Convenient Palladium-Catalyzed Arsination: Direct Synthesis of Functionalized Aryl Arsines, Optically Active *As,N* Ligands, and Their Metal Complexes

Fuk Yee Kwong,[†,‡] Chi Wai Lai,[†] Michael Yu,[†] Duan-Ming Tan,[†] Fuk Loi Lam,[§] Albert S. C. Chan,[§] and Kin Shing Chan*[,†]

Department of Chemistry and Open Laboratory of Chirotechnology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China, and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

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A convenient recipe for the direct preparation of functionalized tertiary arsines has been developed by simple palladium-catalyzed arsination of aryl triflates using triphenylarsine as the arsinating agent. This catalytic arsination was conducted under neutral reaction conditions and was found to be compatible with various functional groups, such as aldehyde, ester, keto, nitrile, and nitro groups. Interestingly, these reactions can be carried out in either DMF or solvent-free conditions with similar reaction rates and product yields. A notable arsination product, (2-cyanophenyl)diphenylarsine, underwent condensation with optically active 2-aminoalkyl alcohols in the presence of $ZnCl_2$ catalyst to afford new chiral *As,N* ligands. The bidentate *As,N*-free ligand **14** and the Pt-*As,N* complex **18** were characterized by single-crystal X-ray crystallography.

Introduction

The organoarsenic compounds are an important class of compounds both as intermediates in organic synthesis and as ligands in catalytic reactions.[1] Tertiary arsines have been reported to be more efficient ligands than phosphines in a number of transition metal-catalyzed organic reactions in terms of rate acceleration and product yield enhancement. Particular examples included Stille,[2] Heck,[3] and Negishi reactions,[4] Suzuki−Miyaura coupling,[5] Ullmann-type homocoupling,[6] epoxidation,[7] cyclization of an allylic enyne,[8] hydroformylation,[9] hydrosilylation,[10] and carbonylation.[11] In view of their potential usefulness as described above, the developments of new methods for the synthesis of arsine ligands are in increasing demand.

Current approaches for the preparation of tertiary arsines can be classified into two categories: classical arsination and catalytic arsination (Scheme 1). The classical methods involved the reaction of Grignard or organolithium reagents with haloarsine; however these reaction conditions are incompatible with many functional groups.[12] Another method is the nucleophilic aromatic substitution of aryl halides with highly reducing Ph_2AsM (M = Li, Na, K), which are usually prepared in situ in liquid ammonia (Scheme 1).[13,14] Additionally, arylarsines can also be obtained by the photoirradiated

* To whom correspondence should be addressed. E-mail: ksc@cuhk.edu.hk.
† The Chinese University of Hong Kong.
‡ Present address: The Hong Kong Polytechnic University.
§ The Hong Kong Polytechnic University.

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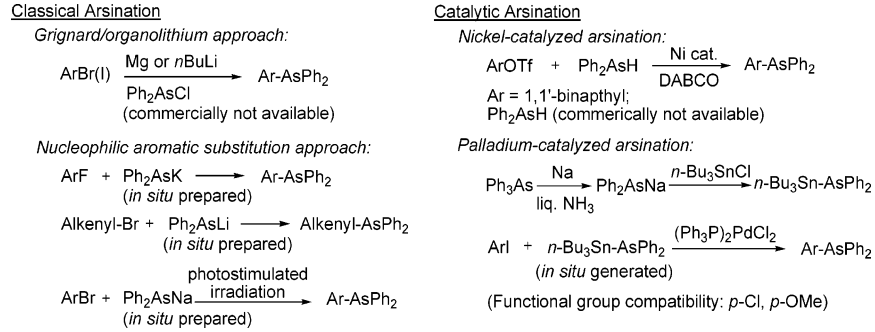
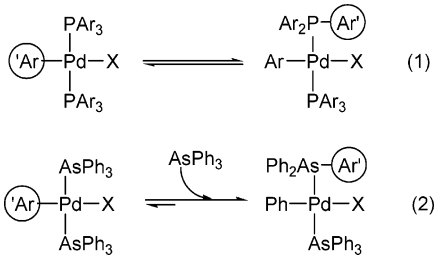
Scheme 1. Methods for the Preparation of Tertiary Arsines



reaction of the Ph_2As^- ion with aryl halides in liquid ammonia; nevertheless, scrambled products were observed.[15]

With a slightly modified catalytic method described by a research group at Merck,[16] Shibasaki and coworkers reported the first nickel-catalyzed arsination of BINOL ditriflate for the synthesis of BINAs ligands (Scheme 1).[17] This method utilized secondary arsine (Ph_2AsH) as the arsinating agent. Recently, a one-pot procedure of palladium-catalyzed As−C(sp^2) bond formation between aryl iodides and *n*-Bu_3Sn-$AsPh_2$ has been described with limited functional group compatibility (−Cl and −OMe groups) (Scheme 1).[18] This *n*-Bu_3-Sn-$AsPh_2$ reagent was prepared in situ by reacting the Ph_2As^- anion (generated from Ph_3As and Na metal in liquid ammonia) with *n*-Bu_3SnCl. The present arsination methods are of limited functional group compatibility because of the utilization of a highly reducible arsinating agent and/or in a basic reaction medium. In view of the drawbacks from current methods, it prompted us to develop a catalytic arsination in milder reaction conditions as well as in a neutral reaction medium with a better functional group compatibility.



The undesirable aryl/aryl exchanges between the palladium-bound Ar′ ring and the phosphorus-bound Ar ring are frequently observed in the palladium-catalyzed cross-coupling reactions[19] and lead to the formation of unwanted scrambled side products (eq 1).[20,21] In contrast, we postulated that this undesirable reaction might be an achievable route for the synthesis of substituted aryl arsine using triphenylarsine as the arsinating agent (eq 2).[22] In fact, the stoichiometric mechanistic studies of the phosphorus analogues, Pd−Ar/P−Ph exchange reactions (eq 1), have been reported by Cheng,[23] Grushin,[24] Norton,[25] and Novak,[26] and the applications have also been recently described.[27,28] Herein, we report our results of the direct arsination of functionalized aryl triflates in neutral reaction medium and the transformation of an aryl arsine into optically active bidentate *As,N* ligands and their corresponding Pd and Pt complexes as well.

Results and Discussions

Palladium-Catalyzed Arsination. In the initial attempt, it was found that the $Pd(OAc)_2$ and Pd/C

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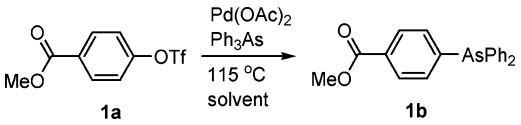
Table 1. Solvent Effect on Palladium-Catalyzed Arsination of 1a[a]

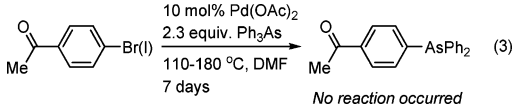


1a **1b**

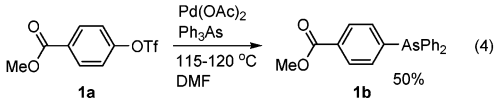
entry	solvent	time/days	% yield[b]
1	DMF	4.5	50
2	NMP	5.0	34
3	DMSO	5.0	40
4	THF	10.0	0
5	solvent-free	5.0	51

[a] Reaction conditions: $Pd(OAc)_2$ (0.1 mmol, 10 mol %), Ph_3As (2.3 mmol), and aryl triflate (1.0 mmol) in solvent (2.0 mL) were heated to 115 °C (±5 °C) under N_2. [b] Isolated yield.

systems failed to catalyze the arsination of 4-bromoacetophenone (or 4-iodoacetophenone) to the corresponding arsine product in the presence of excess Ph_3As, at 110 to 180 °C for 7 days (eq 3). Salt additives, such as $NaBF_4$ or Bu_4NI, were not beneficial in various attempts.[28c]



To our delight, successful palladium-catalyzed arsination was achieved when aryl triflate substrates were examined. Thus, the prototypical aryl triflate **1a** was smoothly transformed to the corresponding arsine **1b** in 50% isolated yield in the presence of 10 mol % of $Pd(OAc)_2$ and 2.3 equiv of triphenylarsine in DMF (eq 4).



