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A Chiral Bis(arsine) Ligand: Synthesis and Applications in Palladium-Catalyzed Asymmetric Allylic Alkylations

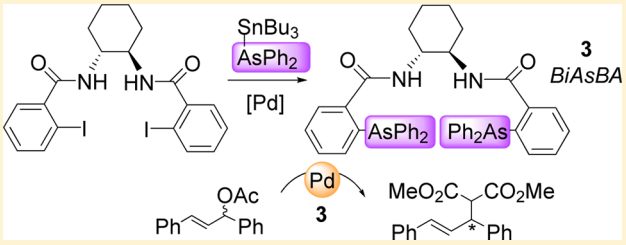
Paula M. Uberman,[†] Mino R. Caira,*[,‡] and Sandra E. Martín*[,†]

[†]INFIQC-CONICET, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Medina Allende y Haya de la Torre, X5000HUA Córdoba, Argentina

[‡]Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

Supporting Information

ABSTRACT: The new chiral bis(arsine) ligand *N*,*N*′-bis[2′-(diphenylarsino)benzoyl]-(1*R*,2*R*)-cyclohexanediamine (*BiAsBA*, **3**), based on the backbone of the Trost modular ligand (TML), was synthesized in three steps. A useful approach to introduce the $-AsPh_2$ group on arsine ligands by Pd-catalyzed arsination was used. The molecular structure and configuration of the *BiAsBA* ligand was determined by single-crystal X-ray crystallography. In the asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate very high to complete conversion and modest enantioselectivity were achieved. Despite the low enantioselectivity obtained, the bis(arsine) ligand *BiAsBA* showed significant potential, since it provided a higher ee value than the phosphorus-containing homologous "Trost standard ligand" (TSL) with the same substrate.



Transition-metal-catalyzed asymmetric allylic substitutions have become some of the most powerful tools for asymmetric C−C and C−heteroatom bond formation,[1,2] finding wide application in the synthesis of valuable molecules and complex natural products.[3] In the past few decades, a large number of chiral ligands have been designed and applied to Pd-catalyzed asymmetric allylic substitutions, affording excellent enantioselectivity.[1,2] Chiral diphosphine ligands have been one of the largest classes of ligands used in asymmetric substitutions.[2c]

Trost and co-workers have reported the development and application of the ligand (*R*,*R*)-**1**, normally referred to as the "Trost standard ligand" (TSL) (Figure 1). This ligand was especially successful with the previously challenging cyclic allylic substrates and played a crucial role in the improvement of Pd-catalyzed asymmetric allylic substitutions.[4] Following this initial report, this ligand has been effectively applied to a large number and range of asymmetric allylic alkylation reactions. Moreover, the Trost modular ligand (TML) system **2** (Figure 1) has been expanded and developed, resulting in a class of ligands broadly applied in asymmetric transition-metal-catalyzed C−C bond formation reactions.[5] However, to our knowledge there have been no reports of arsine ligands derived from the TML system.

Arsines have been shown to be excellent supporting ligands, and there are several examples where arsine complexes give catalysts more active or selective than phosphines in transition-metal-catalyzed reactions.[6] In contrast to the many chiral phosphine-based ligands that have been synthesized, relatively few arsine ligands have been prepared and applied in asymmetric catalysis.[7] The application of enantiomerically pure arsine ligands in asymmetric catalysis remains at a primitive stage. Likewise, the use of chiral arsine ligands still remains unexplored in Pd-catalyzed allylic alkylation. Only diastereoselective allylic alkylation with azlactones using $AsPh_3$[8] and the influence of the ligands, including $AsPh_3$, in (η^3-3-methylbutenyl)palladium (L_2) complexes have been described.[9]

Arsine ligands, to a large extent, have not yet been developed, probably mainly due to the lack of readily available As-containing precursor compounds.[10] The development of new methods to obtain arsines is thus increasingly recognized as central in the synthesis of new ligands. We have developed a versatile methodology that allows for C−As bond formation through a cross-coupling Pd-catalyzed reaction with the arsine−stannane *n*-$Bu_3SnAsPh_2$ (**4**) in a one-pot, two-step reaction.[11,12] This methodology allowed the synthesis of functionalized arsines and arsine ligands.[6,11b]

