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## Rearrangement and redistribution reaction of $\text{Ph}_2\text{PCH}_2\text{TMS}$ with $\text{PhAsCl}_2$ or $\text{AsCl}_3$

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### ABSTRACT

The attempted synthesis of bis(diphenylphosphinomethyl) phenylarsane and tris(diphenylphosphinomethyl) arsane through condensation of chloro arsanes and diphenyl (trimethylsilylmethyl) phosphane yielded a number of side products originating from migratory and redox-reactions in addition to the targeted ligands. An unexpected, 1,3,4-phosphadiarsolan-1-ium salt was obtained and crystallographically characterized as an A-shaped chlorido adduct.

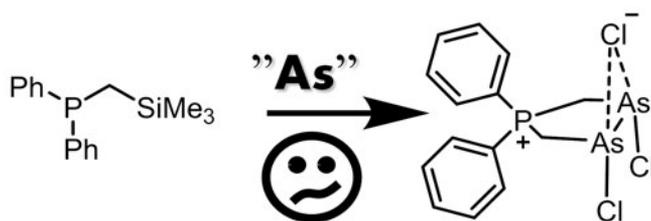
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Phosphonium; arsane;  
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### GRAPHICAL ABSTRACT



## Introduction

Oligophosphanes, in particular the tridentate bis-(diphenylphosphinomethyl) phenyl phosphane (dppp, **1**), have been extensively studied and used to prepare diverse multinuclear coordination compounds of copper,<sup>[1]</sup> silver,<sup>[2]</sup> gold,<sup>[3]</sup> and platinum,<sup>[4]</sup> as well as mixed metallic systems.<sup>[5]</sup> Recently, variations of this motif that alter the phosphane substituents<sup>[6]</sup> or expand the coordination environment<sup>[7,8]</sup> have led to interesting opto-electronic materials (Figure 1).

Elemental substitution of phosphorus with arsenic in the dppm ligand, as seen in bis(diphenylphosphinomethyl) phenylarsane (**2**, dppe) or bis(diphenylarsinomethyl) phenylphosphane (**3**, dpap), gave rise to numerous coordination compounds in which all three or only the two outermost donor sites are involved in the complexation of multi-metallic centers.<sup>[9,10]</sup> Recently, interesting solid state transformations of a dinuclear gold complex have been associated with dramatic optical changes for the bis(diphenylarsino)ethane ligand **4**.<sup>[11]</sup> Our and others efforts to further explore the coordination chemistry of arsine and arsole based ligands has led to materials with interesting optical, electronic and catalytic properties.<sup>[12–16]</sup>

## Results and discussion

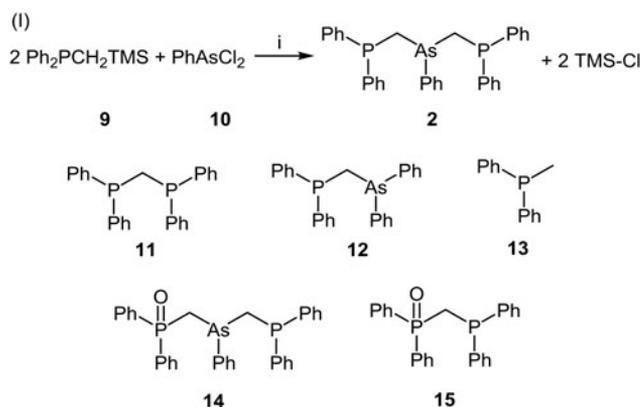
The methylene bridged hexaphosphane ligand bis{[(diphenylphosphinomethyl)phenylphosphino]phenylphosphino} methane (**8**) has previously been prepared in almost quantitative yields by the facile condensation of a silyl-substituted methylene phosphane (**6**) with the chlorophosphane **7**.<sup>[17]</sup> This observed reactivity inspired us to attempt the preparation of the tridentate ligand with mixed pnictogen donors, i.e. dpap (**2**), through the reaction of neat  $\text{Ph}_2\text{PCH}_2\text{TMS}$  (**9**) with  $\text{PhAsCl}_2$  (**10**). Elimination of two equivalents of TMS-Cl was expected to lead to the desired ligand **2** (Scheme 1). Surprisingly, this product was only formed in small amounts, while a multitude of phosphorus-containing side products were observed by <sup>31</sup>P NMR spectroscopy of the crude reaction mixture (Figure 2). Resonances grouped around –22 ppm indicate that a number of different phosphanes were formed, while the downfield shifted signals at around +30 ppm would suggest that serendipitous oxidation or quaternization of the phosphorus centers occurred. Chromatographic work-up of this complex mixture led to the identification of some phosphanes that were formed during this reaction: the symmetric

