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N-Heterocyclic Carbene-Stabilised Arsinidene (AsH)

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A series of novel N-heterocyclic carbene-arsinidene adducts was prepared by two different synthetic routes. Reactions of the difluoro imidazolines (IPr)F$_2$ (**1a**, 1,3-bis(2,6-diisopropylphenyl)-2,2-difluoroimidazoline) and (IMes)F$_2$ (**1b**, 1,3-bis(2,4,6-trimethylphenyl)-2,2-difluoroimidazoline) with tris(trimethylsilyl)arsine, As(SiMe$_3$)$_3$, yielded the corresponding N-heterocyclic carbene supported low-valent As(I) compounds (NHC)AsSiMe$_3$ (NHC = IPr; **2a**, IMes; **2b**). Subsequent methanolysis of the adducts **2a** and **2b** afforded their respective parent arsinidenes (NHC)AsH (NHC = IPr; **3a**, NHC = IMes; **3b**). In addition, the parent arsinidenes **3a**, **3b** and **3c**, (IAr*)AsH (IAr*= 1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene), were also accessible by the reaction of [Na(dioxane)$_{3.31}$][AsCO] with the respective imidazolium salts. Compounds **3a**–**3c** represent the first examples of the parent arsinidene (AsH) stabilized by bulky N-heterocyclic carbenes. The molecular structure and bonding situation in the new compounds was elucidated by X-ray crystallography, microanalysis and NMR (^{1}H and ^{13}C NMR) spectroscopy, and was further investigated computationally using Density Functional Theory methods.

Introduction

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$_5$Me$_5$,[2] Cp = C$_5$H$_4$Me)[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$_2$CH$_2$NSi^{i}Pr$_3$)$_3$], which crystallized with a [K(B15C5)$_2$]$^+$ potassium-crown ether counterion (B15C5 = Benzo-15-crown-5).[7] Isolation of elusive diarsene in [{U(Tren^{TIPS})}$_2$(μ-η^2:η^2-As$_2$H$_2$)] 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 [CH{C(Me)NAr}$_2$SiH=AsH] (**B**, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ = Dipp) represents the only structurally characterised example in which AsH is bound to a p-block element in a terminal fashion (Figure 1).[10]

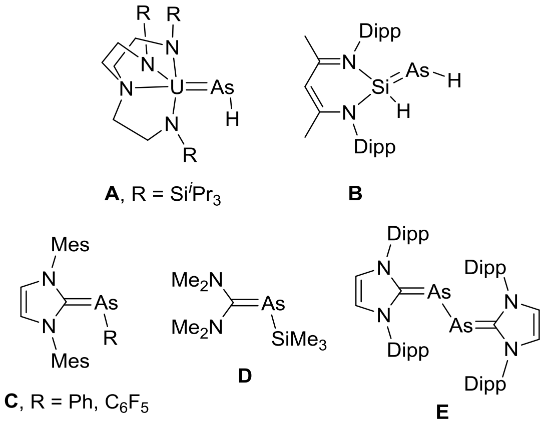

Figure 1: Arsinidene complexes and carbene-arsinidene adducts.

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 oligo-arsinidenes, *i.e.* hexameric (AsPh)$_6$ or tetrameric (AsC$_6$F$_5$)$_4$, respectively.[12,13] Related acyclic carbene adducts such as **D**

