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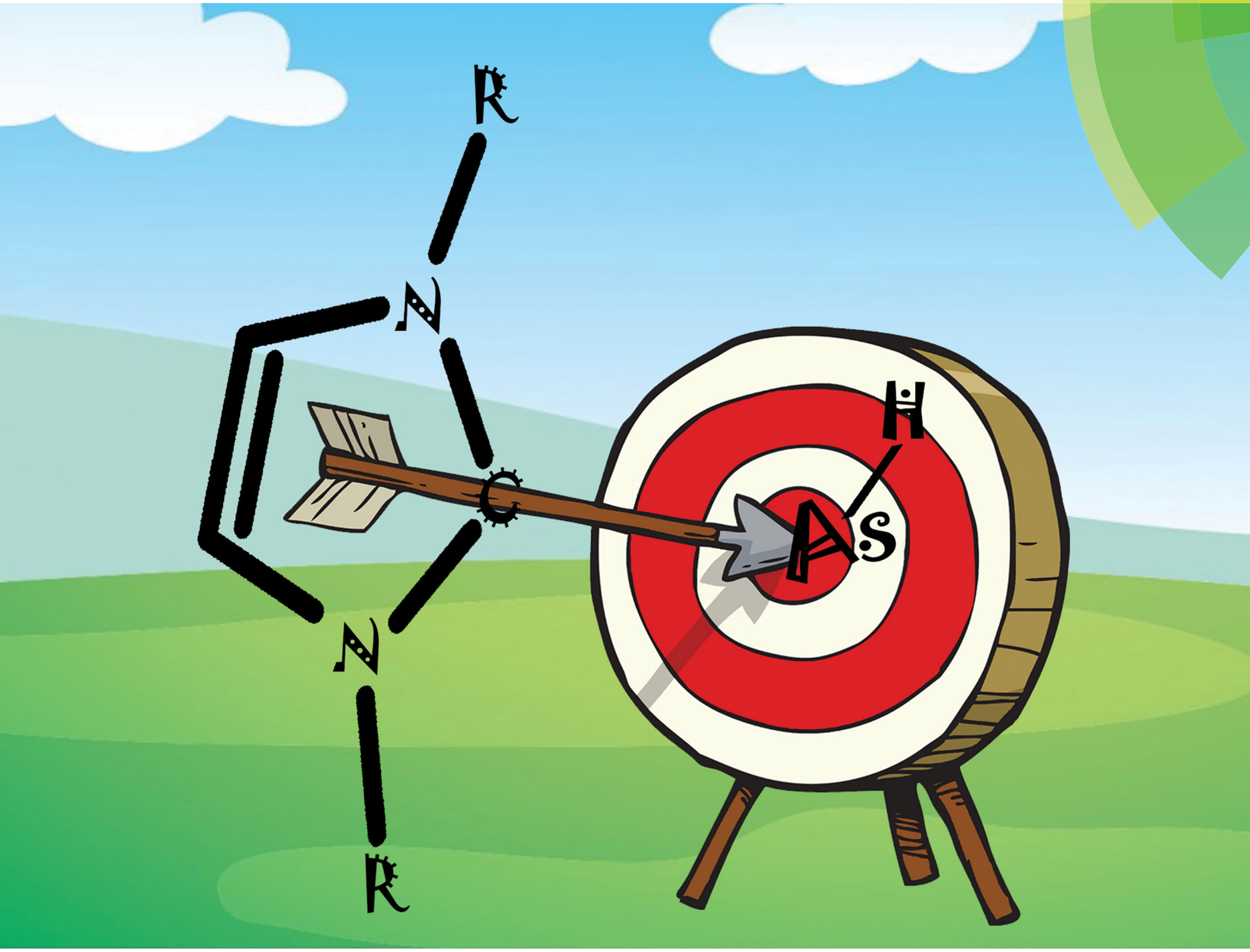

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N-Heterocyclic carbene-stabilised arsinidene (AsH)†

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N-Heterocyclic carbene adducts of the parent arsinidene (AsH) were prepared by two different synthetic routes, either by reaction of $As(SiMe_3)_3$ with 2,2-difluoroimidazolines followed by desilylation or by reaction of $[Na(dioxane)_{3.31}][AsCO]$ with imidazolium chlorides.