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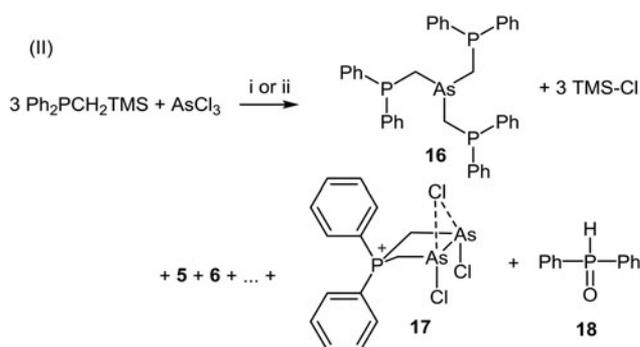
Color versions of one or more of the figures in the article can be found online at [www.tandfonline.com/gpps](http://www.tandfonline.com/gpps).

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**Scheme 1.** Attempted synthesis of the tridentate P-As-P ligand **2**, and the identified side products **11–13** and oxidized derivatives (**14**, **15**) thereof, which were obtained after the purification process. Conditions: i) neat, 90–100 °C.

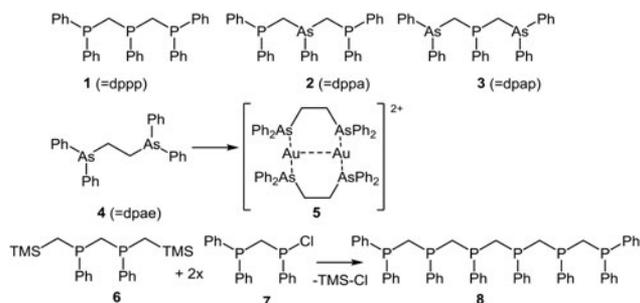


**Scheme 2.** Attempted synthesis of the triphosphane ligand **16** and observed side products in particular the phosphonium salt **17**. (i) room temperature, DCM. (ii) neat, 90–100 °C.

bisdiphenylphosphino methane (**11**, dppm), the mixed diphenylarsino diphenylphosphino methane (**12**, dpma), and diphenylmethylphosphane (**13**, dpmp) were identified based on crystallographic analysis and/or NMR data. These identified products clearly indicate that multiple reactions such as protodesilylation as well as phenyl- and methyl-migrations occur under these conditions. Additional oxidized derivatives have been identified from this complex mixture.

We were also able to chromatographically isolate **2**, and colorless crystals of the desired product were then obtained by slow hexane diffusion into a DCM solution of **2**. The structure solves in the orthorhombic space group  $Pca2(1)$  [ $a = 10.663(3)$ ;  $b = 10.096(3)$ ;  $c = 24.660(6)$ ,  $R1 = 5.1\%$ ]. The ligand exhibits a rather twisted arrangement, in contrast to many of the previously reported coordination compounds.<sup>[1,3,4]</sup> This arrangement leads to a relatively short intramolecular P1...P2 distance of 4.001(4) Å, whereas the phosphorus-arsenic separation is in the expected range (ca. 3 Å) (Figure 3).

