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Synthesis, characterization, and structures of arylaluminum reagents and asymmetric arylation of aldehydes catalyzed by a titanium complex of an N-sulfonylated amino alcohol

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ABSTRACT

A series of phenylaluminum reagents $AlPh_xEt_{3-x}(L)$ ($x = 1–3$) containing adduct ligand L [Et_2O, THF, $OPPh_3$, or 4-dimethylaminopyridine (DMAP)] were synthesized and characterized. NMR studies showed that $AlPh_xEt_{3-x}(L)$ ($x = 1$ or 2) exists as an equilibrium mixture of 3–4 species in solution. Solid-state structures of the phenylaluminum reagents reveal a distorted tetrahedral geometry. Asymmetric additions of phenylaluminum to 2-chlorobenzaldehyde were examined employing a titanium(IV) complex $[TiL^*(OPr^i)_2]_2$ **10** (H_2L^* = (1*R*,2*S*)-2-(*p*-tolylsulfonylamino)-1,3-diphenyl-1-propanol) as a catalyst precursor. It was found that the adduct ligand L had a strong influence on the reactivity and the enantioselectivity in asymmetric phenyl additions to aldehydes. The phenylaluminum reagents with $OPPh_3$ or DMAP were unreactive toward aldehydes, and $AlPh_3(THF)$ was found to be superior to $AlPh_3(OEt_2)$ or $AlPhEt_2(THF)$. Asymmetric aryl additions of $AlAr_3(THF)$ to aldehydes employing a loading of 5 mol % titanium(IV) complex **10** with a strategy of a slow addition of the aldehydes over 20 min were conducted, and the reactions produced optically active secondary alcohols in high yields with excellent enantioselectivities of up to 94% ee.

1. Introduction

The enantioselective addition of organometallic reagents to carbonyl compounds is an important synthetic method that gives optically active alcohols via carbon–carbon bond formation.[1] Among the methods available for the synthesis of chiral diarylmethanols, the asymmetric addition of phenylzinc reagents has achieved much success owing to wide substituent tolerances and mild reaction conditions.[2] Although high enantioselectivities have been achieved, the non-substituted phenyl group as a transferring nucleophile limited the application. Subsequently, a method where arylzinc reagents were prepared by transmetallation between arylboronic acids or arylboranes and diethylzinc as aryl transfer reagents was reported by Bolm et al.[3] and later by others.[4] This modified methodology broadened the scope of the aryl transfer reaction using functionalized arylzinc reagents as nucleophiles. The arylzinc reagents could also be prepared from reactions of zinc halides with metallic aryl reagents.[5] In contrast to zinc reagents, organoaluminum compounds have proven to be more reactive nucleophiles,[6] owing to the greater Lewis acidity of the aluminum center.

The solid-state triarylaluminum compounds were, in general, prepared as dimeric species.[7] However bulky substituted aryl ligands have been used for the preparation of highly reactive monomeric compounds. The first three-coordinate monomeric trimesitylaluminum was reported by Oliver et al.[8] The bulky mesityl ligands provided significant steric hindrances to the metal center and prevented the formation of the dimeric aluminum complex. By providing an additional neutral ligand, a series of four-coordinate triarylaluminum complexes, such as $Al(o\text{-tolyl})_3(OEt_2)$,[7a] $AlMes_3(THF)$ (Mes = mesityl),[9] $AlPh_3(THF)$,[10] $AlMes_3(4\text{-picoline})\cdot(C_7H_8)_{0.5}$,[11] and $AlPh_3(E(SiMe_3)_3)$ (E = P or As)[12] were also synthesized and characterized.

Although many arylaluminum compounds have been synthesized and characterized, there is scarce research on the asymmetric arylation of aldehydes or ketones using the arylaluminum compounds as aryl sources, this led us to investigate asymmetric aryl additions of arylaluminum compounds to aldehydes or ketones. We discovered that arylaluminum compounds are effective reagents in asymmetric aryl additions in short reaction times to aldehydes catalyzed by the titanium catalyst of 10 mol % (*R*)-H_8-BINOL or 20 mol % 1,3-bis[*N*-sulfonyl-(1*R*,2*S*)-1,3-diphenyl-2-aminopropanol]benzene.[13] Furthermore, the $AlAr_3(THF)$ compounds have been proven to be highly enantioselective aryl transfer reagents for additions to aromatic ketones affording tertiary alcohols in excellent enantioselectivities[14] in addition to being coupling

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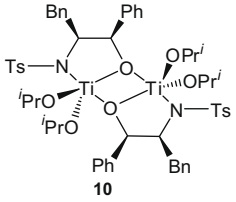
reagents with aryl halides.[15] Subsequently, von Zezschwitz et al.[16] and Hoveyda et al.[17] reported the asymmetric 1,2- or 1,4-additions of arylaluminum reagents to cyclic enones by using $AlPhMe_2$ prepared in situ, respectively. Alexakis et al. also reported a copper-catalyzed asymmetric conjugate addition of $AlArEt_2$ reagents to enones.[18]

In order to further explore arylaluminum reagents for asymmetric catalysis, we herein report the synthesis and structures of a series of arylaluminum reagents containing an adduct of Et_2O, THF, $OPPh_3$, or DMAP and their asymmetric aryl additions to aldehydes employing a loading of 5 mol % titanium(IV) complex **10** as a catalyst precursor.



