

## Geometrically Enforced Donor-Facilitated Dehydrocoupling Leading to an Isolable Arsanylidene-Phosphorane

Brian A. Chalmers, Michael Bühl, Kasun S. Athukorala Arachchige, Alexandra M. Z. Slawin, and Petr Kilian\*

EaStChem School of Chemistry, University of St. Andrews, Fife KY16 9ST, St. Andrews, U.K.

### Supporting Information

**ABSTRACT:** A proximate Lewis basic group facilitates the mild dehydrogenative P–As intramolecular coupling in the phosphine-arsine peri-substituted acenaphthene **3**, affording thermally and hydrolytically stable arsanylidene-phosphorane **4** with a sterically accessible two-coordinate arsenic atom. The formation of **4** is thermoneutral due to the dehydrogenation being concerted with the donor coordination. Reaction of **4** with a limited amount of oxygen reveals arsinidene-like reactivity via formation of cyclooligoarsines, supporting the formulation of the bonding in **4** as base-stabilized arsinidene  $R_3P \rightarrow AsR$ .

The use of dehydrogenative coupling to build up catenated structures (molecular and polymeric) has become a highly topical area of main group chemistry. The newly developed dehydrogenative protocols are viable alternatives to the classical coupling strategies, such as salt eliminations. The growing interest in dehydrogenative coupling stems from the range of possibilities it opens up for new milder and more efficient syntheses of p-block element based materials. The potential is further strengthened by the amenability to catalysis, which is an aspect that received ample attention especially in the past decade.<sup>1</sup> One of the main drivers of the dehydrogenative chemistry is its ability to generate unique new structures, such as the distinctive  $P_{16}$  macrocycle reported by Stephan.<sup>2</sup> We have now used a dehydrogenative heterocoupling strategy to synthesize a two-coordinate arsenic motif, namely the first room temperature stable arsanylidene-phosphorane **4**. The dehydrogenative coupling appears to be indispensable in this case, as **4** has so far been inaccessible by the traditional reductive strategies.

It is generally accepted that low-coordinate arsenic chemistry is much less established than that of related phosphorus congeners. Among two-coordinate arsenic species the most attention has been received by arsaalkenes  $R_2C=AsR'$ , diarsenes  $RA_s=AsR$ ,<sup>3</sup> and phosphine- and carbene-stabilized cationic species.<sup>4,5</sup> In a similar vein, in comparison to their phosphorus relatives, only a very limited number of terminal arsinidene metal complexes  $L_nM=AsR$  are known.<sup>6</sup> Obtaining multiply bonded pnictogen species via dehydrocoupling is synthetically ambitious and, therefore, rare. The examples of low coordinated arsenic species synthesized via  $H_2$ -eliminative strategies include the diarsene  $(dmp)As=As(dmp)$  ( $dmp = 2,6$ -dimesitylphenyl), which was obtained via a catalytic dehydrogenation of  $dmpAsH_2$ ,<sup>7</sup> and an arsinidene complex

$(tBu_3SiO)_3Ta=AsPh$ , which was obtained via a 1,2- $H_2$ -eliminative process starting from  $PhAsH_2$  as the arsenic source.<sup>8</sup>

In addition to its unprecedented thermal stability, **4** displays arsinidene-like reactivity as demonstrated by the formation of the catenated products, cyclooligoarsines **5** and **6**. As mentioned by Weber recently, many of the current pnictinidene-transfer methods suffer from harsh conditions, which limit their synthetic utility.<sup>6</sup> Hence **4**, a new bottleable form of base-protected arsinidene, has the potential to become a welcome alternative arsinidene transfer reagent.<sup>9</sup>

Lithiation of **1** followed by coupling with  $AsCl_3$  afforded the phosphonium-arsoranide **2** in a very good yield (Scheme 1). In addition to the covalent zwitterionic structure of **2**, the compound can also be viewed as a phosphine-donor arsine-acceptor (DA) complex **2'** ( $R_3P \rightarrow AsR'$ , Chart 1). Given the slightly increased Lewis acidity of arsenic halides compared to the respective phosphorus halides, phosphine-arsine DA complexes should be more thermally stable than the related phosphine-phosphine DA complexes.<sup>10</sup> Nevertheless, only two phosphine-arsine DA complexes have previously been structurally characterized.<sup>11</sup>

Single crystal X-ray diffraction (Figure 1)<sup>12</sup> confirmed **2** to have pseudotrigonal bipyramidal geometry around the arsenic atom, with the two chlorine atoms occupying the axial positions and the lone pair occupying one of the equatorial positions. The As1–P1 bond (2.4029(7) Å) is only slightly elongated when compared to a standard covalent P–As single bond.<sup>13</sup> Sequestration of the phosphorus lone pair in bonding to the  $-AsCl_2$  group results in significant deshielding of the (donor) phosphorus atom ( $\delta_p$  65.3 ppm in **2** vs  $\delta_p$  –2.2 ppm in **1**).

