Generation and Identification of the Trifluorosilylarsinidene F$_3$SiAs and Isomeric Perfluorinated Arsasilene FAsSiF$_2$

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The trifluorosilylarsinidene F$_3$SiAs in the triplet ground state has been generated through the reaction of laser-ablated silicon atoms with AsF$_3$ in cryogenic Ne- and Ar-matrices. The reactions proceed with the initial formation of perfluorinated arsasilene FAsSiF$_2$ in the singlet ground state by two As–F bonds insertion reaction on annealing. The trifluorosilylarsinidene F$_3$SiAs was formed via F-migration reactions of FAsSiF$_2$ under irradiation at UV light (λ = 275 nm). The characterization of FAsSiF$_2$ and F$_3$SiAs by IR matrix-isolation spectroscopy is supported by computations at CCSD(T)-F12/aug-cc-pVTZ and B3LYP/aug-cc-pVTZ levels of theory.

Arsinidenes R–As are highly electron-deficient compounds that feature monovalent arsenic analogues of nitrenes (R–N)[1] and phosphinidenes (R–P).[2] Having only a single σ-bond causes the arsenic to have an incomplete valence shell, making arsinidenes highly reactive and fleetingly existent. They can adopt either a singlet or a triplet electronic ground state,[3] which is determined by the nature of different substituents. In contrast to the chemistry of free carbenes and nitrenes,[4] which has been well established, the uncomplexed arsinidenes are generally stabilized by Lewis bases, N-heterocyclic-carbenes (NHCs),[5] N-heterocyclic silylenes (NHSis)[6] or a transition metal.[7] To date, only a handful free arsinidenes have been experimentally characterized. The parent arsinidens diradical, H–As (**1**), has been produced by photolysis of AsH$_3$, and detected by IR, Raman and microwave spectroscopy (Scheme 1).[8] Very recently, triplet phenylarsinidene Ph–As (**2**)[3] and parent vinylarsinidene C$_2$H$_3$–As (**3**)[9] have been generated in an argon matrix through the photolysis of corresponding arsenic diazide. In addition, the phenylarsinidene oxidation to dioxophenylarsine and the rich unimolecular photochemistry of vinylarsinidene were observed. The photogeneration of triplet ethynylarsinidene, HCCAs (**4**), from ethynylarsine has also been reported.[10]

Unlike aryl-, vinyl-, and alkynyl-arsinidenes, silylarsinidene such as F$_3$Si–As have been barely studied, and only the parent molecule H$_3$Si–As has been theoretically investigated.[11] Computational study on H$_3$Si–As indicates a triplet electronic ground state, resembling the phosphinidene H$_3$Si–P, which was achieved through the reaction of atomic silicon with PH$_3$ in low
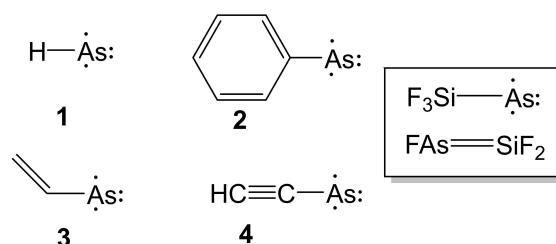
Scheme 1. Experimental known free arsinidene **1**, **2**, **3**, **4**, as well as trifluorosilylarsinidene and its isomer arsasilene from present work.

temperature matrix.[12] However, the silylarsinidene H$_3$Si–As remains experimentally unknown. In addition, silylarsinidene is a key intermediate in the tautomerization of AsH$_2$-substituted silylenes in the coordination sphere of nickel.[13] Reactions of laser-ablated metal atoms (Ti, Zr, Hf, and Th) with arsenic trifluoride will form a terminal arsinidene molecule F$_3$M–As in its triplet ground state, which were identified by matrix-isolation infrared spectroscopy in conjunction with DFT calculations.[14] Inspired by the reaction of silicon atoms with PF$_3$ to form SiPF$_3$, F$_2$SiPF and F$_3$Si–P,[15] our synthetic approach to silylarsinidene F$_3$Si–As utilizes atomic silicon and AsF$_3$ as the precursors.