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2. Results and discussion

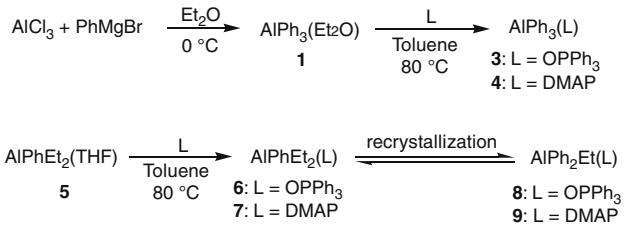
2.1. Syntheses and spectroscopic studies of the aluminum reagents

The aluminum complex $AlPh_3(OEt_2)$ **1** was obtained in high yield from a reaction of $AlCl_3$ with 3 equiv PhMgBr in Et_2O. Further reaction of **1** or $AlPh_3(THF)$ **2** in toluene with $OPPh_3$ or 4-dimethylaminopyridine (DMAP) produced $AlPh_3(OPPh_3)$ **3** and $AlPh_3(DMAP)\cdot C_7H_8$ **4**, respectively. Reactions of $AlPhEt_2(THF)$ **5**[13c] with $OPPh_3$ or DMAP afforded $AlPhEt_2(OPPh_3)$ **6** or $AlPhEt_2(DMAP)$ **7** (Scheme 1). The ^1H NMR spectra of **6** and **7** revealed three sets of ethyl resonances and three sets of phenyl signals, indicating that **6** and **7** in $CDCl_3$ solution contained a mixture of four species represented as $AlPh_xEt_{3-x}(OPPh_3)$ and $AlPh_xEt_{3-x}(DMAP)$ (x = 0, 1, 2, or 3), respectively. Recrystallization of **6** or **7** from toluene gave crystalline solids of $AlPh_2Et(OPPh_3)$ **8** and $AlPh_2Et(DMAP)$ **9**, respectively. It is noteworthy that the ^1H NMR spectra of **8** and **9** showed two sets of ethyl resonances and three sets of phenyl signals, indicating that both **8** and **9** in $CDCl_3$ solution partly converted to $AlPhEt_2(L)$ and $AlPh_3(L)$. Structures of complexes **1**, **3**, **4**, and **9** were further determined by single-crystal X-ray analyses.

2.2. Molecular structures of complexes 1, 3, 4, and 9

Suitable crystals of complexes **1** (Fig. 1), **4** (Fig. 3), and **9** (Fig. 4) for structure determinations were obtained by slowly cooling their respective toluene solutions to 0 °C. Crystals of complex **3** (Fig. 2) were obtained by liquid diffusion of hexane/CH_2Cl_2 solution. The selected bond lengths and angles are listed in Table 1.

A typical feature of all the structures described herein is that three carbon atoms and an oxygen atom (or a nitrogen atom) surround the metal atom in a distorted tetrahedral geometry. The C–Al–O and C–Al–N angles formed around the metal center range



Scheme 1. Syntheses of the aluminum reagents.

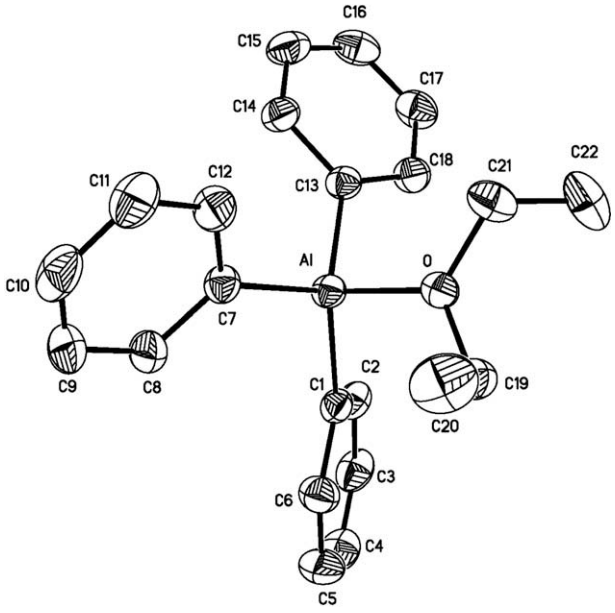


Figure 1. Molecular structure of $AlPh_3(OEt_2)$ **1**. Hydrogen atoms are omitted for clarity.