1a **1b**

By carrying out the side-by-side reactions with a variety of common organic solvents, we found that DMF was the most preferable solvent for the palladium-catalyzed arsination (Table 1, entry 1). Presumably, a more polar solvent favors the arsination through faster oxidative addition of aryl triflates and the formation of arsonium intermediates (as well as stabilization of arsonium salt intermediates; see mechanistic discussion). NMP was found to be a suitable solvent, but a lower yield of the desired product was obtained when compared to DMF (Table 1, entry 1 vs 2). Although DMSO is a more polar solvent than DMF, it may oxidize Ph_3As slowly to give $Ph_3As{=}O$ in an analogous manner to that of DMSO with phosphines.[29] The competitive consumption of arsine reagent and product would therefore account for a lower yield of the desired product (Table 1, entry 3). THF was not effective at all without the consumption of starting material **1a** (Table 1, entry 4). Particularly noteworthy is that the arsination was equally effective in solvent-free conditions.[30] Similar reaction rates and isolated yields were obtained (Table 1, entry 1 vs 5).

Table 2. Effect of Ph_3As Loading on Yield of Arsination in DMF[a]

entry	equiv of Ph_3As	% yield[b]
1	0.0	0
2	1.0	28
3	2.0	45
4	2.3	60
5	2.5	61
6	3.0	60

[a] Reaction conditions: $Pd(OAc)_2$ (0.1 mmol, 10 mol %), Ph_3As (varied), and aryl triflate **1a** (1.0 mmol) in DMF (2.0 mL) were heated to 115−120 °C for 4.5 days under N_2. [b] GC yield.

To further optimize the reaction parameters, the amounts of Ph_3As used in arsination were also investigated. When the Ph_3As loading was increased from 1 to 4 equiv in DMF solvent, the yields of **1b** increased (Table 2). Unlike phosphination,[27b] no decrease of product yield was observed when more than 2.5 equiv of Ph_3As was added. The optimal yield was obtained when 2.3 to 3.0 equiv of Ph_3As was used (Table 2, entries 4−6).

To probe the effectiveness of this methodology, a variety of functionalized aryl triflates were examined in both DMF and solvent-free reaction conditions (Table 3). The redox-sensitive aryl triflates **2a** and **3a**, which bear keto and aldehyde groups, respectively, were directly transformed to the corresponding arsines **2b** and **3b** without complementary protection and deprotection steps (Table 3, entries 2 and 3). The electron-withdrawing and reducible 4-nitrophenyl triflate **4a** was found to be compatible in these arsination conditions to give the corresponding arsine **4b** (Table 3, entry 4) without any reduction of the nitro group into amine.[31] Since both the electron-withdrawing cyano group and electron-donating methoxy group showed similar rates and yields of reaction, no significant electronic effect was observed in this arsination (Table 3, entries 5 and 6). The *meta*-substituted formylphenyl triflate **7a** was transformed to the 3-(diphenylarsino)benzaldehyde (**7b**) in similar yield and reaction time when compared with that of *para*-analogue **3b** (Table 3, entries 3 and 7). It is noteworthy that the sterically congested *ortho*-substituted aryl triflates **8a** and **9a** were also converted to *ortho*-substituted aryl arsines **8b** and **9b** in comparable rate of reaction as their *para*-substituted aryl triflates (Table 3, entries 5, 6 vs 8, 9).[32] Additionally, this palladium-catalyzed arsination was also practical in 20 mmol scale without deleterious effect (Table 3, entry 9). A triflate alternative, aryl nonaflate **10a**,[33] was transformed to the corresponding arsine **1b** slightly faster than the triflate **1a** (Table 3, entry 1 vs 10).[34]

Limitations still exist for the palladium-catalyzed solvent-free arsination. Problematic substrates such as

(29) (a) Fischer, B.; Sheihet, L. *J. Org. Chem.* **1998**, *63*, 393−395. (b) Bae, J. W.; Cho, Y.; J.; Le, S. Hl; Yoon, C. M. *Tetrahedron Lett.* **2002**, *43*, 3537−3539.

(30) For a recent textbook on solvent-free systems, see: Tanaka, K. *Solvent-free Organic Synthesis*; Wiley-VCH: Weinheim, 2003.

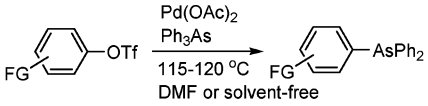
(31) The reduction of an aromatic $-NO_2$ group to an $-NH_2$ group has been observed in the presence of PPh_3 and $Pd(OAc)_2$ catalyst, see: (a) Ref 28c. (b) Fischer, B.; Sheihet, L. *J. Org. Chem.* **1998**, *63*, 393−395. (c) Bae, J. W.; Cho, Y. J.; Lee, S. H.; Yoon, C. M. *Tetrahedron Lett.* **2000**, *41*, 175−177.

(32) Migita et al. reported that the *ortho*-substituted aryl halides retarded the rate of reaction and yield of phosphonium salts formation. Migita, T.; Nagai, T.; Kiuchi, K.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2869−2870.

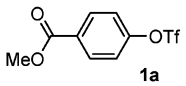
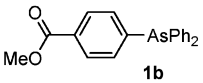
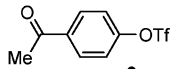
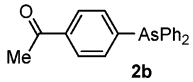
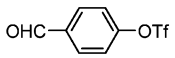
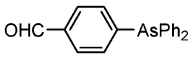
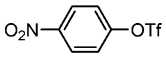
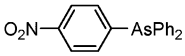
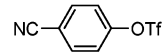
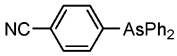
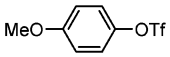
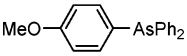
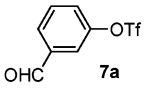
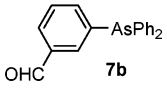
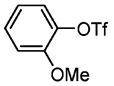
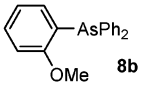
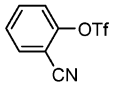
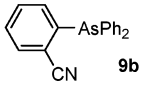
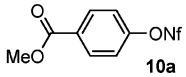
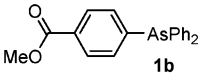
(33) Nonaflate = *n*-nonafluorobutanesulfonate. (a) Niederprüm, H.; Voss, P.; Beyl, V. *Liebigs. Ann. Chem.* **1973**, 20−32. (b) For a review, see: Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85−126.

(34) Knochel and co-workers reported nonaflate has a 1.4 times faster rate of reaction compared with triflate in zinc-mediated coupling. Rottländer, M.; Knochel, P. *J. Org. Chem.* **1998**, *63*, 203−208.