The FAsSiF$_2$, and F$_3$SiAs molecules are produced via the reaction of laser-ablated silicon atoms with AsF$_3$ in solid neon and argon matrices. The infrared spectra in the 1050–450 cm^{-1} region obtained by using a 0.5% AsF$_3$/Ar sample are shown in Figure S1. After 60 min sample deposition at 5 K, very strong AsF$_3$ absorption bands were observed at 731 and 691 cm^{-1} along with new silicon independent bands at 809, 784 cm^{-1} for AsF$_5$ and 699.7, 668.4 cm^{-1} for the AsF$_2$ free radical,[16] which are common reaction products of metal atom reactions with AsF$_3$ molecules. The absorption bands due to silicon fluorides SiF$_2$ (855, 843 cm^{-1}),[17] SiF$_3$ (954, 832 cm^{-1}), and SiF$_4$ (1027 cm^{-1})[18] were also generated during sample co-deposition. In addition to these known absorption bands, new product absorption bands were observed as well. These absorption bands can be classified into two groups according to their identical chemical behaviors. Similar experiments are repeated using a 0.1% AsF$_3$/

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Ne sample. The infrared spectra in the selected region are given in Figure S2. The band positions are collected in Table 1. The difference infrared spectra showing the photochemical transformation of two new reaction products in neon and argon are given in Figure 1.

The 968.7 and 919.2 cm^{-1} absorption bands produced in argon matrices are due to different vibrational modes of the same new species. They are observed right after deposition, and increased by annealing to 20 K, but completely disappear under UV light ($\lambda = 275$ nm) irradiation, whereas only the 921.1 cm^{-1} absorption band was observed in neon matrices. This new species can be safely assigned to the arsasilene isomer FAsSiF$_2$, by comparison with the calculated IR spectra (Table 1

Table 1. Experimentally observed and calculated IR frequencies (cm^{-1}) of FAsSiF$_2$ and F$_3$SiAs molecules (absorption bands above 400 cm^{-1} are listed).

Species	Observed		Calculated	Modes[d]
	Ne-matrix	Ar-matrix	CCSD(T)-F12[b,c]	
FAsSiF$_2$	_[a]	968.7	986 (153)	asym. SiF$_2$ str.
	921.1	919.2	931 (229)	sym. SiF$_2$ str.
	_[a]	_[a]	648 (92)	As–F str.
	_[a]	_[a]	438 (2)	Si–As str.
F$_3$SiAs	958.8	953.5	973 (164)	asym. SiF$_3$ str.
	849.2	847.1	858 (227)	sym. SiF$_3$ str.
	474.3	471.9	476 (81)	Si–As str.

[a] Absorption bands not observed, or overlapped. [b] Harmonic frequencies calculated at the CCSD(T)-F12/aug-cc-pVTZ level as listed. The complete set of vibrational frequencies are provided in Supporting Information Table S1. For the CCSD(T)-F12 calculations no intensities are available. [c] The calculated IR intensities are listed in parentheses in km mol^{-1} at the B3LYP/aug-cc-pVTZ level. [d] Tentative assignments based on calculated vibrational displacement vectors.
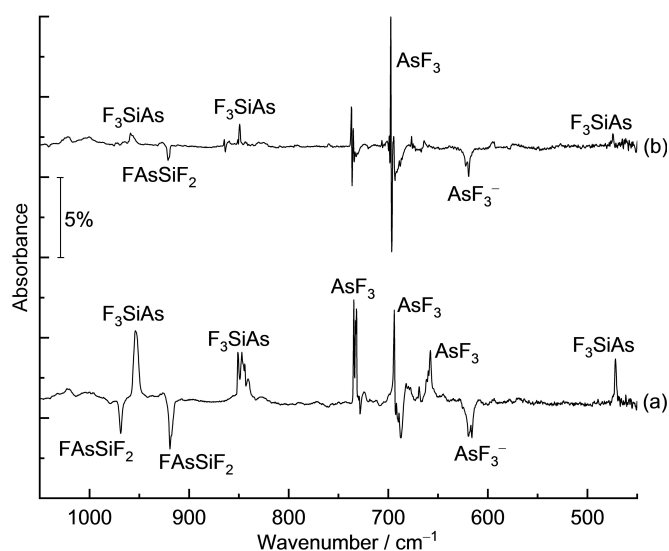