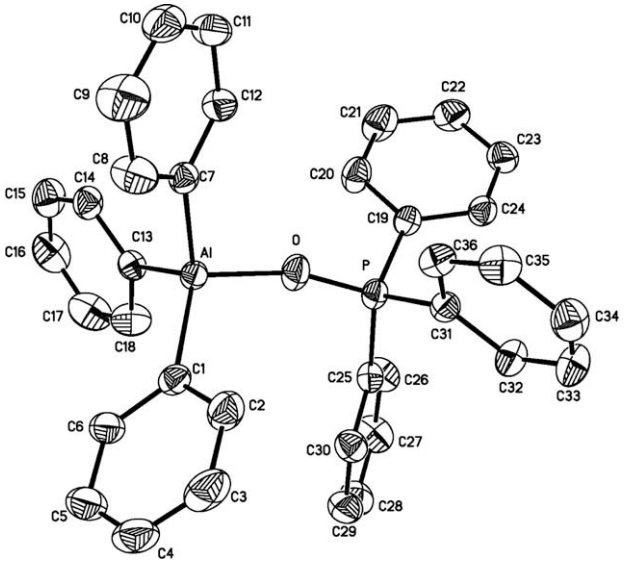


Figure 2. Molecular structure of $AlPh_3(OPPh_3)$ **3**. Hydrogen atoms are omitted for clarity.

from 102° to 108° (Table 1) which are obviously smaller than the C–Al–C angles in the range of 111–117°. Similar results were also observed in complexes such as $Al(o\text{-}Tol)_3(OEt_2)$,[7a] $AlMes_3(THF)$,[9] $AlPh_3(THF)$,[10] and $AlMes_3(4\text{-picoline})\cdot(C_7H_8)_{0.5}$.[11]

From Table 1, it is clear that averaged Al–C bond distances in complexes **1** (1.986(2) Å), **3** (1.986(2) Å), **4** (1.989(2) Å), and **9** (1.990(2) Å) are nearly identical. These averaged Al–C distances are comparable to those in $AlPh_3(THF)$ (1.983(2) Å) and $Al(o\text{-}Tol)_3(OEt_2)$ (1.990(2) Å), but shorter than that of 2.017(7) Å and 2.009(12) Å found in $AlMes_3(THF)$ and $AlMes_3(4\text{-picoline})\cdot(C_7H_8)_{0.5}$, respectively. The Al–O distance of 1.924(1) Å in complex **1** is longer than those of 1.819(1) Å in **3** and 1.897(1) Å in $AlPh_3(THF)$, but shorter than that of 1.969(5) Å in $AlMes_3(THF)$. The Al–N distance (1.962(1) Å) in complex **4** is comparable to that of 1.978(2) Å in **9**, but shorter than that of 2.045(8) Å in $AlMes_3(4\text{-picoline})\cdot(C_7H_8)_{0.5}$. The observed variations of bond distances result from both steric interactions and electronic effect.

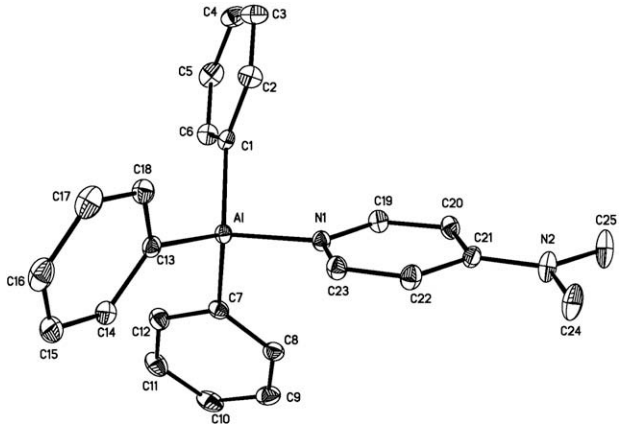


Figure 3. Molecular structure of $AlPh_3(DMAP)\cdot C_7H_8$ **4**. Hydrogen atoms and solvent molecule are omitted for clarity.

