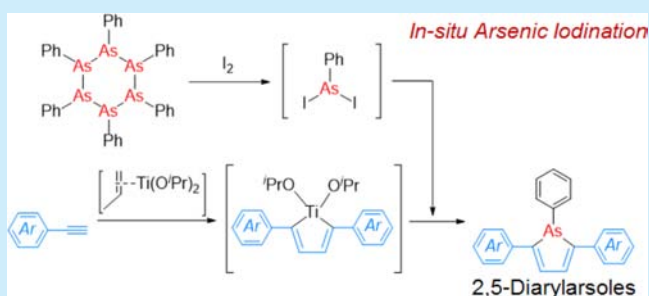


Practical Synthesis and Properties of 2,5-Diarylarsoles

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Supporting Information

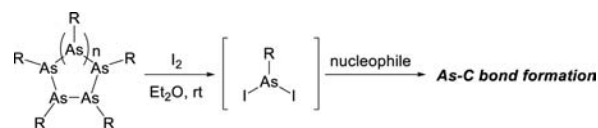
ABSTRACT: 2,5-Diarylarsoles were easily synthesized from nonvolatile arsenic precursors. Diiodoarsine was generated in situ and reacted with titanacyclopentadienes to give 2,5-diarylarsoles. The structures and optical properties were studied in comparison with those of 2,5-diarylphosphole. It was found that the arsoles were much more stable in the air than the phosphole. Single crystal X-ray diffraction revealed the arsenic atoms adopted a trigonal pyramidal structure, reflecting on the s-character of the lone pair. The obtained 2,5-diarylarsoles and 2,5-diarylphosphole showed intense emission in solutions and solid state. In addition, the optical properties were controlled by transition-metal coordination.



Five-membered heterocyclopentadienes “heteroles” have been extensively studied to date. They have been utilized in widespread fields from catalyst to optical and electrical materials. Various kinds of heteroles have been reported: borole,¹ pyrrole,² furan,³ and analogues having heavier main group elements.^{4,5} Among them, arsole is an attractive analogue because the unique electronic properties are predicted by theoretical studies.⁶ Especially, arsole has low aromaticity likely to phosphole,^{5a,6b} which has been widely studied for nonlinear optical materials, light emitting materials, and conductive materials.^{7–10} In addition, arsole is suitable for practical application under oxygen environments because it is highly tolerant to oxygen in comparison with the air-sensitive phosphole.¹¹

Despite the advantage, however, the chemistry of arsole has been highly regulated by the fact that practical synthesis of arsole derivatives remains to be achieved. There is serious concern for the toxicity of volatile arsenic precursors. For example, volatile organoarsines such as phenylarsine and dichlorophenylarsine were employed to obtain arsole derivatives in previous papers.¹²

Recently, we have reported the methodology by which diiodoarsines are generated in situ from nonvolatile organoarsenic homocycles (Scheme 1).¹³ Safely prepared diiodoarsines were converted to 9-arsafluorenes. The synthetic procedure of the in situ iodination of organoarsenic homocycles includes only mixing an organoarsenic homocycle and iodine, and diiodoarsine is generated quantitatively. The resultant solution can be used for the next reaction. The synthetic route

Scheme 1. As–C Bond Formation via in Situ Iodination of Organoarsenic Homocycles¹³

is a strong tool for As–C bond formation toward the construction of various arsenic compounds.

Herein, we investigated the synthesis of arsole derivatives by using the in situ iodination of an organoarsenic homocycle. The generated diiodoarsine was reacted with titanacyclopentadienes. Low-valent titanium complexes can regioselectively form titanacycles with terminal alkynes,¹⁴ and thus, the titanacyclopentadienes are effective for construction of heterole skeletons such as thiophene, selenophene, and phosphole. For example, heterole containing polymers were synthesized by utilizing reactive polymers having titanacyclopentadiene moiety in the main chain.¹⁵ In this work, diiodophenylarsine and 2,5-diaryltitanacyclopentadienes were employed to synthesize 2,5-diarylarsoles. Structures, optical properties, and coordination behavior were examined utilizing 2,5-diarylphosphole for comparison to explore the intrinsic properties of 2,5-diarylarsoles. This is the first study on the practical synthesis and