Arsinidene (or arsanylidene, AsH) is a transient 6-electron triplet species that has been studied intensively by spectroscopic and theoretical methods because of its role in the epitaxial growth of gallium arsenide (GaAs) semiconductor films by metal–organic chemical vapour deposition (MOCVD).[1] Its stabilisation in the condensed phase has been possible by complexation to a metal center in a handful of 3d-transition metal carbonyl complexes such as $[(HAs)\{CpMn(CO)_2\}_2]$ ($Cp = C_5Me_5$,[2] $Cp = C_5H_4Me$)[3] and $[(HAs)\{M(CO)_n\}_3]^{2-}$ (M = Fe, $n = 4$;[4] M = Cr, $n = 5$),[5] in which the arsinidene ligand binds in a μ_2- or μ_3-bridging fashion, respectively. While metal complexes featuring terminal M=AsR functionalities (R = alkyl, aryl) are generally very rare,[6] terminal coordination of the parent AsH was only recently structurally authenticated in the anionic uranium(IV) complex $[U(Tren^{TIPS})(AsH)]^-$ [**A**, $Tren^{TIPS} = N(CH_2CH_2NSi^iPr_3)_3$].[7] Isolation of elusive diarsene in $[\{U(Tren^{TIPS})\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}As_2H_2)]$ was also accomplished at the same uranium moiety.[8] In addition, matrix isolation and characterisation by IR spectroscopy of the complexes HM=AsH (M = Ti, Zr, Hf) was reported recently by the reaction of laser-ablated group 4 metal atoms with AsH_3.[9] Interestingly, the related silaarsene unit HSi=AsH could be stabilised by a 1,3-diketiminate (NacNac) ligand, and to the best of our knowledge, the resulting complex **B** (Ar = 2,6-$^iPr_2C_6H_3$ = Dipp) represents the only structurally characterised example in which AsH is bound to a p-block element in a terminal fashion (Fig. 1).[10]

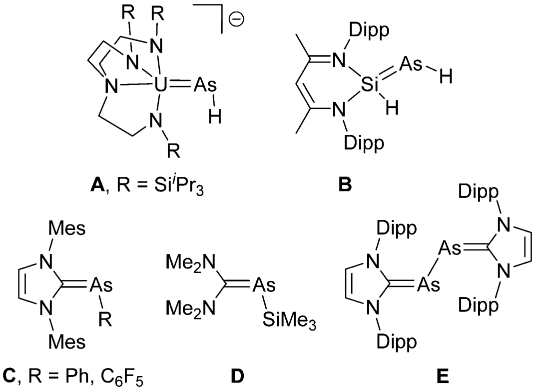

Fig. 1 Arsinidene complexes and carbene–arsinidene adducts.

N-Heterocyclic carbenes (NHC) have become particularly useful for the preparation of unusual main group element compounds,[11] and naturally, the first NHC–arsinidene adducts **C** were prepared by the reaction of 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) with cyclic oligoarsinidenes, *i.e.* hexameric $(AsPh)_6$ or tetrameric $(AsC_6F_5)_4$, respectively.[12] Related acyclic carbene adducts such as **D** were prepared by arsenide addition to formamidinium salts and can be employed as arsinidene-transfer reagents.[13] Carbene stabilisation of diarsenic in $[(IPr)_2As_2]$ [**E**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] was also accomplished (Fig. 1).[14] However, no NHC adducts of the parent AsH are known to date, while several routes were recently reported independently for the preparation of NHC adducts of its lighter congener phosphinidene (PH). In our hands, (IPr)PH was prepared conveniently from the 2,2-difluoroimidazoline $IPrF_2$ (PhenoFluor™) by reaction with $P(SiMe_3)_3$, followed by desilylation.[15] The same compound was also synthesised from the imidazolium salt (IPrH)Cl by the use of sodium 2-phosphaethynolate, Na(OCP), or $P_7(TMS)_3$ (TMS = trimethylsilyl) as phosphorus-transfer reagents.[16] Na(OCP) can also serve as the phosphorus source for the synthesis of (IMes)PH[17] or the more bulky derivative

