

Synthesis and reactions of 1-*t*-butyldimethylsilyl-2,3-diphenyl-1-aza-3-phosphaallyl lithium and potassium. Crystal structures of $[M\{P(Ph)C(Ph)NSiMe_2Bu^t\}(L)]_2$ ($M = Li, L = THF; M = K, L = Et_2O$), $[Sn\{P(Ph)C(Ph)NSiMe_2Bu^t\}_2]$ and $[P(Ph)C(Ph)=NSiMe_2Bu^t]_2$

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Received 12 June 2002; accepted 21 October 2002

Abstract

Reaction of $MP(Ph)SiMe_2Bu^t$ ($M = Li, K$) with an equivalent of $PhCN$ afforded the 1-aza-3-phosphaallyllithium and -potassium complexes $[M\{P(Ph)C(Ph)NSiMe_2Bu^t\}(L)]_2$ (**1**, $M = Li, L = THF$; **2**, $M = K, L = Et_2O$), respectively. After exposing **2** in vacuo at room temperature, the solvent-free complex $[K\{P(Ph)C(Ph)NSiMe_2Bu^t\}]$ (**3**) was obtained. Treatment of **1** with $SnCl_2$ in a 2:1 ratio furnished the homoleptic tin(II) complex $[Sn\{P(Ph)C(Ph)NSiMe_2Bu^t\}_2]$ (**4**). Compound **1** reacted with an equimolar amount of $ClSnN(SiMe_3)_2$ to give $[P(Ph)C(Ph)=NSiMe_2Bu^t]_2$ (**5**) via ligand coupling. Reaction of **3** with $PhCN$ produced $[K\{P(Ph)C(Ph)NC(Ph)NSiMe_2Bu^t\}]$ (**6**) by addition of the nitrogen atom to $PhCN$ followed by a 1,3- $N \rightarrow N'$ migration of the $SiMe_2Bu^t$ group. Structures of compounds **1**, **2**, **4** and **5** have been determined by single crystal X-ray diffraction techniques. The complexes **1** and **2** are dimeric and **4** is both monomeric, while **5** is the product of a ligand coupling with formation of new P–P bond.

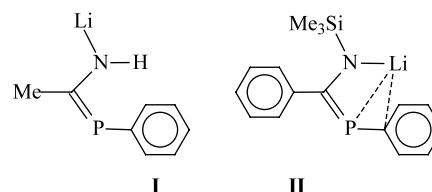
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Keywords: 1-aza-3-Phosphaallyl ligand; Lithium; Potassium; Tin; Complexes; Structures

1. Introduction

P,N-chelating ligands have attracted increasingly attention in recent years due to the presence of a ‘soft’ and a ‘hard’ reaction center [1]. One important property of these ligands is that they can stabilize metal ions in a variety of oxidation states and geometries. These ligands also display quite different coordination modes compared with P,P and N,N ligands [2–4]. Recently 1-aza-3-phosphaallyl anions as mono and bidentate ligands have been reported. The complexes of such ligands with metals such as lithium, alkaline earth metals and even platinum have been synthesized and characterized and show interesting bonding character and reactivity [5–9].

For example, both $[N(H)C(Me)=PPh]^-$ and $[N(SiMe_3)C(Ph)=PPh]^-$ act as monodentate ligands bonding to lithium by the nitrogen atoms of the ligands [5–7], and the latter [7] also reveals a lithium-phosphorus contact of 2.924 Å (see **I** and **II**);

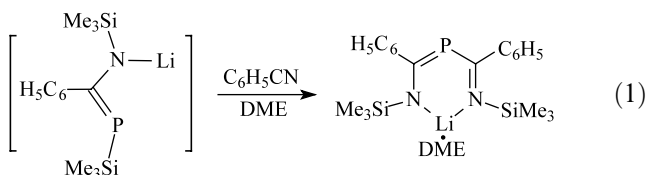


the unstable $[Li\{N(SiMe_3)C(Ph)=PSiMe_3\}]$ acts with $PhCN$ to afford lithium bis{(trimethylsilylimino)benzoyl}phosphanide (Eq. (1)) [8]. However, known complexes with this type of ligands are still rare. Here we report synthesis of a novel 1-aza-3-phosphaallyl ligand, its reactivity towards $SnCl_2$, $Sn(Cl)N(SiMe_3)_2$ and

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PhCN and the crystal structures of $[M\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}_2(L)]_2$ ($M = Li, L = THF; M = K, L = Et_2O$), $[Sn\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}_2]$ and $[P(Ph)C(Ph)=NSiMe_2Bu^t\}_2]$.

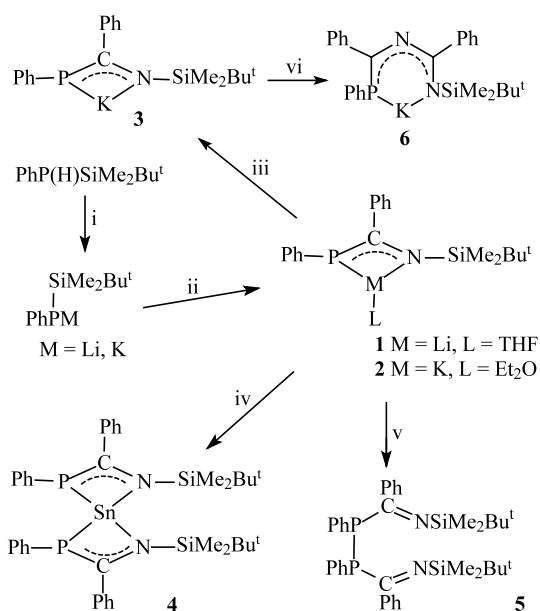


2. Results and discussion

The synthesis of the new 1-aza-3-phosphaallyl lithium and potassium and their reactions are summarized in Scheme 1. Treatment of $LiP(Ph)SiMe_2Bu^t$ prepared from $PhP(H)SiMe_2Bu^t$ and $LiBu^t$ with an equivalent of PhCN in THF gave a deep red solution. Removal of the solvent and crystallization from diethyl ether afforded red orange crystals of $[Li\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}_2(THF)]_2$ (**1**) in high yield. The potassium analogue of **1** was obtained similarly from $KP(Ph)SiMe_2Bu^t$ (prepared by reaction of $PhP(H)SiMe_2Bu^t$ with potassium metal) and PhCN as a diethyl ether adduct, [