Figure 1. Difference infrared spectra in the 1050–450 cm^{-1} region from co-deposition of Si atoms with AsF$_3$ (0.1 % in neon and 0.5 % in argon) in solid matrices. (a) spectrum recorded after 20 min of UV light ($\lambda = 275$ nm) irradiation minus spectrum recorded after 20 K annealing in argon; and (b) spectrum recorded after 20 min of UV light ($\lambda = 275$ nm) irradiation minus spectrum recorded after 10 K annealing in neon.

and Table S1) at the CCSD(T)-F12/aug-cc-pVTZ level. Two absorption bands belong to anti-symmetric and symmetric stretching vibration modes of the SiF$_2$ moiety. The two frequencies are very close to that of FPSiF$_2$ (974.2, 933.1 cm^{-1}, Ar-matrix; 978.5, 933.7 cm^{-1}, Ne-matrix),[15] and lower that in F$_2$Si=S (996, 969 cm^{-1}, Ar-matrix)[19] but higher than that in SiF$_2$ (855, 843 cm^{-1}, Ar-matrix; 864.6, 851.0 cm^{-1}, Ne-matrix).[17] The As–F stretching vibration was predicted at 648 cm^{-1} as a medium strong absorption band and could not be clearly identified due to an overlap with the stronger IR bands of the precursor molecule AsF$_3$ in this region. Other computed bands of the FAsSiF$_2$ molecule are not observed due to the low IR intensity (Table 1 and S1).

The second set of absorption bands at 953.5, 847.1 and 471.9 cm^{-1} (958.8, 849.2 and 474.3 cm^{-1}, Ne-matrix) in the argon matrix belong to another new product molecule. This new product molecule absorption bands increased under UV light ($\lambda = 275$ nm) irradiation at the expense of the FAsSiF$_2$ absorption bands (Figure 1), suggesting that new product is a structural isomer with chemical formula of F$_3$AsSi. Considering the known photoinduced conversion from singlet FPSiF$_2$ to triplet F$_3$SiP in low-temperature matrices.[15] DFT and coupled-cluster calculations on the IR spectra of the most likely candidate species F$_3$SiAs in the singlet and triplet states were performed (Table 1 and S1). In comparison to the experimentally observed spectra for the UV light ($\lambda = 275$ nm) photolysis products of FAsSiF$_2$, the bands observed in Ar matrices are reasonably assigned to the arsinidene intermediate F$_3$SiAs in the triplet ground state based on the good agreement with the predicted three strongest IR bands at 973, 858, and 476 cm^{-1}, respectively. The first two absorption bands can be assigned to the anti-symmetric and symmetric stretching vibration of the SiF$_3$ group, respectively. Both are red-shifted in comparison to those of F$_3$SiPH$_2$ (970, 861 cm^{-1}, gas phase),[20] but close to those of SiF$_3$ radical (954, 832 cm^{-1}, Ar-matrix).[18] Another weak band at 516.0 cm^{-1} is attributed to the Si–As stretching vibration mode. The remaining IR fundamentals of the arsinidene could not be identified in the available IR spectral region (4500–450 cm^{-1}). In addition, a weak absorption band at 619.2 cm^{-1} (616.0 cm^{-1}, Ar-matrix) can be assigned to the AsF$_3^-$ anion, based on its chemical behavior and theoretical frequency calculations (Table S2). Optimized structural parameters of this anion are shown in Figure S3.

