Lithium, Potassium, and Tin(II) Complexes of Novel 3-(Iminophosphorano)-1-phosphaallyl and 2-(Iminophosphorano)-1-phosphaallyl Ligands

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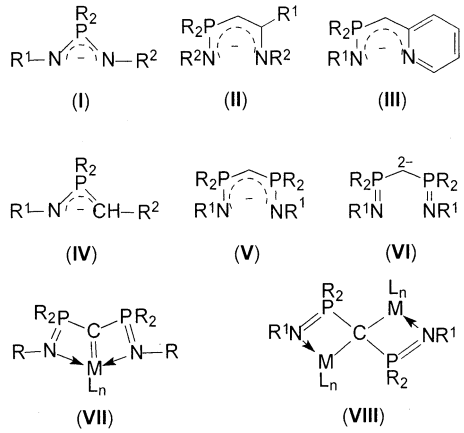
Received May 28, 2002

Reaction of $Ph_2P(C{\equiv}CBu^t){=}NSiMe_3$ (**1**) with KP(H)Ph afforded 3-(iminophosphorano)-1-phosphaallyl potassium, $[K\{P(Ph)C(Bu^t){=}C(H)P(Ph)_2{=}NSiMe_3\}(OEt_2)_3]$ [**3**·$(OEt_2)_3$], which was recrystallized from Et_2O to give a solvent-free complex, $[K\{P(Ph)C(Bu^t){=}C(H)P(Ph)_2{=}NSiMe_3\}]_\infty$ (**3**). Treatment of $Me_2P(C{\equiv}CPh){=}NSiMe_3$ (**2**) with LiP(R)Ph (R = H, $SiMe_2Bu^t$) formed 2-(iminophosphorano)-1-phosphaallyllithium, $[Li\{P(Ph)C\{{=}C(R)Ph\}P(Me)_2{=}NSiMe_3\}(THF)_n]$ (R = H, n = 1.5, **4**; R = $SiMe_2Bu^t$, n = 2, **5**), via a hydrogen or $SiMe_2Bu^t$ group 1,3-P → C migration. Reaction of **4** or **5** with $SnCl_2$ in 2:1 ratio in Et_2O yielded P, N-chelating tin(II) complexes $[Sn\{P(Ph)C\{{=}C(R)Ph\}P(Me)_2{=}NSiMe_3\}_2]$ (R = H, **6**; R = $SiMe_2Bu^t$, **7**). Complex **6** was also obtained by treatment of $ClSnN(SiMe_3)_2$ with 1 equiv of **4**. X-ray data are provided for **3**, **5**, and **6**. Complex **3** is polymeric in the solid state without coordinated solvent molecules, whereas both crystalline **5** and **6** are monomeric.

Introduction

Phosphoraniminato and iminophosphorane ligands, especially functionalized iminophosphorane ligands, have attracted intensive attention in recent years. The nature of the highly polar P−N bond in the ligand makes a compound of this kind versatile in both coordinate and organometallic chemistry.[1−3] Examples include N, N-chelating ligands such as iminophosphoamides (**I** in Chart 1),[4] 3-(iminophosphorano)-1-azaallyls (**II** in Chart 1),[5] and (iminophosphorano)methanides (**III** in Chart 1),[6] and C, N-chelating ligands such as iminophosphoranato with a variety of substituents (**IV** in Chart 1).[7] Bis(iminophosphorano)methanides (**V** in Chart

Chart 1



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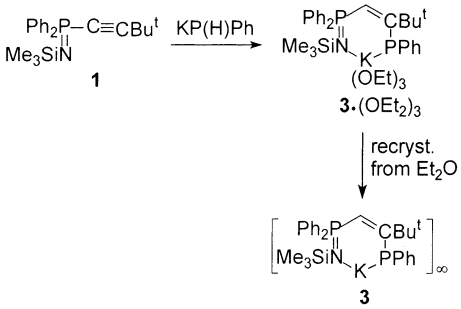
10.1021/om020422c CCC: $22.00
Publication on Web 09/24/2002

1) can act as N, N- or C, N-chelating ligands depending on the nature of the metal atom and other ligands on the metal.[8] These anions are excellent chelating agents for a wide range of metals, including main group and transition metals as well as lanthanides. Recently, new dianionic ligands (**VI**)[9] were reported and a series of main group and transition metal complexes based on these and related ligands have been obtained.[6,10] Such ligands showed versatile bonding modes and reactivity. For example, complexes of group 4 metals and samarium with such ligands reveal carbon−metal double-bond character (**VII** in Chart 1),[10a,11] while the complexes of chromium,[12] aluminum,[13] and group 14 metals[10b] display bonding modes as shown in structure **VIII** (Chart 1) or similar structures. We aimed to design and synthesize new ligands that combine the advantages of iminoposphoranes and phosphides: this class of ligands possess a combination of hard and soft donor (or bonding) atoms and have different features associated with each donor atom that provided unique reactivity to their metal complexes.[14] A number of neutral P, N ligands have been known.[15] However, anionic P, N ligands are relatively rare.[16] We report here the synthesis and characterization of lithium, potassium, and tin(II) derivatives of monoanionic P, N-centered 3- or 2-(iminophosphorano)-1-phosphaallyl ligands.