The reduction of **2** with  $LiAlH_4$  afforded the primary arsine **3** in good yield (Scheme 1). The  $^{31}P\{^1H\}$  NMR spectrum of **3** consists of a singlet at  $\delta_p$  –11.3 ppm, indicating the phosphine group is not involved in any DA interaction with the arsenic functionality. The crystal structure of **3** confirms a repulsive interaction is present between the phosphine and arsine groups, with a  $P \cdots As$  distance of 3.157(2) Å (Figure 2).<sup>14</sup>

The arsine **3** is obtained as a pale pink powder,<sup>15</sup> which can be stored at –30 °C for months without any signs of decomposition. However, solid **3** has been found to release hydrogen slowly at ambient temperature to form the arsanylidene-phosphorane **4** (Scheme 1). This transformation is observed visually as a color change of the solid material from pink to an intense dark red and can be followed by  $^{31}P\{^1H\}$

Received: March 14, 2014

Published: April 15, 2014

Scheme 1. Syntheses Described in the Paper

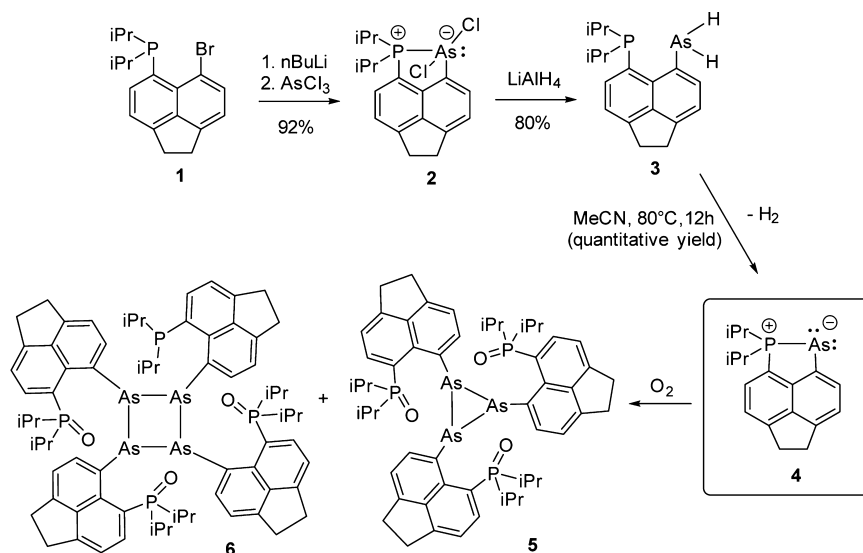


Chart 1. Zwitterionic and Donor–Acceptor Description of Bonding in 2 (Top); Ylide (Left) and Ylene (Right) Resonance Structures of 4 (Bottom)

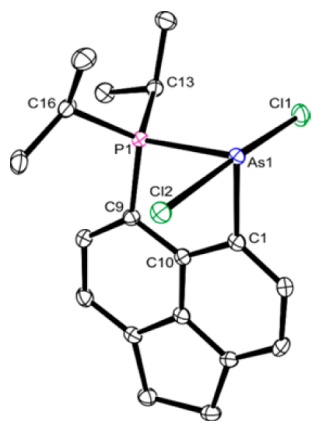
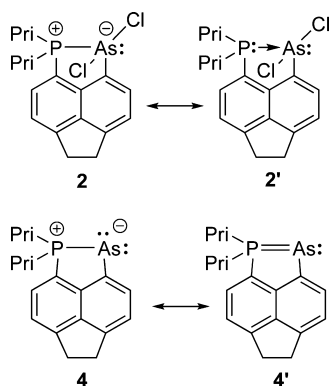


Figure 1. Molecular structure of 2. Hydrogen atoms are omitted for clarity.

