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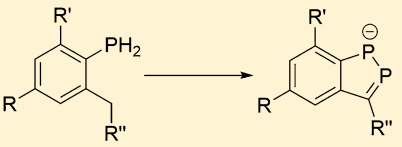
Synthesis of 1,2-Diphospholides Using a Main Group "Superbase"

Lily S. H. Dixon,[†] Schirin Hanf,[†,‡] Jessica E. Waters,[†] Andrew D. Bond,[†] and Dominic S. Wright*[,†]

[†]Chemistry Department, Cambridge University, Lensfield Road, Cambridge CB2 1EW, United Kingdom
[‡]Fäkultät für Chemie und Mineralogie, University of Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

Supporting Information

ABSTRACT: The synthesis of a range of 1,2-diphospholides can be achieved by a one-pot procedure involving the reactions of aromatic primary phosphines bearing *ortho*-CH_2 substituents with the superbase mixture of ^{n}BuLi/Sb(NMe$_2$)$_3$ in the presence of the Lewis base donor TMEDA ($Me_2NCH_2CH_2NMe_2$). The synthesis of the parent benzo-1,2-diphospholide and the substituted derivatives 4-methoxybenzo-1,2-diphospholide, 9-methylbenzo-1,2-diphospholide, and naphtho-1,2-diphospholide are reported from readily prepared primary phosphines. Bulk synthesis of the potassium salt of the previously reported 4,6-dimethylbenzo-1,2-diphospholide anion using this route provides a convenient starting material for reactivity studies.



INTRODUCTION

The ability to tune phosphorus-based compounds by varying the electronic and steric properties of the substituents has made phosphines and related ligands ubiquitous throughout transition metal chemistry.[1] Phosphorus-containing analogues of classically carbon-based frameworks have played an invaluable role in this field.[2] However, development of a more comprehensive library of these types of ligands is often limited by convoluted syntheses as well as a lack of generality of the synthetic methods employed.[3]

The indenyl ligand (Figure 1a) has had an important role in various aspects of organometallic chemistry.[4] The vast increase in the rate of ligand substitution for indenyl complexes relative to cyclopentadienyl complexes has potentially important implications for transition metal catalysis.[5] In contrast, η-coordination of group 15 analogues of indenyl, such as the nitrogen ligand *N*-indazolide (Figure 1b) is rare, and this effect has not yet been exploited in this area.[6] General synthetic access to phosphorus counterparts of indenyl would allow investigation of the reactivity of their transition metal complexes, both in terms of kinetics, and accessible bonding modes. The inclusion of one or more phosphorus atoms into the indenyl framework also introduces the possibility of *bis*-coordination of the phosphorus atom through the π-system as well as the lone pair, providing increased functionality relative to all-carbon analogues.

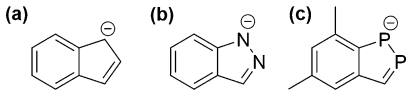


Figure 1. Structures of the indenyl (a), indazolide (b), and 4,6-dimethylbenzo-1,2-diphospholide (c) anions.

Despite the thorough investigations carried out by many groups globally, the 1,2-diphospholides remain under-represented in the literature due to their challenging syntheses.[7,8] Indeed, until recently only two synthetic routes to 1,2-diphospholides had been reported (Scheme 1).[7,8] Both routes make use of uncommon and challenging-to-synthesize starting materials, and require the isolation and purification of intermediates. Furthermore, the highly specific starting materials used in each synthesis preclude the possibility of generating species isoelectronic with the indenyl anion.

Recently, the synthesis of the 4,6-dimethyl-substituted diphospholide anion (**1**) (Figure 1c) was reported concurrently by the Hey-Hawkins group[9] and us,[10] using two different synthetic approaches. Our approach, which involves the one-pot reaction of $MesPH_2$ (Mes = 2,4,6-trimethylphenyl) with the redox-active superbase mixture ^{n}BuLi/Sb(NMe$_2$)$_3$, involves the *in situ* generation of the tetraphosphane-1,4-diide $[MesP]_4^{2-}$ which then ring-closes by a combination of *ortho*-Me deprotonation and oxidation (Scheme 2a). This pathway is related to the Hey-Hawkins route but with the advantage that it does not require the availability of the aryl-substituted tetraphosphane-1,4-diide as a starting material (Scheme 2b), a factor which is likely to limit the synthetic scope.[9]

In this paper we explore the generality of our one-pot approach to 1,2-diphospholides, starting from readily prepared primary phosphines containing *ortho*-CH_2 functionality. DFT calculations are used to compare the electronic structures of the series of new 1,2-diphospholides obtained with the valence-isoelectronic indenyl anion.

RESULTS AND DISCUSSION

While the synthesis of the anion **1** (Figure 1c) was an important first step, our primary aim in the current work was to develop a general method for the synthesis of a range of benzannulated-1,2-diphospholides which could act as ligands in organometallic chemistry. By applying the same method-

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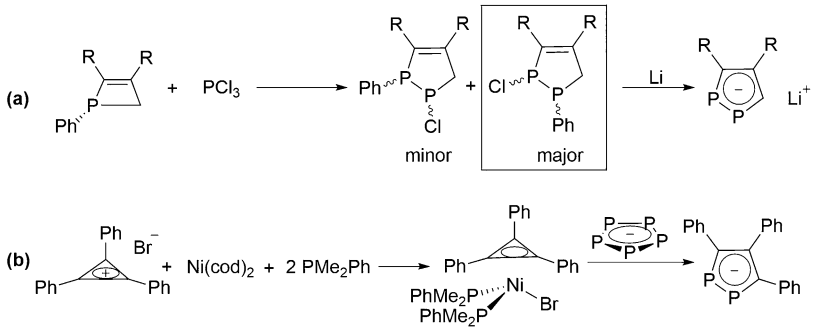
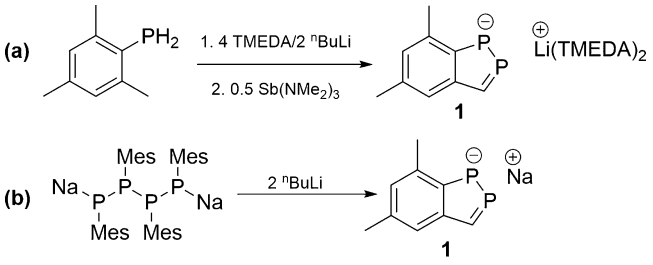
Scheme 1. Previously Reported Syntheses 1,2-Diphospholides[a]