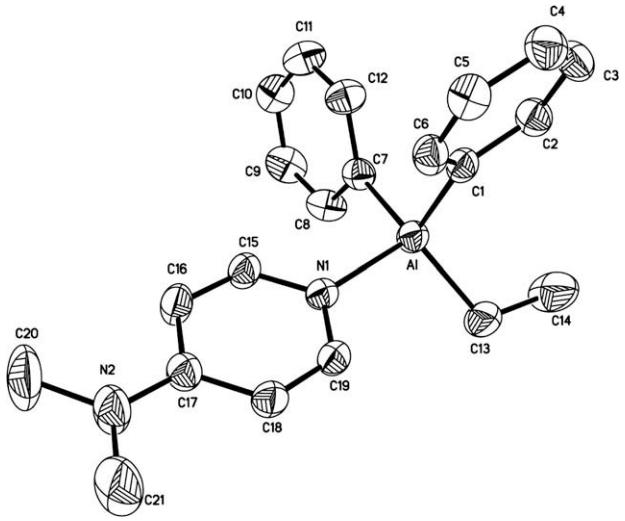


Figure 4. Molecular structure of $AlPh_2Et(DMAP)$ **9**. Hydrogen atoms are omitted for clarity.

2.2.1. Asymmetric addition of aluminum reagents to aldehydes catalyzed by a titanium(IV) complex of an N-sulfonylated amino alcohol

It has been established by us that $AlAr_3(THF)$ and $AlPhEt_2(THF)$ compounds containing a THF adduct are excellent arylation reagents of aldehydes.[13] We also demonstrated that derivatives of amino alcohols were excellent ligands for multiple types of asymmetric carbon–carbon bond formation reactions.[19] In order to study reactivities and enantioselectivities of $AlPh_xEt_{3-x}(L)$ (L = Et_2O, THF, $OPPh_3$, DMAP), asymmetric phenyl additions of $AlPh_xEt_{3-x}(L)$ to 2-chlorobenaldehyde were examined using 10 mol % complex **10** as a catalyst precursor. The results are summarized in Table 2, and it was found that the adduct ligands of the aluminum reagents have a strong influence on both reactivities and enantioselectivities in asymmetric phenylation reactions. Both $AlPh_3(OEt_2)$ **1** and $AlPh_3(THF)$ **2** showed excellent reactivities giving diarylmethanol **12a** in excellent yields of 100% and 91% (entries 1 and 2), respectively. However, the addition of $AlPh_3(OEt_2)$ gave **12a** in a low enantioselectivity of 9% in comparison to 65% for the $AlPh_3(THF)$ addition reaction. The addition of $AlPhEt_2(THF)$ **5** to 2-chlorobenzaldehyde gave diarylmethanol **12a** in 64% yield with a low enantioselectivity of 32%, and an ethyl addition product was also obtained as a by-product in an 11% yield (entry 5). In contrast, the aluminum reagents **3**, **4**, **8**, and **9** were unreactive toward 2-chlorobenaldehyde when they were coordinated by a strong Lewis base such as $OPPh_3$ or DMAP (entries 3, 4, 6, and 7). When the reaction was carried out under the reaction conditions of 10 mol % **10**, 1.25 equiv $Ti(OPr^i)_4$, 1.2 equiv $AlPh_3(THF)$ in THF, the phenyl addition to 2-chlorobenzaldehyde afforded the corresponding diarylmethanol **12a** in 98% yield and 86% ee (entry 8). To examine the requirement of $Ti(OPr^i)_4$ in the catalytic system, a reaction without an addition of $Ti(OPr^i)_4$ was carried out, and **12a** was obtained in a low conversion of 11% (entry 9), suggesting that **10** is not the actual catalyst. Instead, the dititanium complex **10** is a catalyst precursor. In the catalytic solution, $Ti(OPr^i)_4$ exchanges a phenyl group with $AlPh_3(THF)$,[13a] and the resulting species reacts further with **10** to give an active species which has a structure similar to the active species proposed for the asymmetric $ZnEt_2$ addition to aldehydes employing the same **10**/$Ti(OPr^i)_4$ catalytic system.[19d]

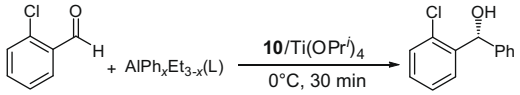
Tuning the amount of $Ti(OPr^i)_4$ to 1.0 and 1.5 equiv led to product **12a** in yields of 78% and 100% with enantioselectivities of 72 and 88% (entries 10 and 11), respectively. When $Ti(OPr^i)_4$ was kept at 1.5 equiv and $AlPh_3(THF)$ was altered to 1.0 and 1.4 equiv (entries 12 and 13), the reactions afforded the product with enantioselectivities of 85% and 82%, respectively. In order to suppress the racemic background reactions that would lower the enantioselectivities of the addition product, a strategy of a slow addition of the aldehyde to a solution containing the catalytic system and the arylaluminum reagent significantly improved the enantioselectivity to 98% (entry 14). To examine the efficiency of the catalytic system, the loading of **10** was decreased to 5 mol%, producing the product in 100% yield and an excellent 92% ee (entry 15). Reducing the loadings of **10** further to 2.5 and 1 mol % resulted in decreasing enantioselectivities to 86% and 62% (entries 16 and 17), respectively. While employing the **10**/$Ti(OPr^i)_4$ catalytic system, it was found that, among the $AlPh_xEt_{3-x}(L)$ reagents, $AlPh_3(THF)$ was the best phenyl source for additions to aldehydes.

