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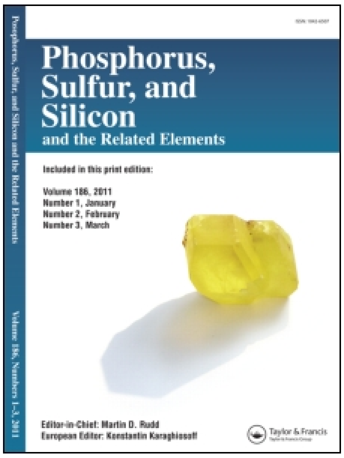

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LOW OXIDATION STATE GROUP 15 ELEMENTS AS PNICTA-WITTIG REAGENTS

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LOW OXIDATION STATE GROUP 15 ELEMENTS AS PNICTA-WITTIG REAGENTS

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We have synthesized a new As(I) salt and performed a Density Functional Theory investigation into the use of such compounds as pnicta-Wittig reagents.

Keywords: Arsenic; DFT; low oxidation state; phosphorus; Wittig

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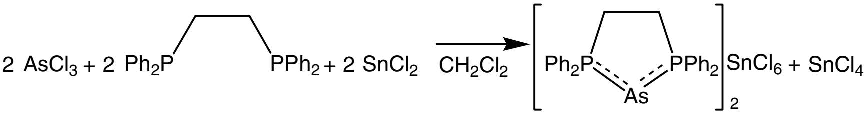
As part of our continuing investigation of the low-oxidation state chemistry of group 13–15 elements,[1] we have synthesized a new salt for use as a source of As(I) centers. In this work, we have begun to study the use of triphosphenium cations, $[(R_3P)_2P]^+$ (**1**),[2] and the heavier arsenic analogues, $[(R_3P)_2As]^+$ (**2**) as pnicta-Wittig reagents for the formation of new group 15-carbon bonds. We have synthesized the new arsenic(I) salt $[(dppe)As]_2[SnCl_6]$ (**3**) (dppe = 1,2-bis(diphenylphosphino)ethane) in 98% yield* using a method analogous to that used by Schmidpeter.[3] Whereas the addition of $AsCl_3$ to one or two equivalents of many phosphines or arsines results in only the formation of adducts,[4] in the presence tin(II) chloride, the arsenic center is reduced from As(III) to As(I) and stabilized by the dppe chelate (Scheme 1).



SCHEME 1

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*Melting point: 122–123°C, $^{31}P\{1H\}$ NMR: $\delta = 61.7$ (s).

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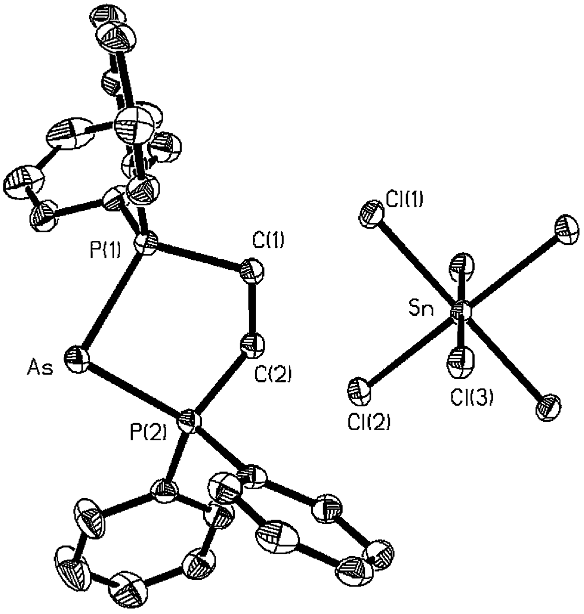

FIGURE 1 Thermal ellipsoid (30%) plot of **3**·2 CH_2Cl_2 (solvent not shown).

There are only five previous examples of such As(I) phosphine-stabilized cyclic compounds comprised of either four-,[5] five-,[6] six-[7] or seven-membered rings,[8] and one acyclic cation[9] that have been structurally characterized. The salt **3** (Figure 1) crystallizes in the space group P-1 with one molecule of CH_2Cl_2 in the asymmetric unit. The cation in **3** has As—P bond lengths of 2.2508(12) and 2.2518(12) Å in the solid state,* which are consistent with the As—P distances in the cyclic examples (2.244 to 2.273 Å), and are intermediate between those of average As—P single bonds (2.331 Å) and double bonds (2.129 Å). The P—As—P angle of 85.63(4) lies between those found in the four-membered rings (avg. angle 69.68°) and that found in the six-membered ring (93.04°).

