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In-situ Iodination of Organoarsenic Homocycles: Facile Synthesis of 9-Arsafluorene

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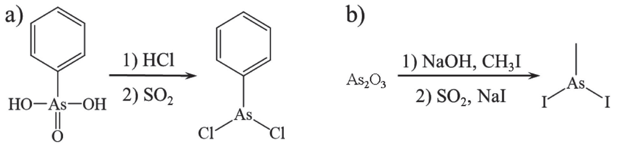
We developed an in-situ iodination of organoarsenic homocycles for facile and general As–C bond formation. Quantitative in-situ generations of arsenic diiodides from organoarsenic homocycles and iodine were confirmed by ^{1}H NMR analysis. 9-Phenyl- and 9-methyl-9-arsafluorenes were prepared by this method and their optical properties were studied.

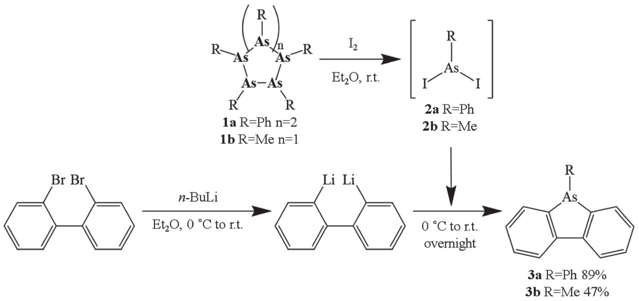
Organophosphorous π-conjugated systems such as 9-phosphafluorenes have recently received much attention as promising optoelectrical materials due to their efficient emission and charge-carrier properties.[1] 9-Phosphafluorene derivatives are generally synthesized by nucleophilic substitution of hydro- or halo-phosphines.[2] However, more convenient synthetic methods are in demand.[2g] The lone pair of electrons on the trivalent phosphorus atom has the ability to complex with transition-metal ions and the catalytic properties of such complexes have been reported.[2d,3] However, these materials have hardly been used for optoelectronic application due to their instability in air.[4]

Trivalent organoarsenic compounds have several potential advantages over their organophosphorus analogues. Their poorer σ-donor and stronger π-acceptor abilities would induce superior ligand properties in transition-metal-catalyzed reactions.[5] Trivalent organoarsenic compounds are generally air stable compared with the corresponding organophosphorus compounds.[6,7] The heavy atom effect of arsenic may contribute to phosphorescence. During our course of studies, we realized that organoarsenic ligands such as 1,4-dihydro-1,4-diarsinines can form strained and unusual complexes, due to flexible bond angles around the arsenic center.[7] However, fundamental studies on organoarsenic compounds as well as on 9-arsafluorenes[6,8] are very limited. This is because most synthetic methods for As–C bond formation use volatile toxic arsenic intermediates such as arsenic halides, prepared from arsenic trioxide or arsonic acid derivatives (Scheme 1).[9] The arsenic halides need purification and their isolation is difficult due to their vesicant nature. Therefore, special care should be taken while working with these substances.

Here, we propose a facile As–C bond formation method for preparing 9-arsafluorenes by in-situ generation of arsenic diiodides from organoarsenic homocycles, i.e. hexaphenylhexacycloarsine (**1a**) and pentamethylpentacycloarsine (**1b**), with iodine (Scheme 2). Although the organoarsenic homocycles can be easily handled in ordinary experimental equipment, their use for As–C bond formation is limited.[10] Advantages of this novel synthetic method are as follows. First, the organoarsenic homocycles are obtained quite easily by reduction of nonvolatile arsonic acid derivatives with hypophosphorus acid.[11] Second, the present in-situ iodination of organoarsenic homocycles is free from isolation and purification of the diiodoarsine intermediates because no salts or by-products are formed. Therefore, the present method provides a conventional approach toward development of organoarsenic chemistry.



Scheme 1. Synthetic examples of arsenic halides.



Scheme 2. Synthesis of 9-arsafluorenes.

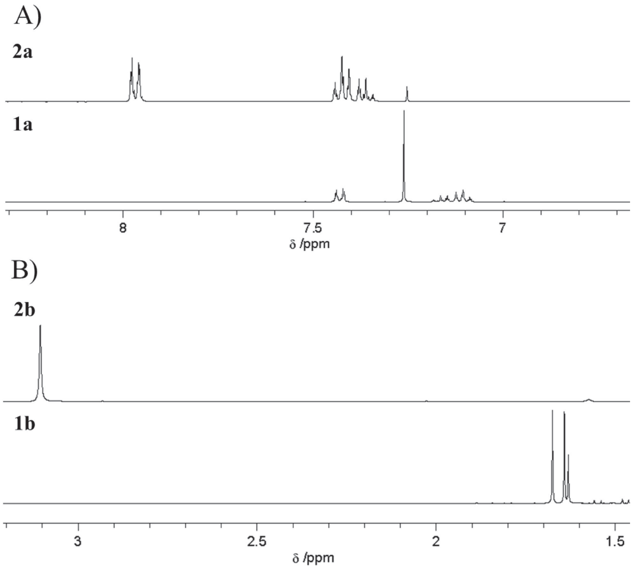


Figure 1. ^{1}H NMR spectra of organoarsenic homocycles (**1a**, **1b**) and in-situ generated diiodoarsines (**2a**, **2b**) after addition of iodine for 30 min at room temperature in $CDCl_3$.

