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Fundamental Study on Arsenic(III) Halides (AsX_3; X = Br, I) toward the Construction of C_3-Symmetrical Monodentate Arsenic Ligands

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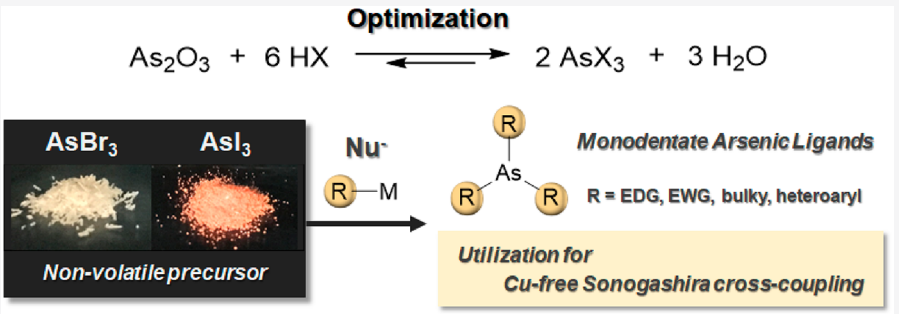

ABSTRACT: Arsenic ligands have attracted considerable attention in coordination chemistry. Arsenic(III) halides are the most important starting materials in the preparation of monodentate arsenic ligands. In this work, we optimized the synthetic methodologies of arsenic(III) halides (AsX_3; X = Br, I) and examined the difference of their physical properties such as solubility to organic solvent and reactivity to nucleophiles. In addition, a wide variety of monodentate arsenic ligands were prepared with the obtained AsX_3. Finally, the obtained monodentate arsenic ligands were utilized for copper-free Sonogashira cross-coupling reaction in the reaction system with porphyrin. The results showed that monodentate arsenic ligands have higher catalytic activity compared with triphenylphosphine because of the difference of the electronic features of lone pairs between arsenic and phosphorus atoms.

INTRODUCTION

In coordination chemistry, arsenic ligands have attracted considerable attention because of their unique coordination ability. Arsenic ligands, in general, possess higher oxidation tolerance in air, more massive steric hindrance, and poorer σ donation compared with phosphorus ones.[1] The characteristic nature of arsenic ligands has so far exhibited some advantages such as high selectivity and reactivity in transition-metal-catalyzed reactions.[2−5] In 1991, for example, Farina and Krishnan reported reaction rate acceleration in Stille cross-coupling with triphenylarsine ($AsPh_3$).[2] More recently, a palladium-catalyzed copper-free Sonogashira cross-coupling reaction with $AsPh_3$ has been developed.[3] A well-designed arsenic−nitrogen−arsenic pincer-type ligand exhibits high catalytic selectivity in the dehydrogenative transformation of benzyl alcohol and benzylamine to form *N*-benzylidenebenzylamine.[4] Considering these pioneering works, it is rational that arsenic ligands would play pivotal roles in the further development of transition-metal catalysts. However, there are few easily accessible arsenic ligands despite the unique catalytic systems. $AsPh_3$ is employed for almost all cases because it is one of the extremely limited commercially available monodentate arsenic ligands. This is because traditional synthetic routes require arsenic chlorides or hydrides, which are misused as chemical weapons because of their high toxicity and volatility.[6]

Recently, we have developed practical synthetic methodologies to access organoarsenic compounds. For example, diiodoarsines[7] and arsenic nucleophiles[8] are generated in situ from arsenic homocycles to afford symmetric (AB_2),[9] asymmetric (ABC), and bidentate types[10] of arsenic ligands (Scheme 1a). The arsenic homocycles must have low volatility at room temperature to be easily handled. These synthetic tools have provided various functional arsenic materials such as conjugated molecules,[11] polymers,[12] and transition-metal complexes.[13] On the other hand, C_3-symmetrical arsenic ligands (A_3) are still difficult to synthesize because of difficulty in the preparation of arsenic homocycles bearing various substituents.[14,15]