Table 3. Palladium-Catalyzed Arsination of Functionalized Aryl Triflates/Nonaflate Using Triphenylarsine[a]

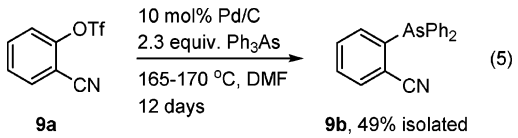


FG = COOMe, COMe, CHO, CN, NO_2, OMe

entry	substrates	products	time/d[c]	yield/%[b,c]
1	 **1a**	 **1b**	5 (4.5)	51 (50)
2	 **2a**	 **2b**	4 (3.5)	47 (51)
3	 **3a**	 **3b**	5 (4)	50 (48)
4	 **4a**	 **4b**	5 (4.5)	40 (41)
5	 **5a**	 **5b**	5 (4)	51 (53)
6	 **6a**	 **6b**	4.5 (4.5)	50 (43)
7	 **7a**	 **7b**	5 (4.5)	48 (46)
8	 **8a**	 **8b**	5 (3.5)	49 (43)
9	 **9a**	 **9b**	5 (5) (5)[d]	41 (31) (56)[d]
10	 **10a**	 **1b**	4 (4.5)	50 (49)

[a] Reaction conditions: $Pd(OAc)_2$ (0.1 mmol, 10 mol %), Ph_3As (2.3 mmol), and aryl triflate/nonaflate (1.0 mmol) were heated to 115−120 °C under N_2. [b] Isolated yields. [c] Results of arsination in DMF (2.0 mL) in parentheses. [d] At 130 °C and aryl triflate (20.0 mmol).

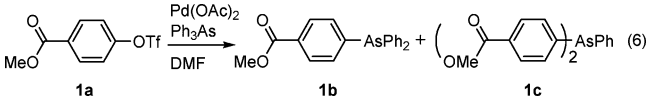
heteroatom-substituted 3-pyridyl triflate, 8-quinolyl triflate, 2-formylphenyl triflate, and 1,1′-binaphthyl-2,2′-ditriflate did not react at all. Presumably, either the steric effect or the pyridyl nitrogen rendered the Pd complex coordinatively saturated, and thus inhibited catalysis.



9a **9b**, 49% isolated (5)

The thermally stable supported catalyst, palladium on charcoal (Pd/C) system was also examined (eq 5). The reaction was best performed at 165−170 °C in DMF. 2-Cyanophenyl triflate **9a** was completely consumed in 12 days to give the corresponding arsine product **9b**. Thus, the arsination can be carried out using the Pd/C catalyst, but at the sacrifice of rate.

Table 4. Effect of Reaction Temperature and Time on Arsination[a]

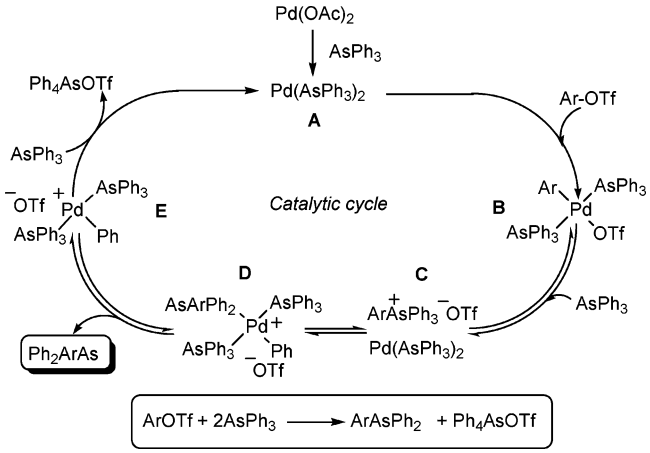


1a **1b** **1c**

entry	temp/°C	time/days	% of **1b**[b]	% of **1c**[b]
1	<110	14	0	0
2	110−115	10	46	0
3	115−120	4.5	48	trace[c]
4	115−120	6	45	4[c]
5	140	3	31	13

[a] Reaction conditions: $Pd(OAc)_2$ (0.1 mmol, 10 mol %), Ph_3As (2.3 mmol), and aryl triflate (1.0 mmol) in DMF (2.0 mL) were heated to specified reaction temperatures under N_2. [b] Isolated yield. [c] GC yield.

Scheme 2. Suggested Mechanism for Palladium-Catalyzed Arsination



In principle, the arsine product **1b** can further react again with aryl triflate **1a** to give a "double aryl transfer" product (eq 6). To further study this methodology to achieve high yields of the desired monoarylated product, we carefully examined both the temperature and reaction time of the arsination reaction of **1a** (eq 6 and Table 4). At temperatures below 110 °C, no arsination occurred even after 14 days (Table 4, entry 1). At 110−115 °C, the reaction of **1a** took 10 days to afford **1b** without any diarylated product **1c**, which formed from double aryl/aryl exchange. At 115−120 °C, the reaction was faster with a trace amount of **1c** formed after 4.5 days (Table 4, entry 3). Only after 6 days was a small amount of diarsinated product in 4% yield observed. At 140 °C in 2.5 days, double aryl/aryl-exchanged product **1c** was isolated in 13% yield together with a reduced yield of **1b** in 31% yield (Table 4, entry 5). Diarylated products were also observed in other substrates when the reactions were conducted for prolonged reaction time.

Scheme 2 illustrates a plausible mechanism. $Pd(OAc)_2$ is proposed to be in situ reduced to Pd(0) by triphenylarsine in a analogous manner to that in the reduction by Ph_3P.[35] Indeed, Ph_3As reduced $Pd(OAc)_2$ at 110 °C to give $Ph_3As{=}O$ as detected by thin-layer chromatography. The Pd(0) complex **A** subsequently undergoes oxidative addition with an aryl triflate to yield the aryl-

(35) Evidence of reduction of Pd(II) to Pd(0) by triphenylphosphine, see: Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009−3013.

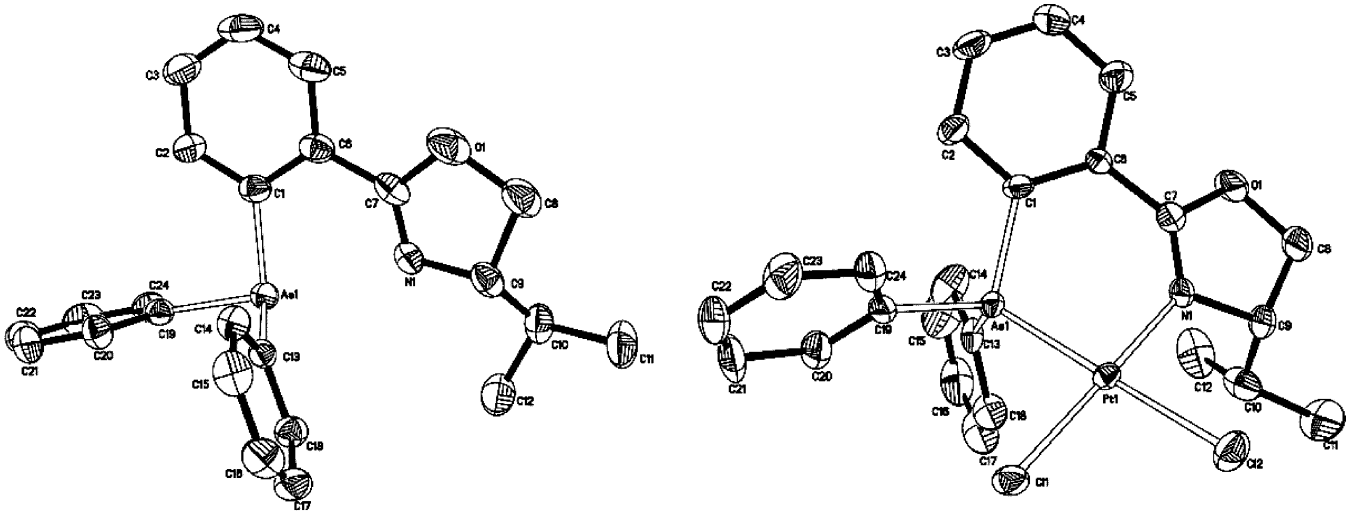
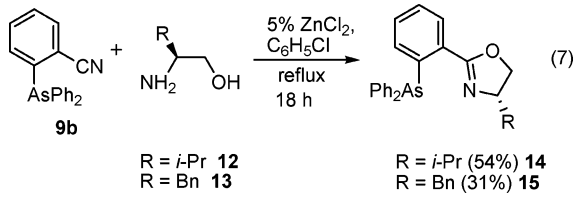


