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Versatile Synthesis of Phospholides from Open-Chain Precursors. Application to Annelated Pyrrole– and Silole–Phosphole Rings

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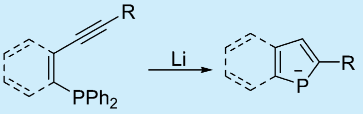
Ⓢ *Supporting Information*

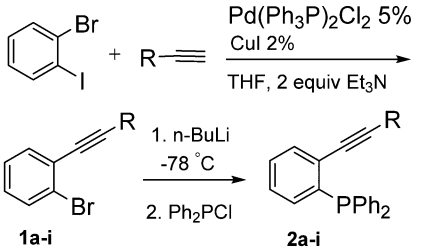
ABSTRACT: Phospholides are easily obtained by treatment of the open-chain acetylenic phosphines shown by an excess of lithium at room temperature in THF (12 examples).



Phospholides are one of the two fundamental aromatic rings of phosphorus–carbon heterocyclic chemistry.[1] However, the number of synthetic routes to these species is very limited in spite of their key role in organophosphorus synthesis and coordination chemistry. In fact, they are practically always synthesized by reductive cleavage of the P–R exocyclic bond of phospholes,[2] the driving force being the conversion of the nonaromatic phosphole into the aromatic phospholide. Alternatively, it is possible to couple the easy [1,5] shift of the sp^2-carbon substituent of phospholes from P to Cα with a deprotonation of the resulting 2*H*-phosphole.[3] To the best of our knowledge, the only case where a noncyclic precursor has been used concerns the formation of a calcium phospholide by reaction of a calcium bis(trimethylsilyl) phosphide with a 1,3-diyne.[4] We wish to report hereafter on a versatile access to phospholides starting from easily made noncyclic phosphines and allowing to synthesis of hitherto unknown annelated species.

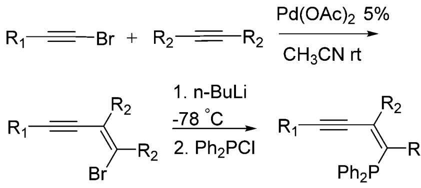
Our work began with the synthesis of two families of open-chain phosphines incorporating a carbon–carbon triple bond at the γ position from the phosphorus center. The first family (**2**) derives from triphenylphosphine. Its synthesis relies on a classical Sonogashira coupling (Scheme 1). Phosphine **2a** has already been described in the literature.[5] The second family (**4**), incorporating a *Z*-enyne functionality, was prepared from the appropriate bromo enynes (**3**) whose synthesis has been recently described[6] (Scheme 2). These two families of phosphines have a backbone similar to those of secondary phosphine oxides that have been previously used in a synthesis of phosphindoles.[7]

Scheme 1. Synthesis of *o*-Alkynyltriphenylphosphines



a: R = Ph
b: R = *p*-Tol
c: R = SiMe$_3$
d: R = *p*-C$_6$H$_4$-OMe
e: R = *n*-Bu
f: R = *p*-C$_6$H$_4$-*n*-Bu
g: R = 1-naphthyl
h: R = 1-methyl-2-indolyl
i: R = *o*-C$_6$H$_4$-SiMe$_3$

Scheme 2. Synthesis of Diphenylphosphinoenynes

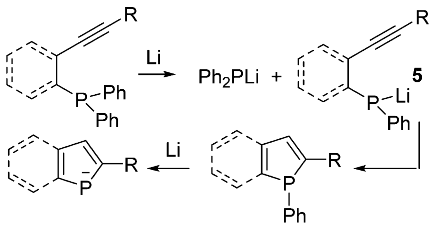


3a R$_1$ = *p*-Tol, R$_2$ = Et — **4a**
3b R$_1$ = Ph, R$_2$ = *n*-Pr — **4b**

This led us to investigate the reaction of lithium with our two families of phosphines. A statistical cleavage of the P–C bonds would lead to a 66% yield of the anion **5** whose cyclization would give a phosphole or a phosphindole (Scheme 3).

The actual results of our experiments with a 5- to 6-fold excess of lithium were more satisfactory than expected. In fact, the formation of Ph$_2$PLi, as detected by its ^{31}P resonance at

Scheme 3. Proposed Synthetic Scheme



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−22 ppm,[8] is negligible, and the cyclization almost exclusively leads to the phospholide and phosphindolide anions **6** and **8** which are easily detected by their characteristic ^{31}P resonances at low fields.[9] The observed shifts are collected in Figure 1. The experiments are described in Schemes 4 and 5.