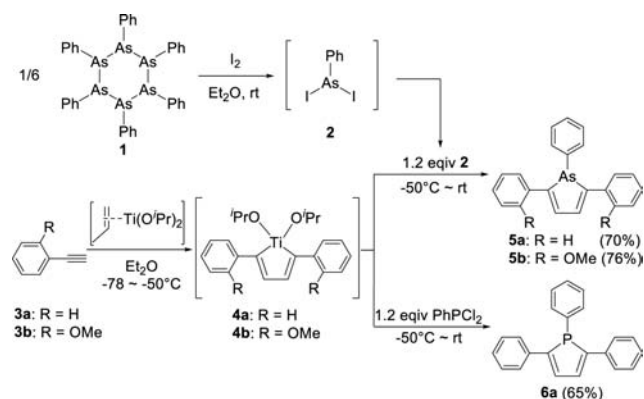
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optical properties of arsole derivatives, to the best of our knowledge.

Synthesis of 2,5-diaryl-1-phenyl-arsoles **5** and 1,2,5-triphenylphosphole **6a** is shown in Scheme 2. Reaction of

Scheme 2. Synthesis of Arsoles **5** and Phosphole **6a**



phenylacetylene derivatives **3** with a low-valent titanium(II) complex gave titanacyclopentadiene derivatives **4**. A diethyl ether (Et_2O) solution of iodine was added to an Et_2O dispersion of hexaphenylcyclohexaarsine **1**¹⁶ for in situ preparation of diiodophenylarsine **2**, and subsequently the solution of **2** was added to the solutions of **4** to obtain arsoles **5**. Instead of **2**, reaction of **4a** with dichlorophenylphosphine gave 1,2,5-triphenylphosphole **6a**. The chemical structures were confirmed by ^1H and ^{13}C NMR, high resolution mass spectroscopy, and single crystal X-ray diffraction.

The oxidation resistance tests were carried out to evaluate the air stability of the products. Chloroform solutions of **5a** and **6a** were aerated to drying air by bubbling at 25°C for 3 h. The extent of the oxidation was estimated by the signal intensity of the ^1H NMR spectra (Figure S13). Despite such mild test conditions, 12% of air-sensitive **6a** was oxidized. In the case of **5a**, less than 2% of it was oxidized, confirming that arsole is more stable in an oxidative atmosphere than phosphole.

Structural analyses for the resulting heteroles were conducted by single crystal X-ray diffraction. The representative perspective drawing of **5a** is shown in Figure 1. The average

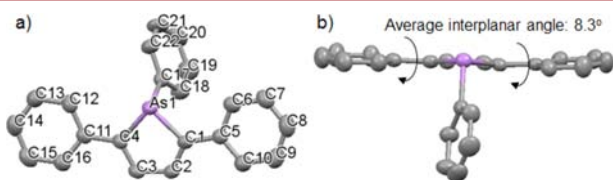


Figure 1. Results of single crystal X-ray diffraction analysis of **5a**. (a) Front view and (b) top view with ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

interplanar angle of the heterole ring and the phenyl groups was 8.3° (Table S3), suggesting that the 2,5-diphenylheterole moiety was highly planar. The bond angles of $\text{C}(1)\text{--As}(1)\text{--C}(4)$, $\text{C}(1)\text{--As}(1)\text{--C}(17)$, and $\text{C}(4)\text{--As}(1)\text{--C}(17)$ of **5a** were 87.0° , 101.7° , and 101.8° , respectively, and the total angles around the arsenic atom was 290.5° . This result means that the trivalent arsenic atom has a trigonal pyramidal structure, differing from trigonal planar pyrrole. In the case of **6a**, the average interplanar angle of the heterole ring and the

phenyl groups was 6.3° (Table S5), and the total angles around the phosphorus atom was 301.7° . This is because As-lone pair exhibits a high *s*-character in comparison to those of N and P.^{5a} In the case of **5b**, the molecular planarity was distorted by the *o*-methoxy groups, and the average interplanar angle of the heterole ring and the phenyl groups was 43.5° (Table S4). The oxygen atoms of **5b** should be interacted to the arsenic atom because the distance of As–O was 3.19 \AA , which was within the total van der Waals radii of arsenic (1.85 \AA) and oxygen (1.52 \AA).¹⁷

The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were estimated by density functional theory (DFT) calculation with the Gaussian 09 suite program at the B3LYP/6-31G+(d,p) level of theory (Figure S26).¹⁸ In all cases, HOMOs were located at diphenyl butadiene moieties, and LUMOs were delocalized across the entirety of the molecules. The energy levels of HOMOs and LUMOs were estimated by cyclic voltammetry (CV) in tetrahydrofuran solutions (Figures S23–S25 and Table S9). The results of **5a** were similar to those of **6a**. On the other hand, those of **5b** were raised by the electron-donating methoxy groups.