[a](a) Mathey (R = Ph, Et)[7] and (b) Hey-Hawkins.[8]

Scheme 2. Previously Reported Syntheses of the (4,6-Dimethylbenzo)-1,2-diphosphlide Anion (1)[a]

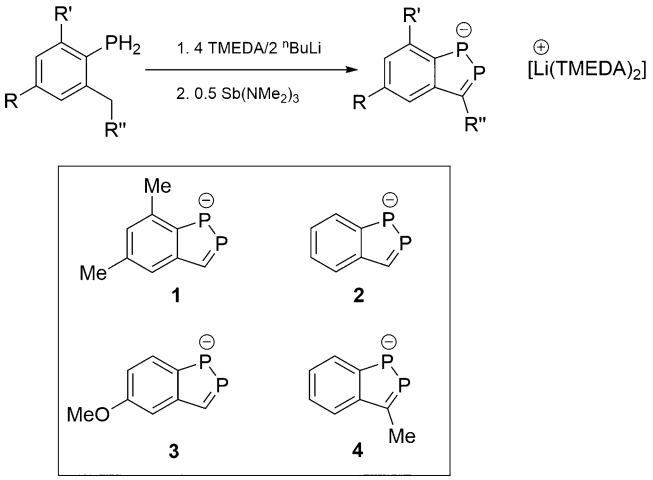


[a]TMEDA = $Me_2NCH_2CH_2NMe_2$.

ology used in the synthesis of **1**, we have been able to access the unsubstituted benzo-1,2-diphospholide (**2**), the 4-methoxy-substituted analogue (**3**), and 9-methylbenzo-1,2-diphospholide (**4**). The synthesis of compounds **2**–**4** was achieved according to Scheme 3 (see the Experimental Section). Our previous studies of **1**, showed that this reaction involving C–H activation of the *o*-CH_2 groups occurs via a series of oligo-phosphorus intermediates.[10]

One potential drawback of our synthetic approach is the fact that the primary phosphine starting materials are not

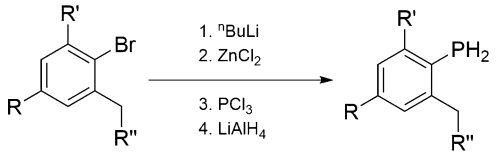
Scheme 3. General Synthesis for Benzo-1,2-diphospholides[a]



[a]**1**: R = R′ = Me, R″ = H, **2**: R = R′ = R″ = H, **3**: R = OMe, R′ = H, R″ = H, **4**: R = R′ = H, R″ = Me. Toluene solvent. (1) Addition at −78 °C then stirred at rt for 1 h. (2) Addition at −78 °C, warmed to rt then heated under reflux for 2 h.

commercially available. However, we have found that the simple one-pot route developed by Vedejs et al. is particularly useful in this respect (see Scheme 4 and the Experimental Section).[11]

Scheme 4. General Synthesis for Primary Arylphosphines[a]



[a]R = R′ = Me, R″ = H; R = R′ = R″ = H; R = OMe, R′ = H, R″ = H; R = R′ = H, R″ = Me. THF solvent. (1) Addition at −78 °C, stirring at −78 °C for 2 h. (2) Addition of THF solution at −78 °C, stirring at −78 °C for 3 h. (3) Slow addition of reagent solution to a THF solution of PCl_3 at −78 °C then slow warming to rt overnight with stirring. Slow addition of reagent solution to a slurry of $LiAlH_4$ at 0 °C followed by slow warming to rt with stirring.

Combining the ease of access to the phosphine starting materials with their facile transformation to the corresponding benzo-1,2-diphospholides provides a simple two-step approach from commercially available aryl bromides. The primary phosphine precursors in the current study (Scheme 4) were selected in order to allow the incorporation of substituents within the C_6- and C_3P_2-ring units of the benzo-1,2-diphospholide anions. Since the reactions occur under highly nucleophilic conditions, the incorporation of highly electrophilic substituents (such as C=O or C≡N) was not considered.

Anions **2**–**4** can be isolated as their $[Li(TMEDA)_2]^+$ salts as powders after filtration and washing with *n*-pentane. All of the isolated products show clean ^1H, ^{31}P, and $^{13}C\{^1H\}$ NMR spectra and high-resolution negative-ion mass spectrometry was able to identify the phospholide anions in the case of **2** and **3** (within 0.0014–0.0037 mass units of the theoretical). However, satisfactory elemental analysis could not be obtained on any of the solid salts, as a result of the presence of variable amounts of finely divided Sb metal and/or Sb Zintl compounds which proved to be impossible to remove fully. We estimate on the basis of elemental analysis and ^1H NMR integration that the percentage of impurities in **2**–**4** range from ca. 5% to 20%, from batch to batch. Our previous work on the mechanism of formation of anion **1** showed that the Sb_7^{3-} Zintl ion is formed concurrently with the diphospholide.[10] The similar solubilities of the diphospholide salts and the antimony Zintl compound formed in the reaction (most likely

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$Li(TMEDA)_2]_3\{Sb_7]\}$[3−10] meant that washing and fractional crystallization were ineffective methods of purification.