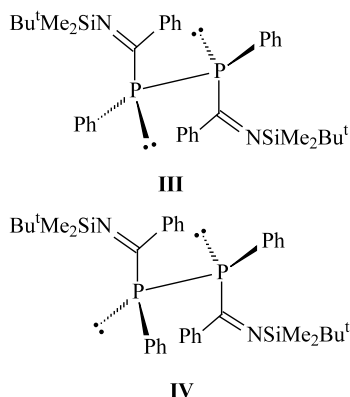
$K\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}_2(OEt_2)]_2$ (**2**). After exposing **2** in vacuo at room temperature, the solvent-free complex $[K\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}]$ (**3**) was obtained. This proved that the diethyl ether molecules were loosely bound in the complex. Treatment of complex **1** with $SnCl_2$ in a 2:1 ratio yielded the homoleptic tin(II) complex $[Sn\{P(Ph)C(Ph)N\}SiMe_2Bu^t\}_2]$ (**4**) as yellow orange crystals in good yield. Attempts to prepare the heteroleptic tin(II) complex by reaction of **1** with one equivalent of $SnCl_2$ were unsuccessful; only an oily species was obtained and the 1H -NMR spectrum showed it to be a mixture. Reaction of **1** with an equimolar amount of $ClSnN(SiMe_3)_2$ in diethyl ether furnished a yellow orange solution with white precipitates. Filtration of the reaction mixture and concentration of the filtrate gave precipitates, which could not be redissolved in organic solvents. The mother liquor was left for about 4 weeks to give yellow crystals which turned out by NMR spectroscopy and single crystal X-ray diffraction to be the ligand coupling species, $[P(Ph)C(Ph)=NSiMe_2Bu^t\}_2]$ (**5**). Presumably the reaction proceeds through the heteroleptic tin(II) complex $[Sn\{P(Ph)C(Ph)=NSiMe_2Bu^t\}\{N(SiMe_3)_2\}]$, and the unstable complex further decomposed to form **5** and other species. Reaction of **3** with PhCN in a 1:1 ratio afforded $[K\{P(Ph)C(Ph)NC(Ph)N\}SiMe_2Bu^t\}]$ (**6**) as yellow crystals, but their quality was not sufficient for an X-ray structure analysis. Apparently the reaction involved not only attack of the nitrogen atom of **3** to PhCN but also a 1,3-silatrip migration. The addition orientation is different from that of the reaction between $[Li\{N(SiMe_3)C(Ph)P(SiMe_3)_2\}]$ and PhCN which yielded $[LiP\{C(Ph)=NSiMe_3\}_2]$ (Eq. (1)) [8]. Complex **6** can also be obtained in a one-pot reaction from $KP(Ph)SiMe_2Bu^t$ and two equivalents of PhCN.

Each of the compounds **1** and **3–6** was characterized by elemental analysis, 1H , $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ -NMR spectroscopy. For example, the 1H -NMR spectrum of **1** showed signals of the appropriate groups, and coordinate THF molecules. The $^{13}C\{^1H\}$ -NMR spectrum displayed the signal of the P–C–N fragment as a doublet due to coupling with the phosphorus atom and other corresponding signals. Complex **3** is not very soluble in benzene, its NMR spectra were recorded in a solvent mixture of C_6D_6 and C_5D_5N . The 1H and $^{13}C\{^1H\}$ -NMR spectra showed signals of the appropriate groups, consistent with the proposed structure. However, its ^{31}P chemical shift of 31.61 ppm was quite different from that of $[K\{N(Ph)C(Bu^t)PPh\}]$ (δ –102 ppm) reported by Issleib and co-workers [9]. This can be attributed to different bonding modes of the two complexes. The $^{31}P\{^1H\}$ -NMR spectral signals of **4** appeared at 6.48 ppm with satellites due to coupling with tin, which proved a bonding interaction between the phosphorus and the tin atom. The 1H and $^{31}P\{^1H\}$ -



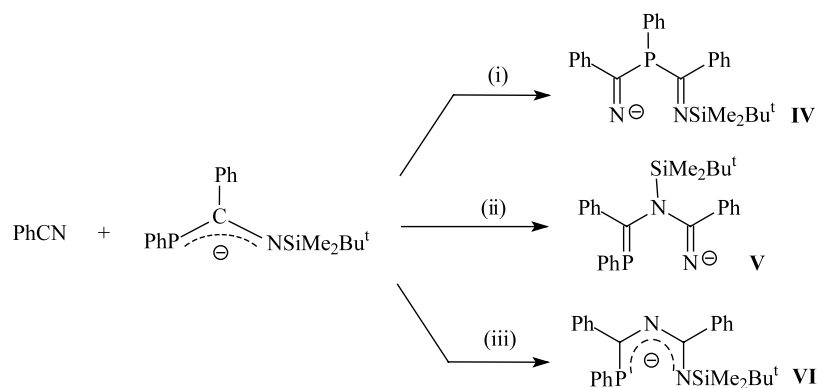
Scheme 1. Syntheses and reactions of 1-*t*-butyldimethylsilyl-2,3-diphenyl-1-aza-3-phosphaallyl lithium and potassium. Reagents and conditions: (i) $LiBu^t$, THF, 0 °C to room temperature, 2 h; K, THF, room temperature, 15 h and reflux for 30 min; (ii) PhCN, –50 °C to room temperature, stirred overnight; (iii) exposing to vacuum, room temperature, 30 min; (iv) 1/2 $SnCl_2$, Et_2O , –80 °C to room temperature, stirred overnight; (v) $ClSnN(SiMe_3)_2$, Et_2O , –70 °C to room temperature, stirred overnight; (vi) PhCN, –70 °C to room temperature, 6 h.