NMR, where the initial singlet of 3 ( $\delta_p$  –11.3 ppm) is gradually replaced with a singlet of 4 ( $\delta_p$  75.3 ppm). While the full conversion in the solid state takes ca. 6 months, full and clean conversion of 3 into 4 was also achieved by heating a solution of 3 in MeCN under reflux for 12 h, or by standing the MeCN solution of 3 at room temperature for 7 days. The

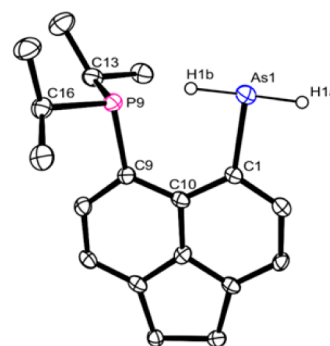


Figure 2. Molecular structure of 3. Carbon-bound hydrogen atoms are omitted for clarity.

transformation of 3 to 4 is very clean under all of the above conditions, with no other side products (except  $H_2$ ,  $\delta_H$  4.55 ppm in  $CD_3CN$ ) being found in the mixtures after the reaction by  $^1H$  and  $^{31}P$  NMR. Indeed, analytically pure 4 was obtained from these reactions as confirmed by microanalysis.

Single crystal X-ray diffraction confirmed the ylidic structure of 4 (Figure 3). The P9–As1 bond lengths in 4 (2.260(1) and 2.262(2) Å in the two molecules in the asymmetric unit) are

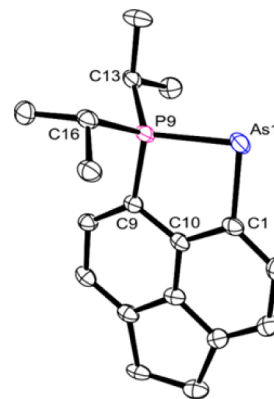


Figure 3. Molecular structure of 4. Hydrogen atoms are omitted for clarity.

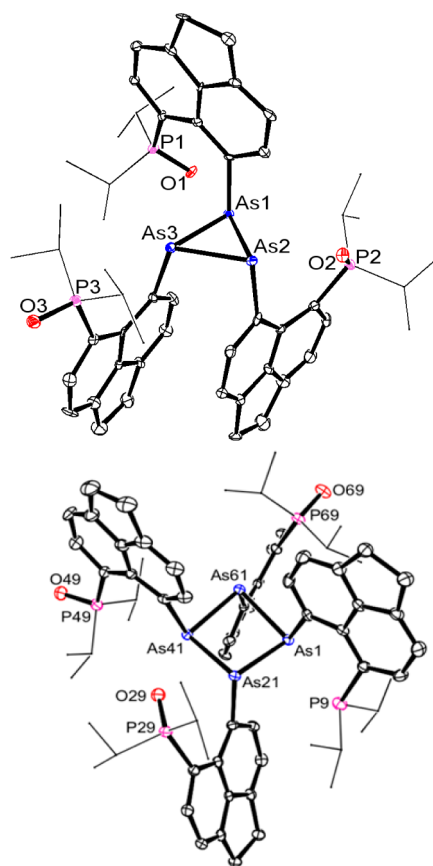
consistent with a P–As single bond with mild double-bond contribution.<sup>13</sup> DFT calculations (see Supporting Information (SI)) reveal that the electronic structure of **4** resembles that of its phosphorus counterpart.<sup>16</sup> Due to the lower electronegativity of arsenic, the P–As bond is less polarized; however, it also has slightly lower double bond character (see calculated natural charges and Wiberg bond indices in Table S1 in the SI). Overall, structural, spectroscopic, and computational data confirm the dominance of the ylidic mesomeric structure **4** over its ylene counterpart **4'** (Chart 1). The electronic structure of (hypothetical) arsanylidene-phosphoranes was the subject of several theoretical papers recently; the theoretical investigations were stimulated by interest in the bonding as well as potential Wittig-like reactivity.<sup>17</sup>

