11 and 12

Single crystals of complexes **3**, **4**, **10**, **11** and **12** were respectively mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Bruker Smart CCD area-detector with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[15] and refined against F^2 by full-matrix least-squares using SHELXL-97.[16] Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 1.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 20572106) and the Foundation for Talents of Anhui Province (Grant No.2008Z011). The authors thank Professors H.-B. Song and D.-Q. Wang for determining the crystal structures.

References

1 (*a*) K. V. Katti and R. G. Cavell, *Comments Inorg. Chem.*, 1990, **10**, 53; (*b*) R. G. Cavell, *Curr. Sci.*, 2000, **78**, 440; (*c*) C. M. Ong, P. McKarns and D. W. Stephan, *Organometallics*, 1999, **18**, 4197; (*d*) K. V. Katti and R. G. Cavell, *Inorg. Chem.*, 1989, **28**, 413; (*e*) K. V. Katti, R. J. Batchelor, F. W. B. Einstein and R. G. Cavell, *Inorg. Chem.*, 1990, **29**, 808; (*f*) K. V. Katti, B. D. Santarsiero, A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 1993, **32**, 5919; (*g*) K. V. Katti, U. Seseke and H. W. Roesky, *Inorg. Chem.*, 1987, **26**, 814; (*h*) M. W. Avis, M. Goosen, C. J. Elsevier, N. Veldman, H. Kooijman and A. L. Spek, *Inorg. Chim. Acta*, 1997, **264**, 43.

2 (*a*) R. P. K. Babu, K. Aparna, R. McDonald and R. G. Cavell, *Inorg. Chem.*, 2000, **39**, 4981; (*b*) R. P. K. Babu, K. Aparna, R. McDonald and R. G. Cavell, *Organometallics*, 2001, **20**, 1451; (*c*) S Wingerter, H. Gornitzka, R. Bertermann, S. K. Pandey, J. Rocha and D. Stalke, *Organometallics*, 2000, **19**, 3890; (*d*) P. B. Hitchcock, M. F. Lappert and Z.-X. Wang, *Chem. Commun*, 1997, 1113; (*e*) A Müller, B. Neumüller and K. Dehnicke, *Chem. Ber.*, 1996, **129**, 253; (*f*) P Wei and D. W. Stephan, *Organometallics*, 2003, **22**, 601; (*g*) M. S. Hill, P. B. Hitchcock and S. M. A. Karagouni, *J. Organomet. Chem.*, 2004, **689**, 722; (*h*) Z.-X. Wang and C.-Y. Qi, *Dalton Trans.*, 2005, 996; (*i*) P. B. Hitchcock, M. F. Lappert and Z.-X. Wang, *J. Chem. Soc. Dalton Trans.*, 1997, 1953; (*j*) W.-P. Leung, K.-P. Chan, K.-W. Kan and T. C. W. Mak, *Organometallics*, 2008, **27**, 2767.

3 (*a*) C. M. Ong and D. W. Stephan, *J. Am. Chem. Soc.*, 1999, **121**, 2939; (*b*) A Kasani, R. P. K. Babu, R. McDonald and R. G. Cavell, *Angew. Chem. Int. Ed.*, 1999, **38**, 1483; (*c*) K Aparna, R. McDonald and R. G. Cavell, *Chem. Commun.*, 1999, 1993; (*d*) R. G. Cavell, R. P. K. Babu and K. Aparna, *J. Organomet. Chem.*, 2001, **617–618**, 158; (*e*) K Aparna, M. Ferguson and R. G. Cavell, *J. Am. Chem. Soc.*, 2000, **122**, 726.

4 (*a*) M Witt and H. W. Roesky, *Chem. Rev.*, 1994, **94**, 1163; (*b*) R Bielsa, R. Navarro, T. Soler and E. P. Urriolabeitia, *Dalton Trans.*, 2008, 1203; (*c*) S. Wingerter, H. Gornitzka, G. Bertrand and D. Stalke, *Eur. J. Inorg. Chem.*, 1999, 173; (*d*) S Wingerter, M. Pfeiffer, T. Stey, M. Bolboacá, W. Kiefer, V. Chandrasekhar and D. Stalke, *Organometallics*, 2001, **20**, 2730; (*e*) M. T. Gamer, S. Dehnen and P. W. Roesky, *Organometallics*, 2001, **20**, 4230; (*f*) D Aguilar, M. A. Aragüés, R. Bielsa, E. Serrano, T. Soler, R. Navarro and E. P. Urriolabeitia, *J. Organomet. Chem.*, 2008, **693**, 417; (*g*) B. Liu, D. Cui, J. Ma, X. Chen and X. Jing, *Chem. Eur. J.*, 2007, **13**, 834; (*h*) M Said, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc. Dalton Trans.*, 2001, 2844.