NMR spectra of **5** displayed two sets of equal intensity signals. The reason is the coupling of the ligands $[\text{P}(\text{Ph})\text{C}(\text{Ph})\text{NSiMe}_2\text{Bu}^t]^-$ form two diastereomers (**III** and **IV** (and its enantiomer)) which exhibit different chemical shifts in the NMR spectra.

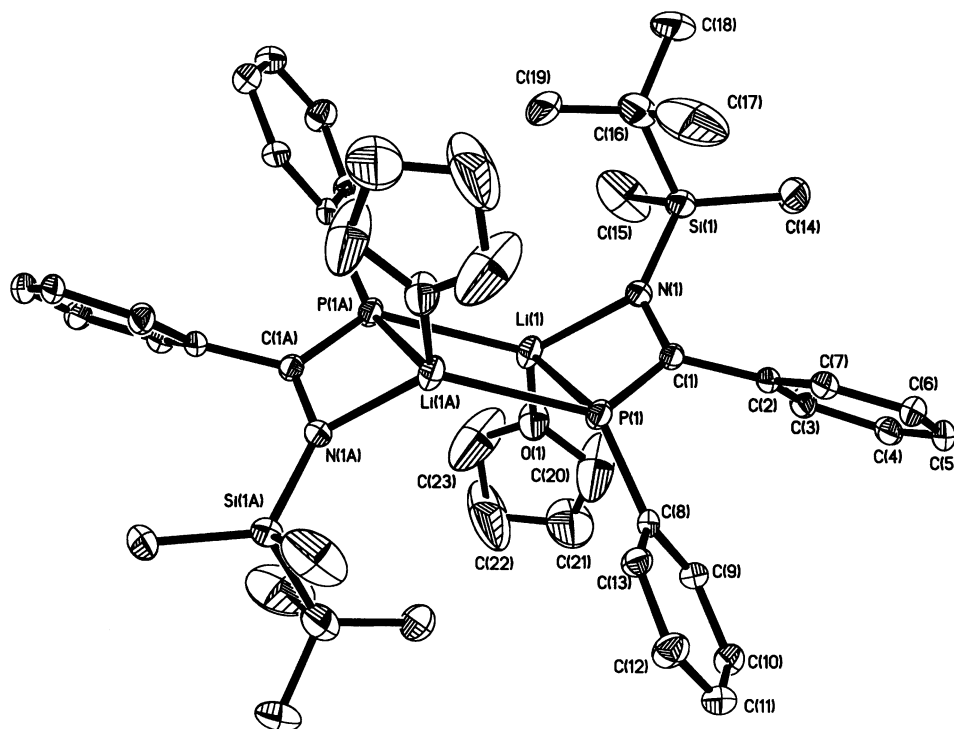


$[\text{K}\{\text{P}(\text{Ph})\text{C}(\text{Ph})\text{NSiMe}_2\text{Bu}^t\}]$ (**3**) has two nucleophilic centers, the phosphorus and the nitrogen atom, respectively. The reaction of **3** with PhCN has, in principle, three possible paths (Scheme 2): (i) the phosphorus atom of **3** attacks PhCN to form **IV**; (ii) the nitrogen atom of **3** attacks PhCN to yield **V** and (iii) the nitrogen atom of **3** attacks PhCN and then the SiMe₂Bu^t group migrates from N to N' affording **VI**. Experimentally, the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **6** showed only one set of P-coupled C=N signals at 207.57 ppm with a coupling constant of 59.36 Hz; hence **IV** is ruled out. Compound **V** contains a C=P double bond, while **VI** is a delocalized system. From the reported spectral data, the ^{31}P chemical shifts for a C=P double bond normally appear downfield compared with a corresponding delocalized system, e.g. the ^{31}P chemical shifts of PhP=C(Me)NH₂ and PhP=C(Me)N(H)SiMe₃ appear at 74.7 and 94.7 ppm, respectively, while those of delocalized $[\text{Li}\{\text{NHC}(\text{Me})\text{PPh}\}(\text{THF})_2]_2$ and $[\text{Li}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Me})\text{PPh}\}(\text{THF})_x]$ at 34.3 and 28.5 ppm, respectively [5]. The $^{31}\text{P}\{^1\text{H}\}$ -NMR signal of **6** was detected at 37.44 ppm, thus **VI** is the most plausible structure.

The structures of compounds **1**, **2**, **4** and **5** were further confirmed by single crystal X-ray diffraction. The complex **1** is a dimer bridged by the phosphorus atoms and crystallizes with two dimeric molecules in the unit cell. For one dimer only, however, an ORTEP representation of the molecular structure is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The skeletal structure is ladder-shaped. Due to a center of inversion the central ring Li(1)P(1)P-(1A)Li(1A) is planar with the angle at P smaller $[72.9(3)^\circ]$ than that at Li $[107.1(3)^\circ]$. Therefore, one of the coordinating THF molecules is situated above the four-membered and the other below. The P(1)C(1)N(1) unit coordinates to the central Li atom in an η^3 mode, different from that found in $[\text{Li}\{\text{NHC}(\text{Me})\text{PPh}\}(\text{THF})_2]_2$ and $[\text{Li}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\text{PPh}\}]$ (see **I** and **II**) [5–7]. The Li(1)–P(1) distance of 2.641(9) Å is slightly longer than that of Li(1)–P(1A) [2.592(7) Å], and the latter is close to those found in $[\{\text{Li}(\text{THF})_2\}_2\{\text{PhPCH}_2\text{CH}_2\text{PPh}\}]$ (av. 2.56 Å) [10] and $[\{\text{Li}(\text{TME-DA})\}_2\{\text{C}_6\text{H}_4(\text{PPh})_{2-1,2}\}]$ (av. 2.58 Å) [11]. The Li(1)–N(1) distance of 1.991(10) Å is shorter than those found in **I** [2.031(8) and 2.090(8) Å] [5] but remains in the usual range. For example, the Li–N distances in $[\text{Li}\{\text{CH}(\text{SiMe}_3)\text{P}(\text{Ph})_2=\text{NSiMe}_3\}]_2$ vary from 1.898(10) to 2.166(9) Å [12], and in $[\text{Li}\{\text{CH}_2\text{P}(\text{Me})_2=\text{NSiMe}_3\}]_4$ from 1.97(1) to 2.12(1) Å [10]. The Li(1)–C(1) distance of 2.499(10) Å is longer than those in $[\text{Li}\{\text{CH}(\text{SiMe}_3)\text{P}(\text{Ph})_2=\text{NSiMe}_3\}]_2$ [2.122(9) and 2.190(9) Å] [12] and $[\text{Li}\{\eta^3\text{-CH}(\text{CHSiMe}_2\text{Bu}^t)\}(\text{TMEDA})]$ [2.11(2)–2.23(2) Å] [13], but comparable with those found in azaallyl lithium compounds such as $[\text{Li}\{\text{CH}(\text{SiMe}_3)\text{C}(\text{Bu}^t)\text{-N}(\text{SiMe}_3)\}]_2$ [2.43(1) and 2.44(1) Å] [14]. Thus, the Li–C distance in complex **1** is within the usual range compared with relevant compounds [15]. At 1.759(5) Å the P(1)–C(1) distance is in between a single and a double bond. However, the 1.321(5) Å of C(1)–N(1) distance is near to a C–N double bond [5]. The Li(1)–Li(1A) distance of 3.110(17) Å implies that it is too long for bond [16].



