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Authors: Jose Manuel Goicoechea, Alexander Hinz, Max Hansmann,
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Intercepting a Transient Phosphino-Arsinidene

Alexander Hinz,^[a] Max M. Hansmann,^[b] Guy Bertrand^{*[c]} and Jose M. Goicoechea^{*[a]}

Abstract: A phosphino-arsinidene derived from a diazaphospholidine scaffold ($\text{Ar}^{**}\text{NCH}_2$)₂PAs (where Ar^{**} = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl) was generated *in situ* and trapped with a range of reagents. Metathesis reactions between ($\text{Ar}^{**}\text{NCH}_2$)₂PCl and either [Na(18-crown-6)][AsCO] or [Na(dioxane)_x][AsCO] are believed to afford an arsaketene, ($\text{Ar}^{**}\text{NCH}_2$)₂PAsCO, which readily loses carbon monoxide under ambient conditions. The resulting transient arsinidene was shown to undergo cycloaddition reactions with excess AsCO[−], but can be stabilised in the presence of Lewis bases. It displays contrasting reactivity from a previously reported phosphino-phosphinidene. With isonitriles, rearrangements occur, however with PPh₃ a phosphine-stabilised arsinidene could be isolated and used for subsequent reactivity studies. This species was found to be a suitable starting material for a transition metal complex of the phosphino-arsinidene, in which the P–As moiety coordinates side-on to the metal centre.

Arsinidenes (R–As) are the heavier analogues of nitrenes and phosphinidenes. The primary arsinidene diradical, AsH, has been detected by IR, Raman and microwave spectroscopy, however the only isolable arsinidenes reported to date require stabilization by complexation to Lewis acids or bases.^[1–5]

Transition metal stabilised arsinidenes were first observed as by-products in the reductive coupling of dichloroarsines with transition metal reducing agents.^[6] Their targeted synthesis was reported by Jutzi in 1990 (Figure 1, A),^[7] but a thorough investigation of their reactivity was not conducted until 2010 when Scheer and co-workers focused on Cp*As[W(CO)₅]₂.^[8–10] Base-stabilised arsinidenes have also been isolated, such as [(tren)U=AsH][−] B,^[11] and NHC=AsH C.^[12] Albeit less stable, a labile anionic arsinidene [Na(18-crown-6)][Ter₂SnAs] was observed in the association and decarbonylation of AsCO[−] with a bulky stannylene.^[13] Driess and co-workers postulated that a germlyenyl-arsinidene was generated as a transient species in the formation of a Ge₂As₂ heterocycle which could be trapped with Lewis bases prior to dimerisation.^[14] So far, the preparation of a free arsinidene has eluded the skills of chemists. However, phosphino-nitrene D,^[15,16] and phosphino-phosphinidene E,^[17,18] have recently been isolated and their reactivity has been investigated. The latter was prepared by photolytic elimination of carbon monoxide from the corresponding phosphanyl-phosphaketene. With AsCO[−] as a potentially suitable source of

arsaketenes and As[−] now being available on a preparatively useful scale,^[12,14,19] we attempted the synthesis of the phosphino-arsinidene F employing the bulky diazaphospholidine backbone utilised in the isolation of E.

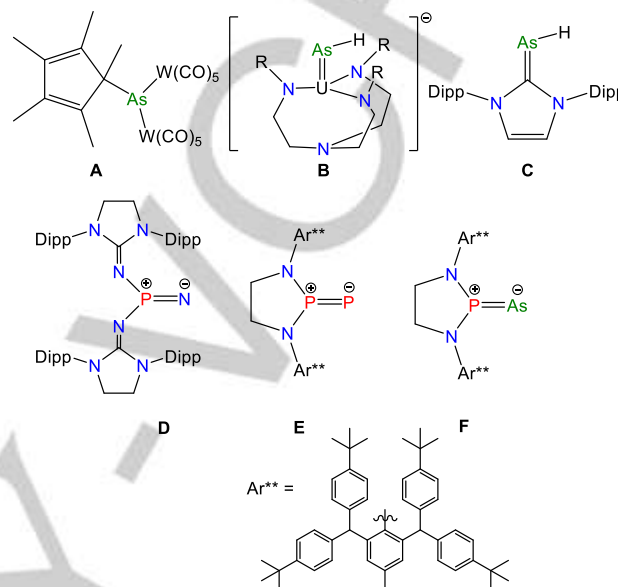


Figure 1. Selected pnictinidene species reported in the literature and the targeted arsinidene F. R = SiPr₃; Ar^{**} = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl.