Results and Discussion

The *P*-alkynyl iminophosphoranes $R_2P(C{\equiv}CR^1){=}NSiMe_3$ (R = Ph, R^1 = Bu^t, **1**; R = Me, R^1 = Ph, **2**) were prepared in good yields by stoichiometric reaction of $R_2P(Br){=}NSiMe_3$ (R = Ph, Me)[17] with appropriate alkynyllithium.[18] Both **1** and **2** are colorless distillable liquids. Their EI mass spectra showed respective molecular ions. The IR spectrum of each compound exhibited carbon−carbon triple-bond absorption. The ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectral data were also consistent with the presumed structures. Treatment of **1** with an equimolar amount of KP(H)Ph in THF resulted in a deep red solution. Removal of THF and crystallization from Et_2O afforded a red crystalline potassium complex, $[K\{P(Ph)C(Bu^t){=}CHP(Ph)_2{=}NSiMe_3\}(OEt_2)_3]$, [**3**·$(OEt_2)_3$], which was recrystallized slowly from Et_2O at room temperature to form solvent-free crystals of **3** (Scheme 1). It seems that the Et_2O molecules in **3**·$(OEt_2)_3$ are loosely bound in **3**. LiP(H)Ph or NaP(H)Ph reacted similarly with **1**, but only oily products were obtained. The ^{1}H NMR spectrum of each oily product showed the presence of appropriate groups with impurities. No attempts were made to further purify them. Formation of complex **3** is postulated to involve a Michael-type addition of $[P(H)Ph]^-$ to iminophosphorane **1** followed by a 1,3-hydrogen shift from phosphorus to carbon. The related examples include base-catalyzed Michael addition of diphenylphosphane to diphenyl vinyl iminophosphoranes[19] and addition of primary amines to 1-alkynyl phosphine oxides.[20] Complex **3**·$(OEt_2)_3$ is soluble in Et_2O and benzene, but solvent-free crystalline **3** is only partly soluble in Et_2O and slightly soluble in benzene. The ^{1}H NMR spectrum of **3**·$(OEt_2)_3$ exhibited two sets of signals of the ligand with the same intensity of corresponding signals, showing that **3**·$(OEt_2)_3$ may be dimeric, and in the dimer the two ligands adopt different coordination patterns. Interestingly, after the solution was left standing for a week at room temperature, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra displayed only one set of signals of the ligand. The $^{31}P\{^1H\}$ NMR spectrum gave P(III) and P(V) signals at 4.48 and 19.64 ppm, respectively. This is attributed to a slow change of the coordination modes on K in solution.

Scheme 1



1 **3**

Crystalline complex **3** is a polymer, revealed by single-crystal X-ray diffraction (Figure 1). Figure 2 illustrates how the structure propagates. Each potassium atom is coordinated by the nitrogen atom and the P(III) atom

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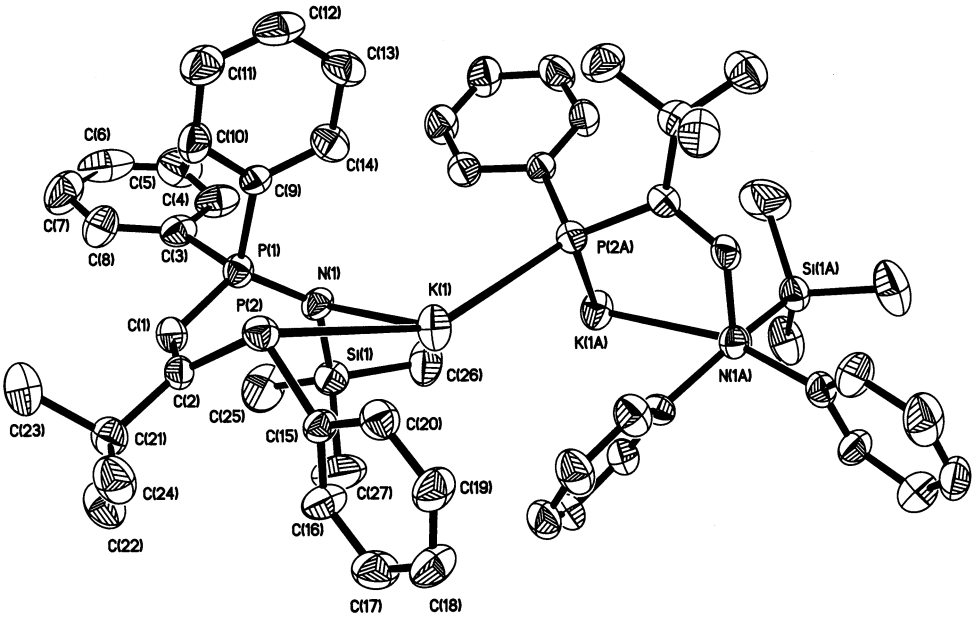

Figure 1. ORTEP representation of [K{P(Ph)C(Bu^t)=C(H)P(Ph)$_2$=NSiMe$_3$}] with neighboring ligand. Selected bond lengths (Å) and angles (deg): K(1)−N(1), 2.831(7); K(1)−C(26A), 3.378(11); K(1)−P(2), 3.265(4); K(1)−Si(1), 3.626(4); K(1)−C(15), 3.276(8); N(1)−P(1), 1.566(7); K(1)−P(2A), 3.278(3); P(1)−C(1), 1.760(8); K(1)−C(11A), 3.309(10); C(1)−C(2), 1.355(10); P(2)−C(2), 1.800(8); N(1)−K(1)−P(2), 77.82(15); P(2)−K(1)−P(2A), 153.25(8); N(1)−K(1)−P(2A), 95.34(15); C(2)−P(2)−K(1), 110.5(3); C(1)−P(1)−N(1), 119.2(4); C(1)−C(2)−P(2), 117.4(6); C(2)−C(1)−P(1),129.3(7).