Figure 1. X-ray crystal structures of chiral *As,N* ligand **14** and *As,N*-Pt complex **18**.

Pd(II) species **B**. The Pd-bound aryl ring then undergoes reductive elimination with $AsPh_3$ to afford the aryltriphenylarsonium salt **C** and Pd(0) species. The crude arsonium salt intermediate was detected by quenching the reaction and was confirmed by mass spectrometry.[36] The substituted arsonium salt then undergoes As−C oxidative addition to yield the desired functionalized aryl arsine (Scheme 2). The Pd(0) complex is regenerated by the reductive elimination of another equivalent of triphenylarsine with the palladium-bound phenyl group to form the arsonium triflate.

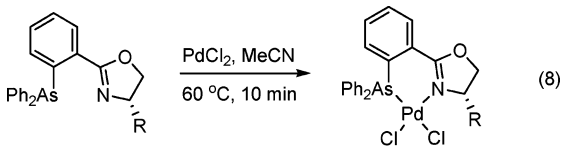
Preparation of Chiral *As,N* Ligands and Metal Complexes. The *o*-cyano arsine **9b** was found to be a versatile precursor for the synthesis of a new type of chiral *As,N* ligands **14** and **15** from readily accessible optically active amino alcohols **12** and **13**, respectively (eq 7).[37,38] Thus, aryl arsine **9b** reacted with (*S*)-2-



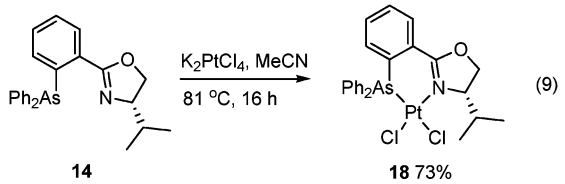
(7)

amino-3-methyl-1-butanol (**12**) in the presence of $ZnCl_2$ catalyst in chlorobenzene to afford the new type of optically active *As,N* ligand, (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (**14**), in 54% yield. Similarly, in the presence of (*S*)-2-amino-3-phenyl-1-propanol, the corresponding (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline (**15**) was obtained. These *As,N* ligands were found to be more stable toward oxidation in air both in solution and in the solid state than the corresponding *P,N* ligands. Thus, they offer the advantage of easier handling in air. Moreover, this new synthetic approach is able to prepare a series of optically active *As,N* ligands, which will likely provide a variety of applications in asymmetric catalysis.

The bidentate *As,N* ligands formed metal complexes smoothly with palladium(II) and platinum(II) dichloride (eqs 8 and 9). These optically active *As,N*-palladium and



(8)



(9)

-platinum complexes were easily prepared in satisfactory yield by reacting with 1 equiv of $PdCl_2$ or K_2PtCl_4 with **14** or **15** in refluxing acetonitrile under nitrogen atmosphere (eqs 8 and 9).

The structures of the *As,N* ligand **14** and the Pt complex **18** were consolidated by single-crystal X-ray analyses (Figure 1). Table 5 lists the data for crystals and refinement. The selected bond lengths and angles for structures **14** and **18** are listed in Tables 6 and 7, respectively. Complex **18** shows that the chiral *As,N* ligand is bidentate by forming a six-membered, puckered chelate ring with the metal. All three carbon atoms C(1)−C(6)−C(7) in this ring reside above the plane of the complex with respect to the isopropyl group C(10)−C(11)−C(12). Hence, the structure of **18** is slightly distorted square-planar in geometry. The bond lengths of C−As in the free ligand range from 1.96 to 1.98 Å. The dihedral angle of the oxazoline and phenyl rings, i.e., C(1)−C(6)−C(7)−N(1), is 8.48°. Upon coordination with $PtCl_2$, the C−As bonds become slightly shorter, to be about 1.93 Å. The dihedral angle C(1)−C(6)−C(7)−N(1) in the Pt complex increases to 26.3°. The bond length of Pt−As in **18** (2.3048(9) Å) is longer than that of the corresponding Pt−P (2.192(5) Å),[39] which is in agreement with the 0.10−0.11 Å difference in the

(36) No attempt at isolation of arsonium salts was performed in this issue.

(37) For a recent review concerning similar chiral *P,N* ligands (PHOX: 2-(2-(diphenylphosphino)phenyl)-4-(isopropyl)oxazoline), see: Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345.

(38) For recent Ru-catalyzed hydrogenation, see: Tan, D.-M.; Chan, K. S. *Tetrahedron Lett*. **2005**, *46*, 503−505.

Table 5. Crystal Data and Structure Refinements for Chiral *As,N* Ligand 14 and *As,N*-Pt Complex 18

	14	18
empirical formula	$C_{24}H_{24}AsNO$	$C_{24}H_{24}AsCl_2NOPt$
fw	417.36	683.35
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	orthorhombic	monoclinic
space group	*P*2(1)2(1)2(1)	*P*2(1)
unit cell dimens	$a = 9.2413(5)$ Å,	$a = 10.1250(8)$ Å,
	$b = 14.7410(8)$ Å,	$b = 12.9507(11)$ Å,
	$c = 15.1499(8)$ Å,	$c = 10.6275(9)$ Å,
	$\alpha = 90°$	$\alpha = 90°$
	$\beta = 90°$	$\beta = 112.380(2)°$
	$\gamma = 90°$	$\gamma = 90°$
volume	2063.81(19) $Å^{-3}$	1288.58(19) $Å^{-3}$
Z	4	2
calcd density	1.343 Mg/m^{-3}	1.761 Mg/m^{-3}
abs coeff	1.660 mm^{-1}	6.941 mm^{-1}
F(000)	864	656
cryst size	0.30 × 0.20 × 0.10 mm	0.30 × 0.20 × 0.10 mm
θ range for data collection/deg	1.93 to 28.03	2.07 to 25.00
limiting indices	$-10 \le h \le 12$,	$-12 \le h \le 11$
	$-19 \le k \le 19$,	$-10 \le k \le 15$,
	$-19 \le l \le 20$	$12 \le l \le 11$
no. of reflns collected	13 849	7003
no. of unique reflns	4960 [R(int) = 0.0412]	3870 [R(int) = 0.0354]
completeness to θ	28.03, 100.0%	25.00, 100.0%
max. and min. transmn	1.0000 and 0.440374	1.0000 and 0.514742
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	4960/0/244	3870/1/271
goodness-of-fit on F^2	0.941	1.030
final R indices [$I > 2\sigma(I)$]	R1 = 0.0299	R1 = 0.0381
	wR2 = 0.0645	wR2 = 0.0929
R indices (all data)	R1 = 0.0375	R1 = 0.0430
	wR2 = 0.0664	wR2 = 0.0966
absolute struct param	0.019(8)	0.013(13)
largest diff peak and hole	0.404 and −0.330 e A^{-3}	3.086 and −1.258 e A^{-3}