With a few exceptions, such as E, most of phosphinidenes have a triplet ground state, and their diradical character prevents their isolation.^[20] Therefore, it was of primary importance to first investigate computationally if the desired arsinidene F would feature a singlet ground state. At the PBE1PBE/6-31G(d,p) level of theory, we found that the singlet–triplet gap amounts to 114 kJ·mol^{−1} with strong preference for the singlet state. The singlet species is computed to possess a very short P–As bond of 2.01 Å, short P–N bonds of 1.68 Å and a planar environment for the phosphorus atom, which is consistent with its description as P^V system (Figure 2). In contrast, in the triplet species, the P–As and P–N bonds are longer (2.27 and 1.72 Å, respectively), and the phosphorus is in a pyramidal environment as expected for a P^{III} centre. The molecular orbitals for singlet F feature a P–As π-antibonding LUMO, an in-plane π-bonding HOMO, and an out-of-plane π-bonding HOMO–1, whilst the σ-bonding interaction is buried in HOMO–38 (Figure S37). In agreement with the rather large singlet–triplet gap, the HOMO–LUMO gap is high (4.34 eV).

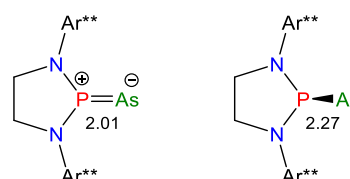
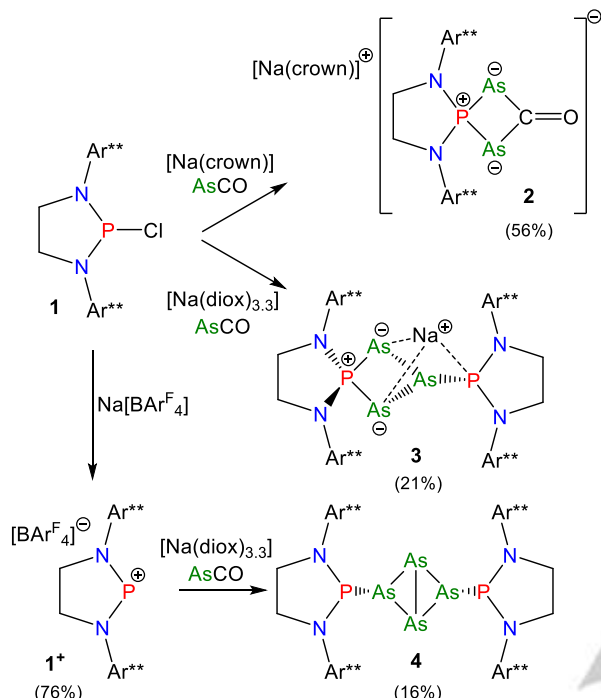


Figure 2. Lewis representations of singlet F (left) and triplet F (right).

- [a] Dr. A. Hinz, Prof. J. M. Goicoechea
Department of Chemistry, University of Oxford, Chemistry Research Laboratory, 12 Mansfield Road, OX1 3TA, Oxford, U.K.
E-mail: jose.goicoechea@chem.ox.ac.uk
- [b] Dr. M. M. Hansmann
Georg-August-Universität, Institute of Organic and Biomolecular Chemistry, Tammannstr. 2, D37077 Göttingen, Germany
- [c] Prof. G. Bertrand
UCSD/CNRS Joint Research Chemistry Laboratory, Department of Chemistry, University of California San Diego, La Jolla, CA 92521–0403, USA
E-mail: guybertrand@ucsd.edu

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Initial attempts to prepare the phosphino-arsinidene **F** were made by metathesis reactions of chlorodiazaphospholidine ($\text{Ar}^{**}\text{NCH}_2)_2\text{PCl}$ (**1**; Ar^{**} = 2,6-bis[(4-*tert*-butylphenyl)methyl]-4-methylphenyl) with a stoichiometric amount of $[\text{Na}(18\text{-crown-6})][\text{AsCO}]$ (Scheme 1).