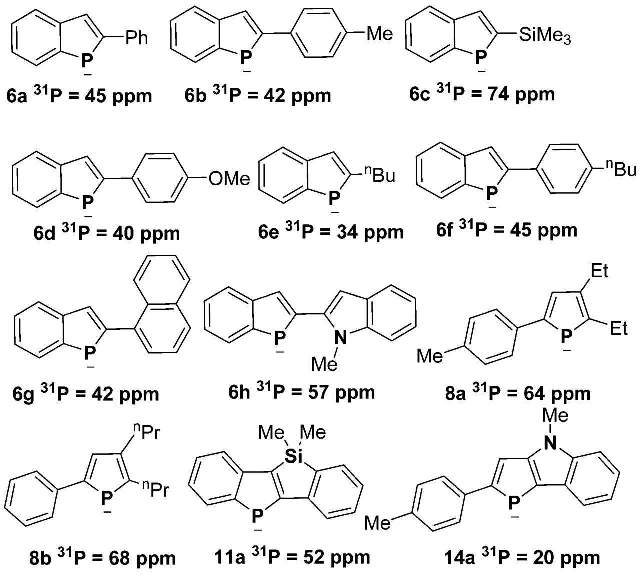
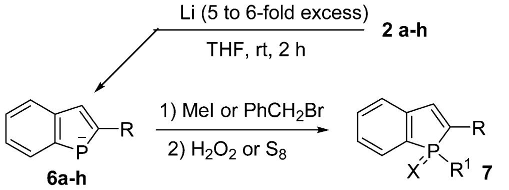


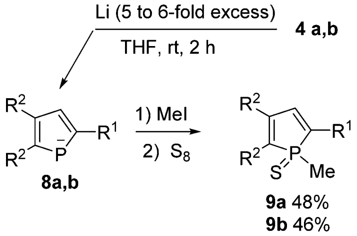
Figure 1. ^{31}P chemical shifts of phospholides and phosphindolides (in THF with Li$^+$ as counterion).

Scheme 4. Synthesis of Phosphindoles



7a R = Ph, R^1= Me, X = O (67%)
7b R = *p*-Tol, R^1= Me, X = S (53%)
7c R = SiMe$_3$, R^1= Me, X = O (46%)
7d R = *p*-C$_6$H$_4$-OMe, R^1= Me, X = S (65%)
7e R = *n*-Bu, R^1= Me, X = S (60%)
7f R = *p*-C$_6$H$_4$-*n*-Bu, R^1= Me, X = O (60%)
7g R = 1-naphthyl, R^1= CH$_2$Ph, X = O (40%)
7h R = 1-methyl-2-indolyl, R^1 = Me, X = O (57%)

Scheme 5. Synthesis of Phospholes



Due to the use of an excess of lithium, the crude solutions containing the anions **6** or **8** also contain phenyllithium which is formed by reduction of the initial phenyl radical by the excess of metal. Treating the solution of **6a** by iodine and sulfur led to **7i** (R = R^1 = Ph, X = S). In order to investigate why lithium almost selectively cleaves the P−Ph bonds of **2** and **4**, we decided to study the electronic structure of radical **10** by DFT at the UB3LYP/6-311G(d,p) level. Radicals such as **10** are known to be involved in the reduction of triarylphosphines by alkali metals.[10] The geometrical structure of **10** is shown in Figure (2). The most striking characteristic of this structure is that the P−C13 (P−Ph) bond at 1.875 Å is significantly longer than the two other P−C bonds at 1.835 Å. The SOMO (Figure 3) is antibonding on this P−C13 bond, whereas it is bonding and highly localized on the two other P−C bonds. These data indicate that the radical evolves preferentially by cleavage of this P−Ph bond.

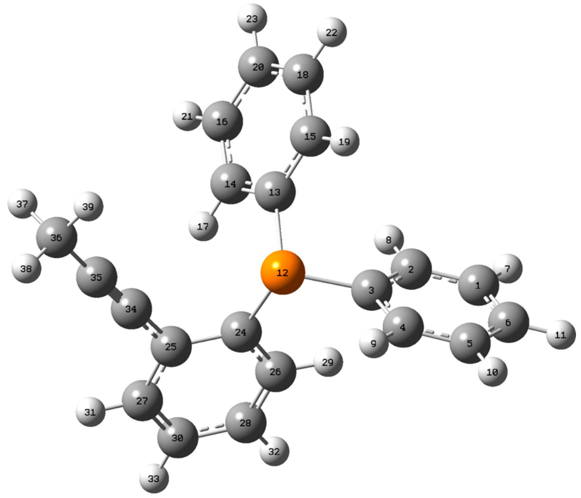


Figure 2. Computed structure of radical anion **10**. Main distances (Å) and angles (deg): P12−C13 1.875, P12−C3 1.835, P12−C24 1.835, C24−C25 1.456, C25−C34 1.411, C34−C35 1.216; C3−P12−C13 101.38, C3−P12−C24 105.06; C13−P12−C24 102.92 C24−C25−C34 122.39.

