5124 *Organometallics* **2004,** *23,* 5124−5126

Arsa-Wittig Complexes ($ArAs{=}PMe_3$) as Intermediates to Diarsenes

Rhett C. Smith,[†] Peter Gantzel,[‡] Arnold L. Rheingold,[‡] and
John D. Protasiewicz*,[†]

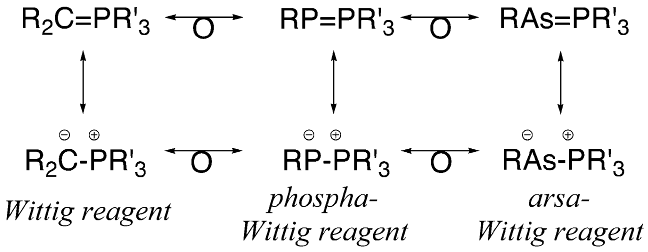
*Departments of Chemistry, Case Western Reserve University, Cleveland, Ohio, and
University of California, San Diego, La Jolla, California*

Received August 23, 2004

Summary: Reactive arsenic analogues of Wittig reagents ($R_2C{=}PR'_3$), arsanylidene-σ^4-phosphoranes ($ArAs{=}PMe_3$), have been generated, and an example has been structurally characterized; these highly reactive functionalities produce diarsenes ($ArAs{=}AsAr$) in quantitative yield upon thermolysis.

Wittig reagents $R_2C{=}PR'_3$ have had a long and rich chemistry since their demonstrated power for the construction of new C=C bonds.[1] Heavier analogues of Wittig reagents, however, are quite rare by comparison. Mathey was the first to show that "phospha-Wittig" reagents can be accessed by coordination to metal centers.[2] Equally important was the ability of these materials to affect P=C bond forming reactions. More recently, we have reported that phospha-Wittig reagents (phosphanylidene-σ^4-phosphoranes) of the form $ArP{=}PR_3$ are isolable when Ar is a sterically demanding aryl group (Scheme 1).[3,4] Reaction of $ArP{=}PR_3$ with aldehydes produces phosphaalkenes, while thermolysis produces diphosphenes ($ArP{=}PAr$) or other products attributable to phosphinidene intermediates.[5−7] While no direct arsenic analogues of these materials appear to have been reported, Cowley and co-workers[8] have isolated carbene adducts of arsanylidenes (**A**, Figure 1). Due to the similar σ-donating properties of carbenes and phosphines, adducts **A** may be thought of as analogues of the phosphine adducts **B** (arsanylidene-σ^4-phosphoranes) that are the target of the current study, but with an inverted distribution of steric bulk. We now report on the preparation of the first heavier analogues featuring the reactive $ArAs{=}PR_3$ functionality which can be considered the first true "arsa-Wittig" reagents[9] and preliminary reports of their chemistry.

Scheme 1



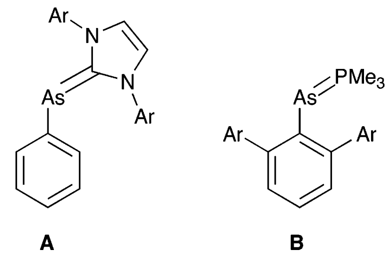


Figure 1. Carbene (**A**) and phosphine (**B**) adducts of arsanylidenes.

Reduction of $2,6\text{-Trip}_2C_6H_3AsCl_2$ [10] (Trip = $2,4,6\text{-}{}^iPr_3C_6H_2$) in the presence of excess PMe_3, the same route employed for synthesis of $ArP{=}PMe_3$, rapidly afforded solutions of the arsa-Wittig species **1a** in quantitative yields. ^{31}P NMR spectroscopy shows a single resonance for the phosphorane atom at δ 16.7 (compare δ −1.6 ppm for the $ArP{=}PMe_3$ analogue). Compound **1a** proved somewhat labile, and purifications were plagued by the presence of the known diarsene $2,6\text{-Trip}_2C_6H_3As{=}As\text{-}2,6\text{-}C_6H_3Trip_2$ (**2a**).[10] Upon heating in THF solution for a few minutes or standing (in solution or in the solid state) for extended periods (days), compound **1a** is quantitatively converted to **2a** (Scheme 2), as judged by ^1H NMR spectroscopy.[12] Regardless, samples of **1a** could be obtained as an orange solid of ca. ≥90% purity contaminated only by the diarsene **2a**.

[†] Case Western Reserve University.

[‡] University of California, San Diego.