Table 6. Selected Bond Lengths and Angles for *As,N* Ligand 14

bond length (Å)		bond angle (deg)	
As(1)−C(1)	1.986(2)	C(13)−As(1)−C(19)	98.34(9)
As(1)−C(13)	1.960(2)	C(19)−As(1)−C(1)	98.57(9)
As(1)−C(19)	1.980(2)	C913)−As(1)−C(1)	99.72(9)
		N(1)−C(9)−C(10)	114.3(2)
		C(1)−C(6)−C(7)−N(1)	8.48

Table 7. Selected Bond Lengths and Angles for *As,N*-Pt Complex 18

bond length (Å)		bond angle (deg)	
Pt(1)−N(1)	2.028(8)	N(1)−Pt(1)−As(1)	88.7(2)
Pt(1)−As(1)	2.3048(9)	N(1)−Pt(1)−Cl(1)	175.5(3)
Pt(1)−Cl(1)	2.285(3)	N(1)−Pt(1)−Cl(2)	92.0(3)
Pt(1)−Cl(2)	2.350(3)	Cl(1)−Pt(1)−As(1)	88.93(8)
As(1)−C(19)	1.919(10)	Cl(2)−Pt(1)−As(1)	176.55(10)
As(1)−C(13)	1.949(10)	Cl(1)−Pt(1)−Cl(2)	90.57(11)
As(1)−C(1)	1.938(9)	N(1)−C(19)−C(10)	110.9(9)
		C(1)−C(6)−C(7)−N(1)	26.31

covalent bond radii of As (1.21 Å) and P (1.10 Å).[40] The *trans*-metal−chloride bond length (2.350(3) Å for Pt complex) to the arsine atom is longer than the *cis* one (2.285(3) for Pt complex), showing the larger *trans*-directing influence of the diphenylarsino group than the imino group.[41]

In summary, we have reported a catalytic application of Pd−Ar/As−Ph exchange in the direct synthesis of functionalized aryl arsines and the synthesis of new chiral *As,N* ligands. This recipe used commercially available, air-stable, and inexpensive triphenylarsine as the arsinating agent and provided an attractive alternative for the preparation of functionalized aryl arsines. A notable feature of this methodology is the essentially high functional group compatibility. Particularly noteworthy is that **9b** was found to be a versatile precursor for the synthesis of a new type of chiral *As,N* bidentate ligands and their metal complexes.

Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used without further purification unless otherwise specified. All palladium-catalyzed arsinations were performed in resealable Rotaflo (England) Teflon screw-cap Schlenk flasks. Dichloromethane and hexane for reaction were distilled from calcium hydride under nitrogen atmosphere. Diethyl ether and THF were distilled under N_2 from sodium benzophenone ketyl prior to use. Hexane for chromatography was distilled from anhydrous calcium chloride. *N,N*-Dimethylformamide (DMF) was distilled from magnesium sulfate under reduced pressure.[42] Acetonitrile was distilled with P_2O_5 under N_2. Chlorobenzene was distilled from CaH_2 under nitrogen. Triphenylarsine was purchased from Acros and used without recrystallization. Palladium(II) acetate was purchased from Strem Chemicals and used as received. Pd/C was purchased from Aldrich. Anhydrous $ZnCl_2$ was vacuum-dried overnight at elevated temperature. All the aryl triflates

(39) For a Pt-PHOX complex, see: Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Humphries, M. E.; Williams, J. M. J. *Chem. Eur. J.* **2000**, *6*, 353−360.

(40) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1967.

(41) Bansolo, F.; Johnson, R. C. *Coordination Chemistry*, 2nd ed.; Science Review: England, 1986.

(42) Perrin, D. D.; Armarego, L. F. *Purification of Laboratory Chemicals*, 3rd ed.; 1988.

were prepared according to the literature methods.[43] Thin-layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70−230 and 230−400 mesh) or neutral aluminum oxide (activity I, 70−230 mesh) was used for column chromatography. Melting points were recorded on a Büchi B-545 melting point instrument (uncorrected). ^{1}H NMR spectra were recorded on a Brüker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard.[44] Chemical shifts (δ) were reported as parts per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were recorded on a Brüker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.0 ppm). Coupling constants (J) were reported in hertz (Hz). Mass spectra (EIMS and FABMS) were recorded on a HP 5989B mass spectrometer. High-resolution mass spectra (HRMS) were performed on a Brüker APEX 47e FT-ICR mass spectrometer (ESIMS). Optical rotation was measured on a polarimeter at 20 °C. GC-MS analysis was conducted on a HP G1800C GCD system using a HP5MS column (30 m × 0.25 mm) with the following temperature programming: initial temperature 100 °C, duration 2 min; increment rate 20 °C/min; final temperature 280 °C, duration 15 min.

General Procedures for Arsination. Procedures for palladium-catalyzed solvent-free arsination are described in example **1b**. A procedure for palladium-catalyzed arsination in DMF are described in example **9b**.

General Procedure for Preparation of Aryl Triflates[33b] (*p*-nitrophenol as an example). *p*-Nitrophenol (10 mmol) was dissolved in dry dichloromethane under nitrogen at room temperature. Pyridine (30 mmol) was added followed by the dropwise addition of trifluoromethanesulfonic anhydride (11 mmol). White fumes evolved, and the color of the solution changed from yellow to red. The reaction mixture was stirred for 2 h at room temperature. Water was added and extracted by dichloromethane (3 × ∼50 mL). The combined organic phase was washed with diluted HCl and brine and dried over $MgSO_4$. Rotary evaporation of the solvent gave a brown residue, which was purified by short flash column chromatography on silica gel using a solvent (hexane/ethyl acetate, 10:1) as the eluent to give a light yellow solid, *p*-nitrophenyl trifluoromethanesulfonate **4a** (80% yield), upon vacuum-drying.

General Procedure for Preparation of Aryl Nonaflates[4545] (methyl 4-hydroxybenzoate as an example). Methyl 4-hydroxybenzoate (3.04 g, 20 mmol) was dissolved in anhydrous ether followed by the addition of triethylamine (4.2 mL, 30 mmol). The reaction mixture was cooled to 0 °C, and perfluorobutanesulfonyl fluoride (5.4 mL, 30 mmol) was added dropwisely. After completed addition, the reaction mixture was gradually warmed to room temperature and stirred overnight. Water was added and extracted by diethyl ether (3 × ∼100 mL). The combined organic phase was washed with brine and dried over $MgSO_4$. Rotary evaporation of the solvent gave a yellow residue, which was purified by short column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 10:1) as the eluent to afford the methyl 4-nonafluorobutanesulfonyloxybenzoate **10a** in 70% yield as a colorless oil.