As part of our studies, we also explored the effect on the reaction of changing the alkali metal counterion. This development is important because the presence of a heavier alkali metal counterion (e.g., Na^+, K^+, vs Li^+) should provide a greater driving force for metathesis reactions of the 1,2-diphospholides with a range of transition and main group metals. The reaction of $MesPH_2$ with KH in the presence of the Lewis base donor PMDETA $[(Me_2CH_2CH_2)_2NMe]$ followed by reaction with $Sb(NMe_2)_3$ at reflux gave [K(PMEDTA)][**1**] in 44% yield. This salt was reported previously by Hey-Hawkins using the reaction of $MesPCl_2$ with K metal but only in 20% yield.[9]

NMR spectroscopic analysis proved to be a powerful tool for the identification and characterization of the benzo-1,2-diphospholides. Figure 2 shows the 1,2-diphospholide region

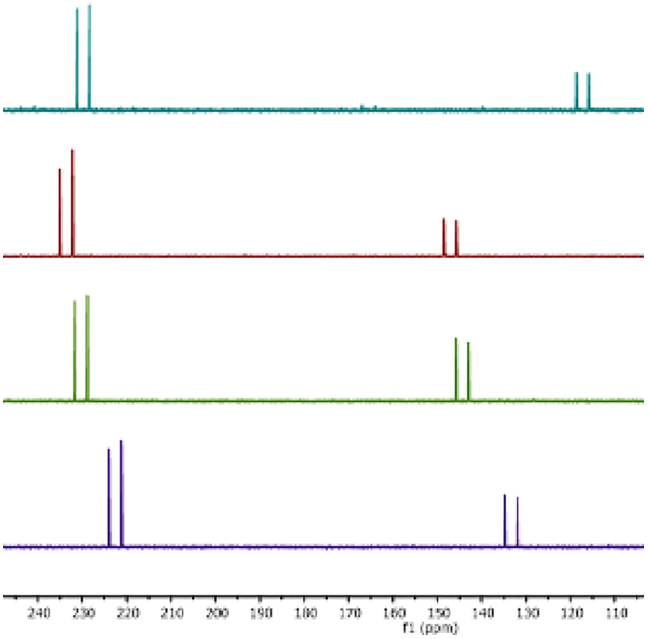

Figure 2. $^{31}P\{^1H\}$ NMR spectra of the $[Li(TMEDA)_2]$ salts of the anions (from bottom to top) **1**−**4**. THF solvent, 298 K. See Scheme 3 for structural formulas.

of the $^{31}P\{^1H\}$ NMR spectrum of the $[Li(TMEDA)_2]^+$ salts of **1**−**4**. A summary of the ^{31}P chemical shifts and coupling constants of each of the anions is shown in Table 1.

The downfield shifts witnessed for these compounds indicate both multiple bond character and delocalization about the 5-membered ring. Further confirmation of the P−P multiple bond character is provided by the large $^1J_{PP}$ coupling constants in each of the anions (448−457 Hz). The significant change in chemical shift of the phosphorus atom that formally bears the negative charge in anion **4** (P1, δ = 117.3 ppm) relative to the anions with unsubstituted 5-membered rings (P1, δ = 133.4−147.1 ppm) demonstrates the way in which substitution of the 5-membered ring influences the properties of the benzo-1,2-diphospholides.

Table 1. ^{31}P NMR Chemical Shifts and $^1J_{PP}$ Coupling Constants for the Anions 1−4[a]

anion	chemical shift (P2, P1, δ ppm)	$^1J_{PP}$ (Hz)
1	222.5, 133.4	449
2	230.3, 144.3	452
3	233.6, 147.1	457
4	229.7, 117.3	448

[a]Chemical shifts relative to 85% H_3PO_4 in D_2O (298 K).

Further confirmation of the formation of the phospholides comes from the structural characterization of the salts $[Li(TMEDA)_2][\mathbf{2}]$ and $[Li(12\text{-crown-}4)_2][\mathbf{4}]$ by single-crystal X-ray diffraction (see the Experimental Section). Despite repeated attempts, no X-ray-quality crystals containing methoxy-substituted anion **3** could be obtained. The $[Li(TMEDA)_2]^+$ salt of **2** was crystallized from a mixture of toluene and THF at room temperature. The structure of $[Li(TMEDA)_2][\mathbf{2}]$ is ion separated, with two independent benzo-1,2-diphospholide anions (**2**), both being disordered over two orientations in an approximate 90:10 ratio. The major orientation of one of the anions is shown in Figure 3.

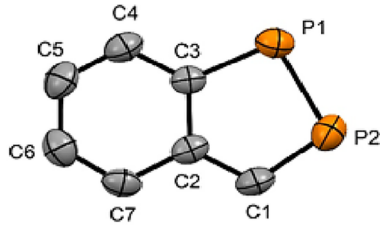

Figure 3. Ortep drawing of the molecular structure of the anion **2**. Displacement ellipsoids with 40% probability at 180(2) K. $[Li(TMEDA)_2]^+$ counterion, hydrogen atoms, and molecular disorder have been omitted for clarity. Selected bond lengths and angles are listed in Table 2.

The $[Li(12\text{-crown-}4)_2]^+$ salt of **4** was obtained by using 12-crown-4 in place of TMEDA in the reaction of Scheme 3. $[Li(12\text{-crown-}4)_2][\mathbf{4}]$ was crystallized by storage of a THF/toluene solution at room temperature, allowing the 9-methylbenzo-1,2-diphospholide (**4**) to be structurally characterized (Figure 4). Comparison of the structural parameters for

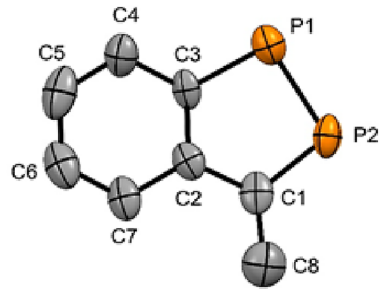

Figure 4. Ortep drawing of the molecular structure of the anion **4**. Displacement ellipsoids with 40% probability at 180(2) K. $[Li(12\text{-crown-}4)_2]^+$ counterion and hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are listed in Table 2.

previously reported anion **1**[10] with new anions **2** and **4** shows that the bond lengths and angles within their five-membered C_3P_2 ring units are nearly identical within the crystallographic errors (Table 2).