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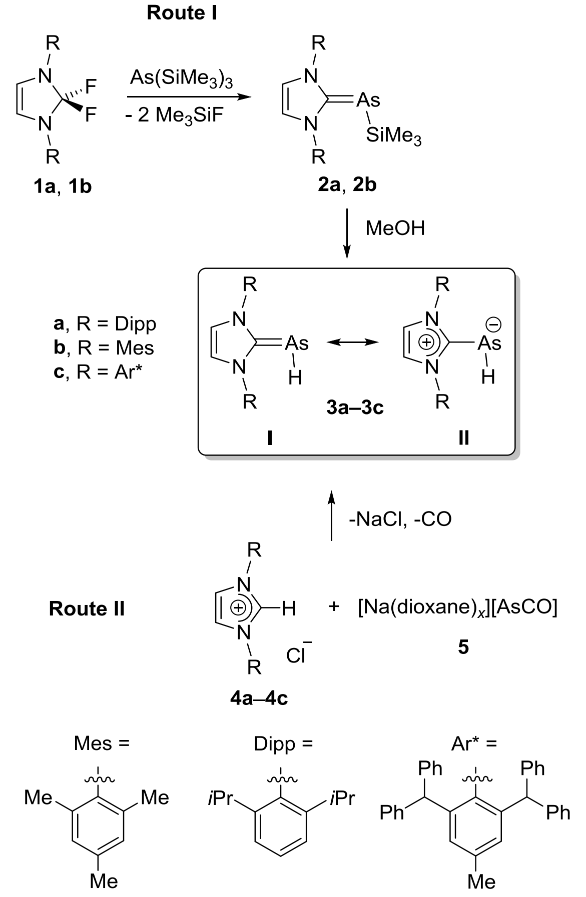
were prepared by arsenide addition to formamidinium salts and can be employed as arsinidene-transfer reagents.[14] Carbene stabilisation of diarsenic [(IPr)$_2$As$_2$] [**E**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene][15] and its oxidation to radical cations and diarsene dications was also accomplished (Figure 1).[16] 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.[17] 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.[18] Na(OCP) can also serve as the phosphorus source for the synthesis of (IMes)PH[19] or the more bulky derivative (IAr*)PH with 2,6-bis(diphenylmethyl)-4-methylphenyl (Ar*) substituents.[20] Various (NHC)PH species, including (IMes)PH, could also be accessed directly from imidazolium salts and P$_4$ or Na$_3$P$_7$,[21] while the 4,5-dihydro form of (IPr)PH was obtained from PH$_3$ and the corresponding imidazol*in*ium chloride.[22]

In view of the current tremendous interest in the use of the carbene-phosphinidene adducts in coordination chemistry,[17,19,20,22,23] 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**),[24] or the recently reported 2-arsaethynolate ion (**route II**),[25,26] 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**).

Results and Discussion

Synthesis and characterisation of N-heterocyclic carbene-arsinidene adducts

For the preparation of the carbene-arsinidene adduct **3a** (R = Dipp) via **route I**,[17] the 2,2-difluoroimidazoline IPrF$_2$ (**1a**, PhenoFluor™) represents a suitable starting material.[27] The corresponding difluoride IMesF$_2$ (**1b**) required for the synthesis of **2b** and **3b** (R = Mes) was unreported when we commenced this research but can be readily synthesised. Treatment of the 2-chloroimidazolium chloride [(IMes)Cl]Cl with ten equivalents of cesium fluoride in boiling toluene afforded **1b** in 80 % yield as a pale brown solid. Like **1a**, **1b** is highly soluble in benzene, toluene and only sparingly soluble in *n*-hexane. **1b** is highly sensitive to moisture, but can be safely stored under a dry argon atmosphere. The molecular composition of **1b** was unambiguously established by NMR spectroscopy, mass spectrometry and elemental analysis. The ^{1}H NMR spectrum in C$_6$D$_6$ shows a triplet at 5.45 ppm ($^3J_{(H,F)}$ = 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.



Scheme 1: Preparation of N-heterocyclic carbene-arsinidene adducts.