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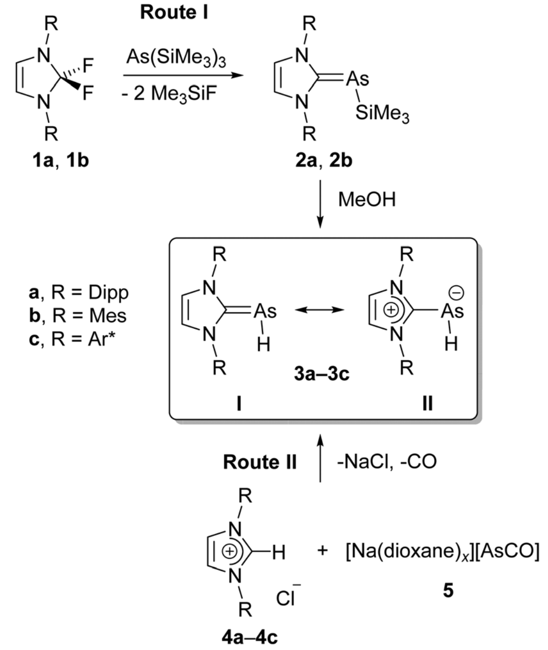
(IAr*)PH with 2,6-bis(diphenylmethyl)-4-methylphenyl (Ar*) substituents.[18] Various (NHC)PH species, including (IMes)PH, could also be accessed directly from imidazolium salts and P_4 or Na_3P_7,[19] while the 4,5-dihydro form of (IPr)PH was obtained from PH_3 and the corresponding imidazolinium chloride.[20] In view of the current tremendous interest in the use of the carbene–phosphinidene adducts in coordination chemistry,[15,17,18,20,21] we reasoned that also the heavier carbene–pnictinidene congeners (NHC)EH (E = As, Sb, Bi) might serve as suitable ligands in transition metal chemistry if they became available. Herein, we report on the development of two synthetic protocols by using $As(SiMe_3)_3$ (**route I**),[22] or the recently reported 2-arsaethynolate ion (**route II**),[23,24] as starting materials for the syntheses of the novel parent N-heterocyclic carbene–arsinidene adducts (IPr)AsH (**3a**), (IMes)AsH (**3b**) and (IAr*)AsH (**3c**).

For the preparation of the carbene–arsinidene adduct **3a** (R = Dipp) *via* **route I**,[15] the 2,2-difluoroimidazoline $IPrF_2$ (**1a**, PhenoFluor™) represents a suitable starting material.[25] The corresponding difluoride $IMesF_2$ (**1b**) required for the synthesis of **2b** and **3b** (R = Mes) was prepared in 80% yield by treatment of the 2-chloroimidazolium chloride [(IMes)Cl]Cl with ten equivalents of CsF in boiling toluene. The ^1H NMR spectrum in C_6D_6 shows a triplet at 5.45 ppm ($^4J_{(H,F)}$ = 1.54 Hz) for the imidazole hydrogen atoms, indicating covalent binding of the two fluorine atoms. The ^{19}F NMR spectrum for **1b** exhibits a sharp singlet at −34.8 ppm, which perfectly matches the chemical shift reported for **1a** (δ = −34.0 ppm) in the same solvent. Reaction of **1a** and **1b** with $As(SiMe_3)_3$[22] afforded the carbene–$AsSiMe_3$ adducts **2a** and **2b** as yellow powders in 52% and 56% yield, respectively (Scheme 1). The ^1H NMR spectra (in C_6D_6) show the expected signals for the Dipp and Mes substituents together with singlets at 6.31 and 5.89 ppm for the two imidazole CH and at 0.11 and 0.15 ppm for the nine Me_3Si hydrogen atoms, respectively. The ^{13}C NMR signals for the carbene carbon atoms in **2a** (δ = 176.8 ppm) and **2b** (δ = 173.6 ppm) are observed as relatively sharp singlets in the same range as reported for the arsinidene adducts **C** (Fig. 1; (IMes)AsPh, δ = 174.3 ppm and (IMes)AsC_6F_5, δ = 172.2 ppm).[12]