The asymmetric aryl transfer of $AlAr_3(THF)$ to a variety of aldehydes was subsequently performed in the presence of 5 mol % **10** with the slow addition of the aldehyde over 20 min; the results are listed in Table 3. Regardless of the electronic nature or the

Table 1
Selected bond lengths (Å) and bond angles (°) for **1**, **3**, **4**, and **9**

	1	3		4	9
Al–O	1.924(1)	1.819(1)	Al–N(1)	1.962(1)	1.978(2)
Al–C(1)	1.981(2)	1.981(2)	Al–C(1)	1.988(2)	2.001(2)
Al–C(7)	1.987(2)	1.986(2)	Al–C(7)	1.985(2)	1.983(2)
Al–C(13)	1.989(2)	1.990(2)	Al–C(13)	1.993(2)	1.978(3)
$Al–C_{(av)}$	1.986(2)	1.986(2)	$Al–C_{(av)}$	1.989(2)	1.990(2)
O–Al–C(1)	105.00(6)	108.80(7)	N(1)–Al–C(1)	102.47(8)	102.82(8)
O–Al–C(7)	103.36(6)	104.97(7)	N(1)–Al–C(7)	106.21(7)	103.47(8)
O–Al–C(13)	103.28(6)	103.94(7)	N(1)–Al–C(13)	103.91(7)	106.08(10)
C(1)–Al–C(7)	115.07(7)	113.29(8)	C(1)–Al–C(7)	111.73(7)	110.81(9)
C(7)–Al–C(13)	114.76(7)	112.60(7)	C(7)–Al–C(13)	114.04(8)	116.95(12)
C(1)–Al–C(13)	113.48(7)	112.44(7)	C(1)–Al–C(13)	116.82(8)	114.84(12)

Table 2
Optimizations of asymmetric $AlPh_xEt_{3-x}(L)$ to 2-chlorobenzaldehyde catalyzed by **10**/$Ti(OPr^i)_4$ catalyst[a]



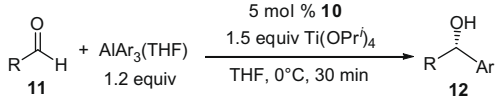
11a 12a

Entry	**10** (mol %)	Solvent	$AlPh_xEt_{3-x}(L)$	$AlPh_xEt_{3-x}(L)$ (equiv)	$Ti(OPr^i)_4$ (equiv)	Conv.[c] (%)	ee[d] (%)
1	10	Toluene	$AlPh_3(OEt_2)$ **1**	1.2	1.25	100	9
2	10	Toluene	$AlPh_3(THF)$ **2**	1.2	1.25	91	65
3	10	Toluene	$AlPh_3(OPPh_3)$ **3**	1.2	1.25	0	—
4	10	Toluene	$AlPh_3(DMAP)$ **4**	1.2	1.25	0	—
5	10	Toluene	$AlPhEt_2(THF)$ **5**	1.2	1.25	64 (11)[e]	32
6	10	Toluene	$AlPh_2Et(OPPh_3)$ **8**	1.2	1.25	0	—
7	10	Toluene	$AlPh_2Et(DMAP)$ **9**	1.2	1.25	0	—
8	10	THF	$AlPh_3(THF)$ **2**	1.2	1.25	98	86
9	10	THF	$AlPh_3(THF)$ **2**	1.2	—	11	—
10	10	THF	$AlPh_3(THF)$ **2**	1.2	1.0	78	72
11	10	THF	$AlPh_3(THF)$ **2**	1.2	1.5	100	88
12	10	THF	$AlPh_3(THF)$ **2**	1.0	1.5	85	85
13	10	THF	$AlPh_3(THF)$ **2**	1.4	1.5	100	82
14[b]	10	THF	$AlPh_3(THF)$ **2**	1.2	1.5	100	98
15[b]	5	THF	$AlPh_3(THF)$ **2**	1.2	1.5	100	92
16[b]	2.5	THF	$AlPh_3(THF)$ **2**	1.2	1.5	100	86
17[b]	1	THF	$AlPh_3(THF)$ **2**	1.2	1.5	100	62