Scheme 2.

Fig. 1. An ORTEP representation of the molecular structure of complex **1**.Table 1
Selected bond lengths (Å) and angles (°) for complex **1** (only one dimer)

Bond lengths			
Li(1)–N(1)	1.991(10)	Li(1)···C(1)	2.499(10)
Li(1)–P(1A)	2.592(7)	Li(1)–P(1)	2.641(9)
Li(1)···Li(1A)	3.110(17)	N(1)–C(1)	1.321(5)
P(1)–C(1)	1.759(5)	N(1)–Si(1)	1.717(4)
Bond angles			
C(1)–N(1)–Li(1)	95.8(4)	N(1)–Li(1)–P(1A)	131.6(5)
C(1)–P(1)–Li(1)	65.7(2)	N(1)–Li(1)–P(1)	68.0(3)
Li(1)–P(1)–Li(1A)	72.9(3)	P(1)–Li(1)–P(1A)	107.1(3)
C(2)–C(1)–P(1)	120.1(4)	C(1)–P(1)–Li(1A)	127.9(3)
C(1)–N(1)–Si(1)	133.5(4)	C(8)–P(1)–Li(1)	133.2(3)
Li(1)–N(1)–Si(1)	129.7(4)	N(1)–C(1)–P(1)	117.6(4)

The molecular structure of **2** is presented in Fig. 2, selected bond lengths and angles are listed in Table 2. The crystalline **2** is also a dimer bridged by phosphorus atoms and the K(1)P(1)K(1A)P(1A) ring is planar due to a center of inversion. The 1-aza-3-phosphaallyl unit binds to the potassium atom in an approximate η^3 -mode and at 3.13(7) Å the K(1)–C(1) distance is too long for a bond. However, the P(1)–C(1) distance of 1.85(3) Å corresponds to a single bond and the N(1)–C(1) distance of 1.33(4) Å approximates a double bond [5]. Each K atom also interacts with the carbon atoms of two phenyl rings attached to the phosphorus atom of a ligand and to the carbon atom of another ligand, respectively. These K···C contacts are as follows:

3.32(7) [K(1)–C(2)], 3.36(7) [K(1)–C(3)], 3.42(8) [K(1)–C(8A)] and 3.34(7) Å [K(1)–C(9A)], comparable with those found in $[K\{\eta^4\text{-N}(\text{SiMe}_2\text{Bu}^t)\text{C}(\text{Bu}^t)(\text{CH})_3\text{-SiMe}_2\text{Bu}^t\}]_\infty$ [17] and $[K_3(\text{THF})_2\{\text{PH}(\text{Mes})\}_3]_\infty$ (Mes = 2,4,6-Me₃C₆H₂) [18]. The mean K–P distance of 3.48 Å is longer than those observed for $[KP(\text{H})\text{-C}_6\text{H}_4\text{Bu}_3\text{-2,4,6}]_x$ ranging from 3.181(2) to 3.357(2) Å [19] and $[KP(\text{H})(\text{DMP})_4]$ (DMP = 2,6-dimesitylphenyl) ranging from 3.043(2) to 3.438(2) Å [20], but still falls into usual range. For example, the P–K distances in $[\text{Cp}_2^*\text{ZrP}_3\text{K}(\text{THF})_{1.5}]$ (Cp* = C₅Me₅) vary from 3.37(1) to 3.61(1) Å [21]. At 2.81(8) Å the K(1)–N(1) distance is quite usual, too.

Table 2
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths			
K(1)–N(1)	2.81(8)	K(1)–C(1)	3.13(7)
K(1)–C(2)	3.32(7)	K(1)–C(9A)	3.34(7)
K(1)–C(3)	3.36(7)	K(1)–C(8A)	3.42(8)
K(1)–P(1A)	3.48(7)	K(1)–P(1)	3.48(9)
K(1)–K(1A)	4.86(13)	P(1)–C(1)	1.85(3)
N(1)–C(1)	1.33(4)	N(1)–Si(1)	1.79(3)
Bond angles			
C(1)–N(1)–Si(1)	136.9(9)	K(1)–N(1)–Si(1)	118.9(17)
P(1)–C(1)–N(1)	132.7(10)	N(1)–K(1)–P(1A)	105.9(11)
P(1)–C(1)–C(8)	107.4(19)	N(1)–K(1)–P(1)	54.1(6)
C(1)–P(1)–C(2)	106.0(19)	P(1A)–K(1)–P(1)	91.3(15)
C(1)–P(1)–K(1)	63.6(18)	C(1)–P(1)–K(1A)	90.1(19)