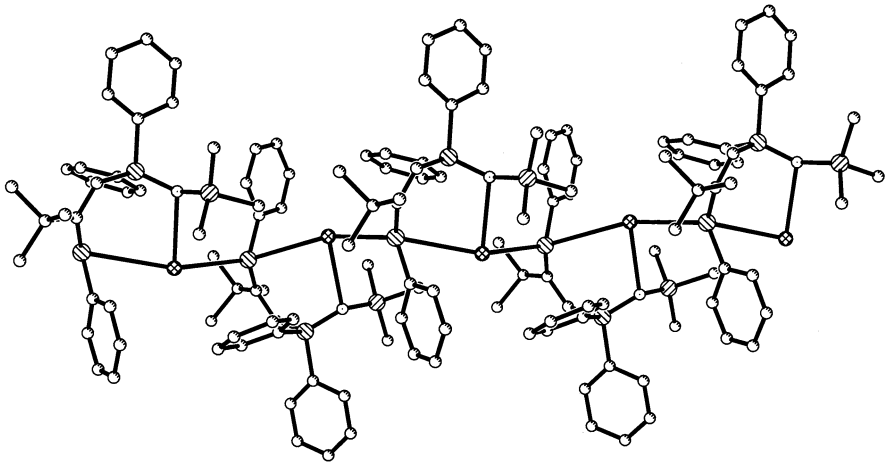

Figure 2. Representation of crystalline complex **3**, showing how the structure propagates.

from one ligand and by the P(III) atom from an adjacent ligand in the polymeric chain. Thus, each P(III) atom acts as a bridge between two potassium atoms and the [P(Ph$_2$)=NSiMe$_3$] group chelates as a sidearm to a potassium via its nitrogen coordination. There are also interactions between K(1) and Si(1), and C(15) and C(11A), respectively [K(1)···Si(1) = 3.626(4) Å, K(1)···C(15) = 3.276(8) Å, K(1)···C(11A) = 3.309(10) Å], and agostic interactions with the protons of the trimethylsilyl methyl groups on Si(1) and Si(1A), respectively [K(1)···H(27c) = 3.017 Å, K(1)···H(26Ac) = 2.793 Å]. The K(1), N(1), P(1), C(1), C(2), and P(2) atoms form a twisted six-membered ring. The K(1)−N(1) distance of 2.831(7) Å is comparable to those found in [K{CH(Ph$_2$P=NSiMe$_3$)$_2$}(THF)$_2$] [2.798(2) and 2.731(2) Å, respectively][8c] and [{{N(SiMe$_3$)C(Ph)CH}$_2$C$_5$H$_3$N-2,6}{K(TMEDA}$_2$] [2.667(4)−2.961(6) Å].[21] The K(1)−P(2) and K(1)−P(2A) distances of 3.265(4) and 3.278(3) Å, respectively, are comparable to those in [KP(H)C$_6$H$_2$-Bu$^t_3$-2,4,6]$_x$, ranging from 3.181(2) to 3.357(2) Å.[22] The P(2)−C(2) distance of 1.800(8) Å is longer than that of a delocalized system, for example, 1.757(6) Å in [Li(TME)$_3$}{2,4,6-Bu$^t_3$C$_6$H$_2$PC(Ph)C(H)Ph}] (**A**),[23] but shorter than a normal P−C single bond, as found in **A** [1.879(7) Å].[23] The 1.355(10) Å C(1)−C(2) distance is comparable to the corresponding distance in **A** [1.366(6) Å].[23] The facts imply that the negative charge is partly delocalized on the P(2)−C(1)−C(2) unit. The C(1), C(2), P(1), and N(1) atoms are not coplanar, and the torsion angle between the C(1)C(2)P(1) plane and the C(2)P(1)N(1) plane is 67.6°. The P(1)−N(1) distance of 1.566(7) Å is indicative of a P−N double bond.[24]

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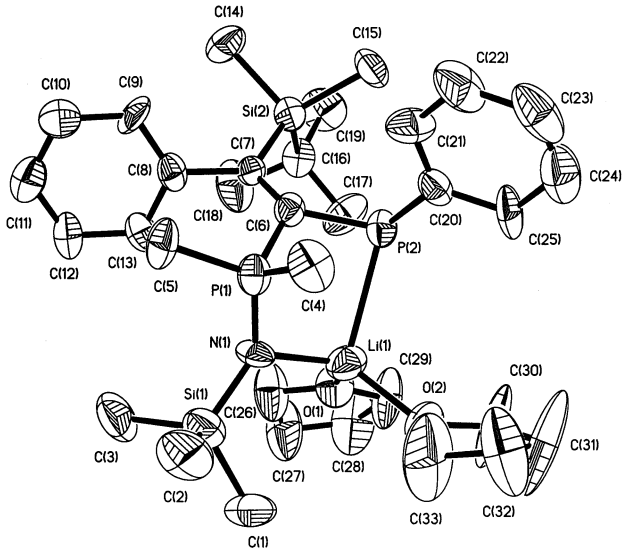
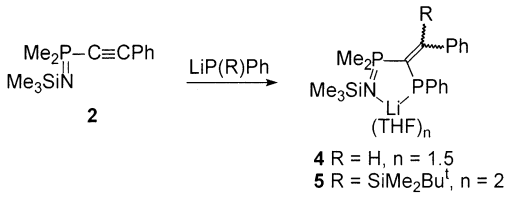


Figure 3. ORTEP representation of complex **5**. Selected bond lengths (Å) and angles (deg): Li(1)−N(1), 2.037(15); Li(1)−P(2), 2.652(12); Li(2)−N(2), 2.022(13); Li(2)−P(4), 2.605(12); P(2)−C(6), 1.835(7); C(6)−C(7), 1.340(8); P(1)−C(6), 1.835(7); P(1)−N(1), 1.567(5); N(1)−Li(1)−P(2), 94.9(5); P(2)−C(6)−C(7),121.0(6); P(2)−C(6)−P(1), 111.5(4); P(1)−N(1)−Li(1), 109.2(4); C(6)−P(2)−Li(1), 86.3(4); C(6)−P(1)−N(1), 110.1(3).