Scheme 1. Attempted synthesis of phosphanyl-arsaketenes. Isolated crystalline yields are given in brackets. AsCO^- salts had to be employed in excess to achieve full conversion of **1**.

The solution immediately turned red and gas evolved, but only 50% conversion to a new product, **2**, which showed a singlet in the ^{31}P NMR spectrum at +59.8 ppm, was observed. When a 1:2 ratio of **1** and $[\text{Na}(18\text{-crown-6})][\text{AsCO}]$ was used, **2** was isolated quantitatively and identified by single crystal X-ray diffraction study as the [2+2] cycloaddition product of the desired phosphino-arsinidene **F** with the AsCO^- anion (Figure S1). The formation of **2** implies, that the arsaketene is thermally unstable with respect to loss of CO, and rapidly forms the phosphino-arsinidene **F**, which reacts faster with another equivalent of $[\text{Na}(18\text{-crown-6})][\text{AsCO}]$ than the metathesis reaction occurs. We then chose the crown-free $[\text{Na}(\text{dioxane})_{3.3}][\text{AsCO}]$ salt as an alternative AsCO^- source.^[12] An excess of the AsCO^- source was necessary to drive the reaction to completion. When $[\text{Na}(\text{dioxane})_{3.3}][\text{AsCO}]$ reacted with the chlorophosphine **1** in toluene, a mixture of products was observed among which the two major species feature an AX system in the ^{31}P NMR spectrum (28.6, 174.1 ppm, $^3J_{\text{P-P}} = 49$ Hz; 37.5, 211.8 ppm, $J_{\text{P-P}} = 4$ Hz; Figure S5) while for a third a singlet was observed (190.9 ppm). Out of this mixture, compound **3** could be crystallised (Figure 3) and consequently assigned to the former AX spin system.

However, when using the phosphonium salt **1+** instead of the chlorophosphine **1**, a clean reaction was observed, and compound **4** was observed as the sole reaction product by ^{31}P

NMR spectroscopy ($\delta = 190.9$ ppm, Scheme 1). Surprisingly, it was identified by X-ray diffraction as the bicyclic tetraarsine (Scheme 1, Figure S14) and not the expected diarsene, which would be a dimer of the phosphino-arsinidene **F**.

Since the singlet-triplet gap of arsinidene **F** (114 $\text{kJ}\cdot\text{mol}^{-1}$) is larger than that of the stable phosphinidene **E** (98.2 $\text{kJ}\cdot\text{mol}^{-1}$), the increased reactivity of **F** can be rationalized by its longer P–As bond distance (2.01 Å) compared to the P–P bond of **E** (1.92 Å), and by the poorer orbital overlap available for the formation of the element–element bond, due to a discrepancy in both the radial extension and energy of the frontier orbitals involved. Consequently, phosphanes seem to be a poor choice of substituent for the stabilisation of a terminal arsinidene. Other functional groups such as amines, to counteract the substituent–arsenic bond distance, or arsines, to counteract the poor orbital match, are potential candidates for the stabilisation of such a species. Consequently, we turned our attention to trapping reactions.