Compound **4** represents the first isolable arsanylidene-phosphorane. The only previously structurally characterized species of this type is 2,6-Trip<sub>2</sub>C<sub>6</sub>H<sub>3</sub>As=PMe<sub>3</sub> (Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) **7**.<sup>18</sup> Despite the excessive steric shielding provided by its bulky terphenyl ligands, arsa-Wittig complex **7** is rather thermally labile, eliminating PMe<sub>3</sub> under ambient conditions to give the corresponding diarsene. This precluded isolation of **7** in pure state and limited its synthetic potential. In sharp contrast, **4** is indefinitely stable at ambient temperature, despite containing a sterically accessible (“naked”) two-coordinate arsenic atom. In addition, no reaction takes place between **4** and degassed water at ambient temperature. We attribute the unprecedented stability of **4** to the special peri-geometry, with the C<sub>3</sub>PAs ring fused into the rigid acenaphthene moiety locking the donor (phosphine) group in close proximity of the low coordinate center.

Although the decomposition pathway via elimination of the phosphine is blocked in **4**, achieving the synthetically attractive deprotection of the arsinidene moiety is possible via quenching the electron-donating ability of the phosphorus atom. Thus, exposure of **4** to a limited amount of air resulted in formation of cyclooligoarsines **5** and **6** (Scheme 1 and Figure 4) as major products. The mechanism of this transformation is likely to involve sequestration of the electron density from the phosphorus atom (via its oxidation to phosphine oxide). This exposes the “free” arsinidene, which undergoes cyclooligomerization to give **5** and **6**. Notably, only three out of four phosphorus atoms are oxidized in **6**; i.e., one of the molecules **4** is incorporated into the ring structure without being oxidized first.

The dehydrogenative transformation of **3** to produce arsanylidene **4** represents a new synthetic strategy to low coordinate arsenic species, namely dehydrocoupling facilitated by a geometrically constrained proximate base. The phosphine group plays a dual role; it acts as a base to stabilize the low-coordinate arsinidene center, and by doing so, it facilitates the dehydrocoupling by making it energetically accessible. Calculations (M06-2X level)<sup>19</sup> show the loss of dihydrogen from **3** to be an essentially thermoneutral process ( $3 \rightarrow 4 + \text{H}_2$ ,  $\Delta H = -0.7 \text{ kcal mol}^{-1}$ ).<sup>20</sup> On the other hand, loss of H<sub>2</sub> from acenaphthene-5-arsine to give the corresponding arsinidene is highly endothermic ( $\Delta H = +52.2 \text{ kcal mol}^{-1}$ ), illustrating the importance of harmonizing the dehydrogenation with the donor coordination.

Notably, our system is conceptually similar to the recently reported reversible P(III)–P(V) redox system, where innovative phosphorus-catalyzed transfer hydrogenation activity was demonstrated.<sup>21</sup> The similarity with our system is that the favorable energetics of the hydrogenation/dehydrogenation



**Figure 4.** Molecular structures of **5** (top) and **6** (bottom). Hydrogen atoms are omitted, and the isopropyl groups are drawn as wireframe for clarity.

process is facilitated by geometrical constraints at the pnictogen center.

We have not been able to reverse the hydrogen evolution from **3** by increasing the H<sub>2</sub> pressure at room temperature. Mechanistic studies are underway to elucidate the reaction pathway of this process and investigate possible ways to facilitate the reversibility of the reaction or to achieve low-valent arsenic catalyzed transfer hydrogenation activity.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental procedures and characterization data of new compounds; additional computational results; X-ray crystallographic data of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

pk7@st-andrews.ac.uk

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by EPSRC, COST action CM0802 PhoSciNet and the EPSRC National Mass Spectrometry Service Centre (NMSSC) Swansea.