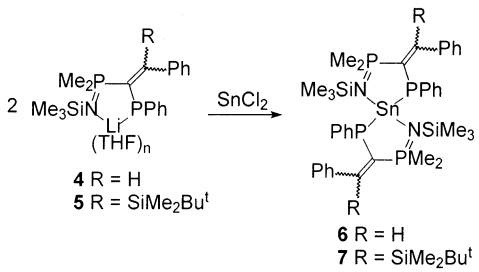
In contrast to the reaction described in Scheme 1, the reaction of **2** with LiP(R)Ph (R = H, $SiMe_2Bu^t$)[25] gave different results (eq 1). In the reaction, $[P(R)Ph]^-$



(1)

attacks at the triple-bond carbon adjacent to P(V), followed by a 1,3 shift of hydrogen or the $SiMe_2Bu^t$ group from phosphorus to carbon. Compared with the reaction shown in Scheme 1, this different addition orientation is attributed to polar reversion of the carbon−carbon triple bond in **2** because of changes of substituted groups on the P(V) and the triple-bond carbon. It seems that the steric factors are nonessential in the reactions. The $^{31}P\{^1H\}$ NMR spectrum of each of **4** and **5** showed two sharp signals corresponding to P(III) and P(V) atoms, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra of each complex showed signals of appropriate groups, consistent with the proposed structures. The structure of **5** was also established by single-crystal X-ray diffraction. The complex is monomeric and crystallizes with two molecules in the asymmetric unit (Figure 3, only one molecule shown). The lithium atom is in a distorted tetrahedral environment and is rounded by N(1) and P(2) of the ligand and two THF molecules. The Li(1), P(2), C(6), P(1), and N(1) atoms constitute a five-membered metallacycle. The $SiMe_2Bu^t$ group is *trans* to the $[P(Me)_2{=}NSiMe_3]$ group. The Bu^t group on Si(2) adopts a *trans* conformation to the phenyl group on P(2), thus minimizing steric repulsions between the groups. The Li(1)−N(1) distance of 2.037(15) Å is within the normal range as observed for lithium amides[26] and lithium iminophosphorances.[7d,f,27] The Li(1)−P(2) distance of 2.652(12) Å is longer than those found in $[\{Li(THF)_2\}_2\{PhPCH_2CH_2PPh\}]$ (av 2.56 Å),[28] $[\{Li(TMEDA)\}_2C_6H_4(PPh)_2\text{-}1,2]$ (av 2.58 Å),[29] and $[Li(THF)_2\{MePC_6H_4\text{-}2\text{-}CH(C_6H_4\text{-}2\text{-}CHNMe_2)NMe_2\}]$[30] (av 2.52 Å), but shorter than those of $[Li\{CH_2P(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}]_4$ (av 2.736 Å).[31] The 1.835(7) Å P(2)−C(6) distance is longer than the corresponding distance in **3** [1.800(8) Å], but slightly shorter than a P−C single bond.[23] The 1.340(8) Å C(6)−C(7) distance is close to a carbon−carbon double bond.[23] The findings reveal that delocalization of charge on the P(1)−C(6)−C(7) unit is very limited. It may be better to describe the P(1)−C(6)−C(7) unit as a combination of a carbon−carbon double bond and an anionic P center.

The ligand transfer reaction was carried out by reaction of **4** and **5**, respectively, with $SnCl_2$ in a 2:1 ratio in Et_2O (eq 2). The homoleptic tin(II) complexes



(2)

with the P, N-chelating ligands, **6** and **7**, were obtained in relatively low yields. Both **6** and **7** are solvent-free red crystals. Complex **6** is air sensitive, while **7** is comparatively stable to the air in the solid state. Crystalline **7** was exposed to the air for a week without decomposition, but is air-sensitive in an ether solution. The ^1H and $^{13}C\{^1H\}$ NMR spectra of each of complexes **6** and **7** exhibited a set of signals, showing an equivalent coordination mode of the two ligands. The NMR spectra also showed that the two *P*-methyls in a ligand had different chemical environments, consistent with their respective chemical structure. The $^{31}P\{^1H\}$ NMR spectrum of each complex showed two signals, and the upfield one displayed satellites by tin coupling.