Reaction of **1a** and **1b** with tris(trimethylsilyl)arsine, As(SiMe$_3$)$_3$,[24] afforded the carbene-AsSiMe$_3$ adducts **2a** and **2b** as yellow powders in 52 % and 56 % yield, respectively (Scheme 1). Both compounds are highly light, moisture and temperature sensitive and require storage under an inert atmosphere at low temperatures to avoid decomposition. The ^{1}H NMR spectra (in C$_6$D$_6$) 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$_3$Si 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** (Figure 1; (IMes)AsPh, δ = 174.3 ppm and (IMes)AsC$_6$F$_5$, δ = 172.2 ppm).[12]

Single crystals suitable for X-ray diffractions analysis of **2a** and **2b** were obtained from hexane solutions at –30 °C. The molecular structure of **2a** is presented in Figure 2, whereas that of **2b** is shown in the Supporting Information (Figure S31). Pertinent structural data are summarised in Table 1. Both compounds crystallise in the monoclinic space group $P2_1/n$ with two independent molecules in the asymmetric unit, and they are also isotypic to the structure of the corresponding phosphinidene (IPr)PSiMe$_3$.[17] 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,[28] and for instance, identical As–C bond lengths of 1.807(3) Å were reported for two polarised fluorenylidene-arsinidene adducts.[29] 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.

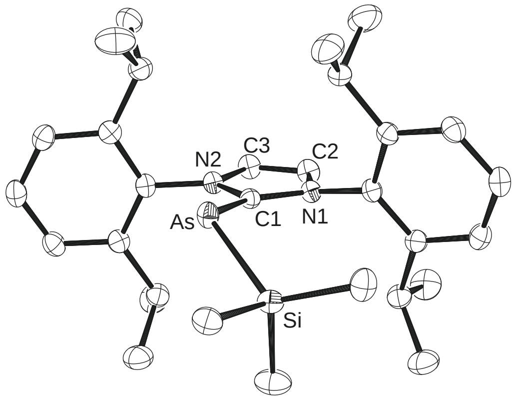


Figure 2: ORTEP diagram of one of the two independent molecules **2a** with thermal displacement parameters drawn at 50% probability level.

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,[25,26] 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 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 resonances at 1.43, 1.47 and 2.26 ppm, which can be assigned to the hydrogen atom of the AsH moiety. 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. In contrast, this coupling is not resolved for the corresponding singlet resonances of **3a** and **3c**. 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 is at lower field in comparison with the $AsSiMe_3$ adducts **3a** and **3b**, and in good agreement with computed values (**3a**: 183.7, **3b**: 175.8, **3c**: 177.5 ppm). 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.[30]

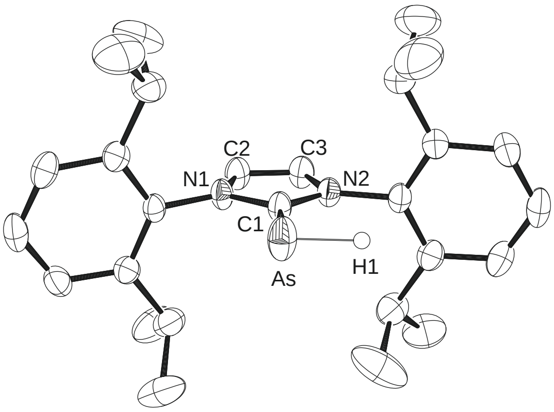


Figure 3: ORTEP diagram of the **3a** in the solid state with thermal displacement parameters drawn at 50% probability level.

The X-ray crystal structures of the three AsH adducts **3a**–**3c** could be established; the molecular structures of **3a** and **3c** are presented in Figures 3 and 4; the structure of **3b** can be found in the Supporting Information (Figure S33) Pertinent structural parameters are summarised in Table 1. The compounds **3a** and **3b** crystallised in the monoclinic space groups *C*2/*c* and $P2_1/c$, respectively, while **3c** crystallised as a toluene solvate in the orthorhombic space group $Pna2_1$**.** 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** (*vide supra*, Figure 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.