Herein, we describe the synthesis and application of the novel chiral bis(arsine) ligand *BiAsBA* (**3**; Figure 1). This ligand was developed on the basis of the successful backbone of TSL, having in mind that the steric and electronic properties of the ligands could be tuned by changing the heteroatom. The *BiAsBA* ligand structure and configuration have been confirmed by single-crystal X-ray crystallography. The chiral bis(arsine) ligand **3** was evaluated in the Pd-catalyzed asymmetric allylic alkylation using the benchmarking reaction with 1,3-diphenyl-2-propenyl acetate and dimethyl malonate.

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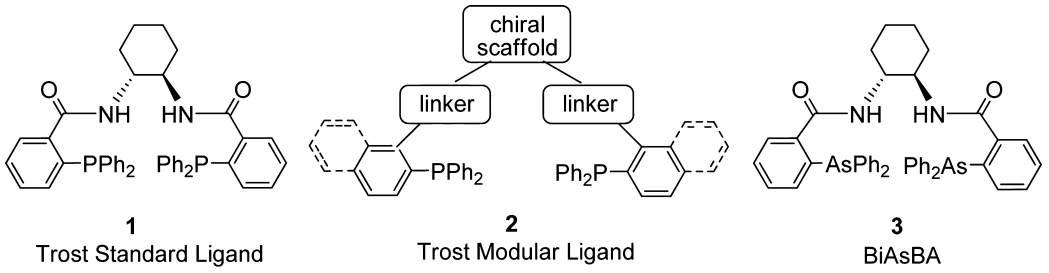
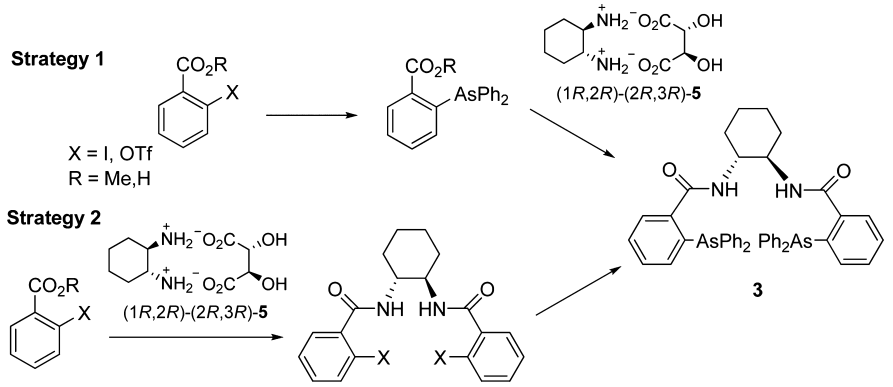
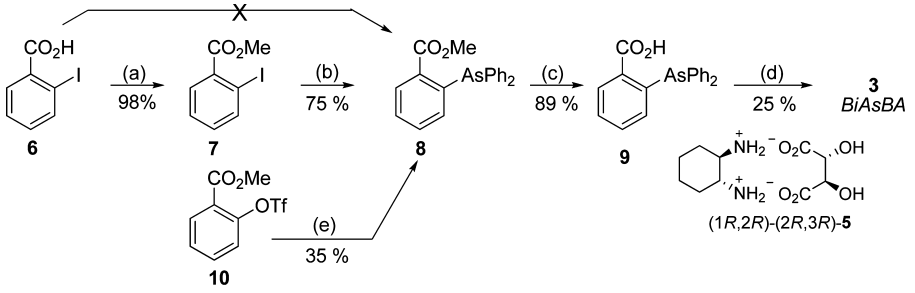


Figure 1. Phosphine and arsine Trost modular ligands.