[a] 0.50 mmol 2-ClC_6H_4CHO, THF (3 mL), 0 °C, equiv of $Ti(OPr^i)_4$ and $AlPh_3(THF)$ are relative to 2-chlorobenzaldehyde.
[b] 2-ClC_6H_4CHO (0.50 mmol) in 0.8 mL THF was added dropwise over 20 min; reaction time of 30 min including the addition time of the substrate to the catalytic solution.
[c] Conversions based on ^1H NMR spectra.
[d] The ee values were determined by HPLC.
[e] The value in parenthesis was conversion of the ethyl addition product.

steric effect of the substituent on the aryl groups, asymmetric phenyl additions to aromatic aldehydes afforded diarylmethanols in high yields with excellent enantioselectivities of 90–94% (entries 1–11). In addition to aromatic aldehydes, the phenyl addition to the α,β-unsaturated (*E*)-cinnamaldehyde was studied to furnish the secondary alcohol **12l** in 92% yield with a good enantioselectivity of 87% (entry 12). In contrast, the phenyl addition to the heterocyclic 2-furylaldehyde gave the addition product **12m** in an excellent 93% yield and a 90% ee (entry 13). For aliphatic aldehydes, the phenyl addition to Bu^tCHO or Pr^iCHO produced the corresponding secondary alcohols in excellent yields but in moderate enantioselectivities of 74% and 77% (entries 14 and 15), respectively. The additions of substituted aryl to benzaldehyde afforded the desired products in good or excellent stereoselectivities of 86% and 91% (entries 16 and 17).

Table 3
Asymmetric $AlAr_3(THF)$ addition to aldehydes catalyzed by **10**/$Ti(OPr^i)_4$ catalyst[a]



11 12

Entry	R	Ar	Product	Yield[b] (%)	ee[c] (%)
1	2-ClC_6H_4	Ph	**12a**	92	93 (*R*)
2	4-ClC_6H_4	Ph	**12b**	91	90 (*R*)
3	2-BrC_6H_4	Ph	**12c**	94	93 (*R*)
4	4-BrC_6H_4	Ph	**12d**	96	90 (*R*)
5	2-$MeOC_6H_4$	Ph	**12e**	94	94 (*R*)
6	4-$MeOC_6H_4$	Ph	**12f**	98	90 (*R*)
7	2-MeC_6H_4	Ph	**12g**	95	91 (*R*)
8	4-MeC_6H_4	Ph	**12h**	93	92 (*R*)
9	4-$CF_3C_6H_4$	Ph	**12i**	80	90 (*R*)
10	1-Naphthyl	Ph	**12j**	96	91 (*R*)
11	2-Naphthyl	Ph	**12k**	94	92 (*R*)
12	(*E*)-Cinnamyl	Ph	**12l**	92	87 (*S*)
13	2-Furyl	Ph	**12m**	93	90 (*R*)
14	Bu^t	Ph	**12n**	93	74 (*S*)
15	Pr^i	Ph	**12o**	92	77 (*S*)
16	Ph	*p*-Tolyl	**12h'**	91	91 (*S*)
17	Ph	2-Napthyl	**12k'**	94	86 (*S*)

[a] Substrate/**10**/$AlAr_3(THF)$/$Ti(OPr^i)_4$ = 0.50/0.025/0.60/0.75 mmol, substrate in 0.8 mL THF was added dropwise over 20 min; reaction time including the addition time of the substrate to the catalytic solution.
[b] Isolated yields after column chromatography.
[c] The ee values were determined by HPLC, Absolute configurations were obtained by comparison with the HPLC data of known compounds.

3. Conclusion

A series of phenylaluminum reagents $AlPh_xEt_{3-x}(L)$ (L = Et_2O, THF, $OPPh_3$, or DMAP) were synthesized. ^1H NMR studies show the existence of 3–4 species for $AlPh_xEt_{3-x}(L)$ (x = 1 or 2) in solution, while solid-state structures reveal a tetrahedral geometry. Asymmetric additions of phenylaluminum reagents to 2-chlorobenzaldehyde catalyzed by the titanium(IV) complex **10** of an N-sulfonylated amino alcohol suggest that the adduct ligands play a key role in both the reactivity and the enantioselectivity in asymmetric phenylations of aldehydes. The phenylaluminum reagents containing a strong Lewis base of $OPPh_3$ or DMAP were unreactive toward aldehydes. For the **10**/$Ti(OPr^i)_4$ catalytic system, $AlPh_3$(THF) was superior to $AlPh_3(OEt_2)$ or $AlPhEt_2$(THF). In this study, 5 mol % **10** was used for the additions of the highly reactive $AlAr_3$(THF) to aldehydes by the strategy of slow addition of aldehydes over 20 min, furnishing optically active secondary alcohols **12** in high yields with excellent enantioselectivities of up to 94%.