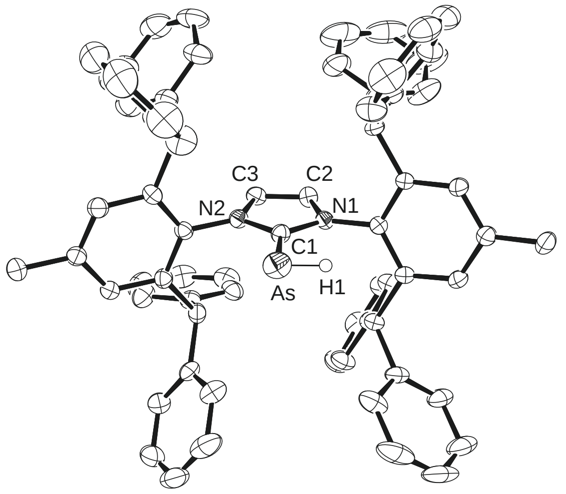


Figure 4: ORTEP diagram of the **3c** in the solid state with thermal displacement parameters drawn at 50% probability level.

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

	C1-As	As-X	C1-As-X	N1-C1-N2
2a (X = $SiMe_3$)[a]	1.9130(15)	2.3110(5)	108.68(5)	104.32(13)
	1.9125(15)	2.3142(5)	104.10(5)	104.34(12)
2b (X = $SiMe_3$)[a]	1.906(2)	2.3234(6)	112.11(7)	104.56(18)
	1.899(2)	2.3243(6)	112.89(6)	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**.

Computational Analysis

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. 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 SI 3.2.1, Figure S37 and S38). 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 bonds 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 SI 3.2.3), 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 SI 3.2.4) 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 (SI 3.2.5). 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 bonds 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.

Conclusions

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 stuctures by X-ray diffraction analyses, which confirm the dicoordinate nature of the arsenic(I) atoms. These species are new members of the familiy 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.

Experimental Section

Materials and methods: Due to the high sensitivity (to oxygen and moisture) of all the compounds reported in this study, all manipulations were performed under a strictly dry argon atmosphere using standard Schlenk line techniques and dry argon-filled glove boxes. All solvents were dried using an MBraun solvent purification system. Fluorobenzene was dried by passing through a column filled with well dried neutral Al_2O_3. ^1H, ^{13}C and ^{31}P NMR spectra were measured on spectrometers (Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz) devices). The chemical shifts are given in parts per million (δ; ppm) relative to residual solvent peaks (δ; 7.15 (C_6D_6), 1.96 (CD_3CN), 5.34 (CD_2Cl_2), 7.24 ($CDCl_3$), 3.58 (THF-d_8) ppm).[32] Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (*singlet*), d (*doublet*), t (*triplet*), m (*multiplet*), sept (*septet*) and br (*broad*). All the spectra were measured at room temperature unless otherwise stated. Mass spectra were recorded on Finnigan MAT 95 (EI) and Finnigan MAT 95 XL (ESI) systems. Elemental analyses were carried out on a Vario Micro Cube System. The starting materials Phenofluor[27], $As(SiMe_3)_3$,[24] [IPrH]Cl[33], [IMesH]Cl[33], [IAr*H]Cl[33], [IMesCl]Cl (1,3-bis(2,4,6-trimethylphenyl)-2-chloroimidazolium chloride)[34] were prepared according to the literature procedures.

Synthesis of 1,3-Bis(2,4,6-trimethylphenyl)-2,2-difluoro-imidazoline, (IMes)F_2 (1b)