Attempts to prepare heteroleptic tin(II) complexes with the P, N ligands by reactions of **4** with an equimolar portion of $SnCl_2$ and $ClSnN(SiMe_3)_2$,[32] re-

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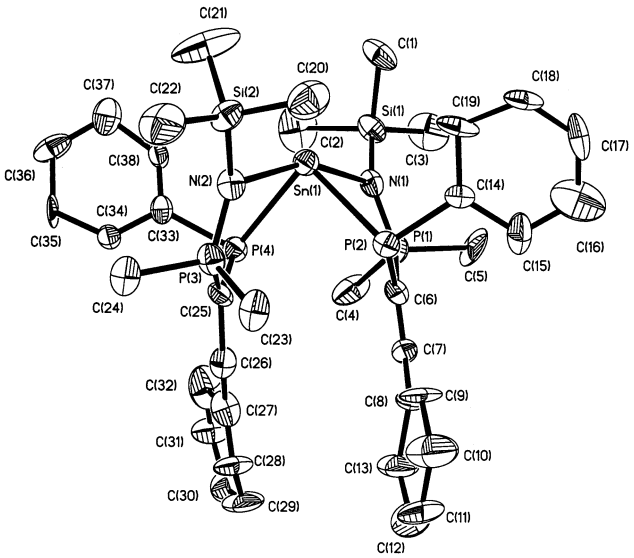

Figure 4. ORTEP representation of complex **6**. Selected bond lengths (Å) and angles (deg): Sn(1)−N(1), 2.532(18); Sn(1)−N(2), 2.562(15); Sn(1)−P(2), 2.591(7); Sn(1)−P(4), 2.598(7); P(1)−N(1), 1.58(2); P(3)−N(2), 1.592(18); P(1)−C(6), 1.82(3); P(2)−C(6), 1.81(3); C(6)−C(7), 1.31(3); N(1)−Sn(1)−N(2),159.80(13); N(2)−Sn(1)−P(4), 78.4(4); N(1)−Sn(1)−P(4), 87.7(5); N(1)−Sn(1)−P(2), 78.7(5); P(2)−Sn(1)−P(4), 92.49(4); P(1)−N(1)−Sn(1), 115.5(10); P(2)−C(6)−P(1), 120.0(13); P(2)−C(6)−C(7), 124(2).

spectively, were unsuccessful. The reaction with the former produced unidentified species, and with the latter afforded complex **6** in 42.1% yield.

The structure of complex **6** was further confirmed by single-crystal X-ray diffraction. The structure (Figure 4) reveals that the molecule is monomeric in the solid state. The coordination number of the central Sn is four, and the lone pair of electrons on tin occupies an additional coordination site. The N(1)−Sn(1)−P(2) angle is almost equal to that of N(2)−Sn(1)−P(4), 78.7(5)° and 78.4(4)°, respectively. The N(1)−Sn(1)−N(2) angle of 159.80(13)° is much wider than that of P(2)−Sn(1)−P(4) [92.49(4)°]. The mean Sn−N distance of 2.547 Å is comparable with the Sn−N(1) distance of 2.511(6) Å in $[Sn[\{N(SiMe_3)_2PPh_2\}_2]$.[33] The Sn−P bond distance of average 2.595 Å falls within the range reported for bonds between the anionic P center and Sn(II) (2.60−2.80 Å).[34] In addition, the structure also shows that the phenyl group on the C−C double bond is *trans* to the $[P(Me)_2{=}NSiMe_3]$ group on the other side of the C−C double bond.

Conclusions

We have described the nucleophilic addition of $[P(R)Ph]^-$ (R = H or $SiMe_2Bu^t$) to a *P*-alkynyl iminophosphorane, and through the reaction novel anionic P, N ligands have been synthesized. Electronic effects of the substituted groups on the carbon−carbon triple bond and on the P(V) determine the addition orientations, while the steric factors are nonessential. In the lithium and potassium complexes, the negative charge is partly delocalized or almost localized on phosphorus through comparison of their bond lengths and geometries with those of delocalized anionic 1-phosphaallyl systems. The 2-(iminophosphorano)-1-phosphaallyl ligands are suitable for the preparation of tin(II) compounds. We are actively investigating the action of the ligands in transition metal chemistry.

Experimental Section

General Procedures. All experiments were performed under nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium-benzophenone (THF, Et_2O, and *n*-hexane) or CaH_2 (CH_2Cl_2) and degassed prior to use. $CDCl_3$ and C_6D_6 were purchased from Acros Organics and degassed and stored over activated molecular sieves ($CDCl_3$) or Na/K alloy (C_6D_6). PhC≡CH and $LiBu^n$ were purchased from Acros Organics and used as obtained. $R_2P(Br){=}NSiMe_3$ (R = Me, Ph),[17] $PhP(SiMe_2Bu^t)Li$,[25] $ClSnN(SiMe_3)_2$,[32] and $Bu^tC{\equiv}CH$[35] were prepared according to the literature. NMR spectra were recorded on a Bruker av400 spectrometer at ambient temperature. The chemical shifts of ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to internal solvent resonances; the $^{31}P\{^1H\}$ NMR spectra are referenced to external 85% H_3PO_4. Infrared spectra were recorded as neat liquid films on a Bruker VECTOR-22 spectrometer. EI mass spectra were measured with a Perkin-Elmer TURBOMASS instrument. Elemental analyses were performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Synthesis of $R_2P(C{\equiv}CR^1){=}NSiMe_3$ (R = Ph, $R^1 = Bu^t$, 1; R = Me, R^1 = Ph, 2). A solution of $LiBu^n$ (14.7 mL of a 2.5 M solution in hexane, 36.6 mmol) was added dropwise to a stirred solution of $Bu^tC{\equiv}CH$ (3.0 g, 36.6 mmol) in 30 mL of Et_2O at −70 °C. The mixture was stirred at room temperature for 2 h and then added dropwise to a cooled (−70 °C) Et_2O solution of $Ph_2P(Br){=}NSiMe_3$ prepared in situ from $Ph_2PN(SiMe_3)_2$ (13.8 g, 40 mmol) and Br_2 (6.4 g, 40 mmol).[17] The mixture was allowed to warm to room temperature and stirred overnight. Solvent was removed in vacuo, and the residue was extracted with *n*-hexane. The extract was concentrated and then distilled at reduced pressure to afford a colorless oil of compound **1** (8.5 g, 66.1%), bp 122−125 °C/0.03 mmHg. IR: $\nu_{C\equiv C}$ (cm^{-1}) 2166. ^1H NMR (400.1 MHz, $CDCl_3$, 298 K): δ 0.07 (s, 9H, $SiMe_3$), 1.35 (s, 9H, Bu^t), 7.39−7.45 (m, 6H, Ph), 7.80−7.85 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K): δ 4.51 (d, J = 4.43 Hz), 28.78 (d, J = 2.31 Hz), 30.43, 76.82 (d, J = 144.26 Hz), 114.00 (d, J = 22.84 Hz), 128.83, 128.96, 131.38, 131.50, 131.53, 137.16, 138.39. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 298 K): δ −20.52. MS(EI): m/z 353 [M^+]. Anal. Calcd for $C_{21}H_{28}NPSi$: C, 71.35; H, 7.98; N, 3.96. Found: C, 71.08; H, 7.75; N, 4.07.