We calculated the structures and vibrational frequencies of the F$_3$AsSi isomers in the electronic singlet and triplet states at the CCSD(T)-F12/aug-cc-pVTZ level of theory, and the results are shown in Figure 2, Figure S4 and Table 1, Table S1. Further details of the calculations are provided in the Supporting Information. According to our calculations, singlet FAsSiF$_2$ and triplet F$_3$SiAs are the two most stable isomers of the F$_3$AsSi (Figure S5). Product FAsSiF$_2$ shows a planar arrangement in C_s symmetry with an electronic ^{1}A' ground state. The predicted Si–As distance of 2.224 Å is rather short and between the values observed for single (2.36 Å) and double bonds (2.16 Å),[21] and very close to that of the donor-stabilized arsasilene (2.218 Å) obtained by single-crystal X-ray analysis.[6]
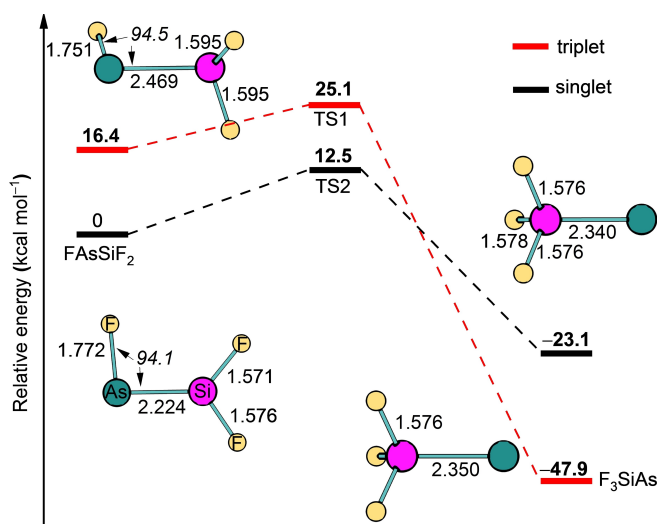
Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202401348

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Figure 2. Calculated potential energy profile for the isomerization of FAsSiF$_2$ in the singlet and triplet states at the CCSD(T)-F12/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level. Molecules structures (bond lengths in Å, angles in ° in italics) calculated at the CCSD(T)-F12/aug-cc-pVTZ level are shown.

Similar to other reported arsinidenes, such as PhAs,[3] C$_2$H$_3$As,[9] and HCCAs,[10] which have been identified to show a triplet ground state, the trifluorosilylarsinidene F$_3$SiAs is also computed to show a $^3A_1$ ground state with C_{3v} symmetry. The predicted singlet-triplet energy gap ΔE_{ST} of trifluorosilylphosphinidene is 27.0 kcal mol^{-1} at B3LYP/aug-cc-pVTZ and 24.3 kcal mol^{-1} at CCSD(T)-F12/aug-cc-pVTZ level. The triplet electronic ground state nature of trifluorosilylarsinidene F$_3$SiAs is close to its structure analogue trifluorosilylphosphinidene F$_3$SiP (ΔE_{ST} = 28.9 kcal mol^{-1} at B3LYP/aug-cc-pVTZ; 25.8 kcal mol^{-1} at CCSD(T)-F12/aug-cc-pVTZ) and trifluorosilylnitrene F$_3$SiN (ΔE_{ST} = 44.0 kcal mol^{-1} at B3LYP/aug-cc-pVTZ; 38.9 kcal mol^{-1} at CCSD(T)-F12/aug-cc-pVTZ) (Table S3). The comparison of the key structural parameters of F$_3$SiAs, F$_3$SiP, and F$_3$SiN are shown in Figure S6. Apparently, the Si–As bond distance (2.350 Å) of F$_3$SiAs is longer than Si–P (2.232 Å) and Si–N (1.777 Å) of F$_3$SiP and F$_3$SiN, respectively. This is consistent with the C–Pn bond length of phenyl pnictinidene (Pn = As, P, N).[3] However, there is only a slight difference observed between the Si–F bonds distance of trifluorosilyl ligand as well as the spin density resides at the pnictinidene atoms (arsenic: 1.94, phosphorus: 1.95, and nitrogen: 1.97). The calculated T_1 diagnostic values for F$_3$SiAs (0.011), F$_3$SiP (0.012), and F$_3$SiN (0.011) all fulfill the quality factor of $T_1 \leq 0.02$ for main-group species, which indicates that single-reference methods provide a reliable description of the systems in question.

