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Article

Synthesis and Structures of Complexes Demonstrating the Coordinative Versatility of the 2,4-Diimino-3-phosphinopentene Anion (γ-Phosphino-β-diketiminate)

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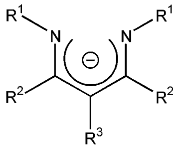
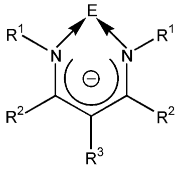
The synthesis and characterization of a 2,4-diimino-3-phosphinopentene anion (γ-phosphino-β-diketiminate) is reported and enables diversification of the β-diketiminate ligand framework, which has been widely employed across the periodic table. Phosphines are observed to adopt the γ-position of the ligand rather than the N,N′ chelate. While aluminum and lithium adopt the familiar N,N′ chelate arrangement with the new 2,4-diimino-3-phosphinopentene anion ligand, reactions with $AsCl_3$ or $SbCl_3$ result in substitution at the β-methyl position on the ligand backbone, realizing novel P→E (E = As or Sb) intramolecular coordination. The chemistry of the 2,4-diimino-3-phosphinopentene anion can be monitored by the ^{31}P NMR chemical shifts, which are distinctively diagnostic of the coordinative engagement of the ligand.

Introduction

β-Diketiminate ligands of the general type **1** (2,4-diiminopentene anion) have been influential in the development of catalytic processes and have facilitated the discovery of unusual bonding arrangements for many elements.[1] Chelate complexes of the type **2** are common, but are not observed for the electron-rich p-block elements. Our attempts to develop phosphorus derivatives of **2** have realized the unusual backbone substitution of the extensively utilized reagent **3Li** (Dipp = 2,6-diisopropylphenyl) with chlorodiphenylphosphine, which gives 2-amino-4-imino-3-phosphinopentene (γ-phosphino-β-diketimine) **4**.[2,3] The auxiliary phosphine of **4** provides a ^{31}P NMR probe for the β-diketiminate moiety so that distinct chemical shifts are observed for the chelate complexes **5E** (E = Li or $AlCl_2$), and the unusual five-membered heterocyclic structures **6E** are formed for E = $AsCl_2$ or $SbCl_2$.



1



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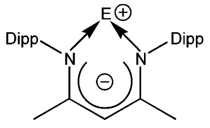
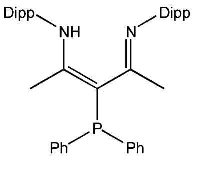


3E (E = H, Li)



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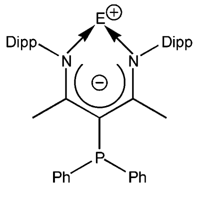
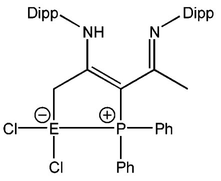


5E



6E

Results and Discussion

Diketiminate anions (**1**) have demonstrated a versatile chelate coordination chemistry with a wide range of metals and some p-block elements.[4−14] Complexes of the electron-rich elements of groups 15,[15,16] 16, and 17 are notably absent

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from the series. The extensive coordination chemistry of phosphines as Lewis acceptors[17−40] prompted us to examine the possibility of incorporating a phosphenium moiety in the N,N′ chelate **2**. However, ^{31}P NMR spectra of reactions between PCl_3 and **3H** or **3Li** show multiple products. In contrast, a quantitative reaction is observed for equimolar combinations of Ph_2PCl with **3Li** (^{31}P NMR −11 ppm). The corresponding product has been isolated and structurally characterized (Figure 1) as a 2-amino-4-imino-3-phosphinopentene **4**. Identification of the amine proton in the ^{1}H NMR ($\delta \approx 12$ ppm) and FT-IR spectra confirms the formulation of **4**, rather than potential isomers such as aminophosphine **7** or phosphenium−nacnac complex **3PPh$_2$**, and similar systems to **4** have been synthesized by alternative methods.[41]