[1] (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635. (b) Wittig, G.; Geissler, G. *Liebigs Ann. Chem.* **1953**, *580*, 44. (c) Wittig, G.; Schollkopf, *U. Chem. Ber.* **1954**, *87*, 1318. (d) Johnson, A. W. In *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (e) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863.

[2] Le Floch, P.; Marinetti, A.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1990**, *112*, 2407.

[3] Shah, S.; Protasiewicz, J. D. *Chem. Commun.* **1998**, 1585.

[4] Shah, S.; Protasiewicz, J. D. *Coord. Chem. Rev.* **2000**, *210/1*, 181.

[5] Smith, R. C.; Ren, T.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2002**, *11*, 2779.

[6] Smith, R. C.; Protasiewicz, J. D. *Eur. J. Inorg. Chem.* **2004**, *5*, 998.

[7] Smith, R. C.; Chen, X.; Protasiewicz, J. D. *Inorg. Chem.* **2003**, *42*, 5468.

[8] Arduengo, A. J.; Calabrese, J. C.; Cowley, A. H.; Rasika Dias, H. V.; Goerlich, J. R.; Marshal, W. J.; Riegel, B. *Inorg. Chem.* **1997**, *36*, 2151.

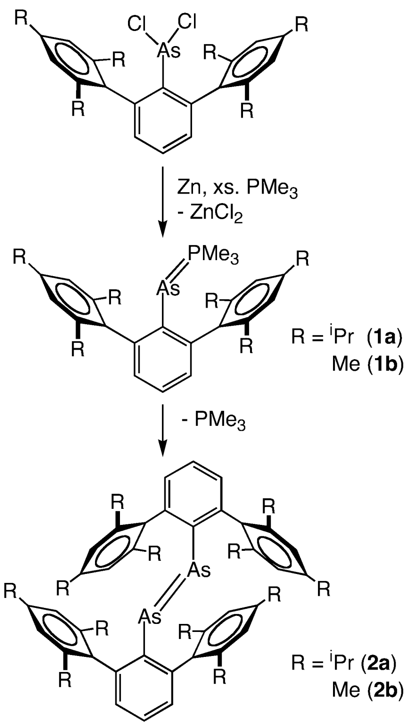
[9] The term "arsa-Wittig" could also conceivably be used for the arsonium-based Wittig reagents $R_2C{=}AsR'_3$. We have chosen to draw analogies to the term "phospha-Wittig", which has been frequently used. See also: Ellis, B. D.; Macdonald, C. L. B. *Phosphorus. Sulfur Silicon Relat. Elem.* **2004**, *179*, 775.

[10] Twamley, B.; Sofield, C. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**. *121*, 3357.

[11] (a) Bouslikhane, M.; Gornitzka, H.; Escudie, J.; Ranaivonjatovo, H. *J. Organomet. Chem.* **2001**, *619*, 275. (b) Twamley, B.; Power, P. P. *Chem. Commun.* **1998**, 1979. (c) Cowley, A. H.; Latsch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *Chem. Commun.* **1983**, 881. (d) Cowley, A. H.; Kildiff, J. E.; Latsch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582.

10.1021/om049340+ CCC: $27.50

Scheme 2



Although reactive and difficult to isolate in pure form, crystals of **1a**·0.5hexane suitable for X-ray diffraction were obtained from hexanes at −35 °C as nonmerohedral twins. The structure (Figure 2) confirms the expected formulation and shows an average (for the twinned structure) As−P bond length of 2.221 Å. This value is somewhat longer than distances reported for the true As=P double bond in structurally characterized arsaphosphenes Mes*As=PMes* (2.1415 Å, Mes* = 2,4,6-tri-*tert*-butylbenzene),[11a] 2,6-Trip$_2$C$_6$H$_3$As=PMes (2.134 Å),[11b] and [(Me$_3$Si)$_2$CH]As=PMes* (2.124 Å).[11c,d] The ^{1}H NMR spectra of **1a** reveal three distinct methyl resonances for the inequivalent isopropyl groups, in accord with the static structure observed in the solid state.[12]

The three As−P−C bond angles in **1a** are notably inequivalent (average values for two crystallographically independent molecules are 105.8, 113.6, and 120.6°) and reminiscent of those observed about the phosphorane atom in 2,6-Mes$_2$C$_6$H$_3$P=PMe$_3$ (P−P−C angles: 102.3(2), 117.4(2), and 121.5°).[13] As previously discussed for the Wittig and phospha-Wittig species, such features indicate that an appropriate description of the E=P multiple bonding involves more of the charge-separated resonance structure (see Scheme 1) coupled with contributions from negative hyperconjugation of E lone pair(s) into symmetry-adapted combinations of σ^* PC orbitals.