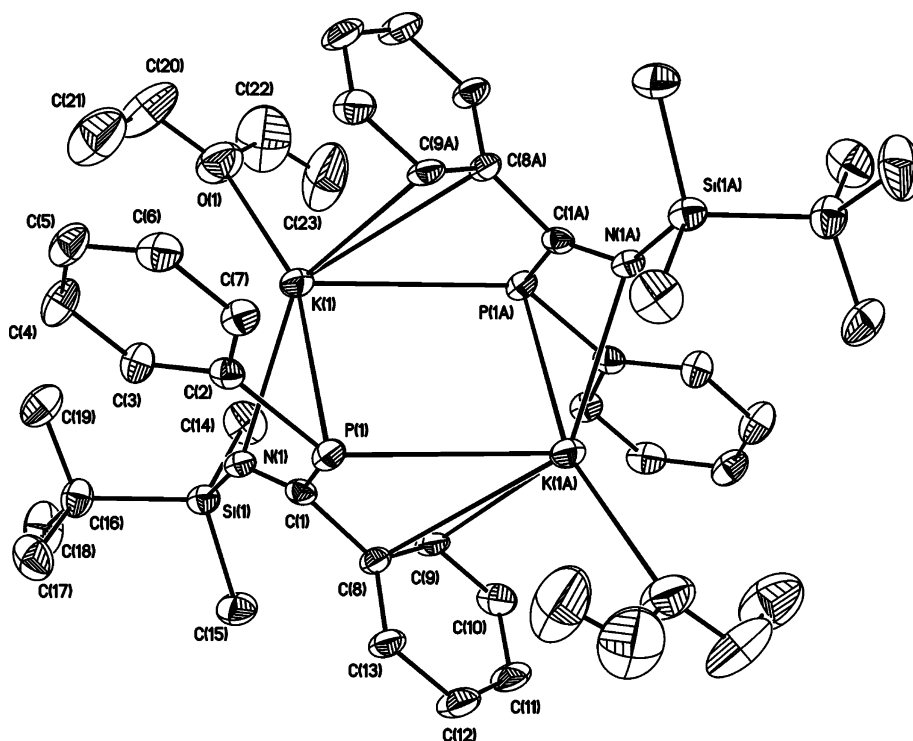


Fig. 2. An ORTEP representation of the molecular structure of complex 2.

The structure of complex 4 is shown in Fig. 3, and selected bond lengths and angles are given in Table 3. The structure reveals that the compound is monomeric in the solid state. The coordination number of the central Sn atom is four and the lone electron pair on tin occupies an additional coordination site. At 2.896 Å the

mean distance between tin and the carbon atom of the PCN unit is too long for a bond [22]. Hence the 1-aza-3-phosphaallyl unit behaves as a bidentate ligand. However, both the four membered rings Sn(1)P(1)C(7)N(1) and Sn(1)P(2)C(26)N(2) are not planar, the torsion angles between the planes Sn(1)–P(1)–C(7) and P(1)–

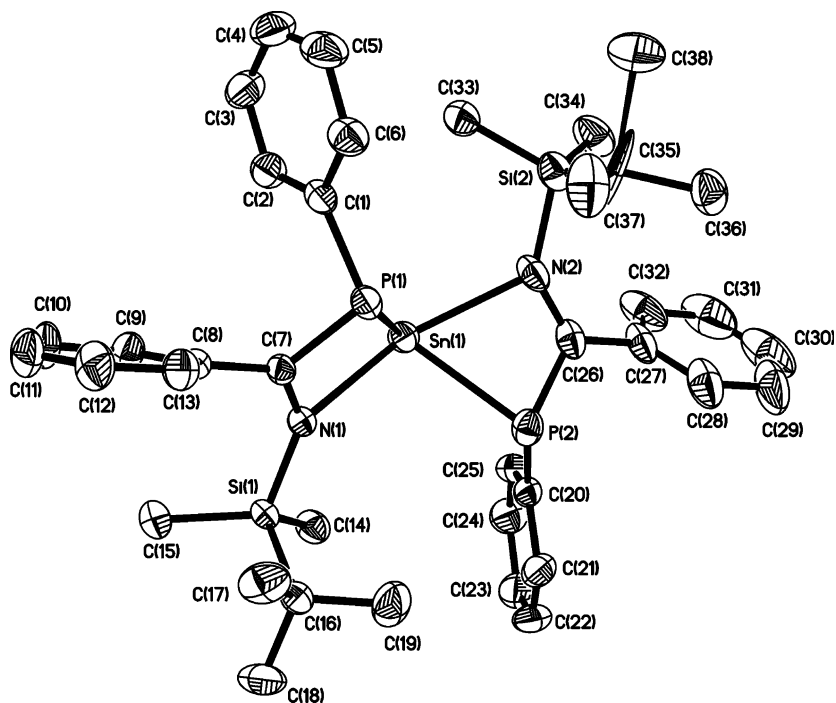


Fig. 3. An ORTEP representation of the molecular structure of complex 4.

Table 3
Selected bond lengths (Å) and angles (°) for complex 4

<i>Bond lengths</i>			
Sn(1)–N(1)	2.459(3)	Sn(1)–N(2)	2.473(4)
Sn(1)–P(2)	2.6127(13)	Sn(1)–P(1)	2.6288(13)
N(1)–C(7)	1.296(5)	N(2)–C(26)	1.330(6)
P(1)–C(7)	1.812(4)	P(2)–C(26)	1.809(5)
N(1)–Si(1)	1.758(4)	N(2)–Si(2)	11.781(4)
P(1)–C(1)	1.829(5)	P(2)–C(20)	1.825(5)
<i>Bond angles</i>			
N(1)–Sn(1)–N(2)	152.53(13)	N(1)–Sn(1)–P(2)	99.73(8)
N(2)–Sn(1)–P(2)	62.82(11)	N(1)–Sn(1)–P(1)	61.90(9)
N(2)–Sn(1)–P(1)	99.25(10)	P(2)–Sn(1)–P(1)	101.86(4)
C(7)–N(1)–Sn(1)	95.5(2)	C(26)–N(2)–Sn(1)	94.8(3)
C(7)–P(1)–C(1)	104.7(2)	C(7)–P(1)–Sn(1)	78.78(14)
C(1)–P(1)–Sn(1)	109.16(15)	C(26)–P(2)–Sn(1)	79.83(17)
N(1)–C(7)–P(1)	113.9(3)	C(20)–P(2)–Sn(1)	109.73(15)
C(20)–P(2)–C(26)	103.9(2)		