Commercially available caesium fluoride was dried at 170 °C for 15 h and was finely ground prior to use. [IMesCl]Cl was finely ground using a mortar and dried under vacuum at 70 °C for 5 h. To a Schlenk tube containing [IMesCl]Cl (4.46 g, 11.81 mmol) and CsF (17.94 g, 118.19 mmol) was added toluene (200 mL). The Schlenk tube was sonicated for 30 min, and then stirred vigorously at 100 °C for 4 days. Formation of a brown solution was observed during the reaction. The reaction mixture was brought to room temperature, filtered through a pad of Celite and the residue washed with toluene (10 mL × 5). The filtrate was concentrated and dried under vacuum, washed with cold *n*-hexane followed by CH_3CN (–10 °C) and dried under vacuum to afford **1b** as a pale brown solid. Yield: 3.23 g (80 %). ^1H NMR (C_6D_6, 300.1 MHz): δ = 6.75–6.74 (m, 4H, *m*-Ar-H), 5.45 (t, 2H, $^3J_{(H,F)}$ = 1.54 Hz, NC*H*), 2.42 (s, 12H, *p*-C*H*$_3$), 2.08 (s, 6H, *o*-C*H*$_3$) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz); δ = 140.2 (N-*C*(Mes)), 138.6 (*o*-*C*(Mes)), 132.8 (*p*-*C*(Mes)), 129.9 (*m*-*C*(Mes)), 127.4 (t, $^1J_{(C,F)}$= 233.4 Hz, CF_2), 111.8 (N*C*H), 21.3 (*p*-CH_3), 18.9 (t, $J_{(C,F)}$ =2.9 Hz, *o*-*C*H$_3$) ppm. ^{19}F NMR (C_6D_6, 282.5 Hz): δ = –34.8 ppm. Anal. Calcd (%) for $C_{21}H_{24}N_2F_2$ (342.425 g/mol): C 73.66, H 7.06, and N 8.18; Found: C 73.39, H 6.97 and N 8.39. HRMS-ESI (*m/z*, CH_3OH) calcd for $C_{21}H_{24}N_2F$ $[M–F]^+$, 323.19180; found, 323.19229. EI-MS (m/z): 342.2 $[M]^{+\cdot}$ (calcd 342.190 g/mol) (60 %), 303.2 $[M–2F]^{+\cdot}$ (30 %).

Synthesis of (IPr)$AsSiMe_3$ (2a)

To a Schlenk tube containing (IPr)F_2 (0.300 g, 0.704 mmol) in fluorobenzene (10 mL) was added $As(SiMe_3)_3$ (0.210 g, 0.713 mmol) in dropwise manner at room temperature. The resulting dark orange reaction mixture was stirred at room temperature for two days. The black precipitate formed was filtered off and the solvent removed under reduced pressure. The brown oily mass obtained was triturated with *n*-pentane until it became a yellow solid and then washed with cold (-90 °C) *n*-pentane (1 mL × 3). This solid was then extracted with *n*-pentane and the solvent removed under reduced pressure affording **2a** as yellow solid. Yield: 0.201 g (52 %). ^1H NMR (C_6D_6, 300.1 MHz): δ = 7.29–7.15 (6H, Ar-*H*), 6.31 (s, 2H, NC*H*), 3.07 (sept, 4H, $^3J_{(H,H)}$ = 6.6 Hz, C*H*(CH_3)$_2$), 1.48 (d, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.09 (d, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.11 (s, 9H, As-SiMe*$_3$*) ppm. ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 176.8 (N*C*N), 147.1 (N*C*(Dipp)), 136.3 (*o*-*C*(Dipp)), 130.6 (*p*-*C*(Dipp)), 125.4 (*m*-*C*(Dipp)), 122.4 (N*C*H), 29.5 (*C*H(CH$_3$)$_2$), 25.3 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$), 5.42 (As-$SiMe_3$) ppm. Anal. Calcd (%) for $C_{30}H_{45}AsN_2Si$ (536.257 g/mol): C 67.14, H 8.45 and N 5.22; Found: C 68.09, H 7.59 and N 5.41. EI-MS (*m/z*): 536.2 (calcd 536.257 g/mol) $[M]^{+\cdot}$ (75 %), 521.2 $[M–CH_3]$ (8 %), 493.2 $[M–^iPr]$ (100 %), 463.2 $[M–SiMe_3]$ (25 %) and 387.3 $[M–As(SiMe_3)]$ (40 %).