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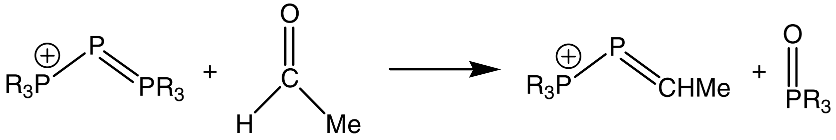
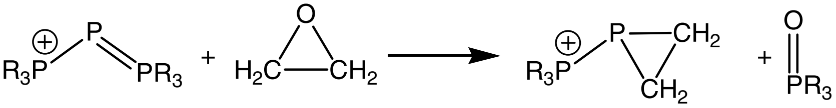
*Crystal data for **3**·$2CH_2Cl_2$: $C_{27}H_{26}AsCl_5P_2Sn_{0.5}$, triclinic, *P*-1, $a = 10.8800(7)$, $b = 11.6470(7)$, $c = 12.9540(8)$ Å, $\alpha = 69.144(1)°$ $\beta = 79.827(1)°$, $\gamma = 81.868(1)°$, $V = 1504.3(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.598$ g cm^{-3}, μ (Mo Kα) = 2.102 mm^{-1}. A total of 13,130 reflections was collected in the range $3.76 < 2\theta < 55.00$. Of these, 6,553 were considered observed ($I > 2.0\sigma$(I)); wR2 = 0.1020, $R = 0.0518$. CCDC 218386 contains the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk)

To assess the suitability of such Pn(I) cations as pnicta-Wittig reagents, we have employed density functional theory (DFT) calculations on a series of model cations. All optimized geometries and energies were calculated by the B3PW91 method[10,11] with the 6-31G(d) basis set using the Gaussian98 suite of programs.[12] The geometries were restricted to the highest reasonable symmetry and each stationary point was confirmed to be a minimum with zero imaginary vibrational frequencies. The electronic energies of the molecules have been corrected by the zero-point vibrational energy (ZPVE).



SCHEME 2



SCHEME 3

The reaction of **1** (**a**: R = H, **b**: R = Me, **c**: R = NH_2, **d**: R = OH) with acetaldehyde (Scheme 2) or oxirane (Scheme 3) was modelled to determine

TABLE I Calculated Energies of Reactants and Products for Reactions Involving Triphosphenium Cations as Phospha-Wittig Reagents with Acetaldehyde

Compound	Symmetry	Energy (au)	ZPVE (au)	Corrected energy (au)	ΔH_{rxn} (kJ mol^{-1})
MeCOH	C_s	−153.77018	0.05593	−153.71425	
$H_3P{-}P{=}PH_3^+$	C_{2v}	−1027.21651	0.05817	−1027.15834	5.9
$H_3P{-}P{=}CHMe^+$	C_s	−762.70591	0.08342	−762.62249	
H_3PO	C_{3v}	−418.27917	0.03133	−418.24784	
$Me_3P{-}P{=}PMe_3^+$	C_{2v}	−1263.14037	0.23349	−1262.90688	1.9
$Me_3P{-}P{=}CHMe^+$	C_s	−880.67504	0.17127	−880.50376	
Me_3PO	C_{3v}	−536.23480	0.11817	−536.11663	
$(H_2N)_3P{-}P{=}P(NH_2)_3^+$	C_2	−1359.38202	0.16929	−1359.21273	−8.0
$(H_2N)_3P{-}P{=}CHMe^+$	C_s	−928.79113	0.13872	−928.65242	
$(H_2N)_3PO$	C_3	−584.36358	0.08595	−584.27763	
$(HO)_3P{-}P{=}P(OH)_3^+$	C_2	−1478.54633	0.09221	−1478.45412	−50.5
$(HO)_3P{-}P{=}CHMe^+$	C_1	−988.36775	0.10050	−988.26725	
$(HO)_3PO$	C_3	−643.96894	0.04859	−643.92034	

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TABLE II Calculated Energies of Reactants and Products for Reactions Involving Triphosphenium Cations as Phospha-Wittig Reagents with Oxirane

Compound	Symmetry	Energy (au)	ZPVE (au)	Corrected energy (au)	ΔH_{rxn} (kJ mol^{-1})
Oxirane	C_{2v}	−153.73037	0.05791	−153.67246	
Me_3P–P=Pme_3^+	C_{2v}	−1263.14037	0.23349	−1262.90688	−114.3
Me_3P–P=$C_2H_4^+$	C_1	−880.67870	0.17245	−880.50625	
Me_3PO	C_{3v}	−536.23480	0.11817	−536.11663	
$(H_2N)_3P$–P=$P(NH_2)_3^+$	C_2	−1359.38202	0.16929	−1359.21273	−135.3
$(H_2N)_3P$–P=$C_2H_4^+$	C_1	−928.79897	0.13986	−928.65911	
$(H_2N)_3PO$	C_3	−584.36358	0.08595	−584.27763	
$(HO)_3P$–P=$P(OH)_3^+$	C_2	−1478.54633	0.09221	−1478.45412	−169.9
$(HO)_3P$–P=$C_2H_4^+$	C_1	−988.37254	0.10161	−988.27094	
$(HO)_3PO$	C_3	−643.96894	0.04859	−643.92034	

the effect of ligand substitution on the effectiveness of triphosphenium cations as Wittig-reagents.

Tables I and II list the calculated energies of the reactants and products involved in each reaction. The calculations predict that phospha-Wittig reactions involving such cations generally should be more favorable with oxiranes than with aldehydes and the results suggest a trend of increasing the thermodynamic favourability for the reactions as the substituents on the phosphines becoming increasingly electronegative.

Experimental investigations of pnicta-Wittig and other reactivity of univalent group 15 compounds are currently underway.

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