The delocalization of the negative charge within the C_3P_2 ring units of **1**, **2**, and **4** is evident from the planarity of the rings as well as from bond length analysis. The phosphorus−

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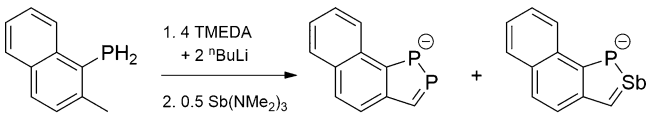
Table 2. Selected Bond Lengths (Å) and Angles (deg) from the Solid State Structures of Anions 1, 2, and 4

	anion **1** (average over three independent anions)	anion **2** (average over two independent anions)	anion **4**
P1–P2	2.119	2.106	2.111(4)
P2–C1	1.703	1.719	1.754(10)
P1–C3	1.792	1.788	1.791(9)
C1–C2	1.417	1.393	1.430(13)
C3–P1–P2	93.1	94.0	92.4(3)
C1–P2–P1	96.1	96.3	98.0(4)
C2–C1–P2	118.2	116.4	114.1(8)

carbon bond lengths of 1.688(13)–1.800(3) Å and the phosphorus–phosphorus bond lengths of 2.1029(15)–2.121(3) Å are shorter than expected for the corresponding single bonds (ca. 1.85 Å for P–C[12] and ca. 2.21 Å for P–P).[13] The observed P–C and P–P bond lengths are also similar to those reported for other aromatic phosphorus-containing heterocycles (P–C ca. 1.74–1.77 Å and P–P 2.11 Å in *cyclo*-P_5^-).[3] Also worth noting is the significant deviation from the ideal 120° angle expected for sp^2 hydridization at the phosphorus centers. The observed range of 90.1(2)–98.7(4)° is far closer to the 90° angle expected for an unhybridized atom, suggesting that the associated nonbonding lone pair of each phosphorus atom is held in an orbital with high s-character.

In further synthetic studies, we attempted to extend our methodology to other polyaromatic backbones. The primary phosphine 1-phosphino-2-methylnaphthalene was prepared according to the procedure outlined in Scheme 4 (see the Experimental Section). Reaction of this phosphine with ^{n}BuLi/$Sb(NMe_2)_3$ in the presence of TMEDA (Scheme 5), however,

Scheme 5. Synthesis of the Naphtha-1,2-diphospholide (5) and Naphtha-1-stiba-2-phospholide (6) Anions[a]



5 **6**

[a]The $[Li(TMEDA)_2]^+$ counterions are not included. The ratio of **5**/**6** is ca. 1.5:1 from integration of the ^{31}P NMR spectrum. Reaction conditions: toluene/THF solvent mixture, reflux 2.5 h.

produced a mixture of two products. The ^{31}P NMR spectrum of the solid product isolated from the reaction showed the presence of a doublet at δ = 152.1 ppm ($^1J_{PP}$ = 455 Hz) and a double doublet at δ 212.6 ppm ($^1J_{PP}$ = 455 Hz, $^2J_{PH}$ = 38 Hz), confirming the formation of desired phospholide anion **5**. However, a singlet at δ = 218.5 ppm was also observed (Figure 5). The downfield shift as well as the absence of any $^1J_{PP}$ or $^2J_{PH}$ coupling is strongly indicative of the formation of antimony-containing naphtha-1-stiba-2-phospholide anion **6** (Scheme 4).

The identity of **6** is further supported by ^1H NMR and ^1H–^{31}P HMBC spectroscopic studies, which show that the proton resonance at δ = 10.30 (d, $^3J_{PH}$ = 3.5 Hz) can be assigned to the C–H of the 5-membered ring of **6**. In our previously published work we showed that the reaction of ^{n}BuLi/$As(NMe_2)_3$ with $MesPH_2$ gives the arsenic–phosphorus heterocycle 4,6-dimethylbenzo-1-arsa-2-phospholide, an arsenic analogue of antimony heterocycle **6**.[10] The NMR spectroscopic characteristics of the $[Li(TMEDA)_2]^+$ salt of the arsenic anion are similar to **6**, displaying a singlet resonance at δ = 175.7 ppm in the ^{31}P NMR spectrum and a singlet at δ = 9.01 in the ^1H NMR spectrum, for the C–H of the 5-membered ring. The proposed mechanism of formation of **6** is shown in Scheme 6. The observed formation of **6** is likely to arise from the greater steric congestion around the phosphine group, allowing competition between intramolecular cyclization and the formation of the tetraphosphane-1,4-diide (which is responsible for the formation of the 1,2-phospholide).

Optimized geometries and frontier molecular orbitals of the anions were calculated using DFT methods.[15] The optimized structures were obtained employing the B3LYP functional[14] in conjunction with a cc-pVTZ basis set (Supporting Information, section 2).[15] Comparison of the HOMOs and LUMOs across the series of diphospholides synthesized shows that the electronic distributions in the indenyl and 1,2-disphospholide anions are similar (Figure 6). Overall, the results are similar to the previously reported DFT calculations on **1**,[9,10] with substituents on the C_6- and C_3P_2-rings having little effect, apart from that on the LUMO of **5** in which the electron density is distributed toward the second C_6-ring unit. Qualitative analysis of the calculated iso-surfaces shows a larger coefficient at the P1 atoms in the HOMO of the benzodiphospholides relative to the (corresponding) C1 atom of the indenyl anion. These data suggest that this series of benzo-1,2-diphospholides would react with electrophiles at P1. This is also suggested by natural population analysis, in which the charges on P1 (i.e., bonded to the arene ring) are all marginally negative (−0.01–0.05e) and the charges on P2 are positive (ca. +0.1e). In contrast, all of the corresponding C atoms of the 5-membered ring in the indenyl anion have significant negative charges. The HOMO–LUMO gaps, obtained from single-point calculations, are significantly smaller in the 1,2-diphospholides compared to those in the indenyl anion (by ca. 0.5–0.7 eV in **1**–**5**), with the MeO-substitution in **3** and the Me-substitution in **4** decreasing the HOMO–LUMO gaps by ca. 0.15 eV compared to those of **1**, **2**, and **5**.