Scheme 1. Synthetic Strategies for the Chiral Bis(arsine) Ligand *BiAsBA* (3)



Scheme 2. Synthesis of Bis(arsine) Ligand 3 by Strategy 1[a]



[a]Reagents and conditions: (a) H_2SO_4, MeOH, reflux, overnight; (b) *n*-$Bu_3SnAsPh_2$ (**4**), $(Ph_3P)_2PdCl_2$, toluene, 100 °C, 24 h; (c) *t*-BuOK, Et_2O, H_2O, 25 °C, 96 h; (d) **5**, DCC, HOBt, CH_2Cl_2/H_2O, 24 h; (e) *n*-$Bu_3SnAsPh_2$ (**4**), $(Ph_3P)_2PdCl_2$, PPh_3, LiCl, DMF, 120 °C, 24 h. All yields correspond to isolated yields.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Chiral Bis(arsine) Ligand *BiAsBA* (3). For the synthesis of the new bis(arsine) ligand *BiAsBA* (**3**), two synthetic strategies were proposed, which are shown in Scheme 1. The key step in the proposed methodologies was to achieve the introduction of the diphenylarsine group. The main difference between them was the stage at which the introduction of the diphenylarsine group (−$AsPh_2$) took place.

Both methods used commercially available, inexpensive starting materials. From (±)-*trans*-1,2-diaminocyclohexane and L-tartaric acid as resolution agent the salt (1*R*,2*R*)-(2*R*,3*R*)-**5** was obtained in high yield and diastereomeric excess (46% yield, 99% de).[13] The tartrate salt **5** was directly derivatized to afford the corresponding bis(amide), avoiding the regeneration of enantiopure free 1,2-diaminocyclohexane, which is troublesome due to its high solubility in water.[14]

In previous works,[11,12] we described the Pd-catalyzed cross-coupling arsination with the stannane *n*-$Bu_3SnAsPh_2$ (**4**), providing examples of the synthesis of Ph_2AsAr from sterically hindered and ortho-substituted arenes.[11b] By this approach the arsination reaction was carried out to obtain the new bis(arsine) chiral ligand **3**. In Scheme 2 are summarized the results achieved by strategy 1.

Direct arsination of carboxylic acid **3** was not successful (Scheme 2).[15] After a Fischer sterification, **7** was obtained. When the ester **7** was allowed to react with stannane **4** in toluene with $(PPh_3)_2PdCl_2$, methyl 2-(diphenylarsino)benzoate (**8**) was obtained (75%). As an alternative, methyl 2-(trifluoromethylsulfonyloxy)benzoate (**10**) was evaluated. The use of triflates in Pd-catalyzed arsination with the arsine−stannane **4** was previously reported.[12b] The arsination was carried out under conventional conditions with triflate **10** and stannane **4** catalyzed by $(PPh_3)_2PdCl_2$ in DMF. However, the yield of the reaction was lower than that with iodide ester **7** (**8**, 35%).

For hydrolyses of arsine ester **8**, the conventional methods with inorganic bases in water or MeOH were not effective, due to the low solubility of **8** in those media. Using the

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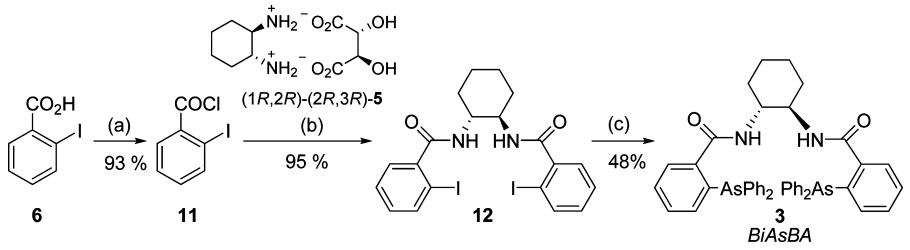
Scheme 3. Synthesis of Bis(arsine) Ligand 3 by Strategy 2[a]



[a]Reagents and conditions: (a) $SOCl_2$, reflux, 4 h; (b) (1*R*,2*R*)-(2*R*,3*R*)-**5**, NaOH, H_2O, Et_2O, overnight; (c) Pd-catalyzed arsination with *n*-$Bu_3SnAsPh_2$ (**4**) (see Table 1).

