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Catalytic Asymmetric C–H Arylation of (η^6-Arene)Chromium Complexes: Facile Access to Planar-Chiral Phosphines

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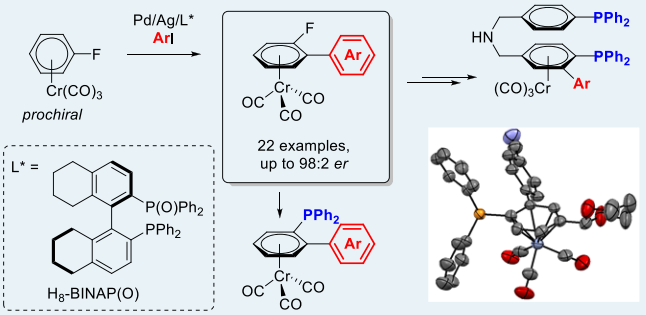
Supporting Information

ABSTRACT: A catalytic asymmetric direct C–H arylation of (η^6-arene)chromium complexes to obtain planar-chiral compounds is reported. The use of the hemilabile ligand H_8-BINAP(O) is key to providing high enantioselectivity in this transformation. We show that this methodology opens the door to the synthesis of a variety of planar-chiral chromium derivatives which can be easily transformed into planar chiral mono- or diphosphines. Mechanistic studies, including synthesis and characterization of Pd and Ag complexes and their detection in the reaction mixture, suggest a Pd-catalyzed/Ag-promoted catalytic system where Ag carries out the C–H activation step.



KEYWORDS: *asymmetric catalysis, C–H activation, (arene)-chromium complexes, planar-chirality, chiral ligands*

1. INTRODUCTION

Unsymmetrically substituted metallocenes and (η^6-arene)chromium complexes are two notable families of planar-chiral transition-metal organometallic complexes, and they have extensively been applied as stoichiometric auxiliaries and/or starting materials for asymmetric synthesis of biologically interesting substances.[1,2] Derivatives of ferrocene have been extensively investigated as optically active ligands in catalysis.[3] In contrast, the use of (arene)chromium complexes as chiral ligands has been significantly less explored with only a small selection of such ligands reported to date (Figure 1). In spite of this, a variety of (arene)$Cr(CO)_3$-based chiral ligands have been successfully used in asymmetric C–C bond formation reactions, such as cross-coupling reactions,[4] addition of dialkylzinc to benzaldehyde,[5] 1,4-additions to Michael acceptors,[5,6] hydrovinylations,[7] 1,2-additions of phenylboroxines to imines[6] and nucleophilic substitutions.[6b,8] Such ligands have also been employed in asymmetric reductions,[8b,9] hydroaminations,[8b] hydroborations,[10] and hydrosilylations.[11]

Formation of optically active (arene)chromium species is usually accomplished by means of either resolution of racemates,[12] or asymmetric synthesis via diastereoselective complexation,[13] diastereo- or enantioselective deprotonation/electrophile quenching,[14] and nucleophilic addition/hydride abstraction sequences[15] (Scheme 1a–c). All these methods employ stoichiometric chiral reagents or auxiliaries. Additionally, many of these processes are hampered by the use of sensitive organometallic reagents, poor functional group compatibility, and/or low atom economy. Conversely, the more attractive access to nonracemic (arene)chromium complexes via asymmetric catalysis has been significantly less explored. Uemura first reported the desymmetrization of *o*-

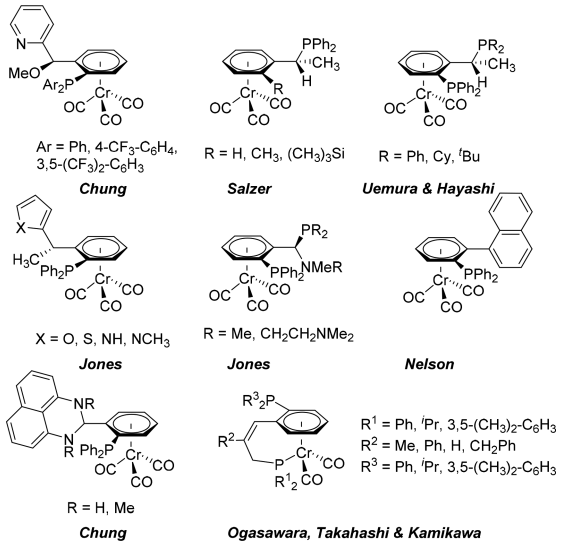


Figure 1. Representative (η^6-arene)$Cr(CO)_3$ complexes used as planar-chiral ligands in asymmetric catalysis.