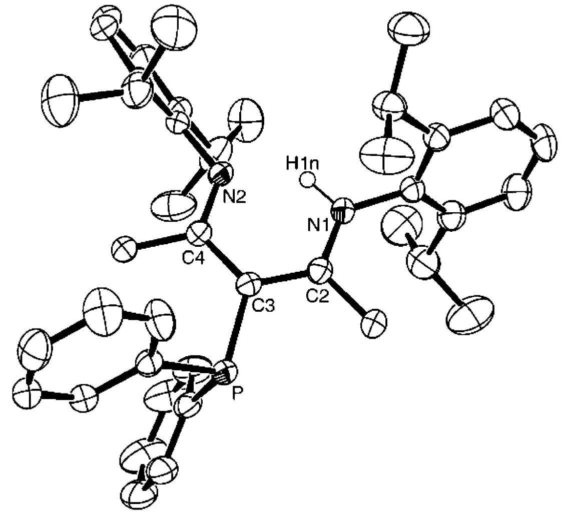
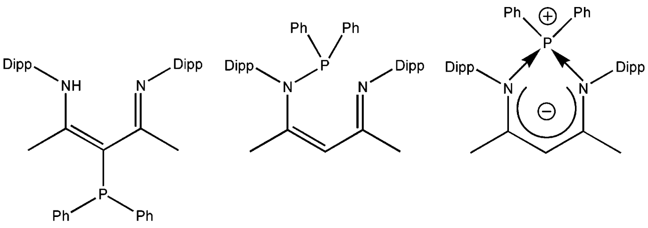


Figure 1. Solid state structure of **4**. Thermal ellipsoids are drawn at 50% probability, and all hydrogen atoms except that bound to nitrogen have been omitted for clarity.



4 **7** **3PPh$_2$**

Isomeric options for **4**

As illustrated in Scheme 1, formation of **4** is envisaged to involve nucleophilic displacement of chloride from Ph_2PCl by C−C π-electron density of the nacnac anion **3**, rather than by the sterically hindered nonbonding electron density at the nitrogen sites. Subsequent migration of the proton at carbon-3 of the intermediate **8** to one of the imine nitrogen centers reestablishes conjugation for the five atom frame to give **4**.

The structure of **4** compares and contrasts the γ-addition product of $GeCl_3$ with **3**, which has been definitively characterized as **9a**, exhibiting N−C_β distances (Table 2) that illustrate a distinct diimine arrangement.[42] The proposed phosphine intermediate **8** is topologically analogous to the conformer **9b**, prompting questions about the stability of the germanium derivative **9a**. Most notable is the distinct

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Table 1. Crystal Data

	4	**5Li**	**6As**	**6Sb**	**5AlCl₂**
empirical formula	$C_{41}H_{51}N_2P$	$C_{41}H_{50}LiN_2P\cdot C_7H_8$	$C_{41}H_{50}AsCl_2N_2P\cdot 1.5C_6H_6$	$C_{41}H_{50}Cl_2N_2PSb\cdot 0.5C_5H_{12}$	$C_{41}H_{50}Al_1Cl_2N_2P$
formula weight	602.81	700.87	864.78	830.52	699.68
crystal system	monoclinic	triclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$Pbca$
a (Å)	10.690(1)	10.1138(4)	11.446(1)	34.699(3)	18.387(1)
b (Å)	36.444(4)	11.1175(5)	12.462(1)	11.305(1)	20.247(1)
c (Å)	10.821(1)	19.644(1)	16.902(1)	20.995(2)	21.232(1)
α (deg)	90	77.193(1)	94.920(2)	90	90
β (deg)	118.846(1)	84.797(1)	104.742(1)	96.025(2)	90
γ (deg)	90	78.208(1)	90.251(2)	90	90
V (Å^3)	3692.7(4)	2106.0(2)	2322.0(3)	8190.0(0)	7904.0(8)
Z	4	2	2	8	8
D_C (Mg m^{-3})	1.084	1.105	1.237	1.347	1.176
R ($I > 2\sigma(I)$)[a]	0.0492	0.0474	0.0374	0.0547	0.0564
wR (all data)[a]	0.1389	0.1312	0.1010	0.1525	0.1092
GOF S[a]	1.057	1.021	1.001	1.040	1.007

[a] $R(F\,[I > 2\sigma(I)]) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR(F^2\,[\text{all data}]) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; S (all data) $= [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program [see Supporting Information]).