Compound 2 was prepared similarly. To a stirred solution of PhC≡CH (8.1 mL, 73.75 mmol) in 100 mL of Et_2O was added dropwise a solution of $LiBu^n$ (29.5 mL of a 2.5 M solution in hexane, 73.75 mmol) at −60 °C. The reaction mixture was stirred at room temperature for 2 h and then was added dropwise to a stirred solution of $Me_2P(Br){=}NSiMe_3$ (16.8 g, 73.68 mmol) in 100 mL of Et_2O at −80 °C. The mixture was stirred overnight at room temperature, and the solvent was removed in vacuo. The residue was extracted with hexane, and then successive concentration and distillation of the extract at reduced pressure yielded a colorless oil identified as **2** (15.47 g, 84.3%), bp 90−93 °C/0.1 mmHg. IR: $\nu_{C\equiv C}$ (cm^{-1}) 2174. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.42 (s, 9H, $SiMe_3$), 1.30 (d, J = 14.07 Hz, 6H, PMe), 6.88−6.95 (m, 3H, Ph), 7.34−7.39

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(m, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 2.52, 18.56 (d, J = 88.53 Hz), 20.66 (d, J = 85.70 Hz), 78.50, 84.34, 123.29, 129.0, 129.26, 132.82. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 38.97. MS (EI): m/z 249 [M^+]. Anal. Calcd for $C_{13}H_{20}NPSi$: C, 62.62; H, 8.08; N, 5.62. Found: C, 62.78; H, 7.85; N, 5.51.

Synthesis of [K{P(Ph)C(Bu^t)C(H)P(Ph)$_2$=NSiMe$_3$}-(OEt$_2$)$_3$] [3·(OEt$_2$)$_3$]. To a suspension of potassium (0.08 g, 2.05 mmol) in 20 mL of THF was added $PhPH_2$ (0.21 g, 1.91 mmol) at room temperature. After the potassium disappeared, the resulting solution was added dropwise to a stirred solution of $Ph_2P(C{\equiv}CBu^t){=}NSiMe_3$ (0.67 g, 1.91 mmol) in 10 mL of THF at −80 °C. The reaction mixture was stirred at room temperature for 6 h. Volatiles were removed at reduced pressure, and the residual solid was washed with *n*-hexane. The solid was dissolved in Et_2O and then filtered. Concentration of the filtrate in vacuo afforded deep red crystals of **3**·$(OEt_2)_3$ (0.58 g, 41.9%), mp >300 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): 0.21 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$), 1.07 (s, 9H, Bu^t), 1.09 (t, J = 7.09 Hz, 36H, Et_2O), 1.57 (s, 9H, Bu^t), 3.24 (q, J = 7.09 Hz, 24H, Et_2O), 5.67−5.77 (m, 2H, CH), 6.72−6.78 (m, 1H, Ph), 6.81−6.98 (m, 10H, Ph), 7.21−7.34 (m, 5H, Ph), 7.43−7.54 (m, 6H, Ph), 7.63−7.72 (m, 3H, Ph), 7.68−7.85 (m, 5H, Ph). After one week the NMR spectra of the sample exhibited only one set of signals. ^1H NMR (400.1 MHz, C_6D_6, 298 K): 0.19 (s, 9H, $SiMe_3$), 1.11 (t, J = 6.94 Hz, 18H, Et_2O), 1.57 (s, 9H, Bu^t), 3.25 (q, J = 6.94 Hz, 12H, Et_2O), 5.83 (t, J = 27.48 Hz, 1H, CH), 6.97−7.13 (m, 11H, Ph), 7.87−7.90 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 5.11, 31.59 (d, J = 8.8 Hz), 34.05, 122.91, 129.93, 130.39, 130.81, 131.74 (d, J = 8.95 Hz), 132.06 (dd, J = 126.14, 19.02 Hz), 133.71 (d, J = 16.20 Hz), 135.87 (d, J = 21.60 Hz), 140.88, 141.87, 155.38. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ 4.48, 19.64. Recrystallization of **3**·$(OEt_2)_3$ from Et_2O at room temperature gave [K{P(Ph)C(Bu^t)C(H)P(Ph)$_2$=NSiMe$_3$}]$_\infty$ identified crystallographically.