Arsenic(III) trichloride ($AsCl_3$) has been traditionally used to this end,[16] although it has high volatility (vapor pressure =

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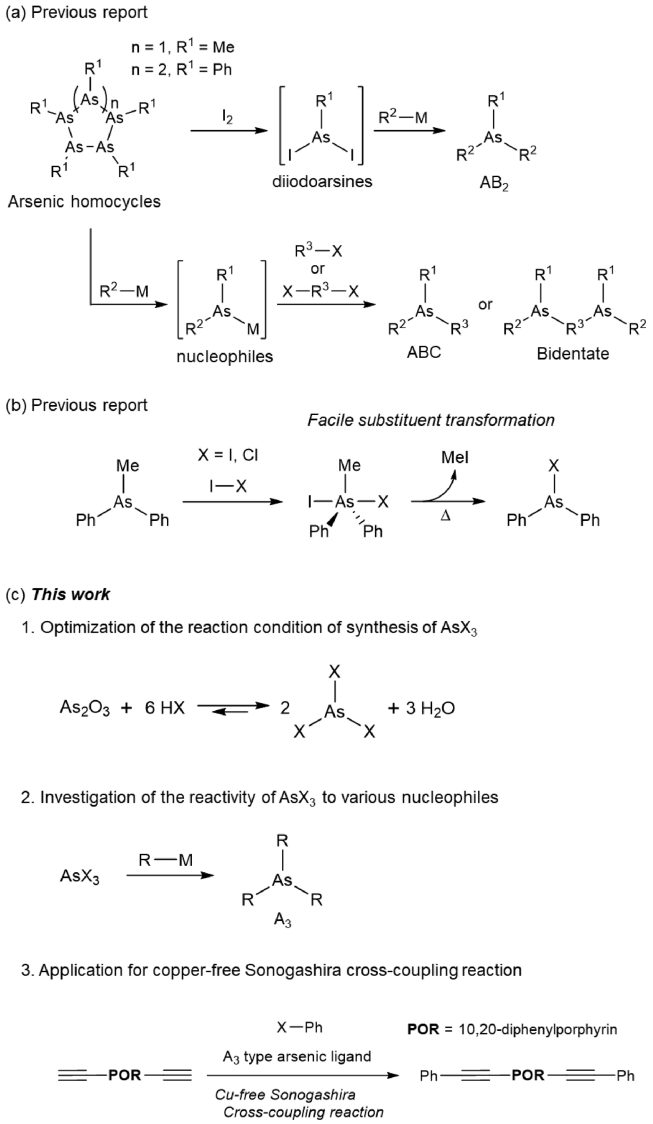
Scheme 1. (a) Practical in Situ Preparation Methods of Diiodoarsine and Arsenic Nucleophiles for the Synthesis of AB_2-, ABC-, and Bidentate-Type Arsenic Ligands, (b) Arsenic Halogenation via As−C Bond Cleavage with the Removal of Iodomethane, and (c) This Work: (1) Optimization of the Reaction Conditions of the Synthesis of AsX_3 (X = Br, I); (2) Investigation of the Reactivity of AsX_3 and Synthesis of A_3-Type Arsenic Ligands; (3) Application for Copper-Free Sonogashira Cross-Coupling Reaction



10 mmHg at 23.5 °C).[17] Actually, $AsCl_3$ and chlorobenzene are reacted in the presence of sodium metal to obtain $AsPh_3$.[18] The severe concern about the hazardous feature prevents us from accessing designed A_3-type ligands. To circumvent the usage of $AsCl_3$, we developed arsenic−halogen bond formation via As−C bond activation with halogen sources to transform the substituents (Scheme 1b).[19] However, this route needs a multistep synthesis to obtain A_3-type ligands, and thus a more efficient strategy has been desired. $AsBr_3$ (vapor pressure = 1 mmHg at 41.8 °C)[17] and AsI_3 (vapor pressure = 2.9 mmHg at 164.0 °C)[20] should be appropriate species to construct them because of the remarkably lower vapor pressure than $AsCl_3$. Previously, the synthetic procedures of $AsBr_3$[21] and AsI_3[22] were concisely introduced. However, the safe preparation method, solubility, and reactivity of arsenic(III) halides (AsX_3; X = Br, I) remain well-studied. There are thus far only a few reports of using $AsBr_3$[23] and AsI_3[24] in actual syntheses of A_3-type ligands. We herein investigated the synthesis and properties of AsX_3. Moreover, the resulting A_3-type arsenic ligands were applied to palladium catalysts for copper-free Sonogashira coupling reaction (Scheme 1c).