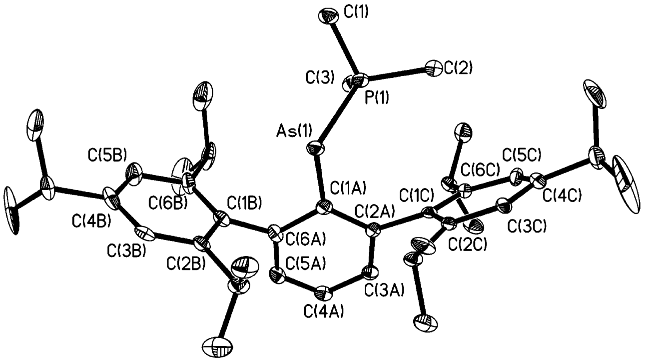


Figure 2. ORTEP diagram of **1a**·0.5hexane (30% probability; hydrogens and hexane molecule omitted for clarity, values given for only one of two crystallographically independent molecules). Select angles (deg) and distances (Å): P(1)−As(1), 2.2190(17); P(1)−C(1), 1.793(6); P(1)−C(2), 1.822(6); P(1)−C(3), 1.804(6); C(1A)−As(1)−P(1), 101.53(17); C(1)−P(1)−As(1), 106.0(2); C(2)−P(1)−As(1), 120.1(2); C(3)−P(1)−As(1), 113.2(2); C(2A)−C(1A)−As(1), 127.0(4); C(6A)−C(1A)−As(1), 114.2(4); C(6)−C(1A)−C(2A) 117.7(5).

Detailed discussions of bonding in Wittig[14−16] and phospha-Wittig[13,17,18] type reagents are presented elsewhere.

Attempts to synthesize the arsa-Wittig reagent 2,6-Mes$_2$C$_6$H$_3$As=PMe$_3$ (**1b**) by reduction of 2,6-Mes$_2$C$_6$H$_3$AsCl$_2$ with Zn and PMe$_3$ led instead to isolation of the previously reported diarsene **2b** (Scheme 2) in quantitative yield.[10,19] It might thus be assumed that **1b** is generated but immediately breaks down to yield the diarsene. This hypothesis was corroborated by the observation of a ^{31}P NMR signal attributable to **1b** at δ 16.1 ppm in a slurry of 2,6-Mes$_2$C$_6$H$_3$AsCl$_2$, Zn, and PMe$_3$ in THF immediately upon mixing. Interestingly, reaction of 2,6-Mes$_2$C$_6$H$_3$AsCl$_2$ with Zn alone does not produce the diarsene, and 2,6-Mes$_2$C$_6$H$_3$AsCl$_2$ was recovered after 24 h. Suspecting that the actual initial reduction of ArAsCl$_2$ might involve PMe$_3$ (and formation of Me$_3$PCl$_2$), the reduction was repeated with a catalytic (10%) amount of PMe$_3$. Indeed, the reaction proceeds to efficiently produce the diarsene in high yield. An overall mechanism for this PMe$_3$-promoted reduction is presented in Scheme 3. Catalytic chlorine atom transfers between ArPCl$_2$ and ArP=PMe$_3$ mediated by PMe$_3$ have been previously noted.[20]

Scheme 3

$$\mathrm{ArAsCl_2 + 2PMe_3 \rightarrow Me_3PCl_2 + ArAs{=}PMe_3}$$

$$\mathrm{2ArAs{=}PMe_3 \rightarrow ArAs{=}AsAr + 2PMe_3}$$

$$\mathrm{Me_3PCl_2 + Zn \rightarrow ZnCl_2 + PMe_3}$$

As the arsa-Wittig reagent **1b** was not isolable, we sought to gain more evidence for its existence by

---

(12) To a suspension of zinc dust (80 mg, 1.3 mmol) and 2,6-Trip$_2$C$_6$H$_3$AsCl$_2$ (200 mg, 0.32 mmol) in THF (10 mL) was added PMe$_3$ (150 mg, 1.9 mmol) with rapid stirring. Over a 24 h period the mixture slowly changed from colorless to light orange. The mixture was then filtered, and all volatiles were removed in vacuo to produce an orange solid (170 mg), which was determined by ^{1}H NMR to be approximately ~90% **1a**. This material could be further purified by recrystallization from a saturated hexanes solution at −35 °C, producing single crystals of **1a** suitable for X-ray diffraction. ^{1}H NMR (C$_6$D$_6$): δ 0.67 (d, 9H, J = 12 Hz), 1.22 (d, 12H, J = 7 Hz), 1.26 (d, 12H, J = 7 Hz), 1.51 (d, 12H, J = 7 Hz), 2.80−3.00 (m, 4H), 3.15−3.30 (m, 2H), 7.08−7.13 (m, 3H), 7.23 (s, 4H). ^{31}P NMR: δ 16.7.