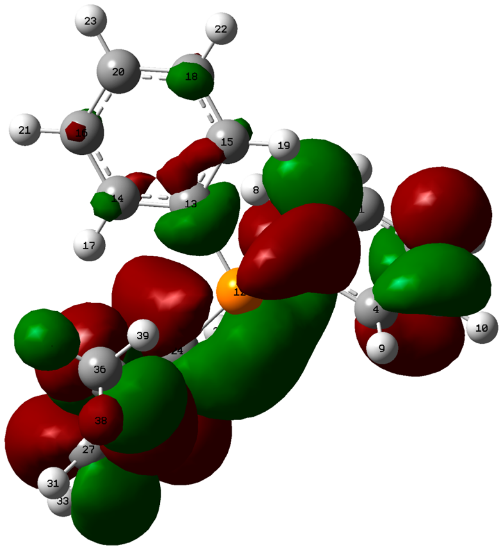
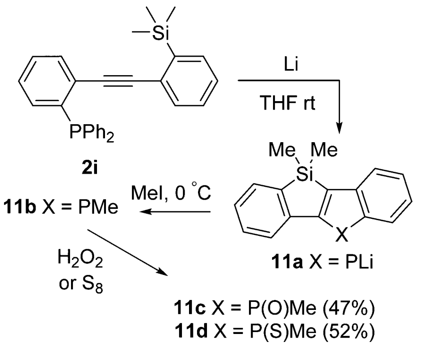


Figure 3. SOMO (Kohn−Sham) of radical anion **10**.

A recent theoretical paper has stressed the interesting properties of ladder-type heterotetracenes with dual bridging atoms for optoelectronic applications.[11] A mixed phosphorus−silicon species **11b** was included among the studied molecules. It is possible to use this new route to phospholides to synthesize **11b** and its derivatives as shown in Scheme 6.

Scheme 6. Synthesis of P,Si-Tetracenes



The initially formed β-lithiated phosphindole spontaneously cyclizes by demethylation of the trimethylsilyl substituent to build the silole ring. Somewhat similar demethylations leading to benzosiloles have been described in the literature.[12,13] The X-ray crystal structure of **11c** is shown in Figure 4. The core of the molecule is slightly bent by 3.2° around the C7–C8 junction between the phosphole and the silole planes.

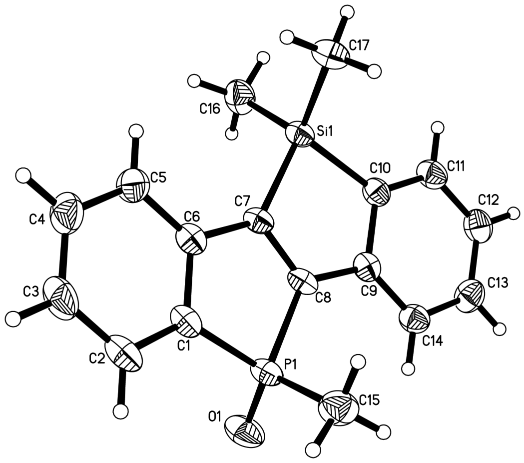
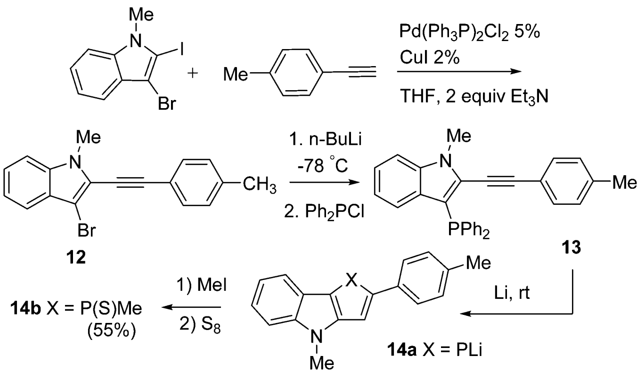


Figure 4. X-ray crystal structure of **11c**. Main distances (Å) and angles (deg): P1–O1 1.481(3), P1–C1 1.811(4), P1–C8 1.821(4), P1–C15 1.813(5), Si1–C7 1.887(4), Si1–C10 1.886(3), C1–C6 1.405(6), C6–C7 1.474(5), C7–C8 1.355(5), C8–C9 1.468(5), C9–C10 1.415(5); C1–P1–C8 91.55(18), C7–Si1–C10 90.72(16).

Another original species **14b** incorporating fused pyrrole and phosphole rings has also been obtained as shown in Scheme 7.

Scheme 7. Synthesis of an Annelated Pyrrole–Phosphole



In conclusion, we have developed the first general synthesis of phospholides and annelated phospholides starting from open-chain precursors. This synthesis has served to prepare a new phosphorus–silicon heterotetracene of interest for optoelectronic studies and a new phosphole–pyrrole annelated system. Many more applications of this new scheme can be envisaged.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, NMR data for **2–14** and X-ray data for **11c** This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This work is dedicated to Prof. Tamotsu Takahashi on the occasion of his 60th birthday.

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