RESULTS AND DISCUSSION

Arsenic(III) oxide (As_2O_3) was selected as a starting material for the preparation of AsX_3. It is known that As_2O_3, being a nonvolatile inorganic compound, reacts with HBr to readily produce $AsBr_3$ and H_2O in an equilibrium reaction.[21] The challenge lies in driving the equilibrium reaction to completion to obtain AsX_3 efficiently. In this context, extraction or precipitation is pivotal in the reaction because the generated AsX_3 should be excluded from the equilibrium in the aqueous solution. We initially optimized the reaction conditions in the syntheses of AsX_3, and the results are summarized in Table 1.

Table 1. Optimization of the Reaction Conditions in Syntheses of AsX_3 (X = Br, I)

$$As_2O_3 + A \text{ equiv of aqueous HX} \overset{T\ (^\circ C),\ t\ (min)}{\rightleftharpoons} AsX_3 + H_2O$$

		conditions				
entry	X	A (equiv)[a]	T (°C)	t (min)	extraction solvent	yield (%)
1	Br	6	100	120	CH_2Cl_2	25
2	Br	6	100	120	hexane	38
3	Br	6	100	120	Et_2O	34
4	Br	8	100	120	hexane	49
5	Br	15	100	120	hexane	70
6	Br	30	100	120	hexane	58
7	Br	15	0	120	hexane	n.d.
8	Br	15	r.t.	120	hexane	17
9	Br	15	100	30	hexane	92
10	Br	15	100	300	hexane	53
11	I	15	100	30		23
12	I	15	100	30		27
13	I	6.4	100	5		33

[a]The equivalents against the number of As−O bonds.

The extraction solvent, amount of acids, temperature, and time were changed for optimization of the reaction conditions. In entries 1−3, hexane was the best extraction solvent because it has poor water solubility to effectively extract AsX_3 from the reaction system. In entries 4−6, excessive amounts of HBr were effective to drive the reaction, and 15 equiv of HBr was the best amount. As_2O_3 was insoluble in HBr at lower temperatures, and the reaction to form $AsBr_3$ was ineffective (entries 7 and 8). When the reaction mixture was stirred for 30 min at 100 °C, $AsBr_3$ was obtained in high yield (92%, entry 9). As the reaction time got longer, a decrease of the product yield was observed (entry 10), although the reason is still unclear. For the preparation of AsI_3 (entries 11−13), there were no suitable extraction solvents because of its poor solubility to aprotic solvents (vide infra). Therefore, reaction conditions such as the amount of HI_{aq}, reaction temperature, and time were optimized; as a result, 6.4 equiv of HI(aq) was added to As_2O_3 and stirred for 5 min at 100 °C to obtain AsI_3 in moderate yield (33%, entry 13).

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Although $AsCl_3$ is a volatile liquid at room temperature, the obtained products of $AsBr_3$ and AsI_3 were colorless and reddish-orange solids, respectively. Their melting points were measured to be within narrow temperature ranges, 31.5−32.1 °C ($AsBr_3$) and 145.8−146.5 °C (AsI_3), which correspond to the literature values.[21,22] This result means that the products obtained in the present procedures have sufficient purity and that they can be easily handled at room temperature. The solubility of AsX_3 to low-polarity and aprotic solvents was evaluated (Table 2). $AsBr_3$ exhibited good solubility to most

Table 2. Solubility of AsX_3 (X = Br, I) to Aprotic Solvent at 25 °C (g/mL)