Absorption spectra and photoluminescence (PL) spectra were measured in chloroform solutions under air conditions (Table 1). The absorption and emission wavelengths of **5b**

Table 1. Optical Properties of the Products

product	in solution ^a			solid state	
	λ_{abs}^b [nm]	λ_{em}^c [nm]	Φ^d	λ_{em}^c [nm]	Φ^d
5a	374	458	0.59	482	0.21
5b	395	476	0.49	485	0.24
6a	375	465	0.56	504	0.39

^aMeasured in chloroform solutions under air condition. ^bAbsorption maxima. ^cEmission maxima (excited at absorption maxima (in solution) or 350 nm (solid state)). ^dAbsolute quantum yields.

were red-shifted from those of **5a**, reflecting on the narrower HOMO–LUMO gap estimated by CV analysis (Table S9). The absorption and PL properties of **5a** were quite similar to those of **6a**, well corresponding to the CV analysis result and the previous literatures.⁶ The lifetimes of the emission were measured; $\tau_{1/2} = 2.92\text{ ns}$ (**5a**), 1.76 ns (**5b**), and 2.06 ns (**6a**). This result implies that the emission is fluorescence (Figures S20–S22, Table S8).

Notably, all the obtained compounds showed intense greenish blue emission in the solid states (Figure 2a). For an understanding of the solid state emission, we investigated the packing structures in the crystalline states. As a representative example, the packing structure of **5a** is shown in Figure 2b and 2c. The planar 2,5-diphenylheterole moieties avoided cofacial $\pi\text{--}\pi$ interactions, which could cause concentration self-quenching, by the bulky phenyl group substituted on the arsenic atom. In the cases of **5b** and **6a**, cofacial $\pi\text{--}\pi$ interactions were also not observed in the crystalline states. This is why **5a**, **5b**, and **6a** exhibited intense emission even in the solid states.

We demonstrated complex formation with Au(I)Cl for emission color tuning. Solutions of Au(I)Cl species and each heterole were stirred at room temperature, and after evaporation, recrystallization from dichloromethane and methanol gave gold complexes (Scheme 3). Gold(I) complexes **5–AuCl** and **6–AuCl** were synthesized from Au(I)Cl and

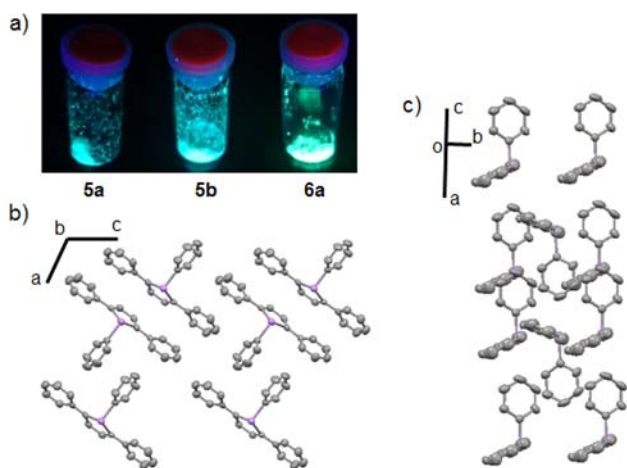
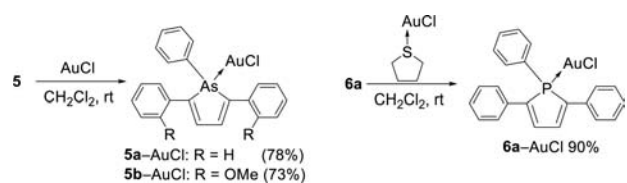


Figure 2. (a) Photographs of solid state emissions under UV irradiation at 365 nm. Packing structures of **5a**: (b) top view and (c) side view. Hydrogen atoms are omitted for clarity.

Scheme 3. Syntheses of Gold Complexes



[Au(I)Cl(tetrahydrothiophene)], respectively.¹⁹ Their chemical structures were confirmed by NMR spectroscopy and single crystal X-ray diffraction. The ¹H NMR spectra of these complexes were shifted downfield in comparison to bare ligands because electron density of the ligands was lowered by the coordination. This result means that the gold complexes were stable in solutions.