CONCLUSIONS

We have shown that a range of new benzo-1,2-diphospholides can be synthesized directly from readily synthesized aromatic primary phosphines. Our approach has allowed the synthesis of parent (unsubstituted) phospholide **2** as well as frameworks containing substituents on the C_6 and C_3P_2 ring units. One drawback of our synthetic approach (at least at first sight) is the presence of antimony metal and/or antimony Zintl ions as contaminants. However, all of the isolated products show no phosphorus-, carbon-, or hydrogen-based impurities and should be useful ligand-transfer reagents for the future development of organometallic chemistry in this area. The HOMOs and LUMOs of the 1,2-diphospholide anions are similar to those of the valence-isoelectronic indenyl anion, but with smaller HOMO–LUMO gaps. The HOMO–LUMO gap shows a marked dependence on the presence of electron-donating groups; strongly electron-donating groups on the C_6-ring unit or electron-donating groups on the C atom of the C_3P_2 unit result in decreased HOMO–LUMO separation. This observation may provide the basis for tuning the donor–

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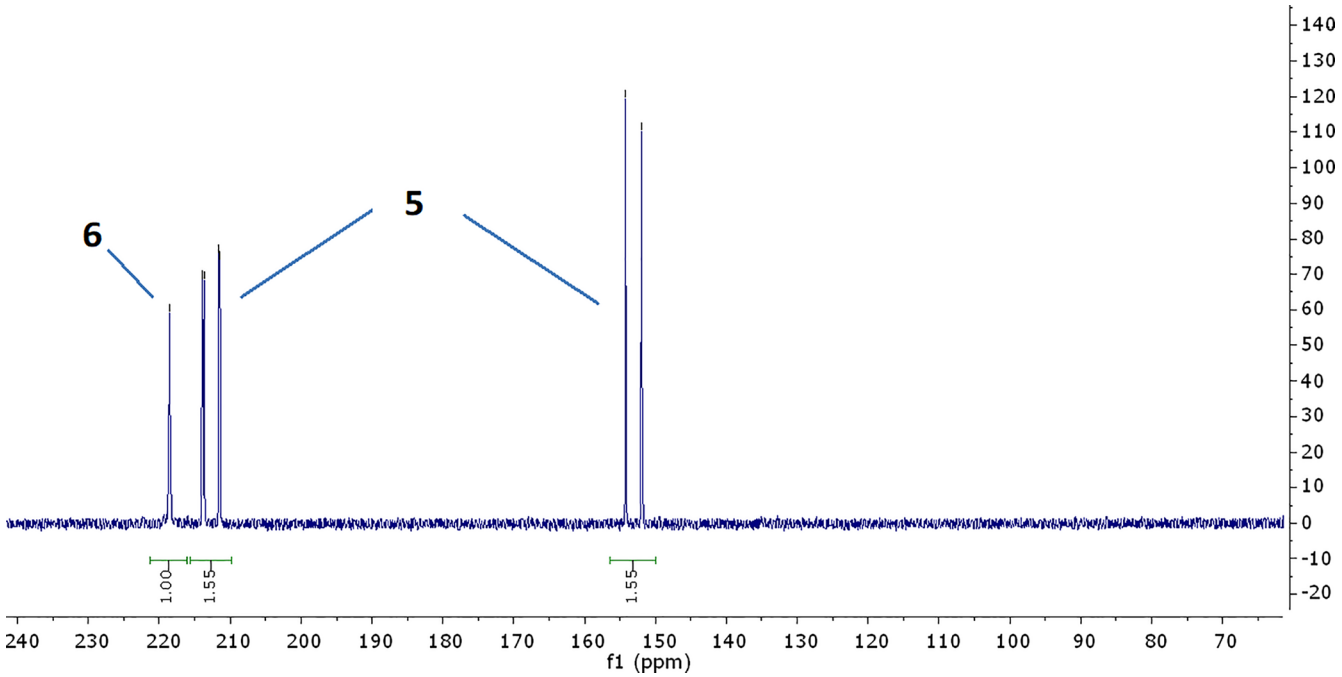
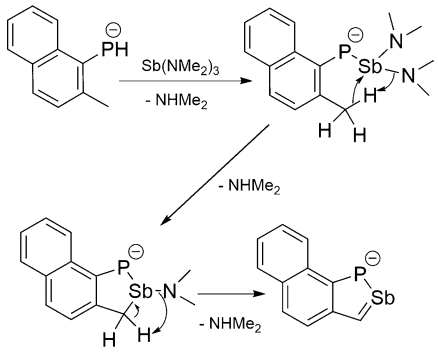


Figure 5. ^{31}P NMR spectrum of Li(TMEDA)$_2$ salts of **5** and **6**, THF solvent. See Scheme 5 for structural formulas.

Scheme 6. Proposed Mechanism for the Formation of the Phosphorus−Antimony Heterocycle Anion 6



acceptor properties of the 1,2-diphospholide anions for metal coordination.

As a final note to the current study, we have been unable to extend this work to the synthesis of the corresponding 1,2-diarsolides, for example, the reaction of $MesAsH_2$ with $Sb(NMe_2)_3/^nBuLi$ under the same conditions as those used for **1**−**5** gives an intractable mixture of products.

EXPERIMENTAL SECTION

General Experimental Techniques. All reactions were carried out at room temperature under dry, oxygen-free nitrogen using standard Schlenk and glovebox techniques and dry and degassed solvents. All solvents were collected freshly distilled over sodium wire/benzophenone (THF, diethyl ether), sodium metal (toluene), or sodium wire (*n*-hexane, *n*-pentane); TMEDA and PMDETA were distilled under nitrogen from CaH_2 and stored over 4 Å molecular sieves under nitrogen. Deuterated NMR solvents were degassed and dried over 4 Å molecular sieves. All other reagents were used as received. Ice/water cooling baths were used to obtain a temperature of 0 °C, ice/acetone baths were used to obtain a temperature of −10 °C, and dry ice/acetone baths were used to obtain a temperature of −78 °C.