Methyl 4-(Diphenylarsino)benzoate (1b). A general procedure for the solvent-free arsination reaction is shown below. Methyl 4-trifluoromethanesulfonyloxybenzoate (**1a**) (284 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), $Pd(OAc)_2$ (22 mg, 0.1 mmol), and a magnetic stirrer bar (3 mm × 10 mm) were charged into a Teflon screw-capped Schlenk flask. The flask was evacuated and backfilled with nitrogen (3 cycles). The reaction mixture was heated to 115−120 °C for 5 days with continuous stirring. The reaction was cooled to room temperature and dissolved in a minimal amount of dichloromethane, which was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (10:1) to yield methyl 4-(diphenylarsino)benzoate (**1b**) (186 mg, 51%) as a white solid: R_f 0.56 (hexane/ethyl acetate, 10:1); mp 109−110.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 3 H), 7.32−7.37 (m, 10 H), 7.41 (dd, 2 H, J = 1.4, 8.3 Hz), 7.98 (dd, 2 H, J = 1.7, 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.1, 128.7, 128.8, 129.4, 130.0, 133.5, 133.7, 138.8, 146.4, 167; IR (neat) 1733 cm^{-1}; MS (EI) *m/z* (relative intensity) 364 (M^+, 17), 227 (27), 210 (36), 181 (100), 152 (52); HRMS (ESIMS) calcd for $C_{20}H_{17}AsO_2$, 364.0445; found, 364.0443. Anal. Calcd for $C_{20}H_{17}AsO_2$: C, 65.94; H 4.70. Found: C, 65.95; H, 4.68.

Bis(methyl 4-benzoate)phenylarsine (1c). Methyl 4-trifluoromethanesulfonyloxybenzoate (**1a**) (284 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were heated to 140 °C for 2 days to yield bis(methyl 4-benzoate)phenylarisne (**1c**) (56 mg, 13%) and methyl 4-(diphenylarsino)benzoate (**1b**) (30%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 5:1) as the eluent: R_f 0.29 (hexane/ethyl acetate, 5:1); mp 121−122.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 6 H), 7.30−7.38 (m, 7 H), 7.40 (d, 2 H, J = 1.8 Hz), 7.98 (dt, 4 H, J = 1.4, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 129.0, 129.1, 129.5, 130.3, 133.6, 133.8, 138.1, 145.5, 166.9; IR (neat) 1735 cm^{-1}; MS (EI) *m/z* (relative intensity) 422 (M^+, 14), 239 (41), 181 (100), 152 (36); HRMS (ESIMS) calcd for $C_{22}H_{19}AsO_4$ H^+, 423.0578; found, 423.0586.

4-(Diphenylarsino)acetophenone (2b). 4-Acetylphenyl trifluoromethanesulfonate (**2a**) (268 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)acetophenone (**2b**) (164 mg, 47%) as a pale yellow solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 10:1) as the eluent: R_f 0.45 (hexane/ethyl acetate, 10:1); mp 120.3−121 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3 H), 7.30−7.35 (m, 10 H), 7.40 (dd, 2 H, J = 1.8, 8.1 Hz), 7.87 (dd, 2 H, J = 1.8, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 128.1, 128.8, 133.7, 136.8, 138.7, 146.8, 198.0; IR (neat) 1718 cm^{-1}; MS (EI) *m/z* (relative intensity) 348 (M^+, 21), 227 (23), 194 (28), 152 (100); HRMS (ESIMS) calcd for $C_{20}H_{17}AsO$, 348.0495; found, 348.0504. Anal. Calcd for $C_{20}H_{17}AsO$: C, 68.97; H 4.92. Found: C, 68.99; H, 4.88.

4-(Diphenylarsino)benzaldehyde (3b). 4-Trifluoromethanesulfonyloxybenzaldehyde (**3a**) (254 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)benzaldehyde (**3b**) (167 mg, 50%) as a pale yellow solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 8:1) as the eluent: R_f 0.21 (hexane/ethyl acetate, 10:1); mp 112.5−113.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30−7.36 (m, 10 H), 7.47 (d, 2 H, J = 8.1 Hz), 7.79 (d, 2 H, J = 7.5 Hz), 9.98 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.5, 130.0, 134.4, 134.7, 136.7, 139.2, 149.5, 192.8; IR (neat) 1700 cm^{-1}; MS (EI) *m/z* (relative intensity) 334 (M^+, 21), 227 (32), 181 (31), 152 (100); HRMS (ESIMS) calcd for $C_{19}H_{15}AsO$, 334.0339; found, 334.0345. Anal. Calcd for $C_{19}H_{15}AsO$: C, 68.27; H 4.52. Found: C, 68.36; H, 4.49.

4-(Diphenylarsino)nitrobenzene (4b). 4-Nitrophenyl trifluoromethanesulfonate (**4a**) (271 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)nitrobenzene (**4b**) (140 mg, 40%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 10:1) as the eluent: R_f 0.72 (hexane/ethyl acetate, 10:1); mp 113−

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114.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31−7.40 (m, 10 H), 7.48 (dt, 2 H, J = 2.1, 8.7 Hz), 8.14 (dt, 2 H, J = 2.0, 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.1, 129.0, 129.1, 133.7, 134.3, 138.1, 148.0, 149.8; IR (neat) 1349, 1521 cm^{-1}; MS (EI) *m/z* (relative intensity) 351 (M^+, 30), 227 (47), 183 (34), 154 (100); HRMS (ESIMS) calcd for $C_{18}H_{14}AsNO_2$, 351.0241; found 351.0227. Anal. Calcd for $C_{18}H_{14}AsNO_2$: C, 61.55; H 4.02; N, 3.99. Found: C, 61.89; H, 3.90; N 4.02.

4-(Diphenylarsino)benzonitrile (5b). 4-Cyanophenyl trifluoromethanesulfonate (**5a**) (251 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)benzonitrile (**5b**) (169 mg, 51%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 5:1) as the eluent: R_f 0.60 (hexane/ethyl acetate, 5:1); mp 116.5−118 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29−7.37 (m, 10 H), 7.40 (dd, 2 H, J = 1.8, 8.1 Hz), 7.56 (dd, 2 H, J = 1.7, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 112.0, 118.8, 129.0, 131.8, 133.7, 134.1, 138.2, 147.2; IR (neat) 2228 cm^{-1}; MS (EI) *m/z* (relative intensity) 331 (M^+, 20), 252 (12), 227 (17), 177 (21), 152 (100); HRMS (ESIMS) calcd for $C_{19}H_{14}AsN$, 331.0342; found, 331.0340. Anal. Calcd for $C_{19}H_{14}AsN$: C, 68.89; H, 4.26; N, 4.23. Found: C, 68.78; H, 4.39; N, 3.99.

4-(Diphenylarsino)anisole (6b). 4-Methoxyphenyltrifluoromethanesulfonate (**6a**) (256 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)anisole (**6b**) (168 mg, 50%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 20:1) as the eluent: R_f 0.58 (hexane/ethyl acetate, 20:1); mp 120.0−121.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3,74 (s, 3 H), 6.77 (d, 1 H, J =1.8 Hz), 6.86 (dd, 2 H, J = 1.8, 8.1 Hz), 7.27−7.35 (m, 11 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.7, 110.2, 121.3, 128.2, 128.5, 130.2, 133.8, 139.2, 161.2; MS (EI) *m/z* (relative intensity) 336 (M^+, 26), 227 (26), 184 (43), 152 (100), 91 (83); HRMS (ESIMS) calcd for $C_{19}H_{17}AsO$, 336.0495; found, 336.0502. Anal. Calcd for $C_{19}H_{17}AsO$: C, 67.87; H 5.10. Found: C, 67.90; H, 5.05.