C(7)–N(1) and between the planes Sn(1)–P(2)–C(26) and P(2)–C(26)–N(2) are 29.1 and 26.5°, respectively. The mean Sn–N distance of 2.466 Å is longer than those found in Sn(II) amide complexes [21], but is comparable with that in Sn{N(SiMe₃)₂PPH₂}₂ [2.511(6) Å] [23]. At 2.6208 Å the mean Sn–P distance is comparable with those of Sn[C(PMe₂)₃]₂ ranging from 2.598(2) to 2.839(2) Å. In addition, in each of the 1-aza-3-phosphaallyl units the N–C bond corresponds to a double bond (av. 1.313 Å) and the mean P–C distance of 1.811 Å approximates roughly the value a single bond.

Compound 5 consists of centrosymmetric molecules with a P–P bond (Fig. 4). Each phosphorus atom is

three coordinate and the lone electron pair occupies the fourth coordination site. The P–P distance of 2.202(5) Å (Table 4) is comparable with those observed for single bonds in diphosphines [2.205(1)–2.260(1) Å] [24]. The P–C distance of 1.886(6) Å agrees fairly well with the value of a single bond and the C–N distance of 1.288(9) Å is indicative of a double bond [5]. The angles at atom C(1) sum up to 359°, therefore, the atoms C(1), N(1), P(1), C(8) lie in a plane.

3. Experimental

All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium–benzophenone (THF, Et₂O and *n*-hexane) or CaH₂ (CH₂Cl₂) and degassed prior to use. CDCl₃, C₅D₅N and C₆D₆ were purchased from Acros Organics, degassed and stored

Table 4
Selected bond lengths (Å) and angles (°) for complex 5

<i>Bond lengths</i>			
N(1)–C(1)	1.288(9)	N(1)–Si(1)	1.724(6)
P(1)–C(2)	1.856(7)	P(1)–C(1)	1.886(6)
P(1)–P(1A)	2.202(5)	C(1)–C(8)	1.512(12)
<i>Bond angles</i>			
C(2)–P(1)–C(1)	98.5(3)	C(2)–P(1)–P(1A)	101.7(3)
C(1)–P(1)–P(1A)	95.3(3)	N(1)–C(1)–C(8)	129.0(5)
N(1)–C(1)–P(1)	121.5(4)	C(8)–C(1)–P(1)	109.5(5)
C(1)–N(1)–Si(1)	140.5(5)		

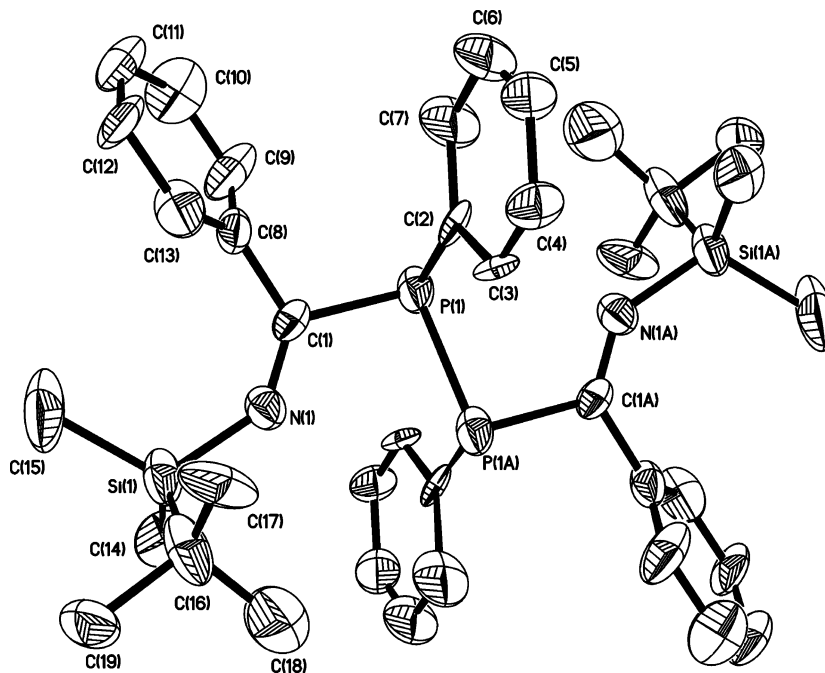


Fig. 4. An ORTEP representation of the molecular structure of complex 5.

over activated molecular sieves (CDCl_3 and $\text{C}_5\text{D}_5\text{N}$) or Na/K alloy (C_6D_6). SnCl_2 and LiBu^n (Acros Organics) were used as received. PhCN was distilled over P_2O_5 and degassed prior to use. $\text{PhP(H)SiMe}_2\text{Bu}^t$ [25] and $\text{ClSnN(SiMe}_3)_2$ [26] were prepared according to the literature. NMR spectra were recorded on a Bruker AV400 or a Bruker DMX500 spectrometer at ambient temperature. The chemical shifts of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra are referenced to internal solvent resonances, the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra to external 85% H_3PO_4 . Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry and the Analytical Center of the University of Science and Technology of China.