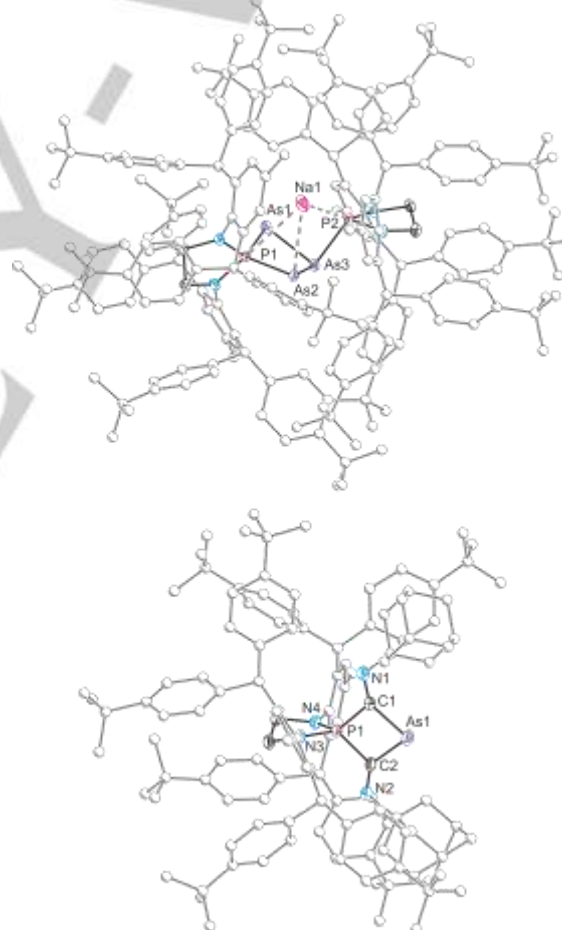
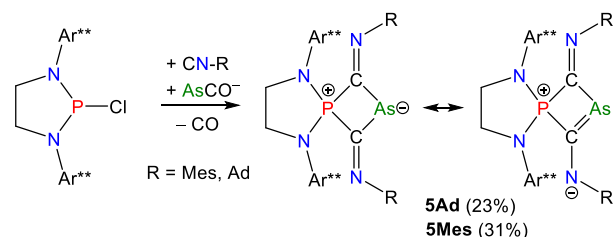


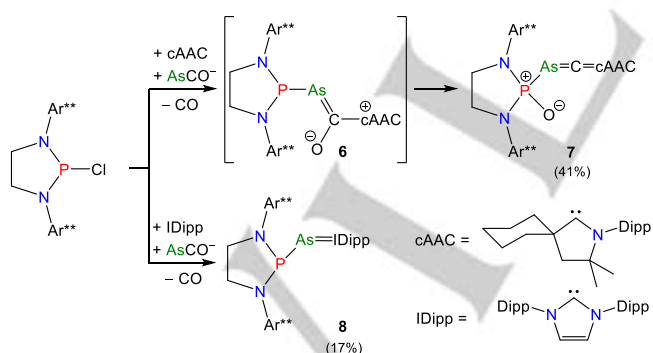
Figure 3. Solid-state structures of **3** (top) and **5Ad** (bottom).

Since isonitriles are known to quickly react with different types of carbenoids,^[21] including nitrene **D**,^[15,16] and phosphinidene **E**,^[17,18] we carried out the reaction of **1** with $[\text{Na}(\text{dioxane})_x][\text{AsCO}]$ in the presence of mesityl- and adamantyl-isonitrile (Scheme 2).



Scheme 2. Trapping of the putative arsinidene with isonitriles. Isolated crystalline yields are given in brackets.

During reaction monitoring, a resonance was observed that likely corresponds to the trapping product $(\text{Ar}^{**}\text{NCH}_2)_2\text{PAsCNR}$ ($\delta(^{31}\text{P})$ R = Mes 186.1, Ad 186.9 ppm), but this only was formed in traces. An excess of the isonitriles had to be employed to suppress formation of **3** and **4** and drive the reaction to completion, but crystallisation was severely hampered by the presence of the excess trapping agents. Consequently, **5Mes** and **5Ad**, were isolated in only 23 and 31% crystalline yields. The ^{31}P NMR spectra showed a singlet [73.8 (**5Mes**) and 90.7 ppm (**5Ad**)], indicating the presence of only one phosphorus nucleus, while the ^1H NMR spectra suggested that two isonitrile units were involved (Figure S18). A single crystal diffraction study of **5Ad** revealed the formation of a spirocyclic product in which no P–As bond is present (Figure 3) which contrasts the behaviour of the phosphinidene **E**.^[18c] The NBO analysis of **5Ad** shows, that the majority of positive charge is accumulated at the P atom ($1.96 e^-$) and to a smaller extent at the As atom ($+0.36 e^-$). In contrast, the N atoms (imine -0.50 , amine $-0.83 e^-$) and the C atoms of the four-membered heterocycle ($-0.44 e^-$) bear the compensating negative charge. The NBO analysis confirms the presence of two lone pairs at the arsenic atom, of which one is of dominant s-character (78% s, $1.97 e^-$), while the p-type lone pair is partially delocalised into the π -system of the heterocycle (100% p, $1.26 e^-$). The ellipticity of the Laplacian of the electron density at the C–As BCP is 0.20, indicating some double bond character.