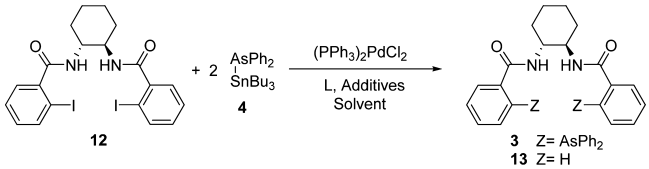
methodology developed for sterically hindered esters with *t*-BuOK/H_2O in ethyl ether, hydrolysis was successfully accomplished (Scheme 2).[16] Finally, the coupling of carboxylic acid **9** with the salt (1*R*,2*R*)-(2*R*,3*R*)-**5** to give the new chiral bis(arsine) **3** was performed, and the *BiAsBA* ligand **3** was obtained in modest yield (25%).

In order to improve the overall yield of chiral bis(arsine) ligand **3** synthesis, an alternative strategy was proposed (strategy 2, Scheme 3). The approach involved in a first step the formation of chiral bis(amide) **12**, from the acid chloride **11** and the diastereomerically pure salt (1*R*,2*R*)-(2*R*,3*R*)-**5**, followed by the introduction of the $-AsPh_2$ group by Pd-catalyzed arsination. Acid chloride **11** was quantitatively obtained and allowed to react under basic conditions with (1*R*,2*R*)-(2*R*,3*R*)-**5**. The novel bis(amide) iodide **12**, which precipitated from the reaction mixture, was obtained in 95% isolated yield. As a final step, direct arsination of bis(amide) **12** was carried out following the methodology previously described for a Pd-catalyzed coupling reaction with stannane **4** in a one-pot, two-step procedure. Several experiments were performed to establish the optimal reaction conditions for the unprecedented disubstitution Pd-catalyzed arsination reaction. The most relevant results are shown in Table 1.

Under the most efficient conditions obtained in the Pd-catalyzed arsination with ester **8** (strategy 1), the reaction did not occur, since bis(amide) **12** was not soluble in toluene (entry 1, Table 1). Likewise, when the reaction was carried out in DMF, bis(arsine) ligand **3** was not obtained. Instead, the dehalogenated bis(amide) **13** was obtained in 70% yield (entry 2, Table 1). An important development in Pd-catalyzed cross-coupling reactions involves the use of Cu(I) as cocatalyst, which increases the rates and yields.[17] When CuI and PPh_3 were added to the reaction mixture, ligand **3** was obtained in 32% yield (entry 3, Table 1). Furthermore, when the reaction was performed in DMF with PPh_3 and CsF as an activator of the organotin reagent,[18] no desired coupling product was obtained (entry 4, Table 1). An improvement in the coupling reaction of **12** was observed by increasing the reaction time to 72 h, when the ligand *BiAsBA* (**3**) was obtained in 48% isolated yield (entry 5, Table 1).

Considering that significant progress has been made based on sterically demanding electron-rich phosphines as ligands for Stille cross-coupling,[19] the phosphine P(*t*-Bu)$_2$Me[20] was examined as a ligand. When the reaction of **12** and **4** was carried out with this ligand, a lower yield of ligand **3** was obtained (entry 6, Table 1). By using other electron-rich phosphine ligands the yield could not be improved. In an attempt to reduce the reaction time, the effect of microwave (MW) radiation on Pd-catalyzed arsination was evaluated (entry 7, Table 1). MW-assisted heating has been proven as a

Table 1. Pd-Catalyzed Arsination of Bis(amide) 12 with *n*-$Bu_3SnAsPh_2$ (4) Catalyzed by $(PPh_3)_2PdCl_2$[a]



		additive[b]			
entry	conditions (time (h))	ligand (L:Pd)	CuI (Cu:Pd)	CsF (equiv)	product (%)[c]
1	toluene, 100 °C (24)				**3** (–)[d]
2	DMF, 120 °C (24)				**3** (–)
					13 (70)
3		PPh_3 (4:1)	2:1		**3** (32)
					13 (16)
4		PPh_3 (4:1)		3	**3** (<5)
					13 (28)
5	DMF, 120 °C (72)	PPh_3 (4:1)	2:1		**3** (48)
					13 (23)
6		P(tBu)$_2$Me (4:1)	2:1		**3** (13)
					13 (28)
7	DMF, microwave (10–11 W), 120 °C (0.33)	PPh_3 (4:1)	2:1		**3** (17)
					13 (40)