Synthesis of Primary Phosphines. A solution of the appropriate aryl bromide (50 mmol) in THF (80 mL) was cooled to −78 °C and treated by slow addition with ^{n}BuLi (1.6 M in hexane, 35 mL, 56 mmol). The resultant white suspension was stirred at −78 °C for 2 h before being added via cannula to a solution of $ZnCl_2$ (8.2 g, 60 mmol) in THF (100 mL) at −78 °C. After stirring for 2 h at −78 °C this solution was added to a solution of PCl_3 (5.5 mL, 63 mmol) in

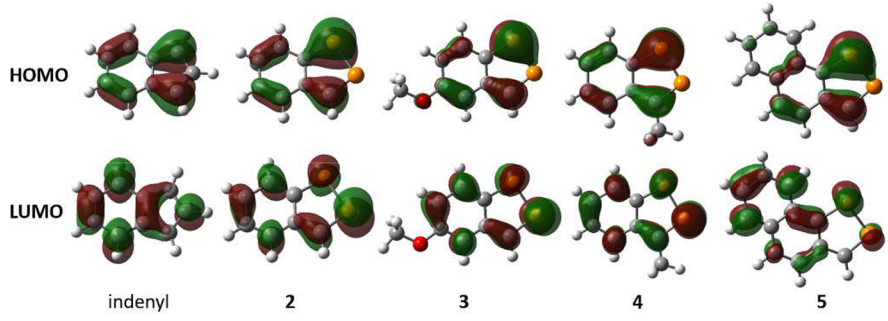


Figure 6. Frontier molecular orbitals of the indenyl anion and anions **2**−**5** at an isovalue of ±0.04. B3LYP functional,[14] cc-pVTZ[15] basis set. Calculations were performed using the Gaussian 09 suite.[16]

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THF (100 mL) at −78 °C over the course of 2 h. The resultant colorless solution was allowed to warm to rt overnight. The crude solution was added dropwise to a slurry of $LiAlH_4$ (3.8 g, 100 mmol) in diethyl ether (200 mL) at −10 °C. After addition was complete, the suspension was allowed to warm to rt slowly overnight. The reaction was cooled to 0 °C and quenched by dropwise addition of deoxygenated 4 M aqueous HCl (150 mL). The reaction mixture was allowed to warm to rt and the organic phase was isolated by cannula transfer. The aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and freed from solvent, giving the desired product as a colorless oil which required no further purification.

o-Tolylphosphine. Yield, 40%. ^{1}H NMR (400.1 MHz, C_6D_6, 25 °C), δ 2.14 (s, 3H, *o*-CH3), 3.70 (d, 2H, PH2, $^1J_{PH}$ = 200 Hz), 6.87−6.92 (m, 2H, aromatic CH), 7.00 (m, 1H, aromatic CH), 7.30 (m, 1H, aromatic CH). ^{31}P NMR (162.0 MHz, C_6D_6, 25 °C), δ −131.6 (t, 1P, PH_2, $^1J_{PH}$ = 200 Hz).

4-Phosphino-3-methylanisole. Yield, 35%. ^{1}H NMR (400.1 MHz, toluene-d_8, 25 °C), δ 2.17 (s, 3H, o-CH3), 3.34 (s, 3H, OCH3), 3.70 (d, 2H, PH2, $^1J_{PH}$ = 200 Hz), 6.48 (dd, 1H, aromatic CH, $^3J_{HH}$ = 8 Hz, $^4J_{PH}$ = 2 Hz), 6.62 (s, 1H, aromatic CH), 7.26 (t, 1H, aromatic CH, *J* = 8 Hz). ^{31}P NMR (162.0 MHz, toluene-d_8, 25 °C), δ −135.9 (t, 1P, PH_2, $^1J_{PH}$ = 199 Hz).

1-Phosphino-2-ethylbenzene. Yield, 64%. ^{1}H NMR (400.1 MHz, C_6D_6, 25 °C), δ 1.06 (t, 3H, *o*-CH_2CH_3, $^3J_{HH}$ = 7.5 Hz), 2.56 (q, 3H, *o*-CH_2CH_3, $^3J_{HH}$ = 7.5 Hz), 3.77 (d, 2H, PH_2, $^1J_{PH}$ = 200 Hz), 6.89 (t, 1H, aromatic CH, $^3J_{HH}$ = 7.5 Hz), 6.69 (m, 1H, aromatic CH), 7.06 (t, 1H, aromatic CH, *J* = 8 Hz), 7.31 (t, 1H, aromatic CH), *J* = 7.5 Hz). ^{31}P NMR (162.0 MHz, C_6D_6, 25 °C), δ −131.2 (t, 1P, PH_2, $^1J_{PH}$ = 200 Hz).

1-Phosphino-2-methylnaphthalene. Yield, 51%. ^{1}H NMR (400.1 MHz, C_6D_6, 25 °C), δ 2.31 (s, 3H, *o*-CH_3), 3.86 (d, 2H, PH_2, $^1J_{PH}$ = 205 Hz), 7.01 (dd, 1H, aromatic CH, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 2 Hz), 7.22 (m, 1H, aromatic CH), 7.31 (m, 1H, aromatic CH), 7.47 (d, 1H, aromatic CH, $^3J_{HH}$ = 8.5 Hz), 7.59 (d, 1H, aromatic CH, $^3J_{HH}$ = 8.5 Hz), 8.17 (d, 1H, aromatic CH, $^3J_{HH}$ = 8.5 Hz). ^{31}P NMR (162.0 MHz, C_6D_6, 25 °C), δ −157.6 (t, 1P, PH2, $^1J_{PH}$ = 205 Hz).

Synthesis of [Li(TMEDA)$_2$] Salts of 2−4. A solution of the appropriate primary phosphine (0.95 mmol) in toluene (10 mL) was treated with TMEDA (0.57 mL, 3.8 mmol) and cooled to −78 °C. Treatment with ^{n}BuLi (1.6 M in hexane, 1.2 mL, 1.9 mmol) and warming to rt yielded a yellow suspension which was stirred for 1 h. After cooling again to −78 °C, $Sb(NMe_2)_3$ (2.0 M in toluene, 0.24 mL, 0.48 mmol) was added, before allowing the solution to warm to rt, then heating under reflux for 2 h. The resultant suspension was allowed to cool to rt before being filtered through glass filter paper. Solvent was removed from the filtrate, and the residue was vigorously stirred in *n*-pentane (10 mL), yielding the desired product as an impure precipitate.