3.1. Synthesis of $[\text{Li}\{\text{P(Ph)C(Ph)NSiMe}_2\text{Bu}^t\}(\text{THF})_2]$ (**1**)

A solution of LiBu^n (1.32 ml of a 2.5M solution in hexane, 3.30 mmol) was added to a stirred solution of $\text{PhP(H)SiMe}_2\text{Bu}^t$ (0.74 g, 3.30 mmol) in 20 ml of THF at 0°C . The mixture was warmed to room temperature (r.t.) and stirred for 2 h. The solution was cooled to -50°C and PhCN (0.34 g, 3.30 mmol) was added using a syringe. The mixture was allowed to come up to r.t. and stirred overnight. The solvent was removed in vacuo and the residual solid was washed with hexane. The solid was dissolved in Et_2O and filtered. Concentration of the filtrate afforded red crystals of complex **1** (1.15 g, 86.0%), melting point (m.p.): $166\text{--}168^\circ\text{C}$. Anal. Found: C, 67.88; H, 8.16; N, 3.63. $\text{C}_{23}\text{H}_{33}\text{LiNOPSi}$ requires: C, 68.12; H, 8.20; N, 3.45%. ^1H -NMR (500.13 MHz, C_6D_6): δ (ppm) 0.08 (s, 6H, SiMe_2), 1.13 (s, 9H, Bu^t), 1.29–1.32 (m, 4H, THF), 3.62–3.64 (m, 4H, THF), 6.81–6.87 (m, 1H, Ph), 6.97–7.05 (m, 5H, Ph), 7.51–7.54 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.77 MHz, C_6D_6): δ (ppm) -1.57 (SiMe_2), 20.15 (Bu^t), 25.76 (THF), 27.77 (Bu^t), 69.28 (THF), 125.44, 127.79, 128.68, 136.06 (d, $J = 13.21$ Hz), 143.87 (d, $J = 30.94$ Hz), 147.46 (d, $J = 12.58$ Hz) (Ph), 218.63 (d, $J = 36.22$ Hz, PCN). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.97 MHz, C_6D_6): δ 53.27.

3.2. Synthesis of $[\text{K}\{\text{P(Ph)C(Ph)NSiMe}_2\text{Bu}^t\}]$ (**3**)

To a suspension of small pieces of potassium (0.15 g, 3.84 mmol) in 20 ml of THF was added $\text{PhP(H)SiMe}_2\text{Bu}^t$ (0.67 g, 2.99 mmol) at r.t. The mixture was stirred for 15 h and then refluxed for 30 min. After cooling to r.t., the mixture was filtered to remove excess potassium. PhCN (0.31 g, 3.01 mmol) was added at -80°C and thereafter the solution was stirred for 14 h at r.t. Volatiles were removed in vacuo, the residual solid was recrystallized from Et_2O and dried in vacuo to give yellow orange solid (1.03 g, 94.3%). M.p.: $220\text{--}222^\circ\text{C}$. Anal. Found: C, 62.01; H, 6.70; N, 3.99. $\text{C}_{19}\text{H}_{25}\text{NKPSi}$ requires: C, 62.43; H, 6.89; N, 3.83%. ^1H -NMR (500.13

MHz, $\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ (ppm) -0.09 (s, 6H, SiMe_2), 1.11 (s, 9H, Bu^t), 6.91–6.99 (m, 6H, Ph), 7.53–7.63 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.62 MHz, $\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ (ppm) -1.65 (SiMe_2), 20.01 (Bu^t), 27.88 (Bu^t), 124.73, 127.68, 128.08, 128.38, 129.26 (d, $J = 16.40$ Hz), 131.87, 132.69 (d, $J = 14.29$ Hz), 150.92 (d, $J = 20.32$ Hz) (Ph), 206.45 (d, $J = 56.44$ Hz, PCN). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.97 MHz, $\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ (ppm) 31.61.

Single crystals were obtained by recrystallization of $[\text{K}\{\text{P(Ph)C(Ph)NSiMe}_2\text{Bu}^t\}]$ from diethyl ether and identified crystallographically as $[\text{K}\{\text{P(Ph)C(Ph)NSiMe}_2\text{Bu}^t\}(\text{OEt}_2)_2]$.

3.3. Synthesis of $[\text{Sn}\{\text{P(Ph)C(Ph)NSiMe}_2\text{Bu}^t\}_2]$ (**4**)

To a stirred solution of **1** (0.63 g, 1.56 mmol) in 20 ml of Et_2O was added SnCl_2 (0.15 g, 0.79 mmol) at -80°C . The mixture was warmed up to r.t. and stirred overnight. The solvent was removed and the residue was extracted with CH_2Cl_2 . The extract was concentrated to about 3 ml and an equal volume of Et_2O was added. Yellow orange crystals were obtained after 1 day (0.45 g, 75.0%), m.p.: $158\text{--}160^\circ\text{C}$. Anal. Found: C, 58.98; H, 6.33; N, 3.54. $\text{C}_{38}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_2\text{Sn}$ requires: C, 59.15; H, 6.53; N, 3.63%. ^1H -NMR (400.13 MHz, C_6D_6): δ (ppm) -0.16 (s, 12H, SiMe_2), 0.86 (s, 18H, Bu^t), 6.81–6.87 (m, 8H, Ph), 6.97 (t, $J = 7.44$ Hz, 4H, Ph), 7.31–7.34 (m, 4H, Ph), 7.61–7.65 (m, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.61 MHz, C_6D_6): δ (ppm) -2.21 (b, SiMe_2), 19.78 (Bu^t), 27.76 (Bu^t), 128.13, 128.60, 130.01, 137.73 (d, $J = 17.13$ Hz), 145.13 (d, $J = 15.22$ Hz) (Ph), 213.06 (d, $J = 27.04$ Hz, PCN). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.97 MHz, C_6D_6): δ (ppm) 6.48 with satellites ($J = 777.29$ Hz).