3-(Diphenylarsino)benzaldehyde (7b). 3-Trifluoromethanesulfonyloxybenzaldhyde (**7a**) (254 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 3-(diphenylarsino)benzaldehyde (**7b**) (160 mg, 48%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 10:1) as the eluent: R_f 0.72 (hexane/ethyl acetate, 10:1); mp 108.5−110 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33−7.38 (m, 10 H), 7.50 (dd, 1 H, J = 1.7, 7.7 Hz), 7.59 (dt, 1 H, J = 1.4, 7.5 Hz), 7.86 (dt, 2 H, J = 1.5, 6.4 Hz) 9.95 (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.8, 128.9, 129.2, 129.3, 133.6, 135.3, 136.4, 138.7, 139.5, 141.4, 192.2; IR (neat) 1699 cm^{-1}; MS (EI) *m/z* (relative intensity) 334 (M^+, 28), 227 (38), 180 (42), 152 (100); HRMS (ESIMS) calcd for $C_{19}H_{15}AsO$, 334.0339; found, 334.0346. Anal. Calcd for $C_{19}H_{15}AsO$: C, 68.27; H 4.52. Found: C, 68.22; H, 4.47.

2-(Diphenylarsino)anisole (8b). 2-Methoxyphenyltrifluoromethanesulfonate (**8a**) (256 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 4-(diphenylarsino)anisole (**8b**) (165 mg, 49%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 40:1) as the eluent: R_f = 0.33 (hexane/ethyl acetate, 20:1); mp 110.5−112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 3 H), 6.84−6.85 (m, 2 H), 6.91 (d, 1 H, J = 7.2 Hz), 7.22−7.28 (m, 1 H), 7.30−7.35 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.1, 114.0, 119.0, 126.0, 128.5, 128.6, 129.5, 133.7, 139.5, 141.0, 159.5; MS (EI) *m/z* (relative intensity) 336 (M^+, 36), 257 (11), 227 (20), 182 (49), 152 (100); HRMS (ESIMS) calcd for $C_{19}H_{17}AsO$, 336.0495; found 336.493. Anal. Calcd for $C_{19}H_{17}AsO$: C, 67.87; H 5.10. Found: C, 67.93; H, 5.08.

2-(Diphenylarsino)benzonitrile (9b). 2-Cyanophenyl trifluoromethanesulfonate (**9a**) (251 mg, 1.0 mmol), $AsPh_3$ (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were used to yield 2-(diphenylarsino)benzonitrile (**9b**) (136 mg, 41%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 5:1) as the eluent: R_f 0.50 (hexane/ethyl acetate, 5:1); mp 111.5−112.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (dd, 1 H, J = 1.7, 6.5 Hz), 7.30−7.39 (m, 10 H), 7.42 (dt, 2 H, J = 1.8, 6.8 Hz), 7.69 (dd, 1 H, J = 1.7, 6.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.9, 118.2, 128.8, 129.0, 132.6, 133.5, 133.8, 133.9, 137.6, 144.9; IR (neat) 2230 cm^{-1}; MS (EI) *m/z* (relative intensity) 331 (M^+, 20), 252 (12), 227 (17), 177 (21), 152 (100); HRMS (ESIMS) calcd for $C_{19}H_{14}AsNH^+$, 332.0420; found, 332.0403. Anal. Calcd for $C_{19}H_{14}AsN$: C, 68.89; H, 4.26; N, 4.23. Found: C, 68.81; H, 4.36; N, 4.19.

2-(Diphenylarsino)benzonitrile (9b). A general procedure for the arsination in DMF using $Pd(OAc)_2$ is shown below. 2-Cyanophenyl trifluoromethanesulfonate (251 mg, 1.0 mmol), triphenylarsine (706 mg, 2.3 mmol), and $Pd(OAc)_2$ (22 mg, 0.1 mmol) were dissolved in dry DMF (2.0 mL) under nitrogen in a Teflon screw-capped Schlenk flask. The solution was degassed and heated to 120 °C for 5 days to yield 2-(diphenylarsino)benzonitrile (**9b**) (172 mg, 0.52 mmol, 52%) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1:5).

Alternatively, 2-cyanophenyl trifluoromethanesulfonate (251 mg, 1.0 mmol), triphenylarsine (706 mg, 2.3 mmol), and 10% Pd/C (106 mg, 0.1 mmol) were suspended in 160−170 °C for 12 days to yield 2-(diphenylarsino)benzonitrile (**9b**) (162 mg, 0.49 mmol, 49%) as a white solid after purification by column chromatography on silica gel eluting with ethyl acetate/hexane (1:5).

Methyl 4-(diphenylarsino)benzoate (1b). The general procedure for the arsination reaction was used. Methyl 4-nonafluorobutanesulfonyloxybenzoate (**10a**) (217 mg, 0.5 mmol), $AsPh_3$ (352 mg, 1.15 mmol), and $Pd(OAc)_2$ (11 mg, 0.05 mmol) were used to yield methyl 4-(diphenylarsino)benzoate (**1b**) (91 mg, 50%) as a white solid after purification by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate, 10:1) as the eluent: R_f 0.56 (hexane/ethyl acetate, 10:1).

(*S*)-(−)-2-(2-(Diphenylarsino)phenyl)-4-(isopropyl)oxazoline (14). 2-(Diphenylarsino)benzonitrile (25.0 mg, 0.08 mmol), anhydrous zinc(II) chloride (11.7 mg, 0.11 mmol), and (*S*)-(+)-2-amino-3-methyl-1-butanol (**12**) (11.7 mg, 0.11 mmol) were dissolved in dry chlorobenzene (0.5 mL) and heated to reflux at 140 °C under N_2 for 18 h to yield (*S*)-(−)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (**14**) (17 mg, 0.04 mmol, 54%) as a white solid after purification by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (1:1). It was further recrystallized from CH_2Cl_2/hexane: R_f 0.43 hexane/CH_2Cl_2 (1:1); mp 140−141 °C; $[\alpha]^{20}_D$ −33.6° (*c* 0.06, MeCN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71 (d, 3 H, J = 6.6 Hz), 0.82 (d, 3 H, J = 6.6 Hz), 1.21 (s, 1 H), 3.84−3.90 (m, 2 H), 4.16 (p, 1 H, 6.3 Hz), 6.99 (dd, 1 H, J = 1.2, 7.5 Hz), 7.28−7.39 (m, 12 H), 7.91 (dd, 1 H, J = 1.2, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ18.3, 18.8, 32.6, 70.4, 128.1, 128.2, 128.5, 129.8, 131.0, 131.5, 133.7, 134.0, 134.5, 141.1, 141.5; MS (EI) *m/z* (relative intensity) 418 (M^+, 50), 340 (100), 254 (20); HRMS (ESIMS) calcd for $C_{24}H_{24}AsNOH^+$, 418.1152; found, 418.1143. Anal. Calcd for $C_{24}H_{24}AsNO$: C, 69.06; H, 5.80; N, 3.36. Found: C, 69.16; H, 5.69; N, 3.24.