[a]Reaction conditions: the Ph_2As^- anion was prepared in liquid ammonia (400 mL) from $AsPh_3$ (1 mmol) and Na metal (2 mmol); then *n*-Bu_3SnCl (1 mmol) was added. The cross-coupling reaction was carried out with bis(amide) **12** (0.35 mmol) and $(PPh_3)_2PdCl_2$ (1.5 mol %), ligand (Pd:L 1:4), CsF (3 equiv), or CuI (Pd:Cu 1:2) [b]Both additives and catalyst were calculated considering that for every millimole of substrate two reactions occur. [c]Isolated yield. The yields reported represent at least the average of two reactions. [d]Bis(amide) **12** was not soluble in toluene.

valuable technology for organic synthesis, and its application in several cases has led to acceleration of reactions and improvement of yields and selectivities.[21] Pd-catalyzed coupling reactions have been carried out under MW conditions;[22] however, the use of MW irradiation in the Stille reaction has a limited scope, and only a few examples have been reported.[23] We started with the optimized reaction conditions and explored different methods and systems for MW irradiation. To our disappointment, it was not possible to achieve results better than those obtained with conventional heating for the reaction

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of bis(amide) **12** and stannane **4**. While the decrease in reaction time was considerable under the best conditions found, the ligand *BiAsBA* (**3**) was obtained in 17% isolated yield with a large amount of product **13** (entry 5 vs 7, Table 1).

It should be noted that, despite the moderate yield achieved in the disubstitution arsination reaction (48%), the new chiral bis(arsine) ligand **3** could be readily prepared in three steps following strategy 2. The *BiAsBA* ligand was obtained as an air-stable solid, and its structure was confirmed by X-ray crystallography. Although ligand **3** was obtained via both strategies, strategy 2 was simpler, involving fewer steps and givng a higher yield. Synthetically, remarkable features that extended the applications of Pd-catalyzed arsination were the two simultaneous cross-coupling reactions, which allowed C–As bond formation for the synthesis of structurally complex arsines. One of the few examples where the introduction of aryl heteroatom groups has been carried out by direct disubstitution was the synthesis of the chiral arsine 2,2′-bis(diphenylarsino)-1,1′-binaphthyl (BINAs).[7g] In this case, the arsination reaction was performed from the corresponding triflate and Ph_2AsH by a Ni-catalyzed reaction, affording only 34% yield after 3 days.

X-ray Crystallographic Study of *BiAsBA* (3). The solid-state structure of the ligand is isostructural with that of the phosphine analogue.[24] Both compounds crystallize in the orthorhombic space group $P2_12_12$ and contain acetonitrile as the common solvent of crystallization. However, since the emphasis of the report describing the P analogue was on the catalytic activity of this species, several interesting features of the X-ray structure were not discussed. Here, some of these features, as they occur in the isostructural arsine analogue, are highlighted for the first time. The unit cell contains six molecules of the ligand **3**, four in general positions (type **A**) and two on crystallographic 2-fold axes (type **B**). Representative molecules **A** and **B**, shown in Figure 2, clearly adopt different overall conformations. While the right-hand halves of molecules **A** and **B** have similar conformations, the two unsubstituted phenyl rings on the left-hand side adopt significantly different spatial arrangements in the two molecules, reflected in differences in all three corresponding C–As–C–C dihedral angles. (For a graphical overlay of molecules **A** and **B** and geometrical data for **3**, see the Supporting Information.) As expected, the As–C distances (Figure 2) are significantly longer than the P–C distances reported for the phosphorus analogue (range 1.828(3)–1.847(3) Å).[24]