X	pentane	hexane	cyclohexane	Et_2O	THF
Br	0.12	0.17	>1.0[a]	>1.0[a]	>1.0[a]
I	<0.001	<0.001	<0.001	0.047	0.062
X	1,4-dioxane		benzene	toluene	xylene
Br	0.71		>1.0[a]	>1.0[a]	>1.0[a]
I	0.034		0.026	0.020	0.013

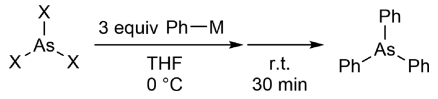
[a]$AsBr_3$ dissolved in the solvents in any proportion.

organic solvents, whereas AsI_3 had much poorer solubility. The dipole moments of $AsBr_3$ and AsI_3 were 1.903 and 0.879 D, respectively, which were calculated by a series of programming works in molecular modeling software *Winmostar* (version 9.3.5); the PM3 method in *MOPAC6* was utilized for full-optimization of AsX_3 (X = Br, I). Although a lower dipole moment leads to higher solubility to low-polarity solvents, $AsBr_3$ showed higher solubility to low-polarity solvents. We thus assumed that the intermolecular interactions in the crystal structure made a difference in the solubility between $AsBr_3$ and AsI_3. The crystal structures of $AsBr_3$ and AsI_3 were investigated in previous reports.[25,26] Single-crystal X-ray diffraction analysis revealed that AsI_3 had intermolecular As−I and I−I interactions.[25] In contrast, no significant intermolecular interactions were observed in the crystal of $AsBr_3$.[26] Higher bond dissociation energy is necessary for cleavage of the intermolecular interactions of AsI_3, resulting in the low solubility.

In order to investigate the reactivity of AsX_3 to nucleophiles, a substitution reaction with phenylmagnesium bromide (PhMgBr) and phenyllithium (PhLi) was performed. To a tetrahydrofuran (THF) solution or dispersion of $AsBr_3$ and AsI_3, respectively, 1 equiv of nucleophiles (against the number of As−X bonds) was added dropwise at 0 °C. After stirring at room temperature for 30 min, $AsPh_3$ was obtained. The reaction conditions and results are summarized in Table 3. In entries 1 and 3, PhLi gave $AsPh_3$ in high yields for $AsBr_3$ (92%) and AsI_3 (85%). In the case of PhMgBr (entries 2 and 4), on the other hand, the isolated yield of $AsPh_3$ generated from $AsBr_3$ (89%) was much higher than that from AsI_3 (54%). These results indicate that the reactivity of $AsBr_3$ is higher than that of AsI_3, which is derived from the difference of the electronegativity in As−Br and As−I. High solubility to aprotic solvents is necessary for substitution reactions with organometallic reagents to prepare A_3-type ligands. $AsBr_3$ was thus employed as an electrophile for the following syntheses of A_3-type ligands because of its higher solubility and higher reactivity in comparison with those of AsI_3.

The syntheses of A_3-type arsenic ligands were performed. A THF solution of $AsBr_3$ was prepared under N_2 and added dropwise to a solution of a nucleophile. The reaction

Table 3. Reaction of AsX_3 with PhMgBr and PhLi

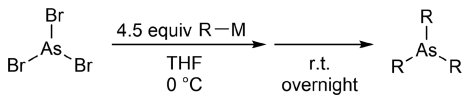


entry	conditions: X	conditions: M	yield[c] (%)
1	Br	Li[a]	92
2	Br	MgBr[b]	89
3	I	Li[a]	85
4	I	MgBr[b]	54

[a]1.6 M in a hexane solution. [b]1.0 M in a diethyl ether solution. [c]Isolated yield.

conditions and results are summarized in Table 4. Organolithium, Grignard, and organocuprate reagents were applicable