We have also reacted  $\text{AsCl}_3$  with three equivalents of **9** in an attempt to synthesize the triphosphane ligand **16** (Scheme 2). Similarly, the allegedly simple reaction afforded a multitude of reaction products, with the exact mixture depending on whether the reaction was carried out neatly or in a solvent (e.g., DCM). When performed in DCM, the reaction initially gave rise to two very broad signals in its  $^{31}\text{P}$ -NMR spectra centered around  $-15$  and  $-7$  ppm, as well as a sharp signal at  $+21.5$  (doublet,  $^1J_{\text{PH}} = 477$  Hz) and a



**Figure 1.** Common polyphosphane and -arsane ligand systems and an example of a dinuclear arsane gold complex. Synthesis of a methylene bridged polyphosphane (**8**) by a condensation reaction and silyl chloride elimination.

singlet at 31.7 ppm. The compound associated with the resonance at 21.5 ppm was assigned to the formation of diphenyl phosphane oxide based on literature data.<sup>[19]</sup> After 18 h, the  $^{31}\text{P}$ -NMR spectrum revealed the major phosphorus-containing products had resonances at ca.  $-7$ ,  $+22$ ,  $30.5$ , and  $33.5$  ppm in an approximate ratio of 6.1:1:2.5. Initial purification by passing the crude reaction mixture through an alumina plug led to the disappearance of the  $-7$  ppm resonance and the appearance of two new peaks at  $-21.0$  and  $-25.9$  ppm, as well as a major peak at  $+31.2$  ppm.

The two phosphanes **11** ( $-25.7$  ppm) and **12** ( $-21.0$  ppm) were again identified as side products in this complex reaction mixture. A similarly complex reaction mixture was obtained when the reaction was carried out without solvent at elevated temperatures. A major product associated with

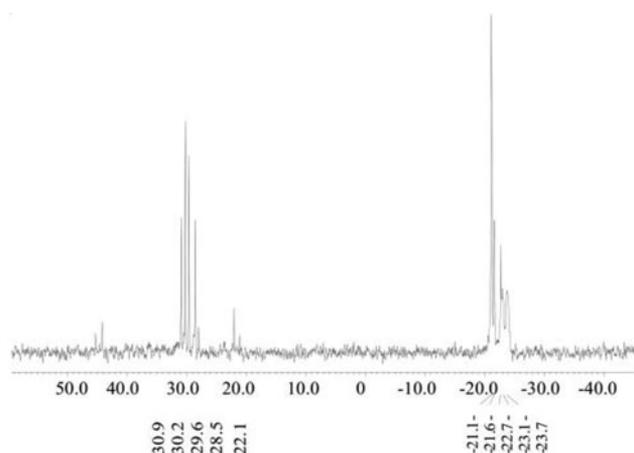


Figure 2. Crude  $^{31}\text{P}\{^1\text{H}\}$ -NMR of reaction (I).

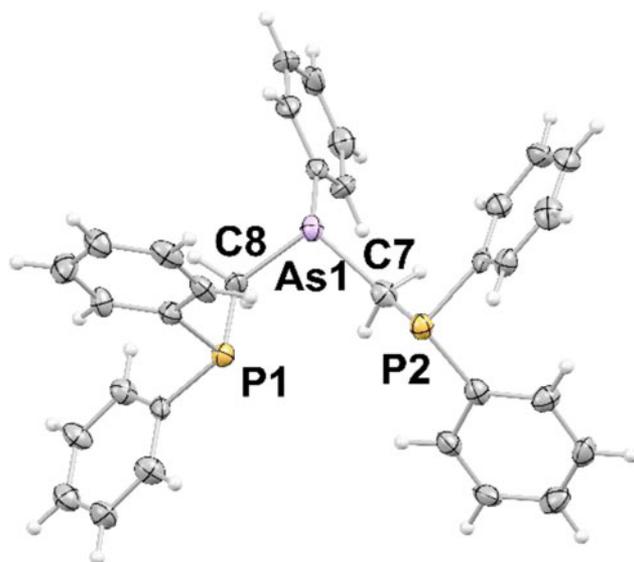


Figure 3. ORTEP<sup>18</sup> representation of the solid state structure of **2**. Ellipsoids are drawn at 50% probability levels. Selected bond lengths [Å] and angles [°]: As1-C8 1.982(9), P1-C8 1.833(8), P2-C7 1.841(9), P1...P2 4.001(4), As1...P2 3.118(3), P1...As1 3.100(3), C7-As1-C8 95.5(3), P2-C7-As1 109.6(4), P1-C8-As1 108.6(4).