Scheme 3. Trapping of the arsaallene and arsinidene by cAAC and IDipp, respectively. Isolated crystalline yields are given in brackets.

The mechanism of the reaction leading from putative $(\text{Ar}^{**}\text{NCH}_2)_2\text{PAsCNR}$ to **5Ad** and **5Mes** is still obscure and the absence of a P–As bond does not prove the transient formation of arsenidene **F**. Carbenes are also known to react with

phosphinidene **E**, and thus the reaction of **1** with $[\text{Na}(\text{dioxane})_x][\text{AsCO}]$ was carried out in the presence of a cyclic (alkyl)(amino)carbene (cAAC),^[22] and a N-heterocyclic carbene (NHC) (Scheme 3).^[23] We first checked that neither the chosen NHC nor the cAAC react with AsCO^- on their own.

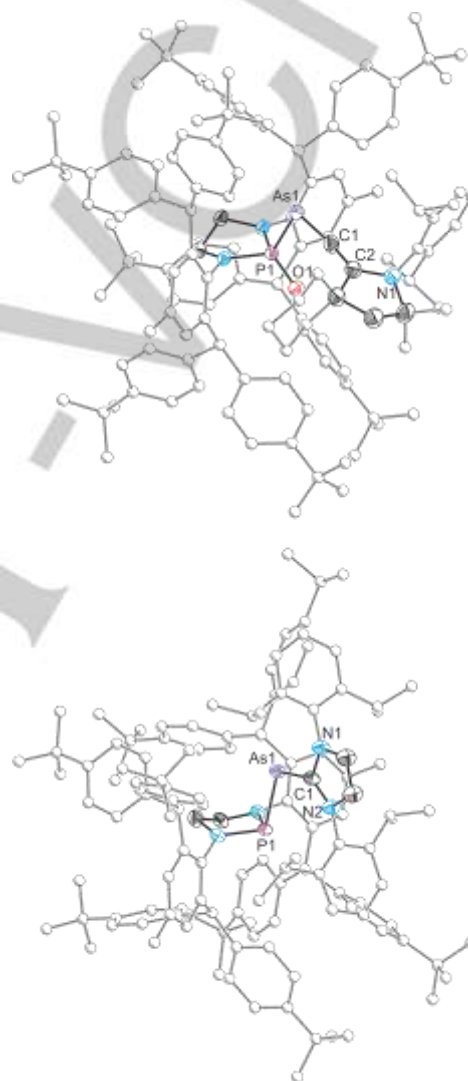


Figure 4. Solid-state structures of **7** (top) and **8** (bottom).

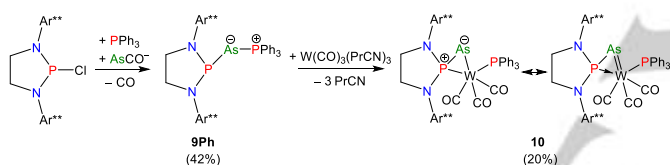
With cAAC, the reaction afforded the arsa-allenyl species **7** which, as expected, features a downfield ^{13}C NMR signal for the allenic carbon (297.0 ppm, $^2J_{\text{C-P}} = 19$ Hz, Figure S26), while the former cAAC carbon resonates at 157.09 ppm ($^3J_{\text{C-P}} = 18$ Hz). The structure of **7** has been ascertained by a single crystal diffraction study (Figure 4) and compares well with the known structure of Escudie's arsaallene (**7**: AsC 1.745(2), CC 1.322(3) vs. 1.754(2), 1.314(3) Å).^[24] The isolation of **7** reveals that the arsaallene is long-lived enough to be trapped by the carbene. Indeed, this product is the analogue of that reported when reacting a cAAC with a stable phosphanyl-phosphaketene.^[25]

Additionally, DFT calculations show that **7** is more thermodynamically stable than its isomer **6** by 103 kJ·mol⁻¹.