Scheme 1. Proposed Mechanism for the Formation of **4**

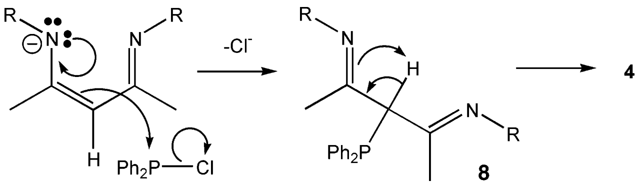
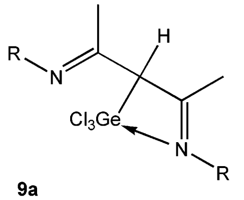


Table 2. Selected Bond Lengths and NMR Parameters for Derivatives of **3**, **4**, **5**, **6**, and **9**

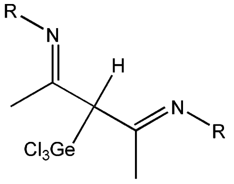
compound	P−C$_\gamma$ (Å)	N−E (Å)	N−C$_\beta$ (Å)	δ ^{1}H[d] (ppm)	δ ^{31}P (ppm)	ref
4	1.813(2)	0.97(2)[a]	1.338(2) 1.307(2)	12.6	−11	this work
3H		0.97(4)[a] 0.92(4)	1.318(3) 1.341(3)	12.1		43
5Li	1.808(2)	1.899(3)[b] 1.908(3)	1.318(2) 1.310(2)	d	−1	this work
Et₂O-3Li		1.917(4)[b] 1.912(4)	1.324(3) 1.325(3)			4
THF-3Li		1.958(5)[b]	1.325(3)			4
Hex-3Li		1.894(7)[b] 1.919(7)	1.323(4) 1.325(4)			4
3Li		1.892(7)[b] 1.903(7)	1.321(5) 1.337(5)			4
6As	1.764(2)	0.82(3)[a]	1.300(3) 1.325(3)	12.5	48	this work
6Sb	1.782(4)	0.85(5)[a]	1.338(5) 1.298(6)	12.7	23	this work
5AlCl₂	1.830(3)	1.861(2)[c] 1.867(2)	1.334(3) 1.339(3)	d	−2	this work
3AlCl₂		1.8843(9)[c] 1.8663(9)	1.341(1) 1.348(1)			4
3Al		1.957(2)[c] 1.957(2)	1.340(3) 1.342(3)			13
9		2.419(2)	1.273(3) 1.268(4)			42

[a] E = H. [b] E = Li. [c] E = Al. [d] Not observed.

intramolecular N−Ge interaction observed in **9a**, which may be responsible for mediating the proton affinity or nucleophilicity of the imine site, and is perhaps due to the greater Lewis acidity of $GeCl_3$ over that of PPh_2.



9a



9b

Retention of the amine/imine bifunctionality upon incorporation of a phosphine substituent in **4** provides the opportunity for subsequent diketiminate metathesis reactions. Furthermore, the backbone phosphine substitution offers a valuable ^{31}P NMR spectroscopic probe. The reaction mixture of **4** with BuLi exhibits a single ^{31}P NMR resonance ($\delta = -1$ ppm), and the isolated solid has been crystallographically characterized as the toluene solvate of **5Li** shown in Figure 2. ^{31}P NMR spectra of equimolar mixtures of **5Li** with $AlCl_3$ in toluene indicate a quantitative reaction ($\delta = -2$ ppm), and the solid state structure (Figure 3) of the isolated product **5AlCl₂** confirms exchange of lithium by dichloroalane in the "mouth" of the chelate. Equimolar mixtures of **5Li** with ECl_3 (E = As, Sb) in toluene also exhibit quantitative metathesis (^{31}P NMR: $\delta = 48$ ppm and 23 ppm, respectively); however, the introduction of ECl_2 contrasts that of $AlCl_2$, engaging the organic backbone of the ligand through auxiliary interaction with the phosphine **6E** (E = As, Sb). The solid state structures are shown in Figures 4 and 5, confirming an amine/imine **6E** formulation with ECl_2 bridges between a β-methylene carbon center and the γ-phosphine. Table 2 lists P−C$_\gamma$, N−E, and N−C$_\beta$ distances as well as ^{1}H and ^{31}P NMR chemical shifts for derivatives of **3**, **4**, **5**, **6**, and **9**.

The As and Sb centers in **6E** both exhibit distorted disphenoidal ("seesaw") geometry with Cl−E−Cl bond angles of 173.85(2)° and 172.12(5)°, respectively, implying stereochemical activity of the lone pair on As and Sb. One E−Cl distance is elongated with respect to the other [As−Cl, 2.3786(6) Å, 2.5243(6) Å; and Sb−Cl, 2.689(2) Å, 2.521(2) Å]. In contrast to the symmetric frameworks of **5Li** and **5AlCl₂**, the N−C$_\beta$ distances in **6As** and **6Sb** are inequivalent (Table 2) due to the remote asymmetric incorporation of the pnictogen fragment and are consistent with imine/amine distinction of the nitrogen centers. The P−C$_\gamma$ distances in