4. Experimental

4.1. General remarks

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium benzophenone ketyl (THF, Et_2O,

toluene, or hexane) or P_2O_5 (dichloromethane) under nitrogen atmosphere prior to use. Aldehydes were dried over $MgSO_4$ or molecular sieves and distilled before use. Ketones, $OPPh_3$, and DMAP were used as received. ^1H NMR and ^{13}C NMR spectra in $CDCl_3$ were recorded on a Varian Mercury-400 spectrometer with chemical shifts given in ppm from the internal TMS. $AlAr_3$(THF)[9a,13a] and $AlPhEt_2$(THF)[13c] were synthesized according to the literature procedure.

4.2. Synthesis of $AlPh_3(OEt_2)$ 1

A solution of phenylmagnesium bromide (90.0 mmol) in Et_2O was slowly added to a solution of $AlCl_3$ (4.00 g, 30.0 mmol) in Et_2O at 0 °C. The mixture was stirred at room temperature for 12 h and the solvent was removed under reduced pressure to afford a residue, which was extracted with toluene (2 × 50 mL). The extracts were combined and concentrated to about 50 mL. Colorless crystals of **1** (8.58 g, 86.0% yield) were obtained by cooling the concentrated solution at 0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80–7.78 (m, 6H), 7.32–7.30 (m, 9H), 4.13 (q, J = 7.2 Hz, 4H), 1.18 (t, J = 7.2 Hz, 6H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.99, 138.23, 127.62, 127.21, 67.64, 13.35 ppm. Anal. Calcd for $C_{22}H_{25}OAl$: C, 79.49; H, 7.58. Found: C, 78.90; H, 7.32.

4.3. Synthesis of $AlPh_3(OPPh_3)$ 3

A toluene (10 mL) solution of $OPPh_3$ (0.278 g, 1.00 mmol) was added to a toluene (20 mL) solution of **1** (0.332 g, 1.00 mmol) at room temperature. The mixture was stirred for 12 h at 80 °C. The solvent was removed under reduced pressure to afford a powder. Colorless crystals of **3** (0.477 g, 89.0% yield) were obtained by liquid diffusion of hexane/CH_2Cl_2 solution. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61–7.55 (m, 9H), 7.49–7.44 (m, 6H), 7.40–7.35 (m, 6H), 7.16–7.10 (m, 9H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.72, 138.16, 133.69, 132.70 (d, $J_{(C-P)}$ = 10.9 Hz), 129.11 (d, $J_{(C-CP)}$ = 13.7 Hz), 127.21, 126.53, 126.34 ppm. Anal. Calcd for $C_{36}H_{30}OPAl$: C, 80.58; H, 5.64. Found: C, 80.33; H 6.01.

4.4. Synthesis of $AlPh_3(DMAP)\cdot C_7H_8$ (4)

A toluene (10 mL) solution of DMAP (0.122 g, 1.00 mmol) was added to a toluene (20 mL) solution of **1** (0.332 g, 1.00 mmol) at room temperature. The mixture was stirred for 12 h at 80 °C. The solvent was removed under reduced pressures to afford a powder which was extracted with toluene (15 mL). Colorless crystals of **4** (0.424 g, 90.0% yield) were obtained by cooling the toluene solution at 0 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.12 (m, 2H), 7.72 (m, 6H), 7.28–7.25 (m, 12H), 7.16 (m, 2H), 6.50 (m, 2H), 3.04 (s, 6H), 2.35 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 155.78, 149.55, 147.57, 138.48, 137.86, 129.04, 128.23, 126.99, 126.95, 125.30, 106.70, 39.28, 21.42 ppm. Anal. Calcd for $C_{32}H_{33}N_2Al$: C, 81.33; H, 7.04; N, 5.96. Found: C, 80.93; H, 7.14; N 5.67.