one of the downfield shifted phosphorus resonances could be isolated by simple extraction of the crude product with acetonitrile. Slow crystallization by evaporation from a saturated solution afforded colorless crystals of the unexpected phosphonium salt **17** (Figure 4). Similarly, the corresponding dichloromethane solvate (**17**·CH<sub>2</sub>Cl<sub>2</sub>) was obtained by diffusion of DCM into an acetonitrile solution of **17**. Formation of this product is associated with a redox reaction at the arsenic center and methyl migrations, but probably involves other migratory steps as well. The  $^{31}\text{P}$ -NMR spectrum shows a single resonance at 36.6 ppm, while the  $^1\text{H}$ -NMR shows a broad singlet for the methylene protons at 1.57 ppm.

The structural analysis of **17** [orthorhombic space group Pna2<sub>1</sub>;  $a = 12.2004(7)$ ,  $b = 18.0162(9)$ ,  $c = 7.8796(4)$  Å] shows the formation of an As-As bond (2.4763(15) Å) together with a phosphonium center. The resulting 1,3,4-phosphodiarsolan-1-ium heterocycle provides an interesting motif with two As-Cl units (2.242(3) and 2.258(2) Å) and

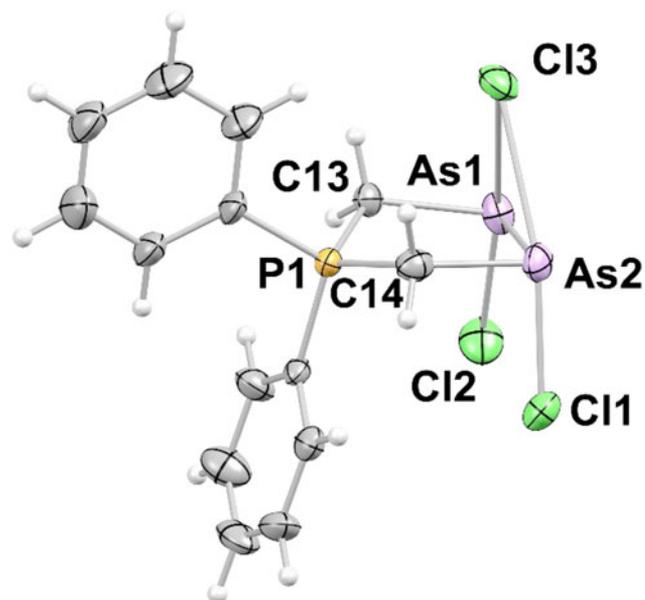


Figure 4. ORTEP<sup>18</sup> representation of the solid state structure of **17**. Ellipsoids are drawn at 50% probability levels. Selected bond lengths [Å] and angles [°]: As1-C13 1.974(8), As1-Cl2 2.242(3), As1-As2 2.4763(15), As2-C14 1.973(9), As2-Cl1 2.258(2), C13-P1 1.796(9), C14-P1 1.789(9), As1-Cl3 2.876(3), As2-Cl3 2.783(3).