Synthesis of (IMes)$AsSiMe_3$ (2b)

To a stirred solution of (IMes)F_2 (0.536 g, 1.566 mmol) in fluorobenzene (20 mL), was added $As(SiMe_3)_3$ (0.461 g, 1.566 mmol) in a drop wise manner. The resulting clear red reaction mixture was stirred for 3.5 h at room temperature. The black precipitate formed was filtered off, and volatiles were then removed *in vacuo*. The residue obtained was quickly washed with *n*-pentane (2 mL × 4) and dried under vacuum to obtain compound **2b** as a pale yellow-brown solid. Yield; 0.401 g (56 % based on (IMes)F_2). ^1H NMR (C_6D_6, 300.13 MHz): δ = 6.76 (br, 4H, *m*-Ar-H), 5.89 (s, 2H, NC*H*), 2.19 (s, 12H, *o*-C*H*$_3$), 2.09 (6H, *p*-CH_3), 0.15 (s, As-SiMe*$_3$*) ppm. ^{13}C {^1H} NMR (C_6D_6, 75.47 MHz): δ = 173.6 (N*C*N), 140.3 (N-*C*(Mes)), 137.5 (*o*-*C*(Mes)), 136.8 (*p*-*C*(Mes)), 131.2 (*m*-*C*(Mes)), 121.5 (N*C*H), 22.4 (*p*-CH_3), 19.9 (*o*-*C*H$_3$), 6.3 (As-$SiMe_3$) ppm. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ= –5.25 (s) ppm. Anal. Calcd (%) for $C_{24}H_{33}N_2AsSi$ (452.593 g/mol): C 63.70, H 7.35, and N 6.19; Found: C 64.95, H 7.29 and N 6.50. EI-MS (*m/z*): 452.1 (calcd 452.162 g/mol) $[M]^{+\cdot}$ (10 %), 437.1 $[M–CH_3]^{+\cdot}$ (4 %), 379.1 $[M–SiMe_3]^{+\cdot}$ (5 %), 303.2 $[M–As(SiMe_3)]^{+\cdot}$(100 %). ***Note:*** The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. The solid can be stored at low-temperatures, but slowly decomposes even under inert conditions to a black solid when stored for hours at room temperature. Furthermore, over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid.

Synthesis of [Na(dioxane)$_x$][AsCO]

Sodium (6.900 g, 300 mmol; in small pieces), arsenic (7.500 g, 100 mmol; powder), and naphthalene (250 mg, 1.95 mmol) were combined in a Schlenk flask. Then, 200 ml of dimethoxyethane (DME) were added, immediately forming a green solution. The mixture was stirred with a glass-covered stirrer bar at 70 °C for three days, forming a dark greenish solution and black microcrystalline precipitate. To the suspension, *tert*-butanol (14.820 g, 200 mmol) was added via syringe. The suspension was stirred for six hours. When all solid had dissolved, the solution had turned greenish-yellow. Diethylcarbonate (11.810 g, 100 mmol) was added via syringe and the suspension was stirred overnight. The initially greenish-yellow suspension turned orange-yellow during this process. All volatiles were removed *in vacuo* at ambient temperature. To the pale yellowish residue 300 ml of THF were added, resulting in the formation of a dark yellow suspension. After vigorous stirring for 1 hour, the mixture was left to settle overnight. The mixture was filtered over a Celite-padded sinter, affording a clear yellow solution, which was then concentrated to approximately half of the original volume. Then an approximate four-fold amount of 1,4-dioxane was added to precipitate the crude product. The solution was filtered off and the yellow solid was redissolved in THF. After filtration, the solution was concentrated and an approximate four-fold amount of 1,4-dioxane was added to precipitate the product. Drying of the bulk sample at ambient temperature under vacuum for an hour afforded an off-white solid (3.31 molecules of dioxane per Na(AsCO) 23.520 g, 56.3 mmol, 56%). The dioxane content was determined via ^{1}H NMR of a sample dissolved in THF-d_8 vs cyclohexane as internal standard. The product, [Na(dioxane)$_{3.31}$][AsCO], is not stable for prolonged storage at ambient temperature in a brown-glass bottle under an argon atmosphere, in coincidence with solvent loss. Also, thorough drying *in vacuo* causes off-white [Na(dioxane)$_{3.31}$][AsCO] to decompose to a black solid. Thus, storage in a freezer is recommended. Anal. Calcd (%) for $C_{14.24}H_{26.48}O_{7.62}NaAs$: C 40.96, H 6.39, N 0.00; no satisfactory analysis could be obtained. ^{1}H NMR (400 MHz, THF-d_8): δ = 3.56 (s, dioxane) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8): δ= 67.63 (s, dioxane), 178.38 (s, As*C*O) ppm. IR (nujol mull, cm^{-1}): 1748 (CO).).