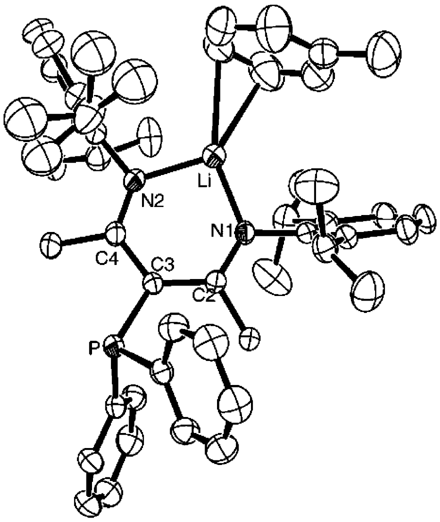


Figure 2. Solid state structure of **5Li**·toluene. Thermal ellipsoids are drawn at 50% probability, and all hydrogen atoms have been omitted for clarity.

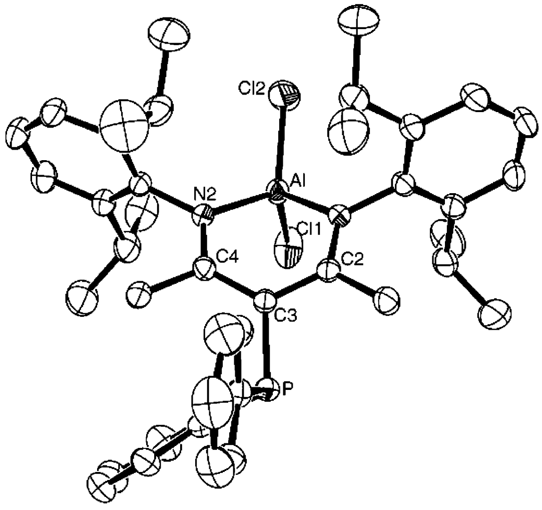


Figure 3. Solid state structure of **5AlCl$_2$**. Thermal ellipsoids are drawn at 50% probability, and all hydrogen atoms have been omitted for clarity.

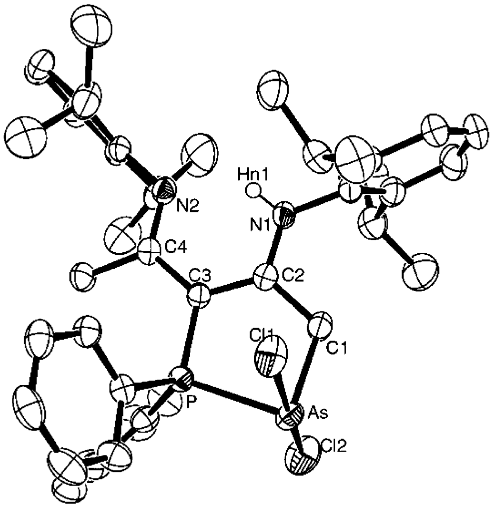


Figure 4. Solid state structure of **6As**. Thermal ellipsoids are drawn at 50% probability, all hydrogen atoms have been omitted for clarity (except that bound to nitrogen), and the 1.5 molecules of benzene solvate are not shown.

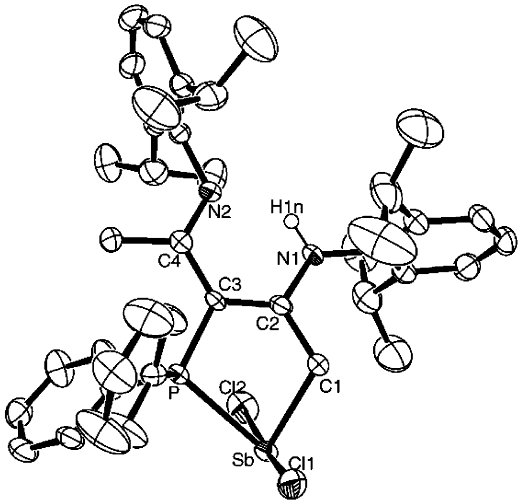


Figure 5. Solid state structure of **6Sb**. Thermal ellipsoids are drawn at 50% probability, all hydrogen atoms have been omitted for clarity (except that bound to nitrogen), and the 0.5 molecule of pentane solvate is not shown.

6E are shorter than in **4**, while those in **5Li** and **5AlCl$_2$** are consistent with **4**.