Quantitative in-situ generation of arsenic diiodides from the corresponding organoarsenic homocycles and iodine was confirmed by ^{1}H NMR analysis (Figure 1). After an equivalent amount of iodine against the arsenic atom in $CDCl_3$ were added to the **1a** or **1b** at room temperature, the color of iodine disappeared a few minutes later. Especially in the case of **1a**, a homogeneous solution was obtained, even though **1a** is insoluble in common organic solvents such as diethyl ether (Et_2O), tetrahydrofuran, toluene, and $CHCl_3$ (Figure S9). The ^1H NMR analysis of the reaction mixtures after 30 min showed disappearance of the original signals for **1a** and **1b** and appearance of new signals corresponding to diiodomethylarsine (**2b**)[9d] and diiodophenylarsine (**2a**), respectively.

After mixing **1a**, and **1b** with an equivalent amount of iodine against the arsenic atom in Et_2O at room temperature, corresponding Et_2O solutions of **2a** and **2b** were obtained. The obtained solutions of **2** were added to an Et_2O solution of 2,2′-dilithiobiphenyl at 0 °C and the reaction mixtures were allowed to warm to room temperature. After stirring the reaction mixtures overnight, 9-phenyl-9-arsafluorene (**3a**) and 9-methyl-9-arsafluorene (**3b**) were obtained in 89% and 47% yields, respectively (Scheme 2).[12] To compare with an organophosphorus analog, 9-phenyl-9-phosphafluorene (**4**) was prepared following a reported procedure.[2d]

Air-stability was studied by bubbling air through $CHCl_3$ solutions of **3a**, **3b**, and **4** for 8 h at room temperature. Although 8 mol % of **4** was oxidized to 9-phenyl-9-phosphafluorene oxide according to ^1H NMR analysis, no oxidation for **3a** and **3b** was observed (Figures S5 and S6). Superior air stability of **3** to that of **4** is expected to be a factor in using **3a** and **3b** as optoelectrical materials.

No room-temperature photoluminescence (PL) was observed for **3a** in solutions. This observation is in agreement with the previous reports, i.e., quantum yields of PL for **3a**[8c] and a phenyl-substituted arsole[13] were quit low compared with a phosphorus analogue in solution, due to increased quenching efficiency of the heavier atom. However, we found for the first time that **3a** displayed solid-state PL ($\lambda_{max} = 390$ nm, $\Phi = 0.03$) at room temperature; at 77 K, in addition to the 387 nm peak, an intense peak at $\lambda_{max} = 515$ nm was observed (Figure S8). Solid-state PL spectrum of **3b** at 77 K also showed two emission maxima similar to that of **3a** (Figure 2), but neither solution-state nor solid-sate PL was observed for **3b** at room temperature. The emission bands at around 500 nm are probably attributed to phosphorescence, while those at around 400 nm are attributed to fluorescence, because phosphorescence is expected to be enhanced with decreasing temperature and the emission band of phosphorescence is of lower energy than that of fluorescence. Compared with **4**, the organoarsenic analogues **3a** showed relatively prominent phosphorescence (Figure 2) and the quantum yield of **4** ($\Phi = 0.09$) is less than that of **3a** ($\Phi = 0.31$) (Table 1), which suggests efficient intersystem crossing by heavy-atom effect of the arsenic atom. The emission maxima of **3a** were red-shifted compared with those of **3b**, suggesting a lower energy photoexcitation process for **3a**. This observation was correlated to the UV–vis adsorption maxima i.e., the UV–vis adsorption maximum of **3a** was slightly red-shifted compared with that of **3b**.

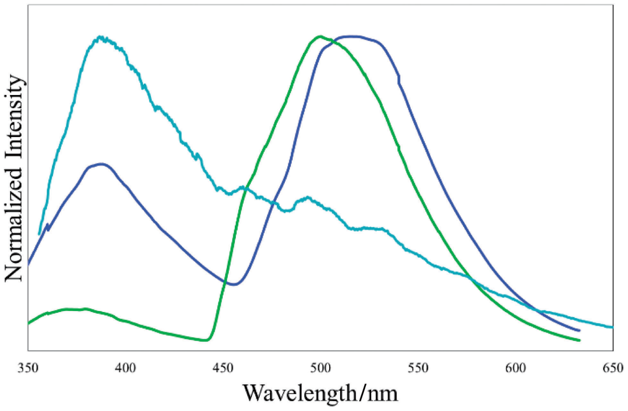


Figure 2. Solid-state PL spectra of **3a** (blue), **3b** (green) ($\lambda_{ex} = 322$ nm), and **4** (light blue) ($\lambda_{ex} = 342$ nm) at 77 K.

Table 1. Optical properties of 9-arsafluorenes (**3a**, **3b**)

	λ_{ex}[a] /nm	λ_{em}[b] /nm	Φ_{PL}[c]	λ_{abs}[d] /nm
3a	324	387, 515	0.31	281
3b	321	370, 500	0.33	279

[a]Excitation maxima determined by 510 nm emission at 77 K. [b]Local emission maxima excited at 322 nm at 77 K. [c]Quantum yields in solid state under 322 nm irradiation for excitation at 77 K. [d]UV–vis absorption maxima in $CHCl_3$ at r.t.

In summary, we have developed a novel and facile As–C bond formation method. The key step of this method is the in-situ generation of arsenic diiodides from organoarsenic homocycles and iodine. We applied this method for preparing 9-arsafluorenes and studied their optical properties. The 9-arsafluorenes showed intense solid-state PL at 77 K and excellent air-stability. 9-Arsafluorenes are promising superior candidates for optoelectrical materials due to inherent properties derived from the arsenic atom. Detailed studies for emission properties, coordination behavior and polymerization for poly-arsafluorenes are currently in progress in our laboratory.

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Supporting Information is available electronically on J-STAGE.

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12 The melting points of **3a** and **3b** were in agreement with those of reported values.[8a,8b] The structures of **3a** and **3b** were also confirmed by ^{1}H and ^{13}C NMR, mass spectroscopy and elemental analysis (See Supporting Information).

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