2. Yield 22% (assuming pure sample). ^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ 2.15 (s, 24H, TMEDA, CH_3), 2.30 (s, 8H, TMEDA, CH_2), 6.49 (t, 1H, $^3J_{HH}$ = 7.0 Hz, aromatic C*H*), 6.65 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, 6.5 Hz, aromatic C*H*), 7.58 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic C*H*), 7.89 (t, 1H, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.0 Hz, aromatic C*H*), 7.90 (d, $^2J_{PH}$ = 38.0 Hz, PC*H*). ^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ 146.0 (dd, 1P, $^1J_{PP}$ = 455 Hz, $^3J_{PH}$ = 7 Hz, *P*PCH), 222.3 (dd, 1P, $^1J_{PP}$ = 455 Hz, $^2J_{PH}$ = 38 Hz, P*P*CH). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 25 °C) δ 46.2 (s, TMEDA, CH_3), 58.4 (s, TMEDA, CH_2), 114.3 (dd, $^3J_{PC}$ = 15 Hz, aromatic), 117.9 (d, $^4J_{PC}$ = 2 Hz, aromatic), 122.7 (d, $^3J_{PC}$ = 10.5 Hz, aromatic), 129.3 (d, $^2J_{PC}$ = 25.5 Hz, $^3J_{PC}$ = 4 Hz, aromatic), 138.8 (dd, $^1J_{PC}$ = 57.5 Hz, $^2J_{PC}$ = 4 Hz, PPCH), 151.5 (dd, $^2J_{PC}$ = 9 Hz, $^3J_{PC}$ = 4 Hz, aromatic), 162.4 (d, $^1J_{PC}$ = 60 Hz, aromatic). LR-ESI-MS (negative): *m*/*z* 151 (**2**, 100%). HR-ESI-MS (negative): Calcd for $C_7H_5P_2$ (**2**) *m*/*z* = 150.9866. Found *m*/*z* = 150.9852. X-ray data, formula $C_7H_5P_2{\cdot}Li(C_6H_{16}N_2)_2$, MW = 390.40, crystal system monoclinic, space group *C*2/*c*, *Z* = 16, *a* = 32.3894(7), *b* = 17.6315(4), *c* = 16.9036(4) Å, β = 103.1995(11)°, *V* = 9398.2(4) Å^3, ρ_{calc} = 1.104 Mg m^{-3}, *T* = 180(2) K, μ(Cu Kα) = 1.735 mm^{-1}, total reflections 35 584, unique reflections 8792, R_{int} = 0.046, R_1 [$I < 2\sigma(I)$] = 0.072, wR_2 (all data) = 0.218.

3. Yield 30% (assuming pure sample). ^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ 2.15 (s, 24H, TMEDA, CH_3), 2.30 (s, 8H, TMEDA, CH_2), 3.71 (s, 3H, OCH_3), 6.25 (d, 1H, $^3J_{HH}$ = 8.5 Hz, aromatic C*H*), 7.06 (bs, 1H, aromatic C*H*), 7.69 (dd, 1H, $^3J_{HH}$ = 8.5 Hz, 6.0 Hz, aromatic C*H*), 7.70 (d, $^2J_{PH}$ = 39.0 Hz, PC*H*). ^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ 147.1 (d, 1P, $^1J_{PP}$ = 457 Hz, *P*PCH), 233.7 (dd, 1P, $^1J_{PP}$ = 457 Hz, $^2J_{PH}$ = 39 Hz, P*P*CH). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 25 °C) δ 46.2 (s, TMEDA, CH_3), 54.9 (s, OCH_3), 58.4 (s, TMEDA, CH_2), 102.3 (dd, $^3J_{PC}$ = 9 Hz, aromatic), 106.6 (dd, $^3J_{PC}$ = 15 Hz, $^4J_{PC}$ = 2 Hz, aromatic), 129.4 (d, $^2J_{PC}$ = 26 Hz, aromatic), 136.1 (dd, $^2J_{PC}$ = 25.5 Hz, $^3J_{PC}$ = 4 Hz, aromatic), 138.8 (dd, $^1J_{PC}$ = 58 Hz, $^2J_{PC}$ = 4 Hz, PPCH), 150.9 (dd, $^2J_{PC}$ = 9 Hz, $^3J_{PC}$ = 4 Hz, aromatic), 154.4 (s, aromatic), 155.1 (d, $^1J_{PC}$ = 58 Hz, aromatic). LR-ESI-MS (negative): *m*/*z* 181 (**3**, 1%), 166 (**3** − Me, 20%), 151 (**3** − OMe, 100%). HR-ESI-MS (negative): Calcd for $C_8H_7OP_2$ (**3**) *m*/*z* = 180.9972. Found *m*/*z* = 181.0009.

4. Yield 39% (assuming pure sample). ^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ 2.15 (s, 24H, TMEDA, CH_3), 2.30 (s, 8H, TMEDA, CH_2), 2.72 (d, 3H, $^3J_{PH}$ = 13 Hz, CH_3), 6.52 (t, 1H, $^3J_{HH}$ = 7.0 Hz, aromatic C*H*), 6.73 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, 7.0 Hz, aromatic C*H*), 7.40 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic C*H*), 7.80 (t, $^3J_{HH}$ = 7.0 Hz, aromatic C*H*). ^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ 117.3 (d, 1P, $^1J_{PP}$ = 448 Hz, *P*PCMe), 222.3 (dq, 1P, $^1J_{PP}$ = 457 Hz, $^3J_{PH}$ = 13 Hz, P*P*CMe). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 25 °C) δ 19.7 (dd, $^2J_{PC}$ = 35 Hz, $^3J_{PC}$ = 32 Hz, CH_3), 46.2 (s, TMEDA, CH_3), 58.4 (s, TMEDA, CH_2), 114.0 (d, $^3J_{PC}$ = 16 Hz, aromatic), 117.4 (s, aromatic), 119.0 (d, $^2J_{PC}$ = 10 Hz, aromatic), 129.8 (d, $^2J_{PC}$ = 25 Hz, aromatic), 163.6 (d, $^1J_{PC}$ = 56 Hz, aromatic). X-ray data, formula $C_8H_7P_2{\cdot}Li(C_8H_{16}O_4)_2$, MW = 524.43, crystal system triclinic, space group $P\bar{1}$, *Z* = 2, *a* = 8.4645(4), *b* = 12.2344(6), *c* = 14.0658(7) Å, α = 95.494(3), β = 95.576(4), γ = 110.021(3)°, *V* = 1349.13(12) Å^3, ρ_{calc} = 1.291 Mg m^{-3}, *T* = 180(2) K, μ(Cu Kα) = 1.835 mm^{-1}, total reflections 16 339, unique reflections 3241, R_{int} = 0.082, R_1 [$I < 2\sigma(I)$] = 0.127, wR_2 (all data) = 0.311.