(13) Shah, S.; Yap, G. P. A.; Protasiewicz, J. D. *J. Organomet. Chem.* **2000**, *608*, 12.

(14) Gilheany, D. G. In *Structure and Bonding in Phosphonium Ylides, Salts and Phosphoranes*; Hartley, F. R., Ed.; Wiley: New York, 1994; Vol. 3, pp 1−44.

(15) Gilheany, D. G. *Chem. Rev.* **1994**, *94*, 1339.

(16) Dobado, J. A.; Martínez-García, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1144.

(17) Sudhakar, P. V.; Lammertsma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1899.

(18) Rak, J.; Skurski, P.; Liwo, A.; Blazejowski, J. *J. Am. Chem. Soc.* **1995**, *117*, 2638.

(19) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958.

(20) Smith, R. C.; Shah, S.; Urnezius, E.; Protasiewicz, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 40.

trapping with benzaldehyde by an “arsa-Wittig” reaction that might generate an arsaalkene (ArAs=C(H)Ph) and O=PMe$_3$. Attempts to trap DmpAs=PMe$_3$ with 3 equiv of benzaldehyde, however, were inconclusive. Although the presence of O=PMe$_3$ in the ^{31}P NMR spectrum suggested that the reaction had taken place, significant amounts of **2b** complicated analysis, and the desired arsaalkene was not cleanly separated and identified. Arsaalkenes are far less stable than phosphaalkenes, and materials of the type ArAs=C(H)Ph do not appear to be known. It may also be that these materials are themselves unstable, even with the bulky substituents.[21]

Finally, preliminary efforts have also been undertaken to extend the “pnicta-Wittig” analogy to antimony. In this vein, reaction of 2,6-Mes$_2$C$_6$H$_3$SbCl$_2$ with Zn and PMe$_3$ does produce 2,6-Mes$_2$C$_6$H$_3$Sb=SbMes$_2$C$_6$H$_3$-2,6 (possibly through a 2,6-Mes$_2$C$_6$H$_3$Sb=PMe$_3$ intermediate), but only in about 80% yield (as judged by ^{1}H NMR), along with unidentified side products. Further efforts are underway to explore the possibility of utilizing this protocol to prepare other heavy-element multiple bonds.

In conclusion, we have isolated and structurally characterized the first example of the arsanylidene-σ^4-phosphorane **1a** by employing the bulky 2,6-Trip$_2$C$_6$H$_3$ ligand. The less bulky 2,6-Mes$_2$C$_6$H$_3$As=PMe$_3$ (**1b**) is not isolable but proceeds directly to the diarsene **2b** in quantitative yields at room temperature. Compound **1a** also proceeds quantitatively to a diarsene upon thermolysis. This method represents a new route to diarsenes, materials that remain relatively few in number.[18,22]

Acknowledgment. The authors thank the National Science Foundation (CHE-0202040) for support and Professor Charles L. B. Macdonald (University of Windsor) for helpful discussions.

Supporting Information Available: Text giving experimental details and a CIF file giving X-ray crystallographic data for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049340+

---

[21] Weber, L. *Chem. Ber.* **1996**, *129*, 367.

[22] (a) Tokitoh, N.; Sasamori, T.; Takeda, N.; Nagase, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 1473. (b) Bouslikhane, M.; Gornitzka, H.; Escudie, J.; Ranaivonjatovo, H. *J. Organomet. Chem.* **2001**, *619*, 275. (c) Weber, L. *Chem. Rev.* **1992**, *92*, 1839. (d) Cowley, A. H.; Norman, N. C.; Pakulski, M. *J. Chem. Soc., Dalton Trans.* **1985**, 383. (e) Tisnes, P.; Madaule, Y.; Wolf, J. G.; Couret, C.; Escudie, J. *J. Chem. Res., Synop.* **1984**, 274. (f) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Mehrotra, S. K.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R.; Atwood, J. L.; Hunter, W. E. *Inorg. Chem.* **1984**, *23*, 2582. (g) Couret, C.; Escudie, J.; Madaule, Y.; Ranaivonjatovo, H.; Wolf, J. G. *Tetrahedron Lett.* **1983**, *24*, 2769. (h) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M. *J. Am. Chem. Soc.* **1983**, *105*, 5506.