^{1}H NMR spectra of **6E** derivatives display a characteristic resonance at $\delta \approx 12$ ppm (Table 2) consistent with the presence of an N$-$H proton, while this signal is not observed for **5Li** and **5AlCl$_2$**. The ^{31}P NMR chemical shifts of these complexes (Table 2) are diagnostic of the coordination mode of the ligand, with P,C chelate complexes (**6E**) more dramatically downfield shifted from the free ligand (**4**) than N,N′ chelated complexes (**5**).

The formation of **6E** (E = As, Sb) is envisaged to occur via Scheme 2. Inter- or intramolecular tautomerism gives access to a methylene site at the β-carbon center. In this context, deprotonation of anion **3** is rare but a complex of the dianionic conjugate base of **3** has recently been reported,[44] and a methylene isomer has been observed for a germanium complex.[45] Nucleophilic attack at ECl$_3$ (E = As, Sb) will promote chloride elimination, supported by coordination by the neighboring phosphine center to give a 5-membered ring system, not uncommon for phosphorus.[23,26,46]

Conclusions

A series of complexes of the 2,4-diimino-3-phosphinopentene anion demonstrate unusual coordinative versatility that goes beyond conventional wisdom for the extensively studied and exploited diketiminate framework. N,N′ chelate complexes are observed for lithium and aluminum while the electron-rich elements of group 15 (P, As, Sb) access remote sites by proton substitution of the organic backbone. Consequential introduction of the Ph$_2$P substituent at the γ

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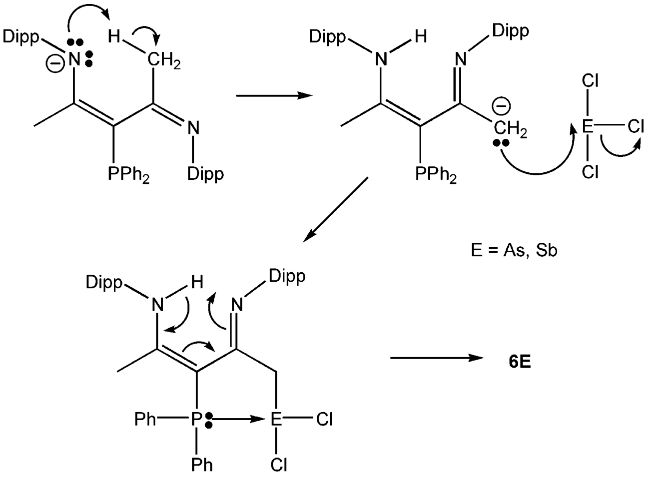
Scheme 2. Proposed Mechanism for the Formation of **6E**



position provides a useful and diagnostic ^{31}P NMR probe for the analysis of reaction mixtures in situ.

Experimental Section

General. All manipulations were carried out in a N_2 filled Innovative Technologies Drybox. All solvents were distilled prior to use and dispensed in the drybox. CH_2Cl_2 was dried at reflux over CaH_2, P_2O_5, and again over CaH_2. Hexane was dried at reflux over K, Et_2O was dried at reflux over Na/benzophenone, and toluene was dried over Na. **3**Li(Et_2O) was prepared from literature methods,[4] and Ph_2PCl, ^{n}BuLi (1.6 M in hexane), $AsCl_3$, $SbCl_3$, and $AlCl_3$ were purchased from Aldrich Chemical Co. and used as received. Solid samples were evacuated for 12 h and submitted to Desert Analytics, Tucson, AZ, for determination of elemental composition. IR spectra were collected on a Bruker VECTOR 22 FT-IR using Nujol mulls and are reported with ranked intensities in parentheses. Solution NMR data were collected on a Bruker AC-250 NMR spectrometer at room temperature unless otherwise indicated. Chemical shifts are reported in ppm relative to a reference standard [100% $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P); 1.0 M LiCl (^{7}Li)], and both ^{1}H and ^{13}C NMR data were calibrated to an internal reference signal (^{1}H, $CHDCl_2$, 5.32 ppm; ^{13}C, CD_2Cl_2, 54.00 ppm). Crystals were mounted under oil (Paratone or perfluoropolyether) and placed in a cold stream of N_2. X-ray diffraction data were collected on a Bruker PLATFORM diffractometer with a sealed tube generator and a SMART 1000 CCD detector at 193(2) K using graphite-monochromated Mo Kα ($\lambda = 0.71073$) radiation (Table 1).