(*S*)-2-(2-(Diphenylarsino)phenyl)-4-(benzyl)oxazoline (15). 2-(Diphenylarsino)benzonitrile (25.0 mg, 0.08 mmol), anhydrous zinc(II) chloride (11.7 mg, 0.11 mmol), and (*S*)-(−)-2-amino-3-phenyl-1-propanol (**13**) (16.6 mg, 0.11 mmol) were dissolved in chlorobenzene (0.5 mL) and heated to reflux at 140 °C under N_2 for 18 h to yield (*S*)-2-(2-(diphenylarsino)-phenyl)-4-(benzyl)oxazoline (**15**) (10.6 mg, 0.02 mmol, 31%) as a white solid after purification by column chromatography on silica gel eluting with hexane/CH_2Cl_2 (1:1). It was further recrystallized from CH_2Cl_2/hexane: R_f 0.34 CH_2Cl_2/hexane (1:1); mp 153−154 °C; $[\alpha]^{20}_D$ 12.5° (*c* 0.20, MeCN); ^{1}H NMR (300

MHz, $CDCl_3$) δ 2.11 (dd, 1 H, J = 9.0, 13.8 Hz), 2.86 (dd, 1 H, J = 5.4, 13.8 Hz), 3.78 (t, 1 H, J = 8.4 Hz), 4.05 (t, 1 H, J = 8.4 Hz), 4.31 (quint, 1 H, J = 5.4 Hz), 7.00 (d, 1 H, J = 7.5 Hz), 7.06 (d, 2 H, J = 6.6 Hz), 7.18−7.25 (m, 4 H), 7.28−7.39 (m, 11 H), 7.89 (d, 1 H, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.7, 41.1, 68.0, 71.5, 126.3, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1, 129.7, 130.8, 131.8, 133.7, 134.2, 134.4, 138.2, 141.2, 141.3, 141.8; MS (EI) *m/z* (relative intensity) 466 (M^+, 30), 388 (100), 256 (15); HRMS (ESIMS) calcd for $C_{28}H_{24}AsNOH^+$, 466.1147; found 466.1147. Anal. Calcd for $C_{28}H_{24}AsNO$: C, 72.26; H, 5.20; N, 3.01. Found: C, 72.18; H, 5.55; N, 2.82.

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)-oxazoline]palladium(II) (16). A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL) was added to a clear orange mixture of $PdCl_2$ (6.4 mg, 0.04 mmol) in acetonitrile (0.5 mL) at 60 °C and stirred for 10 min. The color changed from orange to yellow. The solution mixture was then cooled to room temperature. A yellow precipitate was formed and was collected by filtration and washed with cold acetonitrile and then diethyl ether to give dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]palladium(II) (**16**) (16.1 mg, 0.03 mmol, 75%) as a yellow solid: mp 250 °C (dec); $[\alpha]^{20}_D$ 290.5° (*c* 0.07, MeCN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (d, 3 H, J = 6.9 Hz), 0.83 (d, 3 H, J = 6.9 Hz), 2.76 (dt, 1 H, J = 2.7, 7.0 Hz), 4.33 (dd, 1 H, J = 5.1, 9.2 Hz), 4.44 (t, 1 H, J = 9.2 Hz) 5.51 (dquint, 1 H, J = 1.8, 5.2 Hz), 7.10 (d, 1 H, J = 7.6 Hz), 7.43−7.68 (m, 12 H), 8.11 (d, 1 H, J = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.3, 18.6, 30.8, 68.7, 71.7, 128.7, 128.8, 128.9, 129.2, 129.7, 131.6, 132.0, 132.7, 133.0, 133.5, 133.7,133.8; MS (EI) *m/z* (relative intensity) 593 (M^+, 5), 558 (100), 523 (20), 460 (20); HRMS (ESIMS) calcd for $C_{24}H_{24}AsNOPdCl^+$, 557.9792; found 557.9804. Anal. Calcd for $C_{24}H_{24}AsNOPdCl_2$: C. 48.47; H. 4.07; N, 2.36. Found: C, 47.96; H, 3.86; N, 2.10.

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)-oxazoline]palladium(II) (17). A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(benzyl)oxazoline (**15**) (15.0 mg, 0.03 mmol) in acetonitrile (0.5 mL) was added to a clear orange mixture of $PdCl_2$ (5.7 mg, 0.03 mmol) in acetonitrile (0.5 mL) at 60 °C and stirred for 5 min. The color changed from orange to yellow. A yellow precipitate formed and the reaction mixture was cooled to room temperature. The yellow precipitate was collected by filtration and washed with cold acetonitrile and then diethyl ether to give dichloro[(*S*)-2-(2-(diphenylarsino)-phenyl)-4-(benzyl)oxazoline]palladium(II) (**17**) (15.7 mg, 0.02 mmol, 76%) as a yellow solid. Single crystals were grown from $CHCl_3$/hexane for X-ray crystallography analysis: $[\alpha]^{20}_D$ 215.1° (*c* 0.015, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.82 (t, 1 H, J = 11.1 Hz), 3.95 (dd, 1 H, J = 3.8, 13.2 Hz), 4.26 (dd, 1 H, J = 4.8, 8.9 Hz), 4.34 (t, 1 H, J = 9.4 Hz), 5.72 (dquint, 1 H, J = 2.1, 3.9 Hz), 7.14 (d, 1 H, J = 7.0 Hz), 7.20 (s, 5 H), 7.68−7.44 (m, 12 H), 8.09 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.0, 68.3, 72.0, 125.9, 127.1, 128.5, 128.7, 129.4, 129.9, 131.8, 132.0, 132.5, 133.1, 133.2, 133.8, 133.9, 135.6; MS (EI) *m/z* (relative intensity) 641 (M^+, 2), 606 (100), 573 (50), 530 (50); HRMS (ESIMS) calcd for $C_{28}H_{24}AsNOPdCl^+$, 605.9792; found 605.9802. Anal. Calcd for $C_{28}H_{24}AsNOPdCl_2$: C, 52.32; H, 3.76; N, 2.18. Found: C, 52.39; H, 3.53; N, 1.98.

Dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)-oxazoline]platinum(II) (18). A solution of (*S*)-(+)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL) was added to a mixture of potassium tetrachloroplatinate(II) (15.0 mg, 0.04 mmol) in acetonitrile (0.5 mL). The solution was heated to reflux at 85 °C under N_2. After 16 h, a mixture of yellowish and white precipitates formed and the reaction mixture was cooled to room temperature. The yellow precipitate was collected by filtration and washed with cold acetonitrile and then diethyl ether to give dichloro[(*S*)-2-(2-(diphenylarsino)phenyl)-4-(isopropyl)oxazoline]platinum(II) (**18**) (17.9 mg, 0.03 mmol, 73%). The product was further recrystallized from CH_2Cl_2/hexane, from which single crystals were obtained: mp 305 °C (dec); $[\alpha]^{20}_D$ 217.9° (*c* 0.015, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.10 (d, 3 H, J = 6.9 Hz), 0.84 (d, 3 H, J = 6.9 Hz), 2.86 (dt, 1 H, J = 3.6, 9.7 Hz), 4.34 (dd, 1 H, J = 4.9, 9.2 Hz), 4.43 (t, 1 H, J = 9.96 Hz), 5.71 (dquint, 1 H, J = 2.3, 5.1 Hz), 7.15 (d, 1 H, J = 7.4 Hz), 7.40−7.80 (m, 12 H), 8.10 (d, 1 H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 18.4, 18.5, 30.5, 129.1, 129.6, 131.5, 131.8, 132.9, 133.4, 133.5, 133.6; MS (EI) *m/z* (relative intensity) 682 (M^+, 5), 646 (100), 534 (50), 457 (50); HRMS (ESIMS) calcd for $C_{24}H_{24}AsNOPtCl^+$, 647.0405; found 647.0405. Anal. Calcd for $C_{24}H_{24}AsNOPtCl_2$: C, 42.18,; H, 3.54; N, 2.05. Found: C, 42.08; H, 3.84; N, 1.86.

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Supporting Information Available: X-ray crystallographic data (CIF) for ligand **14** and complex **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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