Table 4. Synthesis of A_3-Type Arsenic Ligands



entry	conditions: R	conditions: M	product	yield[b] (%)
1	*p*-tolyl	MgCl	**1**	91
2	*o*-tolyl	MgBr	**2**	81
3	*p*-anisyl	Li	**3**	85
4	*o*-anisyl	Li	**4**	68
5	*p*-trifluoromethylphenyl	Li	**5**	78
6	*o*-trifluoromethylphenyl	Li	**6**	52
7	naphthyl	Li	**7**	55
8	cyclohexyl	MgCl	**8**[c]	20[c]
9	pyridyl	Li	**9**	22
10	mesityl	Cu[a]	**10**	72
11	mesityl	Li	**10**	25

[a]Organocopper reagent [RCu] was prepared from mesityllithium and CuI. [b]Isolated yield. [c]The yield of palladium(II) complex was calculated because tricyclohexylarsine is easily oxidized in air.

as nucleophiles for the substitution reaction. To maximize the isolated yields, 4.5 equiv of nucleophiles was used here; it was confirmed that the yields remained the same or declined when using 3 equiv of nucleophiles. Aryl (entries 1−7), alkyl (entry 8), and heteroaryl (entry 9) groups were introduced by selecting the corresponding nucleophiles. Tuning of the electron-donation ability was easily accomplished by the introduction of electron-donating or -withdrawing groups (entries 3−6). In entry 10, a bulky substituent such as a mesityl group was efficiently introduced with the organocopper reagent prepared from mesityllithium and copper(I) iodide. The product yields significantly decreased when using organolithium reagents (entry 11). These results indicate that $AsBr_3$ is an excellent starting material for the synthesis of A_3-type arsenic ligands.

R_2EX (E = element) is a promising precursor for the development of highly active catalysts, e.g., Buchwald-type backbone.[27] However, it is difficult to prepare R_2EX through a one-step reaction of 1 equiv of EX_3 with 2 equiv of nucleophile (RM; M = metal) because of the generation of byproducts such as R_3E or REX_2. In the present case, we confirmed that the reaction of $AsBr_3$ with 2 equiv of PhLi gave only $AsPh_3$ (for details, see the Supporting Information). To address this

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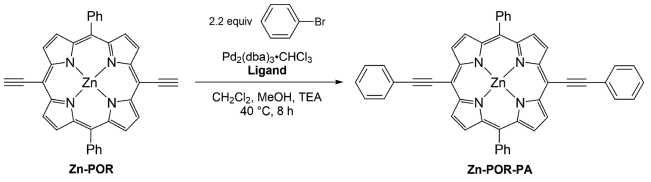
problem, a redistribution reaction with R_3E and EX_3 is often employed. It is well-known that such a redistribution reaction can be observed in heavy-main-group chemistry such as antimony and organobismuth in group 15 elements.[28] On the other hand, there are few reports about the redistribution reaction with arsenic.[29] Therefore, we considered that $AsBr_3$ could be converted to bromoarsine derivatives (R_2AsBr) through redistribution reactions with AsR_3. We selected tri(*p*-tolyl)arsine (**1**) as a reactant for the redistribution reaction. A diethyl ether solution of $AsBr_3$ (1 equiv) and **1** (2 equiv) was refluxed overnight, and $(p\text{-tolyl})_2AsBr$ was obtained in 69% yield (Figure S1), which was determined by ^1H NMR integration.[30] However, we failed to isolate the target product $(p\text{-tolyl})_2AsBr$ because the starting materials and byproducts were not sufficiently removed. A more versatile design for arsenic ligands will be attained by using the redistribution reaction, although there is still a drawback in the isolation step.