The molecular structures of **2a** and **2b** were determined by X-ray diffraction analysis and are presented in Fig. 2 (for **2a**) and in Fig. S33 (for **2b**, ESI†). Pertinent structural data are summarised in Table 1. The As–C bond lengths of 1.9130(15)/1.9125(15) Å and 1.906(2)/1.899(2) Å in **2a** and **2b** fall in the range reported for related N-heterocyclic carbene–arsinidene adducts such as **C**, *viz.* 1.899(3) Å in (IMes)AsPh and 1.902(7) Å in (IMes)AsC_6F_5,[12] whereas a shorter As–C bond length of 1.881(2) Å was reported for $[(IPr)_2As_2]$ (**E**). Arsaalkenes of the general formulae RR′C=AsR″ exhibit usually somewhat shorter arsenic–carbon bonds,[26] and for instance, identical As–C bond lengths of 1.807(3) Å were reported for two polarised fluorenylidene–arsinidene adducts.[27] The presence of the sterically more demanding Dipp substituents in **2a** in comparison with the Mes groups in **2b** leads to a pronounced deviation from the expected coplanar arrangement of the As–Si axis, and the TMS group is oriented with its silicon atom outside the plane of the imidazole ring, by 1.14/0.98 Å in the two independent molecules. In contrast, the silicon atom in **2b** is displaced by only 0.04/0.24 Å.



Scheme 1 Preparation of N-heterocyclic carbene–arsinidene adducts; Mes = 2,4,6-trimethylphenyl; Dipp = 2,6-diisopropylphenyl, Ar* = 2,6-bis(diphenylmethyl)-4-methylphenyl.

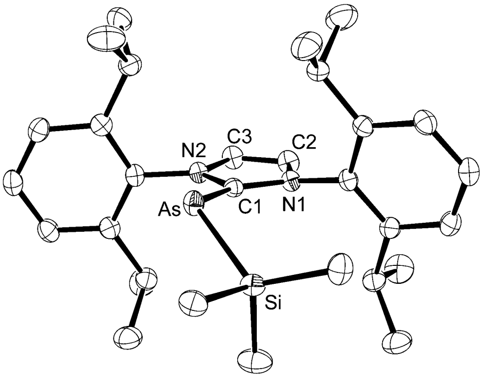


Fig. 2 ORTEP diagram of one of the two independent molecules **2a** with thermal displacement parameters drawn at 50% probability level.

Completing the synthesis of the parent carbene–arsinidene adducts **3a** and **3b** *via* **route I** requires desilylation of **2a** and **2b**, which was successfully performed by stirring them in dry methanol for several hours to afford yellow solids in 58% (**3a**) and 64% (**3b**) yield. An alternative synthesis of these parent compounds should be possible using the 2-arsaethynolate salt [Na(18-crown-6)][AsCO], which has recently become available,[23,24] however, all attempts to generate parent carbene–arsinidene adducts with this compound failed. Hence, crown ether-free $[Na(dioxane)_x][AsCO]$ (x = 3.31) had to be prepared to access **3a** and **3b** directly *via* **route II** from the imidazolium chlorides **4a** (R = Dipp) and **4b** (R = Mes) by the reaction in THF at room temperature (Scheme 1). In addition, the imidazolium salt **4c** with the larger

Table 1 Comparison of selected bond lengths (Å) and angles (°) of the carbene–pnictinidene adducts (X = H or $SiMe_3$)

Compound	C1–As	As–X	C1–As–X	N1–C1–N2
2a (X = $SiMe_3$)[a]	1.9130(15) 1.9125(15)	2.3110(5) 2.3142(5)	108.68(5) 104.10(5)	104.32(13) 104.34(12)
2b (X = $SiMe_3$)[a]	1.906(2) 1.899(2)	2.3234(6) 2.3243(6)	112.11(7) 112.89(6)	104.56(18) 103.84(17)
(IMes)AsPh[12]	1.899(3)	1.845(2)	97.3(1)	104.2(2)
(IMes)AsC_6F_5[12]	1.902(7)	1.976(7)	99.8(3)	104.6(6)
3a (X = H)	1.883(2)	1.47(5)	90.2(19)	104.58(18)
3b (X = H)	1.896(2)	1.42(4)	97.8(13)	105.2(2)
3c (X = H)	1.886(4)	—[b]	—[b]	104.5(3)

[a] Values for two independent molecules. [b] The As–H bond length in **3c** was restrained, whereas the position of the hydrogen atom was freely refined in **3a** and **3b**.