Synthesis of [Li{P(Ph)C{=C(H)Ph}P(Me)$_2$=NSiMe$_3$}-(THF)$_{1.5}$] (4). A solution of LiBu^n (1.74 mL of a 2.5 M solution in hexane, 4.35 mmol) was added dropwise to a stirred solution of $PhPH_2$ (0.48 g, 4.36 mmol) in 15 mL of THF at 0 °C. The mixture was stirred at room temperature for 2 h and then added dropwise to a solution of $Me_2P(C{\equiv}CPh){=}NSiMe_3$ (1.1 g, 4.42 mmol) in 10 mL of THF at −80 °C. The mixture was stirred at room temperature for 6 h. Volatiles were removed in vacuo. The residue was dissolved in Et_2O and filtered. Concentration of the filtrate gave purple crystals of complex **4** (1.07 g, 51.2%), mp 120 °C (dec). ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.23 (s, 9H, $SiMe_3$), 1.44 (d, J = 11.68 Hz, 6H, PMe), 1.23−1.26 (m, 6H, THF), 3.44−3.47 (m, 6H, THF), 6.74−6.80 (m, 1H, =CH), 6.92−7.02 (m, 4H, Ph), 7.13−7.17 (m, 2H, Ph), 7.32−7.36 (t, J = 7.32 Hz, 2H, Ph), 7.93 (d, J = 7.96 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 4.91, 19.81 (d, J = 59.58 Hz), 25.88, 68.83, 121.32, 126.61, 127.72 (d, J = 7.04 Hz), 129.15, 130.25 (d, J = 18.91 Hz), 131.00 (d, J = 2.31 Hz), 131.51, 134.70 (d, J = 17.20 Hz), 137.25 (d, J = 23.23 Hz), 139.63 (d, J = 24.75 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ −46.60, 25.76. Anal. Calcd for $C_{19}H_{26}NP_2SiLi$ (THF escaped from the complex): C, 62.46; H, 7.17; N, 3.83. Found: C, 62.11; H, 7.55; N, 3.51.

Synthesis of [Li{P(Ph)C{=C(Ph)SiMe$_2$Bu^t}P(Me)$_2$=NSiMe$_3$}(THF)$_2$] (5). A solution of LiBu^n (0.89 mL of a 2.5 M solution in hexane, 2.23 mmol) was added dropwise to a stirred solution of $PhP(H)SiMe_2Bu^t$ (0.5 g, 2.23 mmol) in 15 mL of THF at room temperature. The mixture was stirred for 2 h and then added dropwise to a solution of $Me_2P(C{\equiv}CPh){=}NSiMe_3$ (0.57 g, 2.29 mmol) in 10 mL of THF at −80 °C. The mixture was stirred at room temperature for 6 h. Volatiles were removed in vacuo, and the residue was extracted with *n*-hexane. Concentration of the extract afforded purple crystals of complex **5** (0.73 g, 51.1%), mp 142−144 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.06 (s, 9H, $SiMe_3$), 0.14−0.50 (b, 3H, SiMe), 0.82−1.14 (b, 3H, SiMe), 1.29 (s, 9H, Bu^t), 1.42−1.46 (m, 8H, THF), 3.61−3.64 (m, 8H, THF), 6.83 (t, J = 7.21 Hz, 1H, Ph), 7.03−7.07 (m, 1H, Ph), 7.11−7.18 (m, 6H, Ph), 7.38 (t, J = 6.87 Hz, 2H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 0.85, 4.86, 20.29, 26.05, 30.76, 68.97, 158.26 (dd, J = 63.38, 58.95 Hz), 166.27 (dd, J = 30.58, 8.35 Hz), 19.75, 126.39, 127.99 (d, J = 4.23 Hz), 129.18 (d, J = 8.81 Hz), 129.43, 148.26 (t, J = 11.67 Hz), 159.03, 159.62. $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ −27.72, 17.74. Anal. Calcd for $C_{25}H_{40}NP_2SiLi$: C, 62.60; H, 8.41; N, 2.92. Found: C, 62.89; H, 8.27; N, 3.69.

Synthesis of [Sn{P(Ph)C{=C(H)Ph}P(Me)$_2$=NSiMe$_3$}$_2$] (6). $SnCl_2$ (0.30 g, 1.58 mmol) was added to a stirred solution of **4** (1.67 g, 3.25 mmol) in 30 mL of Et_2O at −80 °C. The mixture was warmed to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2. Concentration of the extract in vacuo yielded red crystals of complex **6** (0.60 g, 45.0%), mp 274.5−275.5 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.26 (s, 18H, $SiMe_3$), 0.94 (d, J = 12.19 Hz, 6H, PMe), 6.72 (dd, J = 18.76, 25.30 Hz, 2H, CH), 6.91−6.97 (m, 4H, Ph), 7.05−7.13 (m, 8H, Ph), 7.82−7.85 (m, 4H, Ph), 7,96 (d, J = 7.25 Hz, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 5.41, 20.97 (dd, J = 59.45, 11.97 Hz), 24.68 (d, J = 52.51 Hz), 126.17, 129.00, 129.10, 132.28 (d, J = 10.56 Hz), 133.26 (d, J = 12.78 Hz), 138.48(d, J = 22.03 Hz), 140.37 (d, J = 33.30 Hz), 145.50 (dd, J = 59.66, 81.99 Hz), 147.30 (t, J = 17.30 Hz). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ −42.28 with satellites (J = 1077.59 Hz), 31.09. Anal. Calcd for $C_{38}H_{52}N_2P_4Si_2Sn$: C, 54.62; H, 6.27; N, 3.35. Found: C, 54.63; H, 6.23; N, 3.38.