3.4. Reaction of **1** with $\text{ClSnN(SiMe}_3)_2$

A solution of $\text{ClSnN(SiMe}_3)_2$ (0.42 g, 1.34 mmol) in 10 ml of Et_2O was added dropwise at -70°C to a stirred solution of **1** (0.53 g, 1.31 mmol) in 10 ml of Et_2O . The suspension formed was warmed up to r.t. and stirring was continued overnight. White precipitates were removed by filtration and the filtrate was concentrated to form insoluble products which could not be redissolved in organic solvents. The mother liquor was left for about 4 weeks to yield yellow crystals identified as $[\text{P(Ph)C(Ph)=NSiMe}_2\text{Bu}^t]_2$ (**5**) (0.17 g, 39.8%), m.p.: $114\text{--}117^\circ\text{C}$. Anal. Found: C, 69.63; H, 7.49; N, 4.46. $\text{C}_{38}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_2$ requires: C, 69.91; H, 7.73; N, 4.29%. ^1H -NMR (400.13 MHz, C_6D_6): δ (ppm) -0.31 to -0.08 (b, 6H, SiMe_2), -0.02 to 0.15 (b, 6H, SiMe_2), 1.00 (s, 9H, Bu^t), 1.25 (s, 9H, Bu^t), 6.61–7.09 (m, 14H, Ph), 7.30–7.56 (m, 4H, Ph), 7.68–7.88 (b, 4H, Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.61 MHz, C_6D_6): δ (ppm) -3.22 , 3.09 (SiMe_2), 18.49–19.22 (b), 27.25 (Bu^t), 127.09, 128.38, 128.86, 129.34, 136.41–137.42 (m), 145.09 (d, $J = 16.60$

Hz), 145.26 (d, $J = 16.70$ Hz) (Ph), 189.59 (C=N). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.97 MHz, C_6D_6): δ (ppm) 10.45, 16.44.

3.5. Reaction of **3** with PhCN

To a stirred solution of **3** (1.0 g, 2.74 mmol) in 20 ml of THF was added PhCN (0.29 g, 2.82 mmol) at -70°C . The solution was warmed up to r.t. and stirred for 6 h. Volatile compounds were removed in vacuo and the residual solid was dissolved in Et_2O . Filtration of the solution and concentration of the filtrate afforded yellow crystals of **6** (0.91 g, 71.0%), m.p.: $213\text{--}215^\circ\text{C}$. Anal. Found: C, 67.03; H, 6.39; N, 5.76. $\text{C}_{26}\text{H}_{30}\text{N}_2\text{PSiK}$ requires: C, 66.63; H, 6.45; N, 5.98%. ^1H -NMR (400.13 MHz, $\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ (ppm) -0.09 (s, 6H, SiMe_2), 1.10 (s, 9H, Bu^t), 6.68–6.87 (m, 2H, Ph), 6.97–7.03 (m, 3H, Ph), 7.08–7.20 (m, 5H, Ph), 7.61 (d, $J = 7.76$ Hz, 3H, Ph), 8.39 (b, 2H, Ph). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100.61 MHz, $\text{C}_6\text{D}_6 + \text{C}_5\text{D}_5\text{N}$): δ (ppm) -1.49 (SiMe_2), 20.12, 27.99 (Bu^t), 123.41, 124.02, 127.20, 127.74, 129.25 (d, $J = 9.36$ Hz), 132.86 (d, $J = 14.99$ Hz), 135.74, 136.07, 151.73 (d, $J = 37.02$ Hz) (Ph), 169.24 (NCN), 207.57 (d, $J = 59.36$ Hz) (PCN). $^{31}\text{P}\{^1\text{H}\}$ -NMR (161.97 MHz, $\text{C}_6\text{D}_6/\text{C}_5\text{D}_5\text{N}$): δ (ppm) 37.44.

3.6. Crystal structure solution and refinement for compounds **1**, **2**, **4** and **5**

Crystals were mounted in Lindemann capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied to the data. The structures were solved by direct methods using SHELXS-97 [27] and refined against F^2 by full-matrix least-squares using SHELXL-97 [28]. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 5. Since the poor quality of the single-crystal of complex **2**, the quality of the X-ray structure determination is low and that the standard deviations are relatively high.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC no. 186908–186911 for **1**, **2**, **4** and **5**, respectively. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge

Table 5
Details of the X-ray structure determinations of compounds **1**, **2**, **4** and **5**

	1	2	4	5
Empirical formula	$\text{C}_{46}\text{H}_{66}\text{Li}_2\text{N}_2\text{O}_2\text{P}_2\text{Si}_2$	$\text{C}_{23}\text{H}_{35}\text{KNOPSi}$	$\text{C}_{38}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_2\text{Sn}$	$\text{C}_{38}\text{H}_{50}\text{N}_2\text{P}_2\text{Si}_2$
F_w	811.01	439.68	771.61	652.92
Temperature T (K)	293(2)	293(2)	298(2)	293(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.861(3)	14.1(4)	13.269(2)	9.333(16)
b (Å)	14.870(4)	15.1(4)	13.969(3)	10.96(2)
c (Å)	15.096(4)	14.1(4)	14.136(3)	11.13(2)
α ($^\circ$)	78.361(5)	90	100.541(3)	66.96(2)
β ($^\circ$)	74.194(4)	109.3(6)	108.340(2)	75.92(3)
γ ($^\circ$)	81.446(5)	90	117.781(2)	69.54(3)
V (Å ³)	2496.7(11)	2824(145)	2023.9(7)	974(3)
Z	2	4	2	1
μ (mm ^{−1})	0.170	0.299	0.796	0.200
θ Range for data collection ($^\circ$)	1.79–23.37	2.23–24.47	1.65–24.77	2.37–25.02
Number of reflections collected	10904	5815	9967	1723
Number of independent reflections (R_{int})	6891 ($R_{\text{int}} = 0.0603$)	3516 ($R_{\text{int}} = 0.1702$)	6604 ($R_{\text{int}} = 0.0252$)	1720 ($R_{\text{int}} = 0.0017$)
Goodness-of-fit on F^2	0.772	0.832	0.916	0.932
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0575$; $wR_2 = 0.0892$	$R_1 = 0.0664$; $wR_2 = 0.1028$	$R_1 = 0.0444$; $wR_2 = 0.0872$	$R_1 = 0.0583$; $wR_2 = 0.1181$
R indices (all data)	$R_1 = 0.2090$; $wR_2 = 0.1251$	$R_1 = 0.1539$; $wR_2 = 0.1295$	$R_1 = 0.0779$; $wR_2 = 0.0979$	$R_1 = 0.1353$; $wR_2 = 0.1541$
Largest difference peak and hole (e Å ^{−3})	0.197 and -0.133	0.202 and -0.168	0.963 and -0.855	0.113 and -0.131

^a $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

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Acknowledgements

We are grateful for financial support of this work from NSFC (Project Code 20072035) and the Ministry of Education, PRC.

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