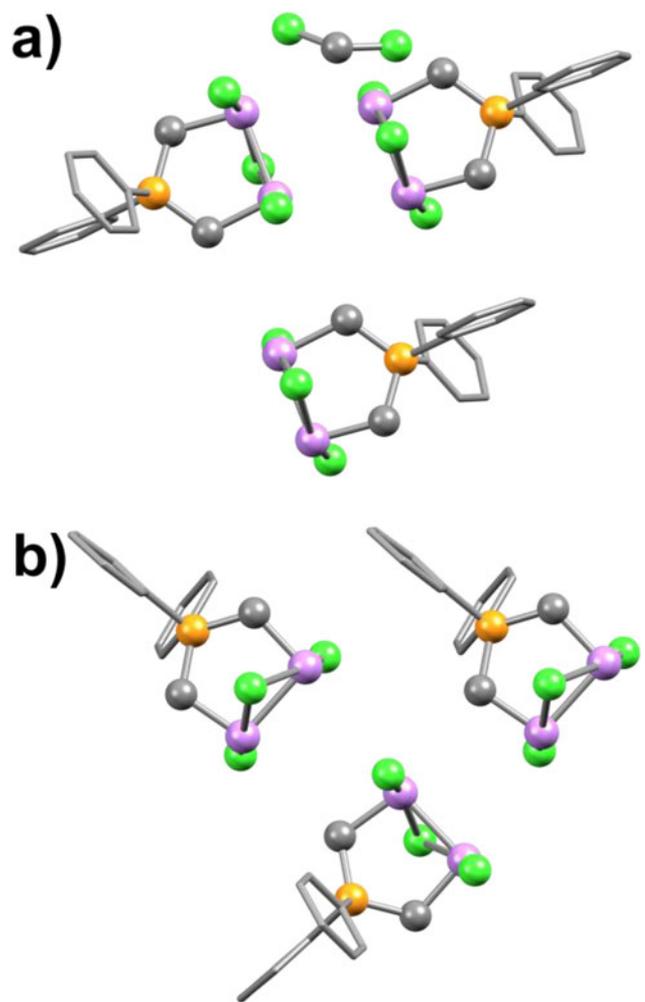


Figure 5. Different packing motifs seen in the solid-state structures of **10**-DCM (a) and **10** (b).

the third chloride atom bridging between the two arsenic centers (As-Cl3 2.783(3) and 2.876(3) Å) giving a unique A-shaped arrangement. The Cl3 chloride has long distances to the nearest phosphonium centers (intramolecular: 3.272(3) and intermolecular: 4.238(3) Å); however, it also displays a weak C-H...Cl interaction with one of the phenyl substituents (Cl3-H2 3.086 Å). The sums of the angles around both arsenic centers (excluding the As-Cl3 contacts) are 293.0 and 290.8°, resulting in a rather peculiar bonding situation. Moreover, the As-As single bond distance (2.4763(15) Å) is relatively long compared to previously reported diarsanes (2.40–2.45 Å<sup>[20]</sup>) but significantly shorter than in the sterically encumbered dimer of the latent and stable arsinyl radical (TMS<sub>2</sub>CH)<sub>2</sub>As· (2.587 Å).<sup>[21]</sup> A related five membered heterocycle - a dihalo-diarsa-cyclopentane derivative - has previously been reported as a halogenation product of As<sub>3</sub>-nortricyclane.<sup>[22]</sup> Similar to our observations, a complex equilibrium of products was observed under these experimental conditions.

The structure solution of the DCM solvate gives very similar metrics to the phosphonium salt, however the packing motifs differ significantly. While the DCM solvate leads to a shifted face-to-face arrangement of the A-motif (Figure 5a) the solvent free structure shows the A-motifs in a side-on packing motif (Figure 5b).

## Conclusions

The simple TMS-Cl elimination in the reaction of chlorophosphanes with silyl-substituted methylene phosphanes contrasts the complex behavior for chloro arsanes (Ph-AsCl<sub>2</sub> and AsCl<sub>3</sub>). The mixed pnictogen ligand bis(diphenylphosphinomethyl) phenylarsane was crystallographically characterized. The observed reactivities indicate that migratory and redox reactions are responsible for the complexity of this allegedly simple condensation reaction ultimately giving the unexpected 1,3,4-phosphadiarsolan-1-ium salt, with an A shaped As<sub>2</sub>Cl<sub>3</sub> motif.

## Experimental

Experiments are carried out under inert conditions unless stated otherwise. NMR data are recorded on a JEOL EXC operating at a proton frequency of 400 MHz. X-ray crystallography: All the measurements were performed using graphite-monochromatized MoK<sub>α</sub> radiation at 150 K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques against F<sup>2</sup> (SHELXL).<sup>[23]</sup>

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