Finally, the obtained A_3-type arsenic ligands were utilized for palladium-catalyzed copper-free Sonogashira cross-coupling reaction. It is a powerful tool for substrates sensitive to the presence of copper. For example, in the case of structural modification of metal-centered-porphyrins, copper-free Sonogashira cross-coupling reaction is necessary because transmetalation from the centered metal to copper could occur in porphyrins to give contamination of the byproducts.[31] Entering the 2000s, some chemists reported that the weaker σ donation of the arsenic ligand can improve the efficiency of the coupling reaction compared with phosphorus ones.[3] $AsPh_3$ was the only applicable ligand in those reports because it is one of the few commercially available arsines. We thus applied the A_3-type arsenic ligands obtained in the present work to the copper-free Sonogashira cross-coupling reaction of 515-bis-(ethynyl)-substituted zinc(II) porphyrin derivative (**Zn-POR**; Table 5). For the reaction conditions, refer to the literature procedure,[3a] and details are described in the Supporting Information. In entry 1, the target 5,15-diphenyl-10,20-bis(phenylethynyl)-substituted porphyrin (**Zn-POR-PA**) was obtained with PPh_3 in low yield (12%); small amounts of free-base porphyrin were concomitantly obtained. On the other hand, no side reactions were observed in the case of $AsPh_3$ (entry 2). This result exhibited that the weaker coordination ability of arsenic suppressed decomplexation of the Zn ions from the porphyrin. In entries 3−6, the yields of **Zn-POR-PA** from the ligands possessing electron-donating groups were higher than those from arsenic ligands containing an electron-withdrawing group such as a trifluoromethylphenyl one. This is probably because the rate-limiting step in copper-free Sonogashira cross-coupling reaction is an oxidative addition in the catalytic cycle, and the electron-rich ligands lowered the activation energy. In entries 9 and 11, the bulky ligands gave quite low yields (up to 5%), suggesting that the steric hindrance prevented coordination to the palladium center. In fact, we confirmed that the mesityl-group-substituted ligand **10** did not coordinate to palladium(II) through the reaction with *cis*-$PdCl_2(PhCN)_2$. To understand the relationship between the steric hindrance and catalytic activity, single-crystal X-ray diffraction analysis was carried out for the palladium dichloride complexes of **1**−**5**. The results are summarized in Tables S1−S8. The Tolman ligand cone angles of $PdCl_2(ligand)_2$ (ligand = $AsPh_3$, **1**, **2**, **3**, **4**, and **5**) were 145°,[32] 147°, 173°, 142°, 179°, and 151°, respectively. This result implies that a less sterically hindered arsenic ligand tended to show higher catalytic activity when the electron-donating ability is the same. The screening that we conducted here successfully demonstrates the structure−catalytic activity relationships between monodentate arsenic ligands.

Table 5. Copper-Free Sonogashira Cross-Coupling Reaction in the Reaction System with Porphyrin



entry	ligand	yield (%)
1	PPh_3	12
2	$AsPh_3$	23
3	**1**	25
4	**2**	16
5	**3**	35
6	**4**	30
7	**5**	n.d.
8	**6**	n.d.
9	**7**	5
10	**8**[a]	13
11	**10**	n.d.

[a]The palladium complex of tricyclohexylasrsine was used instead of $Pd_2(dba)_3{\cdot}CHCl_3$ and ligand.

CONCLUSION

We optimized the reaction conditions for syntheses of AsX_3 (X = Br, I) by changing the molar ratio of hydrohalic acid, reaction temperature, reaction time, and extraction solvents to AsX_3. $AsBr_3$ was employed as the starting material to synthesize monodentate arsenic ligands because of its higher reactivity and solubility to aprotic solvents in comparison with those of AsI_3. The substitution reaction with nucleophiles readily provided monodentate arsenic ligands possessing various substituents such as aryl, alkyl, electron-withdrawing, electron-donating, bulky, and heteroaryl groups. Finally, the monodentate arsenic ligands were applied for the palladium-catalyzed copper-free Sonogashira cross-coupling reaction of **Zn-POR** with bromobenzene. Upon screening of the arsine ligands, the coupling reaction with tri-*p*-anisylarsine **3** afforded the highest yield of **Zn-POR-PA** among the prepared arsenic ligands. In the present work, we demonstrated that $AsBr_3$ is a proper starting material for safely accessing various monodentate arsenic compounds and believe that it has the potential for accessing the novel arsenic ligands utilized in outstanding transition-metal-catalyzed reaction systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00598.

Experimental procedures, X-ray crystallographic data, and NMR spectra (PDF)

Accession Codes

CCDC 1998397−1998401 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by

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emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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