2,6-bis(diphenylmethyl)-4-methylphenyl (Ar*) substituents was also employed. The reactions were terminated by filtration through Celite, and crystallisation from concentrated THF solutions furnished **3a–3c** as microcrystalline yellow solids in comparatively low yield, *i.e.* 13% (**3a**), 15% (**3b**) and 9% (**3c**). This is due to the high light sensitivity and instability of the products in solution at ambient temperature. As decomposition products, the free carbenes were identified indicating the easy removal of the parent arsinidene moiety. Their similar solubility decreases dramatically the isolated yields of the analytically pure products **3a–3c**.

The ^1H NMR spectra (in C_6D_6) of **3a–3c** display signals at 1.43, 1.47 and 2.26 ppm, which can be assigned to the hydrogen atom of the As–H moiety. The shift to lower field of the latter resonance can be ascribed to an interaction with the Ar* substituents. In the spectrum of **3b**, this signal appears as a triplet with a $^5J_{(H,H)}$ coupling of 0.45 Hz together with a doublet at 6.00 ppm for the imidazole hydrogen atoms. For the latter, a variable-temperature ^1H NMR study of **3b** in toluene-d_8 afforded two resolved signals below a coalescence temperature of T_C = 195 K, which allowed to establish a barrier of rotation around the As–C bond of $\Delta G^{\#} = 9.7 \pm 0.2$ kcal mol^{-1} (ESI,† Section 2.9). The ^{13}C NMR spectra reveal relatively sharp signals for the carbene–carbon atoms at 184.5 ppm (**3a**), 179.4 ppm (**3b**) and 180.9 ppm (**3c**), which are at lower field in comparison with the $AsSiMe_3$ adducts **3a** and **3b**. The IR spectra (Nujol) of **3a–3c** exhibit bands at 2080, 2059 and 2090 cm^{-1}, which can be assigned to respective As–H stretching frequencies. It should be noted that a significantly lower stretching frequency was reported for the uranium arsinidene complex **1** (1857 cm^{-1}),[7] whereas similar values were found for instance in metal arsenido complexes.[28]

The X-ray crystal structures of the three AsH adducts **3a–3c** could be established; the molecular structures are presented in Fig. 3 (for **3a**) and in Fig. S35 and S36 (for **3b** and **3c**, ESI†). Pertinent structural parameters are summarised in Table 1. The As–C bond lengths of 1.883(2) Å (**3a**), 1.896(2) Å (**3b**) and 1.886(4) Å (**3c**) are slightly shorter than those in the silylated derivatives **2a** and **2b** and those in the arsinidene adducts **C** (Fig. 1).[12] The C–As–H angles are close to 90°, reflecting the high degree of p-character for the heavier main group element–element covalent bonds.

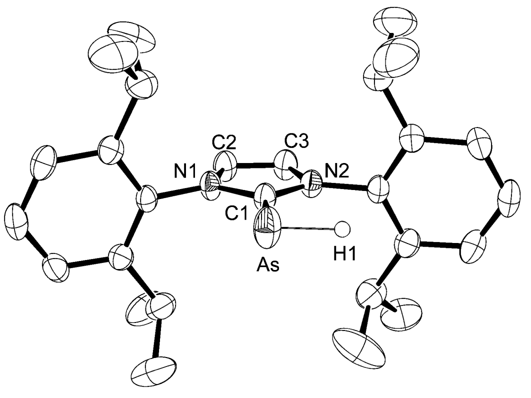


Fig. 3 ORTEP diagram of the **3a** in the solid state with thermal displacement parameters drawn at 50% probability level.