## ■ REFERENCES

- (1) For recent reviews, see: Leitao, E. M.; Jurca, T.; Manners, I. *Nat. Chem.* **2013**, *5*, 817–829. Waterman, R. *Chem. Soc. Rev.* **2013**, *42*, 5629–5641. Less, R. J.; Melen, R. L.; Wright, D. S. *RSC Adv.* **2012**, *2*, 2191–2199. Less, R. J.; Melen, R. L.; Naseri, V.; Wright, D. S. *Chem. Commun.* **2009**, 4929–4937. Greenberg, S.; Stephan, D. W. *Chem. Soc. Rev.* **2008**, *37*, 1482–1489. Clark, T. J.; Lee, K.; Manners, I. *Chem.—Eur. J.* **2006**, *12*, 8634–8648.
- (2) Etkin, N.; Fermin, M. C.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 2954–2955. Masuda, J. D.; Hoskin, A. J.; Graham, T. W.; Beddie, C.; Fermin, M. C.; Etkin, N.; Stephan, D. W. *Chem.—Eur. J.* **2006**, *12*, 8696–8707.
- (3) For reviews, see: Fisher, R. C.; Power, P. P. *Chem. Rev.* **2010**, *110*, 3877–3923. Weber, L. *Chem. Rev.* **1992**, *82*, 1839–1906.
- (4) Ellis, B. D.; Macdonald, C. L. B. *Coord. Chem. Rev.* **2007**, *251*, 936–973. Coffey, P. K.; Dillon, K. B. *Coord. Chem. Rev.* **2013**, *257*, 910–923.
- (5) Abraham, M. Y.; Wang, Y.; Xie, Y.; Gilliard, R. J., Jr.; Wei, P.; Vaccaro, B. J.; Johnson, M. K.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2013**, *135*, 2486–2488.
- (6) For a microreview, see: Weber, L. *Eur. J. Inorg. Chem.* **2007**, 4095–4117.
- (7) Roering, A. J.; Davidson, J. J.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. *Dalton Trans.* **2008**, 4488–4498.
- (8) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159–11160.
- (9) For examples of phosphanylidene-phosphorane used as a phosphinidene-transfer reagent, see: Kilgore, U. J.; Fan, H.; Pink, M.; Urnezus, E.; Protasiewicz, J. D.; Mendiola, D. J. *Chem. Commun.* **2009**, 4521–4523.
- (10) Wawrzyniak, P.; Fuller, A. L.; Slawin, A. M. Z.; Kilian, P. *Inorg. Chem.* **2009**, *48*, 2500–2506.
- (11) Ragogna, P. J.; Burford, N.; D'eon, M.; McDonald, R. *Chem. Commun.* **2003**, 1052–1053. Burford, N.; D'eon, M.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *Inorg. Chem.* **2004**, *43*, 734–738. Hill, N. J.; Levason, W.; Reid, G. *Dalton Trans.* **2002**, 1188–1192.
- (12) See the SI for synthetic and crystallographic details.
- (13) According to CCDC, the single  $\lambda^3\text{P}-\lambda^3\text{As}$  bond length range is 2.32–2.37 Å.
- (14) Although the P...As distance in **3** (3.157(2) Å) is well below the sum of van der Waals radii (3.65 Å), this is not an indication of a bonding interaction. For other examples of such sub-van der Waals contacts in peri-substituted species, see: Kilian, P.; Knight, F. R.; Woollins, J. D. *Chem.—Eur. J.* **2011**, *17*, 2302–2328. Kilian, P.; Knight, F. R.; Woollins, J. D. *Coord. Chem. Rev.* **2011**, *255*, 1387–1413.
- (15) Notably, the single crystals of **3** used for X-ray work displayed pleochroism; when observed from one angle crystals appear colorless, but from another angle they appear pink.
- (16) Surgenor, B. A.; Bühl, M.; Slawin, A. M. Z.; Woollins, J. D.; Kilian, P. *Angew. Chem., Int. Ed.* **2012**, *51*, 10150–10153.
- (17) Sanchez-Gonzalez, A.; Melchor, S.; Dobado, J. A.; Silvi, B.; Andres, J. J. *Phys. Chem. A* **2011**, *115*, 8316–8326. Liao, H. J. *Chinese Chem. Soc.* **2011**, *58*, 645–652.
- (18) Smith, R. C.; Gantzel, P.; Rheingold, A. L.; Protasiewicz, J. D. *Organometallics* **2004**, *23*, 5124–5126.
- (19) The M06-2X/6-311+G\*\*//B3LYP/6-31+G\*(\*) level; this level turned out to be slightly superior to B3LYP for this kind of reaction (see Table S2 in the SI).
- (20) For comparison, the counterpart reaction for the phosphorus congener is predicted to be notably endothermic, with  $\Delta H = +6.8$  kcal mol<sup>-1</sup>) at the same level.
- (21) Dunn, N. L.; Ha, M.; Radosevich, A. T. *J. Am. Chem. Soc.* **2012**, *134*, 11330–11333. Coyle, E. E.; O'Brien, C. J. *Nat. Chem.* **2012**, *4*, 779–780.