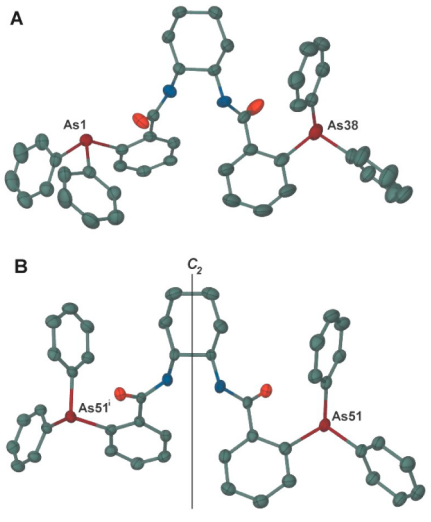

Figure 2. Perspective views of the two crystallographically independent molecules of ligand **3** with displacement ellipsoids at the 40% probability level. H atoms are omitted for clarity. Molecule **A** is in a general equivalent position, while molecule **B** is located on a 2-fold axis. (Symmetry transformation used to generate equivalent atoms in **B**: (i) $1 - x, 1 - y, z$.) The As–C bond distance ranges are As1–C = 1.962(5)–1.972(5) Å, As38–C = 1.956(6)–1.975(6) Å, and As51–C = 1.970(5)–1.984(5) Å.

The supramolecular assembly of ligand **3** in the crystal (Figure 3) is also interesting, involving the formation of hydrogen-bonded motifs that comprise two molecules of **A** and one molecule of **B**, as well as acetonitrile molecules. Two distinct N–H···O hydrogen bonds (N72–H72···O31, with N···O = 2.888(7) Å and bond angle 168°; and N22–H22···O71^i, with N···O = 2.910(5) Å and bond angle 165°) link molecules **A** and **B**, creating a large ring motif. At the top of the figure, a third hydrogen bond (N29–H29···N76, with N···N = 2.81(1) Å and bond angle 164°) links the acetonitrile molecule to the ligand molecule **A**. The complete supramolecular motif has C_2 symmetry. The configurations at the chiral centers of the *BiAsBA* ligand were assigned on the basis of the known configuration of the starting material, the salt (1*R*,2*R*)-(2*R*,3*R*)-**5**, and were confirmed as 1*R*,2*R* on the basis of the value of the Flack parameter.

Catalytic Applications of the new Chiral Bis(arsine) Ligand *BiAsBA* (3) in Pd-Catalyzed Asymmetric Allylic Substitutions. The substrate 1,3-diphenyl-2-propenyl acetate was often used to compare the activity of different ligands in the so-called standard catalyzed reaction for the asymmetric Pd-catalyzed nucleophilic allylic substitutions.[2] In order to explore the application of the new chiral ligand *BiAsBA* (**3**) in Pd-catalyzed asymmetric allylic alkylation, we evaluated the reaction of 1,3-diphenylpropenyl acetate (**14**) with dimethyl malonate (**15**) under several reaction conditions. The reactions were carried out at room temperature in the presence of the catalyst formed in situ from $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ and ligand **3**. The results are summarized in Table 2.

First, we examined the complex derived from ligand **3** under the standard conditions reported by Trost et al.,[25] which involve NaH as base in THF (entry 1, Table 2). Under these conditions the complex [Pd-*BiAsBA*] was found to be an effective catalyst for allylic alkylation, since the alkylated malonate **16** was obtained in 98% yield: however, with only 23% ee. Despite the low enantioselectivity obtained, this result showed the significant potential of the bis(arsine) ligand *BiAsBA*, since the TSL **1** gave allylic malonate **16** in only 29% yield and 12% ee under the same reaction conditions (entry 2, Table 2).[25] It is very important to highlight the greater reactivity of ligand **3** in comparison to that of TSL **1**. The remarkable improvement in catalytic activity with ligand **3** is an example of a ligand-acceleration effect,[26] which offers a powerful approach to increasing reaction efficiency and provides new opportunities to accelerate allylic alkylation reactions with arsine ligands. Considering that the structure of the *BiAsBA* ligand is isostructural with that of TSL, it seems that the electronic changes of the chiral arsine ligand **3** achieved by modifying the heteroatom are relevant for catalytic activity. The general catalytic cycle involving oxidative addition to afford a [Pd-allyl]$^+$ intermediate, followed by nucleophilic attack, has become firmly established in the literature. Considering the general assumption that under catalytic conditions the [Pd-allyl]$^+$ intermediate is the "resting state" of the catalytic cycle,[27]