Preparative Procedures and Characterization Data. 4. A solution of **3Li**(Et_2O) (3.24 g, 6.50 mmol) in toluene (50 mL) was added to a cooled (−78 °C) solution of $ClPPh_2$ (1.43 g, 6.50 mmol) in toluene (15 mL). The reaction mixture was stirred for 12 h, warmed to room temperature, and filtered. Slow removal of solvent gave yellow crystals 3.22 g, 82.0%; mp 144−147 °C. Anal. Calcd for $C_{41}H_{51}N_2P$ (found): C 81.7 (82.4), H 8.5 (8.2), N 4.7 (4.2). FT-IR (cm^{-1}): 1526(1), 1322(8), 1191(10), 1028(4), 795(9), 769(5), 742(3), 696(2), 555(6), 427(7). ^{31}P{^{1}H} NMR: −11 ppm.

5Li. ^{n}BuLi in hexanes (1.6 M, 0.11 mL) was added dropwise to a solution of **4** (0.11 g, 0.18 mmol) in toluene (3 mL) at RT. The mixture was stirred for 2 h, concentrated in vacuo (≈0.5 mL), and crystallized at −30 °C. Subsequent washing with cold *n*-pentane gave clear, colorless crystals, 0.05 g, 42%. mp 270−274 °C. FT-IR (cm^{-1}): solid material is extremely air sensitive and as such, a reliable IR spectrum could not be obtained. Anal. Calcd for $C_{41}H_{50}Li_1N_2P$ (found): C: 80.9 (80.6), H: 8.3 (8.0), N: 4.6 (4.2). ^{31}P{^{1}H} NMR: −1 ppm. ^{7}Li NMR: −0.4 ppm.

6As. 1.6 M ^{n}BuLi in hexanes (0.10 mL) was added dropwise to a solution of **4** (0.10 g, 0.17 mmol) in toluene (3 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and then added to a solution of $AsCl_3$ (0.003 g, 0.17 mmol) in toluene (3 mL) −30 °C. The mixture was stirred for 12 h at RT. LiCl was filtered and the solvent was removed and the solid was recrystallized from benzene to give brown crystals, 0.06 g, 44%. mp (dec): 177 °C. Anal. Calcd for $C_{41}H_{50}AsCl_2N_2P$ (found): 65.8 (66.1); H, 6.7 (6.8); N, 3.8 (3.8). FT-IR (cm^{-1}): 1537(1), 1190(9), 1101(5), 801(10), 778(3), 746(8), 688(6), 523(4), 477(2), 436(7). ^{31}P{^{1}H} NMR: 48 ppm.

6Sb, 1.6 M ^{n}BuLi in hexanes (0.10 mL) was added dropwise to a solution of **4** (0.10 g, 0.17 mmol) in toluene (3 mL) at RT; the mixture was stirred for 2 h and then added to a solution of $SbCl_3$ (0.04 g, 0.17 mmol) in toluene (3 mL) at −78 °C. The mixture was stirred for 12 h and allowed to warm to RT. LiCl was filtered, and the solvent was removed; the solid was recrystallized using vapor diffusion (toluene/pentane) to give colorless crystals, 0.03 g, 22%. mp (dec): 124 °C. Anal. Calcd for $C_{41}H_{50}SbCl_2N_2P$ (found): C 62.0 (60.8); H 6.3 (6.7); N 3.5 (2.7). FT-IR (cm^{-1}): 693(8), 745(3), 778(5), 796(4), 1258(7), 1295(9), 1321(10), 1406(6), 1436(2), 1564(1). ^{31}P{^{1}H} NMR: 23 ppm.

5AlCl$_2$. 5Li (0.10 g, 0.14 mmol) in toluene was added to a solution of $AlCl_3$ in toluene (0.02 g, 0.14 mmol) at RT. The mixture was stirred for 12 h at RT, LiCl was filtered, and the solvent was removed. The solid was recrystallized using vapor diffusion (toluene/pentane) to give clear crystals, 0.07 g, 58%. mp: 202−206 °C. Anal. Calcd for $C_{41}H_{50}AlCl_2N_2P$ (found): C 70.4 (70.2); H 7.2 (7.2); N 4.0 (4.2). FT-IR (cm^{-1}): 470(14), 511(10), 535(6), 569(9), 596(7), 802(11), 901(18), 925(19), 1017(8), 1051(20), 1100(17), 1174(13), 1256(12), 1314(2), 1336(1), 1435(4), 1496(3), 1585(15), 3060(16). ^{31}P{^{1}H} NMR: −2 ppm.

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Supporting Information Available: Figures depicting solid state structures, tables of crystallographic data, and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.

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