Interestingly, when IDipp (1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) was employed as trapping agent, we were able to isolate the desired arsinidene-NHC adduct **8**, which was fully characterized including an X-ray diffraction study (Figure 4).

Following the successful trapping of the transient phosphino-arsinidene, we then investigated the reaction with phosphines such as triphenylphosphine (Scheme 4), which led to the expected arsinidene adducts **9Ph** (³¹P NMR: 181.7 (d, ²J_{P-P} = 80 Hz), 35.7 (d, ²J_{P-P} = 80 Hz, ³J_{P-H} = 11 Hz, Figure S31) and **9Me** (180.3 (d, ²J_{P-P} = 110 Hz, N₂PAs), -1.1 (d-dec, ²J_{P-P} = 110 Hz, ³J_{P-H} = 12 Hz, Figure S34).

Interestingly, the triphenylphosphine-stabilised arsinidene was successfully subjected to complexation experiments (Scheme 4). A low oxidation state transition metal is required, as the arsinidene is a strong reductant. Three products were reproducibly formed by reacting **9Ph** with W(CO)₃(PrCN)₃, two of them being identified as **4** and W(CO)₃(PPh₃)(PrCN)₂ by NMR spectroscopy. The third component (**10**) appears on the ³¹P NMR spectrum as an AX spin system, accompanied by W satellites at +151.8 ppm (d, ²J_{P-P} = 34.8, ¹J_{P-W} = 207 Hz; N₂PAs) and 33.0 ppm (d, ²J_{P-P} = 34.8 Hz, ¹J_{P-W} = 116 Hz, PPh₃), and its structure was revealed by a single crystal X-ray diffraction study (Figure 5).



Scheme 4. Trapping of the arsinidene with phosphines and subsequent complexation. Isolated crystalline yields are given in brackets.

The formation of **10** reveals that the arsinidene fragment can act as a nucleophile as well. This distinguishes the phosphino-arsinidene from the phosphino-phosphinidene reported previously by Bertrand and co-workers, as they typically are electrophilic. Our attempts to prepare the related tungsten complex of the phosphinidene were not successful. The P1–As1 bond is slightly shorter [2.1723(8) Å] than in the starting material **9Ph** [2.2082(5) Å], while the P2–As1 distance of 3.256(1) Å precludes a direct bond. Consequently, the PAsW moiety forms a triangle with acute inner angles (66.27(2)°, 61.88(2)°, 51.86(2)°) and W–P and W–As distances of 2.4359(7) and 2.5284(4) Å, respectively, while the triphenylphosphine P–W bond has a length of 2.5350(8) Å.

To have more insight into the bonding situation in this very unusual complex **10**, DFT calculations were carried out. The LUMO of the complex **10** bears semblance to the HOMO of the free arsinidene **F**, possessing large coefficients at the As atom for an in-plane p orbital. The HOMO of **10** is P–As and P–W σ-bonding, while the bonding interaction between As and W is evident from a π-type HOMO–3 and a s-type HOMO–6 (see SI, 3.11). The NBO analysis reveals, that both the P (+1.08 e⁻) and As (+0.19 e⁻) atoms of the triangle are positively charged, while the N (–0.75 e⁻) and W (–1.85 e⁻) atoms bear negative charges.

There are two NBOs for the W–P and W–As interaction, respectively, that are occupied (W–P 1.80, 1.85; W–As 1.79, 1.67 e⁻), while one lone pair remains at the arsenic atom (1.94 e⁻). The P–As bond is a σ-bond occupied by 1.93 e⁻. From the QTAIM perspective, the Laplacian of the electron density at the P–W, As–W and P–As bonding critical point amounts to 0.15, 0.19 and 0.04, respectively, which also implies double bond character between P–W and As–W and single bond character between P–As. This implies, that the phosphino-arsinidene is best described as a four-electron donor, which is different from analogous complexes of alkynes and arsaalkynes, [Mes⁺CC(H)]W(CO)₄ and [Mes⁺CAs]W(CO)₄.^[26] In these two computed examples, W (0.87, 0.82 e⁻) is positively charged and NBO reveals two C–C (1.97, 1.82 e⁻) and C–As (1.96, 1.78 e⁻) bonds, respectively, while there are only single bonds to tungsten (W–C 1.75, 1.75; W–C 1.83, W–As 1.68 e⁻). This bonding situation also contrasts strongly with Scheer's tungsten complex of diphosphino-diarsene [Pr₂P{W(CO)₅As]₂W(CO)₅] in which tungsten is coordinated either by the P lone pair or by the diarsene double bond.^[27]