The photoisomerization of arsasilene FAsSiF$_2$ to F$_3$SiAs is similar to the photochemistry of those phosphasilene, such as HPSiH$_2$, FPSiF$_2$, both of them isomerize to phosphinidene H$_3$SiP and F$_3$SiP under UV-vis light irradiation, respectively.[12,15] The calculated potential energy profile for the isomerization of FAsSiF$_2$ (Figure 2) unravels the underlying reaction mechanism. The spectra shown in Figure S1 and Figure S2 indicate that the arsasilene FAsSiF$_2$ molecule is produced by the reactions of ground state silicon (^{3}P) atoms with arsenic trifluoride AsF$_3$ in

solid argon and neon matrices. This insertion reaction is predicted to be exothermic by 96.1 kcal mol^{-1} (CCSD(T)-F12/aug-cc-pVTZ level, Figure S5), and require negligible activation energy, as the FAsSiF$_2$ absorption bands increase on annealing. EOM-CCSD/aug-cc-pVTZ calculation find a very strong UV/vis absorption for FAsSiF$_2$ around 250 nm (Figure S7). The UV/vis spectrum of triplet F$_3$SiAs is also shown in Figure S8. This explains why the experimentally observed rearrangement from FAsSiF$_2$ to F$_3$SiAs only occurs upon irradiation with 275 nm UV light rather than visible light, although the barriers to isomerization, either in the singlet or triplet state, are less than 15 kcal mol^{-1}.

In summary, we report the preparation and spectroscopic identification of the trifluorosilylarsinidene F$_3$SiAs and perfluorinated arsasilene FAsSiF$_2$ by the reactions of laser-ablated silicon atoms with AsF$_3$ in low-temperature neon and argon matrices. Arsasilene FAsSiF$_2$ has a singlet electronic ground state with planar structure. Upon the 275 nm UV light irradiation, FAsSiF$_2$ isomerizes to trifluorosilylarsinidene F$_3$SiAs, which was identified to have a triplet electronic ground state. The results presented here extend our fundamental understanding of arsasilene and silylarsinidene and deepen the fluorine-specific interaction in the chemistry of pnictinidenes.

Acknowledgements

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] a) J. Sun, J. Abbenseth, H. Verplancke, M. Diefenbach, B. de Bruin, D. Hunger, C. Würtele, J. van Slageren, M. C. Holthausen, S. Schneider, *Nat. Chem.* **2020**, *12*, 1054–1059; b) F. Dielmann, O. Back, M. Henry-Ellinger, P. Jerabek, G. Frenking, G. Bertrand, *Science* **2012**, *337*, 1526–1528.

[2] a) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem.* **2016**, *1*, 147–153; b) H. Aktaş, J. C. Slootweg, K. Lammertsma, *Angew. Chem. Int. Ed.* **2010**, *49*, 2102–2113; *Angew. Chem.* **2010**, *122*, 2148–2159.

[3] W. Qian, P. R. Schreiner, A. Mardyukov, *J. Am. Chem. Soc.* **2023**, *145*, 12755–12759.

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[4] C. Wentrup, *Angew. Chem. Int. Ed.* **2018**, *57*, 1508–11521; *Angew. Chem.* **2018**, *130*, 11680–11693.