Synthesis of [Sn{P(Ph)C{=C(Ph)SiMe$_2$Bu^t}P(Me)$_2$=NSiMe$_3$}$_2$] (7). $SnCl_2$ (0.26 g, 1.37 mmol) was added to a stirred solution of complex **5** (1.63 g, 2.62 mmol) in 30 mL of Et_2O at −80 °C. The mixture was allowed to reach room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2. The volume of the extract was reduced to about 3 mL, and then 3 mL of Et_2O was added. The solution was stored overnight at 0 °C to afford red crystals of complex **7** (0.38 g, 26.0%), mp 282−284 °C. ^1H NMR (400.1 MHz, C_6D_6, 298 K): δ 0.16 (s, 18H, $SiMe_3$), 0.25 (s, 6H, SiMe), 0.63 (s, 6H, SiMe), 1.04 (s, 18H, SiMe), 1.11 (d, J = 14.04 Hz, 6H, PMe), 1.53 (d, J = 12.68 Hz, 6H, PMe), 6.97−7.06 (m, 10H, Ph), 7.27 (t, J = 7.2 Hz, 4H, Ph), 7.34 (t, J = 7.6 Hz, 2H, Ph), 7.65−7.68 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 298 K): δ 1.28, 2.55, 6.16, 20.44, 29.84, 24.31 (d, J = 48.36 Hz), 25.84 (d, J = 6.80 Hz), 124.96, 127.26, 129.61(d, J = 4.93 Hz), 131.11(d, J = 14.69 Hz), 145.36 (t, J = 27.87 Hz), 149.67 (m), 156.89 (m). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6, 298 K): δ −26.02 with satellites (J = 1031.26 Hz), 24.92. Anal. Calcd for $C_{50}H_{80}N_2P_4Si_4Sn$: C, 56.37; H, 7.58; N, 2.63. Found: C, 56.22; H, 7.46; N, 2.61.

Reaction of [Li{P(Ph)C{=C(H)Ph}P(Me)$_2$=NSiMe$_3$}-(THF)$_{1.5}$] with ClSnN(SiMe$_3$)$_2$. A solution of complex **4** (0.86 g, 1.82 mmol) in 20 mL of Et_2O was added to a stirred solution of $ClSnN(SiMe_3)_2$ (0.57 g, 1.81 mmol) in 20 mL of Et_2O at −80 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed in vacuo, and the residue was extracted with CH_2Cl_2. Crystallization from CH_2Cl_2 gave red crystals identified as **6** (0.32 g, 42.1% based on **4**).

Crystal Structure Solution and Refinement for Complexes 3, 5, and 6. Crystals were mounted in Lindemann Capillaries under nitrogen. Diffraction data were collected on a Siemens CCD area-detector at 298(2) K (for **3**) and 299(2) K (for **5** and **6**, respectively) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A semiempirical absorption

Table 1. Details of the X-ray Structure Determinations of Complexes 3, 5, and 6

	3	5	6
empirical formula	$C_{27}H_{34}KNP_2Si$	$C_{66}H_{112}Li_2N_2O_4P_4Si_4$	$C_{38}H_{52}N_2P_4Si_2Sn$
fw	501.68	1247.70	835.57
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2(1)/n$	$P\bar{1}$	Cc
a (Å)	13.655(11)	10.655(3)	19.605(4)
b (Å)	10.678(8)	17.776(5)	11.840(2)
c (Å)	21.348(17)	21.218(6)	18.611(4)
α (deg)	90	103.262(6)	90
β (deg)	100.412(15)	97.354(6)	96.580(3)
γ (deg)	90	94.270(5)	90
V (Å^3)	3061(4)	3857(2)	4291.4(15)
Z	4	4	4
D_{calcd} (g/cm^3)	1.089	2.149	1.293
$F(000)$	1064	2704	1728
μ (mm^{-1})	0.331	0.403	0.828
θ range for data collecn (deg)	1.94 to 23.34	1.94 to 23.37	2.01 to 24.78
no. of reflns collected	12 860	13 982	10 545
no. of indep reflns (R_{int})	4316 (R_{int} = 0.1654)	10463 (R_{int} = 0.0895)	6513 (R_{int} = 0.0410)
no. of data/restraints/params	4316/1/293	10 463/0/739	6513/2/436
goodness of fit on F^2	0.794	0.644	0.877
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0637	R1 = 0.0556	R1 = 0.0420
	wR2 = 0.1395	wR2 = 0.0653	wR2 = 0.0584
R indices (all data)	R1 = 0.2344	R1 = 0.2863	R1 = 0.0873
	wR2 = 0.1915	wR2 = 0.1081	wR2 = 0.0698
largest diff peak and hole (e·Å^{-3})	0.665 and −0.294	0.191 and −0.170	0.299 and −0.463

[a] $R1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $wR2 = [\{\sum w(F_o^2 - F_c^2)^2\}/\{\sum w(F_o^4)\}]^{1/2}$.

correction was applied to the data. The structures were solved by direct methods (SHELXS-97)[36] and refined against F^2 by full-matrix least-squares using SHELXL-97.[37] Hydrogen atoms were placed in calculated positions. The anomalous thermal parameters on C(18) and C(35) in Figure 4 infer some disorder, but attempts to model the disorder were unsatisfactory. Crystal data and experimental details of the structure determinations are listed in Table 1.

(36) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(37) Sheldrick, G. M. *SHELXL97*, Programs for structure refinement; Universität Göttingen, 1997.

Acknowledgment. We are grateful for financial support of this work from NSFC (Grant No. 20072035). We wish to acknowledge Professors D.-Q. Wang and J.-M. Dou for determining the crystal structures.

Supporting Information Available: Details of the X-ray structure determinations of **3**, **5**, and **6**. Crystallographic files in CIF format for the structure determinations of **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020422C