To investigate the bonding situation in the N-heterocyclic carbene–arsinidene adducts **3a–3c**, various computations were carried out by using Gaussian09 at the PBE1PBE level of theory and the 6-31G(d,p) basis sets for all atoms. Besides the structural optimisation of the three compounds **3a–3c**, methylarsine (H_3CAsH_2) featuring a C–As single bond, as well as the arsaalkenes H_2CAsH and Ph_2CAsH as archetypical species exhibiting C=As double bonds were calculated for comparison. All computational data are assembled in Table S7 (ESI†). While the computed As–H bond lengths vary only slightly (1.509–1.519 Å) the C–As–H angle is significantly closer to 90° for **3a–3c** (91.96°–92.95°) than for H_3CAsH_2 (95.22°), H_2CAsH (96.13°) or Ph_2CAsH (95.69°). This is due to weak C–H bonding contributions (*e.g.* in HOMO−1, HOMO−5, see ESI,† Section 4.2.1, Fig. S41 and S42). The computed C–As bond lengths of **3a–3c** (1.851–1.860 Å) are slightly shorter than the distances determined by X-ray diffraction (1.883–1.896), but are in between the values for a single bond (H_3CAsH_2: 1.961 Å) and a double bond (H_2CAsH: 1.766, Ph_2CAsH: 1.803 Å). Similarly, the Wiberg bond indices for the C–As bond of **3a–3c** (1.26–1.27) were found to be between the values for single bond (H_3CAsH_2: 0.97) and double bond (H_2CAsH: 1.93, Ph_2CAsH: 1.62).

Natural Resonance Theory (NRT) shows three major resonance structures (see ESI,† Section 4.2.3), weighing the one with the C=As double bond at 33% (Scheme 1, **I**) and the corresponding zwitterionic formulations (N^+, As^-) at 38% (Scheme 1, **II**). An ELF analysis (see ESI,† Section 4.2.4) shows the typical dumbbell-shaped surface at an isovalue of 0.85 for H_2CAsH and similarly, but slightly less pronounced, for **3b**. Another tool to estimate the degree of multiple bonding is the ellipticity of the electron density perpendicular to the bonding path at the bonding critical point within QTAIM (see ESI,† Section 4.2.5). The ellipticity of the C–As bond in H_3CAsH_2 (0.05) is considerably smaller than for the arsaalkenes (0.28) or **3a–3c** (0.31–0.32), which also points to the presence of a C=As double bond in **3a–3c**. The computed NBO charges q(H) are similar for all considered species (−0.033 to −0.070 e), but with dramatically differences for C and As: whereas the C atoms in H_3CAsH_2 (−1.034 e), H_2CAsH (−0.866 e) or Ph_2CAsH (−0.371 e) bear a negative charge, in **3a–3c** the charge on the carbon amounts to +0.094, +0.091 and +0.094 *e*. On the other hand, the As atom is negatively polarised in **3a–3c** (−0.045, −0.058, −0.073, respectively) and bears positive charge in H_3CAsH_2 (+0.333 *e*), H_2CAsH (+0.436 *e*) or Ph_2CAsH (+0.399). Hence, it is similarly justified to rationalise the adducts of the parent arsinidene (AsH) and NHCs as inversely polarised arsaalkenes.

In summary, we have introduced two different synthetic protocols for the preparation of the first N-heterocyclic carbene adducts of the parent arsinidene (AsH). Three adducts of the type (NHC)AsH were fully characterised, including the determination of their molecular structures by X-ray diffraction analyses, which confirm the dicoordinate nature of the arsenic(I) atoms. These species are new members of the family of N-heterocyclic carbene adducts of parent pnictinidenes, which now comprises EH = NH, PH and AsH. An extension to the heavier antimony (SbH) and bismuth (BiH) analogues might also become possible by application of similar synthetic routes. These new (NHC)AsH species are ideally suited to serve as starting materials, *e.g.* for the preparation of unusual arsenic-containing main-group element compounds and as novel arsenic-donor ligands in transition metal chemistry.

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