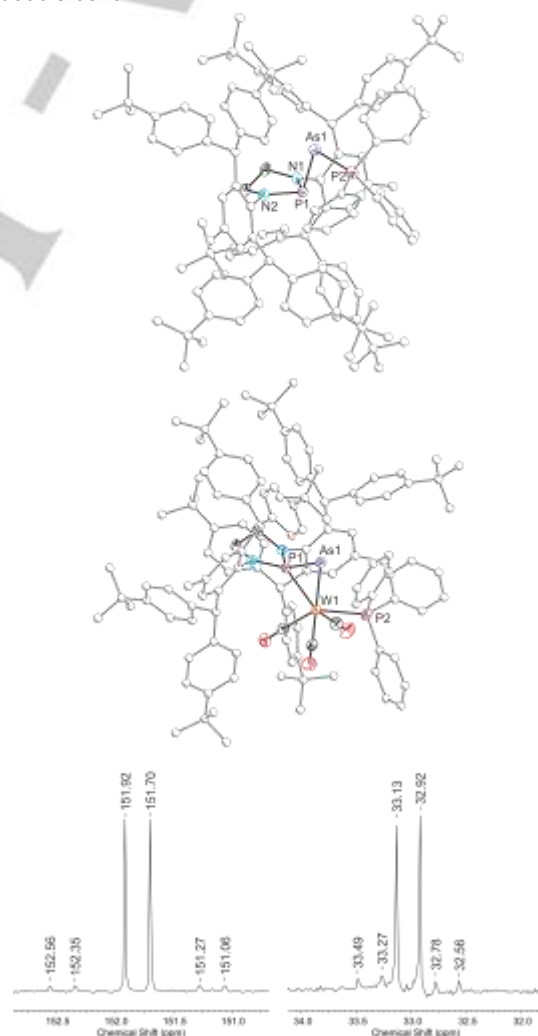


Figure 5. Molecular structure of **9Ph** (top) and **10** (middle) and sections from the ³¹P NMR spectrum of **10** (bottom).

Conclusions

Even though the targeted phosphino-arsinidene as well as its phosphino-arsaketene precursor eluded structural and spectroscopic characterisation, their reactivity could be studied by trapping experiments. It was shown that the phosphino-arsaketene can be trapped by cAACs, while the phosphino-arsinidene could be stabilized by an NHC and a phosphine. From the triphenylphosphine-adduct, a novel alkyne-type complex featuring side-on coordination of the P–As moiety was synthesised.

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Keywords: arsinidene • trapping experiments • arsenic • phosphorus • diazaphospholidine ligands

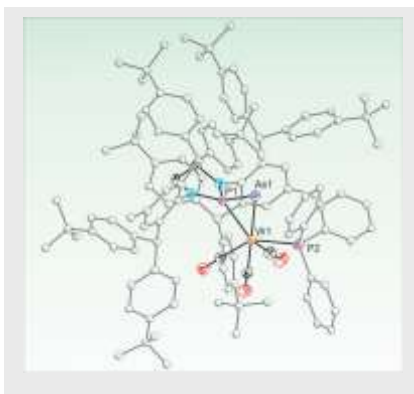
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

We report the formation of a transient phosphino-arsinidene and the result of trapping experiments with Lewis bases and a transition metal centre.



Alexander Hinz, Max M. Hansmann,
Guy Bertrand* and Jose M. Goicoechea*

Page No. – Page No.

Intercepting a Transient Phosphino-
Arsinidene