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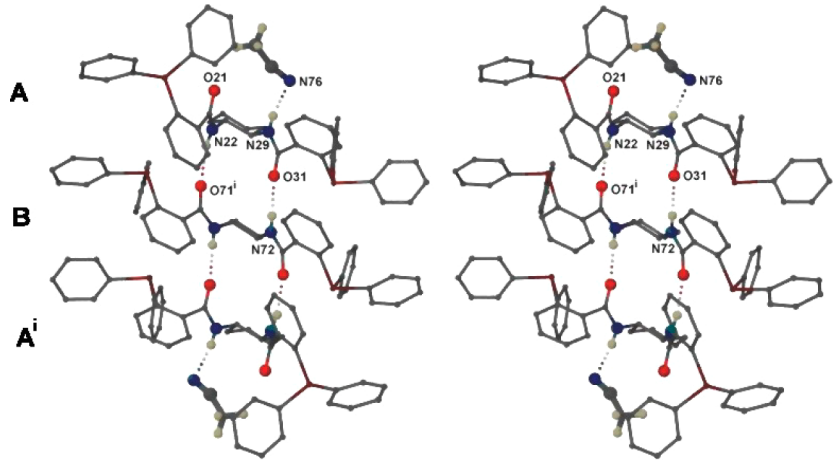
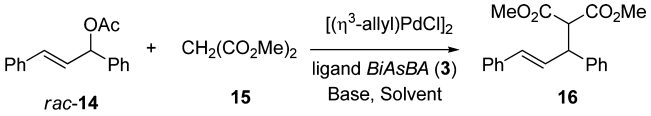


Figure 3. Stereoview of the supramolecular hydrogen-bonded motif in the crystal structure of ligand **3**. The view direction is parallel to the C_2 axis in molecule **B**.

Table 2. Pd-Catalyzed Allylic Alkylation of 1,3-Diphenyl-2-propenyl Acetate (14) with Dimethyl Malonate (15) Catalyzed by [Pd-*BiAsBA*][a]



entry	base	solvent	yield (%)[b]	config[c]	ee (%)[d]
1	NaH[e]	THF	98	*R*	23
2[f]	NaH[e]	THF	29	*R*	12
3	NaH	CH_2Cl_2	95	*S*	6
4	NaH	toluene	<5		
5	NaAcO/*BSA*[g]	THF	<5		
6	LiAcO/*BSA*[g]	CH_3CN	61	*S*	22
7	LiAcO/*BSA*[g]	CH_2Cl_2	95	*S*	49
8	NaAcO/*BSA*[g]	CH_2Cl_2	94	*S*	30
9	KAcO/*BSA*[g]	CH_2Cl_2	93	*S*	*rac*
10	CsAcO/*BSA*[g]	CH_2Cl_2	90	*S*	9

[a]Reaction conditions: reactions were carried out with [Pd] (2.5 mol %) and the chiral ligand *BiAsBA* **3** (7.5 mol %), in 1 mL of solvent at room temperature for 24 h under a nitrogen atmosphere. [b]Determined by GC with an internal standard method. [c]The assignment is based on the sign of the optical rotation and comparison with literature.[29] [d]Enantiomeric excesses were determined by ^{1}H NMR using Eu(hfc)$_3$ as the chiral shift reagent. [e]The reactions were carried out with 3 equiv of base. [f]The reaction was carried out under the standard conditions reported by Trost with **1**.[25] [g]The reactions were carried out with 1 mol % of MAcO and 3 equiv of *BSA*.

a weaker σ-donor arsine ligand could increase the electrophilicity of the [Pd-allyl]$^+$ intermediate and promote the nucleophilic attack by malonate **15**.

Additionally, catalytic reactions involving Pd complexes bearing ligand **1** suffer from a competing reaction in which the Pd(0) complex undergoes oxidation to generate a neutral P,P,N,N-tetradentate-coordinated Pd(II) complex that is catalytically inactive.[28] A possible deactivation of catalyst Pd/**1** could occur through oxidation with dioxygen, although reactions were achieved in degassed solvents under an inert atmosphere.[28b] Consequently, to explain the higher conversion with the bis(arsine) ligand **3** in comparison to TSL **1**, we should take into account the possibility that a reduced amount of catalyst deactivation by formation of the inactive Pd(II) complex may be occurring with the arsine ligand.