[5] A. Doddi, M. Weinhart, A. Hinz, D. Bockfeld, J. M. Goicoechea, M. Scheer, M. Tamm, *Chem. Commun.* **2017**, *53*, 6069–6072.

[6] C. Präsang, M. Stoelzel, S. Inoue, A. Meltzer, M. Driess, *Angew. Chem. Int. Ed.* **2010**, *49*, 10002–10005; *Angew. Chem.* **2010**, *122*, 10199–10202.

[7] a) E. P. Wildman, G. Balázs, A. J. Wooles, M. Scheer, S. T. Liddle, *Nat. Commun.* **2017**, *8*, 14769; b) T. Pugh, A. Kerridge, R. A. Layfield, *Angew. Chem. Int. Ed.* **2015**, *54*, 4255–4258; *Angew. Chem.* **2015**, *127*, 4329–4332.

[8] a) R. N. Dixon, H. M. Lamberton, *J. Mol. Spectrosc.* **1968**, *25*, 12–33; b) M. Arens, W. Richter, *J. Chem. Phys.* **1990**, *93*, 7094–7096; c) Y. Monteil, R. Favre, P. Raffin, J. Bouix, M. Vaille, P. Gibart, *J. Cryst. Growth* **1988**, *93*, 159–164; d) K. D. Hensel, R. A. Hughes, J. M. Brown, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 2999–3004.

[9] W. Qian, P. R. Schreiner, A. Mardyukov, *J. Am. Chem. Soc.* **2024**, *146*, 930–935.

[10] A.-L. Lawzer, E. Ganesan, M. Gronowski, T. Custer, J.-C. Guillemin, R. Kołos, *Chem. Eur. J.* **2023**, *29*, e202300887.

[11] Z. Havlas, M. Kývala, J. Michl, *Coll. Czech. Chem. Comm.* **2003**, *68*, 2335–2343.

[12] J. Glatthaar, G. Maier, *Angew. Chem. Int. Ed.* **2004**, *43*, 1294–1296; *Angew. Chem.* **2004**, *116*, 1314–1317.

[13] T. J. Hadlington, T. Szilvási, M. Driess, *J. Am. Chem. Soc.* **2019**, *141*, 3304–3314.

[14] a) X. Wang, L. Andrews, *Dalton Trans.* **2009**, 9260–9265; b) X. Wang, J. T. Lyon, L. Andrews, *Inorg. Chem.* **2009**, *48*, 6297–6302.

[15] G. Deng, M. Reimann, C. Müller, Y. Lu, M. Kaupp, S. Riedel, *Inorg. Chem.* **2024**, *63*, 7286–7292.

[16] a) J. L. Brum, J. W. Hudgens, *J. Chem. Phys.* **1997**, *106*, 485–488; b) A. L. K. Aljibury, R. L. Redington, *J. Chem. Phys.* **1970**, *52*, 453–459.

[17] J. W. Hastie, R. H. Hauge, J. L. Margrave, *J. Am. Chem. Soc.* **1969**, *91*, 2536–2538.

[18] M. E. Jacox, K. K. Irikura, W. E. Thompson, *J. Chem. Phys.* **1995**, *103*, 5308–5314.

[19] H. Beckers, J. Breidung, H. Bürger, R. Köppe, C. Kötting, W. Sander, H. Schnöckel, W. Thiel, *Eur. J. Inorg. Chem.* **1999**, 2013–2019.

[20] G. Fritz, H. Schfer, R. Demuth, J. Grobe, *Z. Anorg. Allg. Chem.* **1974**, *407*, 287–294.

[21] a) M. Driess, S. Rell, H. Pritzkow, *J. Chem. Soc. Chem. Commun.* **1995**, 253–254; b) M. Driess, *Coord. Chem. Rev.* **1995**, *145*, 1–25; c) M. Driess, H. Pritzkow, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 316–319; *Angew. Chem.* **1992**, *104*, 350–353.