Synthesis of (IPr)AsH (3a)

Route I: To a Schlenk tube containing (IPr)AsSiMe$_3$ (0.050 g, 0.093 mmol) in toluene (5 mL) was added CH_3OH (0.4 mL) at room temperature. The resulting reaction mixture was stirred for 1 h at the same temperature. All the volatiles were removed under reduced pressure, washed the residue with cold (–80° C) *n*-pentane (1 mL × 3) and dried under vacuum affording **3a** as pale yellow solid. Yield: 0.025 g (58 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 7.27–7.19 (m, 4H, Ar-H), 7.13 (m, 2H, Ar-H), 6.31 (s, 2H, NC*H*), 3.01 (sept, 4H, $^3J_{(H,H)}$= 7.0 Hz, C*H*(CH$_3$)$_2$), 1.49 (d, 12H, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H$_3$*)$_2$), 1.43 (s, 1H, As-*H*), 1.14 (d, 12H, $^3J_{(H,H)}$ = 6.9 Hz, CH(C*H$_3$*)$_2$) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 184.5 (N*C*N), 147.5 (N*C*(Dipp)), 135.5 (*o-C*(Dipp)), 130.6 (*p-C*(Dipp)), 125.3 (*m-C*(Dipp)), 121.1 (N*C*H), 29.4 (*C*H(C*H$_3$*)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$) ppm. EI-MS (*m/z*): 464.2 (calcd 464.217 g/mol) [M]$^{+\cdot}$ (100 %), 421.1 [M–^{i}Pr] (55 %), 387.3 [M–AsH] (90 %).

Route II: The reaction procedure was carried out under rigorous exclusion of light: 0.110 g (0.24 mmol, 1 eq.) of [IPr-H][Cl] and 0.150 g (0.36 mmol, 1.5 eq.) of [Na(dioxane)$_{3.31}$][AsCO] were suspended in ca. 10 mL THF. The grey suspension was stirred at room temperature overnight. After removal of the solvent *in vacuo* the brownish solid was suspended in hexane and filtered over Celite. The volume of the obtained yellow solution was reduced to 3 mL and stored at –30 °C. After 2 days, the product was isolated as yellow crystalline solid. Yield: 14 mg (13 %). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I. Anal. Calcd (%) for $C_{27}H_{37}N_2As$ (464.217 g/mol): C 69.81, H 8.03 and N 6.03; Found: C 68.49, H 7.73 and N 6.65. IR (nujol mull, cm^{-1}): 2080 (As-H).