In an effort to optimize the performance of the [Pd-*BiAsBA*] catalyst with diphenylpropenyl acetate **14**, the effect of the solvent was investigated. When the reaction was performed in CH_2Cl_2, the yield of product **16** was practically the same, without improvement of the enantioselectivity (entry 3, Table 2). When the solvent was changed to toluene, practically no reaction was observed, and the allylic substrate **14** was recovered in 90% yield (entry 4, Table 2).

It is well-known that the structure of the nucleophile affects the enantioselectivity of these reactions.[5] Consequently, *N,O*-bis(trimethylsilyl)acetamide (*BSA*)[30] and catalytic amounts of MAcO as base were employed to facilitate the deprotonation of dimethyl malonate **15** and produced the nucleophile in situ (entries 5−10, Table 2). When NaAcO/*BSA* was employed in THF as solvent, the substrate **14** was recovered unreacted (entry 5, Table 2). The best results in CH_3CN were achieved using LiAcO/*BSA* as base, and the product **16** was obtained in only 61% yield and low ee value (entry 6, Table 2). In this solvent the conversion was complete and the reduced substrate was obtained. Changing the solvent to CH_2Cl_2 led to improved results: total conversion and modest enantioselectivity were accomplished (entry 7, Table 2).

The change of the acetate countercation provided a slight decrease in the yield and decreased the ee value (entries 8−10, Table 2). In general, as the basicity of the acetate increased, the ee value decreased. The dependence of ee values on metal cations reveals that the structure of the ion pair that forms the nucleophile is critical for the molecular recognition.

To explain the asymmetric induction produced by TSL, an empirically derived C_2-symmetric "wall-flap" cartoon model was developed by Trost,[31] and the newly developed Lloyd−Jones−Norrby model[32] involves two regiochemically distinct NH positions for hydrogen bonding of the ligand with the incoming nucleophile. Taking into account that the structure of the *BiAsBA* ligand is isostructural with that of TSL and that the TSL bound to Pd catalyst exhibits optimal catalytic and asymmetric efficiency when the allylic substrate is of a smaller size,[25] the modest asymmetric induction observed with ligand **3**, although slightly better than that with TSL **1**, could be attributed to structural dynamics associated with the steric strain being induced in [Pd-allyl]$^+$ by a clash of the Ph-As

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moiety with the allyl termini. Thus, it is presumed that the palladium-bound ligand **3** should experience significant steric hindrance when interacting with the 1,3-diphenylpropenyl acetate substrate.

In summary, the new chiral bis(arsine) ligand *BiAsBA* derived from TML was synthesized. The key step was the introduction of the $-AsPh_2$ group by Pd-catalyzed arsination. This reaction proved to be a direct and simple synthetic methodology, which could be employed effectively for the synthesis of arsine ligands. The best results were obtained when two simultaneous coupling arsination reactions were performed on bis(amide) **12**.

The new chiral bis(arsine) ligand *BiAsBA* was found to be a very good ligand for the asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate, where very high to complete conversion was observed. Even though the asymmetric alkylation reactions with the [Pd-*BiAsBA*] complex proceed with modest enantioselectivity, the bis(arsine) ligand *BiAsBA* provided a higher ee value than the phosphorus-containing homologous TSL with 1,3-diphenyl acetate **14** under the same reaction conditions. On the basis of the results obtained, the potential of chiral arsine ligands in asymmetric allylic alkylation has been established. Further studies to explore the scope of this ligand in asymmetric catalytic reactions are currently in progress.

■ ASSOCIATED CONTENT

Supporting Information

A CIF file giving X-ray crystal structure data for **3**·0.4-(acetonitrile), a figure showing an overlay of molecules **A** and **B**, text giving experimental procedures or details, and figures giving full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available through the Cambridge Crystallographic Database for compound **3** (CCDC 903122).

■ AUTHOR INFORMATION

Corresponding Author

*S.E.M.: tel, 54-351-4334170; fax, 54-351-4333030; e-mail, martins@fcq.unc.edu.ar. M.R.C.: e-mail, Mino.Caira@uct.ac.za.

Notes

The authors declare no competing financial interest.

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