5 (*a*) Z.-X. Wang and C.-Y. Qi, *Organometallics*, 2007, **26**, 2243; (*b*) M. S. Hill and P. B. Hitchcock, *J. Chem. Soc. Dalton Trans.*, 2002, 4694; (*c*) Z.-Y. Chai, C. Zhang and Z.-X. Wang, *Organometallics*, 2008, **27**, 1626; (*d*) C. A. Wheaton, B. J. Ireland and P. G. Hayes, *Organometallics*, 2009, **28**, 1282; (*e*) S Al-Benna, M. J. Sarsfield, M. Thornton-Pett, D. L. Ormsby, P. J. Maddox and M. Bochmann, *J. Chem. Soc. Dalton Trans.*, 2000, 4247; (*f*) C. Zhang, W.-H. Sun and Z.-X. Wang, *Eur. J. Inorg. Chem.*, 2006, 4895; (*g*) A Buchard, A. Auffrant, C. Klemps, L. Vu-Do, L. Boubekeur, X. F. Le Goff and Pascal Le Floch, *Chem. Commun.*, 2007, 1502; (*h*) Z.-X. Wang and L. Wang, *Chem. Commun.*, 2007, 2423; (*i*) L Wang and Z.-X. Wang, *Org. Lett.*, 2007, **9**, 4335; (*j*) K Sun, L. Wang and Z.-X. Wang, *Organometallics*, 2008, **27**, 5649; (*k*) L Orzechowski and S. Harder, *Organometallics*, 2007, **26**, 2144; (*l*) D Aguilar, M. Contel, R. Navarro and E. P. Urriolabeitia, *Organometallics*, 2007, **26**, 4604; (*m*) B. Liu and D. Cui, *Dalton Trans.*, 2009, 550.

6 (*a*) A Kasani, R. McDonald and R. G. Cavell, *Organometallics*, 1999, **18**, 3775; (*b*) A Kasani, R. McDonald and R. G. Cavell, *J. Am. Chem. Soc.*, 2000, **122**, 9314; (*c*) W.-P. Leung, C.-W. So, J.-Z. Wang and T. C. W. Mak, *Chem. Commun.*, 2003, 248; (*d*) B Liu, X. Liu, D. Cui and L. Liu, *Organometallics*, 2009, **28**, 1453; (*e*) V Cadierno, J. Díez, J. García-Álvarez and José Gimeno, *Organometallics*, 2008, **27**, 1809; (*f*) P Oulié, C. Freund, N. Saffon, B. Martín-Vaca, L. Maron and D. Bourissou, *Organometallics*, 2007, **26**, 6793; (*g*) K. Kubo, T. Baba, T. Mizuta and K. Miyoshi, *Organometallics*, 2006, **25**, 3238; (*h*) V Cadierno, J. Díez, J. García-Álvarez, J. Gimeno, N. Nebra and J. Rubio-García, *Dalton Trans.*, 2006, 5593.

7 (*a*) N. D. Jones and R. G. Cavell, *J. Organomet. Chem.*, 2005, **690**, 5485; (*b*) N. D. Jones, G. Lin, R. A. Gossage, R. McDonald and R. G. Cavell, *Organometallics*, 2003, **22**, 2841; (*c*) K Aparna, R. McDonald, M. Ferguson and R. G. Cavell, *Organometallics*, 1999, **18**, 4241; (*d*) A Kasani, R. P. K. Babu, R. McDonald and R. G. Cavell, *Angew. Chem. Int. Ed.*, 2006, **45**, 3097; (*e*) W.-P. Leung, Z.-X. Wang, H.-W. Li and T. C. W. Mak, *Angew. Chem. Int. Ed.*, 2001, **40**, 2501; (*f*) R. P. K. Babu, R. McDonald and R. G. Cavell, *Chem. Commun.*, 2000, 481; (*g*) R. P. K. Babu, R. McDonald, S. A. Decker, M. Klobukowski and R. G. Cavell, *Organometallics*, 1999, **18**, 4226; (*h*) K Aparna, R. P. K. Babu, R. McDonald and R. G. Cavell, *Angew. Chem. Int. Ed.*, 2001, **40**, 4400; (*i*) G Lin, N. D. Jones, R. A. Gossage and R. G. Cavell, *Angew. Chem. Int. Ed.*, 2003, **42**, 4054; (*j*) W.-P. Leung, C.-W. So, Z.-X. Wang, J.-Z. Wang and T. C. W. Mak, *Organometallics*, 2003, **22**, 4305; (*k*) W.-P. Leung, Q. W.-Y. Ip, S.-Y. Wong and T. C. W. Mak, *Organometallics*, 2003, **22**, 4604.

8 (*a*) W.-P. Leung, Z.-X. Wang, H.-W. Li, Q.-C. Yang and T. C. W. Mak, *J. Am. Chem. Soc.*, 2001, **123**, 8123; (*b*) W.-P. Leung, K.-W. Wong, Z.-X. Wang and T. C. W. Mak, *Organometallics*, 2006, **25**, 2037.

9 C.-Y. Qi and Z.-X. Wang, *J. Polym. Sci.: Part A: Polym. Chem.*, 2006, **44**, 4621.

10 T. Fieldberg, H. Hope, M. F. Lappert, P. P. Power and A. J. Thorne, *J. Chem. Soc. Chem. Commun.*, 1983, 639.

11 P. B. Hitchcock, J. Hu, M. F. Lappert, M. Layh and J. R. Severn, *J. Chem. Soc. Chem. Commun.*, 1997, 1189.

12 (*a*) T. K. Panda, A. Zulys, M. T. Gamer and P. W. Roesky, *J. Organomet. Chem.*, 2005, **690**, 5078; (*b*) L Lee, D. J. Berg and G. W. Bushnell, *Inorg. Chem.*, 1994, **33**, 5302; (*c*) T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725; (*d*) T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271; (*e*) S Datta, M. T. Gamer and P. W. Roesky, *Organometallics*, 2008, **27**, 1207.

13 B. Wrackmeyer, A. Pedall and J. Weidinger, *Z. Naturforsch. B*, 2001, **56b**, 1009.

14 Y. F. Rad'kov, E. A. Fedorova, S. Y. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *J. Gen. Chem. USSR (Engl. Transl.)*, 1985, **55**, 1911.

15 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.

16 G. M. Sheldrick, *SHELXL97, Programs for structure refinement*, Universität Göttingen, 1997.