Single crystals suitable for X-ray diffraction analysis were obtained in the case of **5a**-AuCl and **6a**-AuCl. As shown in **Figure 3a**, **5a** formed monodentate coordination to the gold

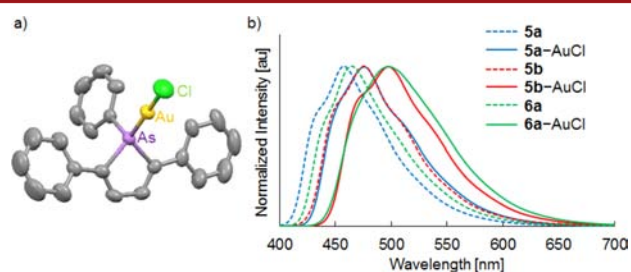


Figure 3. (a) Results of single crystal X-ray diffraction analysis of **5a**-AuCl with ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. (b) PL spectra measured in chloroform under air condition before (dash lines) and after (solid lines) the coordination.

center. The UV-vis and PL spectra of **5**-AuCl and **6**-AuCl were measured (**Figure 3b** and **Table 2**). The solutions of **5**-AuCl and **6**-AuCl showed green emission, while greenish blue emission was observed before the coordination. The emission maxima of **5a**-AuCl, **5b**-AuCl, and **6a**-AuCl were 476, 498, and 498 nm, respectively, and the red shift caused by the coordination were 49, 53, and 65 nm, respectively. The effect of coordination of **6a** was a little more profound than those of **5** because the P-lone pair has a larger contribution to π -

Table 2. Optical Properties of AuCl Complexes

ligand	in solution ^a			solid state	
	λ_{abs}^b [nm]	λ_{em}^c [nm]	Φ^d	λ_{em}^c [nm]	Φ^d
5a	383	476	0.86	498	0.17
5b	411	498	0.77	522	0.13
6a	391	498	0.81	508	0.25

^aMeasured in chloroform solutions under air conditions. ^bAbsorption maxima. ^cEmission maxima (excited at absorption maxima (in solution) or 350 nm (solid state)). ^dAbsolute quantum yields.

conjugation than the As-lone pair. Actually, a previous paper reported that the aromatic stabilization energy (ASE) and nucleus independent chemical shift (NICS) of phosphole were 3.20 kcal/mol and -5.43 , respectively, while the ASE and NICS of arsole were 1.71 kcal/mol and -3.93 , respectively.^{6b} Even though there is a minor difference, the emission color of arsole can be controlled by metal coordination as several papers reported about phosphole.^{10b,c,20} The quantum yields of the gold complexes were relatively high in solutions ($\Phi = 0.77$ – 0.86), and those in solid states were moderate ($\Phi = 0.13$ – 0.25). The quantum yields in the solid states were slightly lowered after coordination because partial overlap of the π -conjugated systems was observed in the packing structure (**Figure S14**). Arsoles can serve as ligands for intensely emissive transition metal complexes.

In conclusion, 2,5-diarylarsoles were readily synthesized from nonvolatile arsenic precursors by employing the in situ iodination of an organoarsenic homocycle. Titanacyclopentadienes worked as excellent nucleophiles to construct the arsole skeleton. The arsenic atoms in **5** adopted a trigonal pyramidal structure because of the relatively high s-character of the lone pair. Compounds **5** showed intense emission in solutions and solid states. The optical properties of **5a** were similar to those of **6**, as theoretically studied. The emission color of **5** was controlled by coordination to Au(I)Cl, and after coordination, the complexes had high quantum yields (up to 0.86 in solutions). These results imply that arsole is a potential candidate for air-stable and intensely emissive materials. Arsole containing π -conjugated polymer materials based on the synthetic strategy proposed in this work will be reported soon.

■ ASSOCIATED CONTENT

Supporting Information

and X-ray crystallographic data. The Supporting Information is available free of charge on the [ACS Publications website](https://doi.org/10.1021/acs.orglett.5b02416) at DOI: 10.1021/acs.orglett.5b02416.

Detailed experimental procedures, spectral data of products (PDF)

X-ray crystallographic data for **5a** (CIF)

X-ray crystallographic data for **5a**-AuCl (CIF)

X-ray crystallographic data for **5b** (CIF)

X-ray crystallographic data for **6a** (CIF)

X-ray crystallographic data for **6a**-AuCl (CIF)

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Notes

The authors declare no competing financial interest.

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