Synthesis of (IMes)AsH (3b)

***Route I*:** To a stirred solution of (IMes)AsSiMe$_3$ (0.230 g, 0.508 mmol) in toluene (15 mL), excess dry CH_3OH (0.652 mL, 20.349 mmol) was added at room temperature. The resulting solution was stirred for 5 h at 45 °C. All volatiles were then removed *in vacuo*, extracted with toluene and the solvent removed under vacuum. The residue obtained was quickly washed with *n*-pentane (1 mL × 7) and dried to afford compound **3b** as a pale yellow to white solid. Yield; 0.123 g (64 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 6.76–6.74 (m, 4H, *m*-Ar-H), 6.00 (d, 2H, $^5J_{(H,H)}$ = 0.45 Hz, NC*H*), 2.19 (s, 12H, *o*-C*H$_3$*), 2.07 (6H, *p*-C*H$_3$*), 1.47 (t, $^5J_{(H,H)}$ = 0.45 Hz, As-*H*) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ = 179.4 (N*C*N), 139.3 (N-*C*(Mes)), 136.5 (*o-C*(Mes)), 135.4 (*p-C*(Mes)), 130.1 (*m-C*(Mes)), 119.5 (N*C*H), 21.4 (*p*-*C*H$_3$), 18.6 (*o*-*C*H$_3$) ppm. Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.123 g/mol): C 66.31, H 6.62 and N 7.37; Found: C 66.86, H 6.57 and N 7.59. EI-MS (*m/z*): 380.1 (calcd 380.1233) [M]$^{+\cdot}$ (60 %), 365.1 [M-CH$_3$] (8 %), [M-AsH] (100 %). ***Note*:** The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. Over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid at room temperature.

Route II: A grey suspension of 0.200 g (0.59 mmol, 1 eq.) [(IMes)H][Cl] and 0.290 g (0.70 mmol, 1.2 eq.) [Na(dioxane)$_{3.31}$][AsCO] in 10 mL THF was stirred at room temperature for 2 h. After removal of the solvent *in vacuo*, the brownish solid was suspended in toluene and filtrated over Celite. The resulting yellow solution was concentrated to a volume of 5 mL and stored at –30 °C. After 2 days the yellow blocks formed were filtered and dried under vacuum to obtain **3b**. Yield: 30 mg (15%). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I. Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.358 g/mol): C 66.31, H 6.62 and N 7.37; found: C 66.89, H 6.70 and N 7.38. IR (nujol mull, cm^{-1}): 2059 (As-H).

Synthesis of (IAr*)AsH (3c)

Route II: The reaction procedure was carried out under rigorous exclusion of light. A light brown suspension of 0.200 g (0.21 mmol, 1 eq.) [(IAr*)H]Cl and 0.110 g (0.27 mmol, 1.3 eq.) [Na(dioxane)$_{3.31}$][AsCO] in ca. 10 mL THF was stirred at room temperature overnight. After the removal of the solvent under vacuum, the brown solid was suspended in toluene and filtered over Celite. The volume of the brownish solution was reduced to 3 mL and stored at –30 °C. After 5 days, the product was obtained as light yellow crystalline solid. Yield: 18 mg (9 %). ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.85 (d, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *o*-C*H*$_{Ph}$), 7.20 (t, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *m*-C*H*$_{Ph}$),7.10 (s, 4 H, *p*-C*H*$_{Ph}$), 6.96 (s, 20 H, C*H*$_{Ph}$), 5.96 (s, 4 H, *m*-C*H*), 5.19 (s, 2 H, NC*H*), 2.26 (s, 1 H, As*H*), 1.72 (s, 6 H, C*H*$_3$), ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz); δ = 180.9 (N*C*N), 143.6 (s, *C*), 144.4 (s, *C*), 143.0 (s, *C*), 140.2 (s, *C*), 134.7 (s, *C*), 131.1 (s, *C*H), 130.8 (s, *C*H), 130.0 (s, *C*H), 128.7 (s, *C*H), 128.4 (s, *C*H), 127.0 (s, *C*H), 126.5 (s, *C*H), 120.9 (s, *C*H), 52.3 (s, Ph$_2$*C*H), 21.4 (s, *C*H$_3$) ppm. Anal. Calcd (%) for $C_{69}H_{57}N_2As$ (988.373 g/mol): C 83.78, H 5.81 and N 2.83; Found: C 83.44, H 5.82 and N 2.89. IR (nujol mull, cm^{-1}): 2090 (As-H).

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