Synthesis of [K(PMDETA)] (1). A suspension of KH (0.126 g, 3.1 mmol) in toluene (18 mL) was treated with PMDETA (0.66 mL, 3.1 mmol) and $MesPH_2$ (0.24 g, 1.6 mmol) at −78 °C. The resulting mixture was allowed to warm to rt, than heated to reflux for 5 min, after which a yellow suspension was present. This was allowed to cool to rt before being cooled to −78 °C and treated with $Sb(NMe_2)_3$ (2.0 M solution in toluene, 0.56 mL, 1.1 mmol). After warming to rt, the reaction was heated under reflux for 3 h. Once at rt, the black suspension was filtered through glass filter paper, yielding a yellow/orange solution. This was freed from volatiles under vacuum and suspended in pentane (10 mL). The resultant yellow precipitate was isolated by cannula filtration, then washed with pentane (2 × 10 mL) (0.130 g, 0.33 mmol, 44%). ^{1}H NMR (400 MHz, THF-d_8) δ 7.98 (d, $^2J_{PH}$ = 38 Hz, 1H, P(CH)C), 7.38 (s, 1H, C(CH)C), 6.37 (s, 1H, C(CH)C), 2.63 (s, 3H, CH_3), 2.41 (m, 4H, PMDETA CH_2), 2.30 (s, 3H, CH_3), 2.30 (m, 4H, PMDTA CH_2), 2.18 (s, 3H, PMDTA CH_3), 2.14 (s, 12H, PMDETA CH_3). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8) δ 223.7 (d, $^1J_{PP}$ = 447 Hz, 1P, PPCH), 137.7 (d, $^1J_{PP}$ = 447 Hz, 1P, PPCH).

Synthesis of [Li(TMEDA)$_2$] Salts of 5 and 6. A solution of 1-phosphino-2-methylnaphthalene (0.20 g, 1.15 mmol) in toluene (12 mL) and THF (3 mL) was treated with TMEDA (0.69 mL, 4.60 mmol) and cooled to −78 °C. Next, 1.6 M ^{n}BuLi in hexane (1.45 mL, 2.30 mmol) was added dropwise to the stirred solution causing the color to change to bright orange. After stirring for 1 h at rt, the now deep-red solution was cooled to −78 °C and treated with 2.0 M $Sb(NMe_2)_3$ in toluene (0.30 mL, 0.60 mmol). Once at rt, the brown solution was heated under reflex for 2.5 h. After cooling to rt, THF (5 mL) was added, and the dark brown solution was filtered through glass filter paper. The filtrate was freed from volatiles under vacuum, and the solid residue was stirred with *n*-pentane (20 mL). Filtration of this suspension yielded a mixture of the [Li(TMEDA)$_2$] salts of **5** and **6** in a ratio of 2:1 as a brown precipitate.

*Spectral Data for [Li(TMEDA)$_2$][**5**].* ^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ 2.15 (s, 24H, TMEDA CH_3), 2.30 (s, 8H, TMEDA, CH_2), 6.95 (d, 1H, $^3J_{HH}$ = 8.5 Hz, aromatic C*H*), 7.00 (m, 1H,

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aromatic C*H*), 7.10 (m, 1H, aromatic C*H*), 7.48 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic C*H*), 7.62 (d, $^3J_{HH}$ = 8.5 Hz, aromatic C*H*), 8.01 (d, $^2J_{PH}$ = 38 Hz, PPC*H*), 8.70 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 3.5 Hz, aromatic C*H*). ^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ 152.1 (d, 1P, $^1J_{PP}$ = 455 Hz, *P*PCH), 212.6 (dd, 1P, $^1J_{PP}$ = 455 Hz, $^2J_{PH}$ = 38 Hz, P*P*CH).^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 25 °C) δ 46.2 (s, TMEDA CH_3), 58.4 (s, TMEDA CH_2), 118.8 (s, aromatic), 121.4 (s, aromatic), 123.8 (s, aromatic), 125.1 (d, $^3J_{PC}$ = 10 Hz, aromatic), 126.2 (d, $^3J_{PC}$ = 22 Hz, aromatic), 128.0 (s, aromatic), 141.2 (d, $^1J_{PC}$ = 56 Hz, PP*C*H), 148.7 (aromatic), 159.3 (aromatic). HR-ESI-MS (negative): Calcd for $C_{11}H_7P_2$ (S) m/z = 201.0023. Found m/z = 201.0070.

*Spectral Data for [Li(TMEDA)$_2$][**6**].* ^{1}H NMR (400.1 MHz, THF-d_8, 25 °C) δ 2.15 (s, 24H, TMEDA CH_3), 2.30 (s, 8H, TMEDA CH_2), 6.85 (d, 1H, $^3J_{HH}$ = 8.5 Hz, aromatic C*H*), 7.02−7.06 (m, 2H, aromatic C*H*), 7.38 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic C*H*), 7.60 (d, $^3J_{HH}$ = 8.5 Hz, aromatic C*H*), 8.87 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 3 Hz, aromatic C*H*), 10.30 (d, $^3J_{PH}$ = 3.5 Hz, PSbC*H*). ^{31}P NMR (162.0 MHz, THF-d_8, 25 °C) δ 218.6 (s, 1P, *P*SbCH).^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 25 °C) δ 46.2 (s, TMEDA CH_3), 58.4 (s, TMEDA CH_2), 119.2 (s, aromatic), 121.0 (s, aromatic), 123.9 (s, aromatic), 127.3 (d, $^3J_{PC}$ = 30 Hz, aromatic), 127.7 (s, aromatic), 128.5 (aromatic), 159.3 (aromatic), 162.5 (PSbCH).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00480.

General experimental techniques, ^{1}H and ^{31}P NMR spectroscopic characterization, computational details, X-ray single-crystal analysis of [Li(TMEDA)$_2$][**2**] and [Li(18-crown-6)$_2$][**4**] (DOCX)

Accession Codes

CCDC 1852044−1852045 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail dsw1000@cam.ac.uk.

ORCID

Andrew D. Bond: 0000-0002-1744-0489

Dominic S. Wright: 0000-0002-9952-3877

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Notes

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