4.5. Synthesis of 6 and 8

To a toluene (30 mL) solution of $OPPh_3$ (0.834 g, 3.00 mmol) was added **5** (0.703 g, 3.00 mmol) at room temperature. The mixture was stirred for 12 h at 80 °C. The solvent was removed under reduced pressures to give an oily solid of **6**. ^1H NMR ($CDCl_3$, 400 MHz): $AlEt_3(OPPh_3)$, δ 0.92 (t, J = 8.2 Hz, 9H), −0.33 (q, J = 8.2 Hz, 6H) ppm; $AlPhEt_2(OPPh_3)$, δ 7.63–7.48 (m, br, 17H), 7.15–7.11 (m, 3H), 0.99 (t, J = 8.2 Hz, 3H), −0.09 (q, J = 8.0 Hz, 2H) ppm; $AlPh_2Et(OPPh_3)$, δ 7.63–7.48 (m, br, 19H), 7.15–7.11 (m, 6H), 1.03 (t, J = 8.2 Hz, 3H), −0.09 (m, 2H) ppm; $AlPh_3(OPPh_3)$, δ 7.63–7.48 (m, br, 24H), 7.15–7.11 (m, 6H) ppm. Recrystallization of the crude product **6** from toluene gave colorless crystalline solid of $AlPh_2Et(OPPh_3)$ **8**. The ^1H NMR spectrum indicates that complex **8** in $CDCl_3$ solution contains a mixture of three major species of $AlPhEt_2(OPPh_3)$, $AlEtPh_2(OPPh_3)$, and $AlEtPh_2(OPPh_3)$. Anal. Calcd for $C_{32}H_{30}OPAl$ **8**: C, 78.67; H, 6.19. Found: C, 78.19; H, 6.67.

4.6. Synthesis of 7 and 9

To a toluene (30 mL) solution of DMAP (0.488 g, 4.00 mmol) was added **5** (0.937 g, 4.00 mmol) at room temperature. The mixture was stirred for 12 h at 80 °C. The solvent was removed under reduced pressures to give an oily solid of **7**. ^1H NMR ($CDCl_3$, 400 MHz): $AlEt_3$(DMAP), δ 8.07 (d, J = 6.8 Hz), 6.52 (d, J = 6.8 Hz, 2H), 3.05 (s, 6H), 0.95 (t, J = 7.6 Hz, 9H), −0.16 (q, J = 8.0 Hz, 6H) ppm; $AlPhEt_2$(DMAP), δ 8.07 (d, J = 6.8 Hz, 2H), 7.62–7.59 (m, 2H), 7.28–7.16 (m, 3H), 6.52 (d, J = 6.8 Hz, 2H), 3.05 (s, 6H), 1.06 (t, J = 8.2 Hz, 6H), 0.08 (q, J = 8.2 Hz, 4H) ppm; $AlPh_2Et$(DMAP), δ 8.07 (d, J = 6.8 Hz, 2H), 7.66–7.32 (m, 4H), 7.28–7.16 (m, 6H), 6.52 (d, J = 6.8 Hz, 2H), 3.05 (s, 6H), 1.13 (t, J = 8.2 Hz, 3H), 0.35 (q, J = 8.0 Hz, 2H); $AlPh_3$(DMAP), δ 8.07 (d, J = 6.8 Hz, 2H), 7.72–7.70 (m, 6H), 7.28–7.16 (m, 9H), 6.52 (d, J = 6.8 Hz, 2H), 3.05 (s, 6H) ppm. Recrystallization of the crude product **7** from toluene gave colorless crystals of $AlPh_2Et$(DMAP) **9**. The ^1H NMR spectrum indicates that complex **9** in $CDCl_3$ solution contains a mixture of three major species of $AlPhEt_2$(DMAP), $AlPh_2Et$(DMAP), and $AlPh_3$(DMAP). Anal. Calcd for $C_{21}H_{25}N_2Al$ **9**: C, 75.88; H, 7.58; N 8.43. Found: C, 75.52; H, 7.39; N 8.69.

4.7. X-ray crystallography

Suitable crystals of complexes **1**, **3**, **4**, and **9** were mounted under nitrogen atmospheres in sealed capillaries. Diffraction was performed on a Bruker AXS SMART 1000 or an Oxyford Gemini S diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); temperature 293(2) K for complexes **1**, **3**, and **9**, and 100(2) K for complex **4**; φ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections. All structures were solved by direct methods (SHELXTL-97),[20] completed by subsequent difference Fourier syntheses, and refined by full-matrix least squares calculations based on F^2 (SHELXTL-97). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-710552 (**1**), CCDC-710554 (**3**), CCDC-710553 (**4**), and CCDC-710551 (**9**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.8. General procedure for the asymmetric aryl addition of aldehydes

Under a dry nitrogen atmosphere, **10** (0.027 g, 0.025 mmol) and $Ti(OPr^i)_4$ (0.22 mL, 0.75 mmol) were mixed in dry THF (3 mL) at room temperature. After stirring for 30 min, $AlPh_3$(THF) (0.198 g, 0.600 mmol) in dry THF (2 mL) was added at 0 °C. The mixture was stirred for another 10 min, and an aldehyde (0.50 mmol) in THF (0.8 mL) was added dropwise to the resulting solution over 20 min at 0 °C. The mixture was allowed to react for 10 min at this temperature, and then quenched with 2 M NaOH. The aqueous phase was extracted with diethyl ether (3 × 10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography to give the secondary alcohol. Enantiomeric excesses of products were determined by HPLC using suitable chiral columns from Daicel.

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