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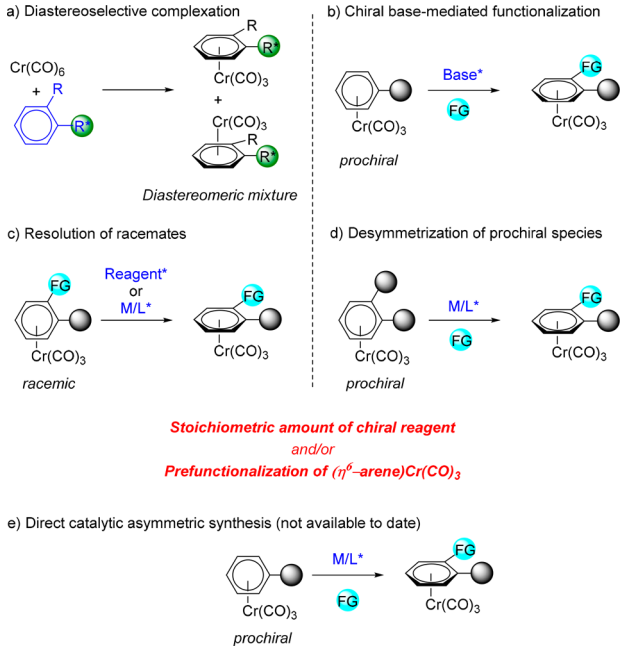
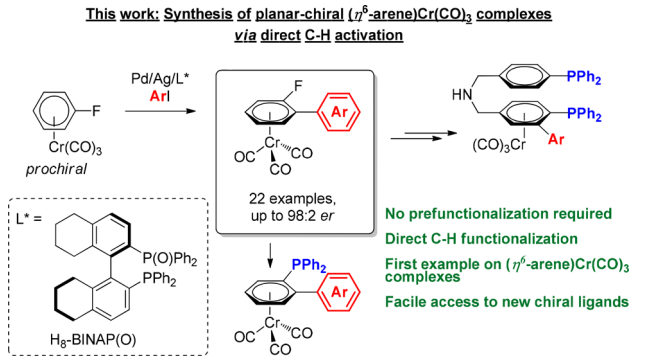
Scheme 1. Synthesis of Planar-Chiral (Arene)$Cr(CO)_3$ Complexes



Scheme 2. Synthesis of Planar-Chiral (Arene)$Cr(CO)_3$ Complexes via C−H Activation



dichlorobenzene chromium tricarbonyl complexes via asymmetric Pd-catalyzed cross-coupling with various vinylic metals.[16] Subsequently, several examples of desymmetrization of suitably difunctionalized (arene)chromium complexes have been reported, including methoxycarbonylation[17] or hydrogenolysis of haloarene-chromium derivatives,[18] intramolecular Mizoroki-Heck reactions,[19] gold-catalyzed intramolecular nucleophilic additions[20] and Mo-catalyzed kinetic resolution[6a] (Scheme 1d). In all of these cases, prefunctionalization of the η^6-complexed arene is required. In contrast, a catalytic asymmetric approach to planar-chiral (arene)chromium complexes from nonprefunctionalized starting materials has never been reported (Scheme 1e).

While transition-metal catalyzed asymmetric C−H functionalization faces the challenge of discriminating between "inert" enantiotopic C−H bonds, it provides a straightforward approach for the preparation of chiral molecules.[21] Several strategies have been developed to introduce central- and axial-chirality by enantioselective C−H bond activation.[22] However, the use of asymmetric C−H bond functionalization for the creation of planar chirality has been relatively underexplored and limited exclusively to ferrocenes.[23] These methods all rely on the formation of a chiral metallacyclic intermediate via an intramolecularly directed C−H activation.[24,25] Thus, they are limited to substrates with suitable directing groups, reducing the generality and applicability of the process. To the best of our knowledge, there are no methods reported to synthesize enantioenriched planar-chiral chromium tricarbonyl complexes from unfunctionalized precursors in a catalytic fashion. In this paper, we report the first catalytic direct asymmetric C−H arylation of simple prochiral (η^6-fluoroarene)chromium complexes (Scheme 2). In addition, we demonstrate that the enantioenriched products can be easily converted into planar-chiral phosphines providing access to an array of novel (arene)chromium-based chiral phosphine ligands.

2. RESULTS AND DISCUSSION

2.1. Optimization of the Conditions of the Direct Asymmetric C−H Arylation. We have recently demonstrated that (fluoroarene)$Cr(CO)_3$ complexes such as **1a** can undergo Pd-catalyzed/Ag-mediated direct arylation affording excellent yields of *ortho*-substituted biaryls with high regioselectivity.[26] A combination of stoichiometric and kinetic mechanistic studies showed that PPh_3 ligated Ag(I)-carboxylates are responsible for the C−H activation step.[27] With this in mind, we envisaged that the process could be rendered asymmetric in the presence of a chiral phosphine ligand suitable for distinguishing between the two enantiotopic C−H bonds of a prochiral complex. Furthermore, the presence of a C−F bond in the aromatic core should allow for the subsequent easy transformation of the resulting products into chiral arylphosphine derivatives via phosphination.[28]

We started our investigation testing similar conditions to those reported for the (nonasymmetric) *ortho*-arylation of (fluorobenzene)$Cr(CO)_3$ (**1a**) complexes[26a] as a benchmark for reactivity. Under these conditions good reactivity was observed with 41% of racemic monoarylated product **3aa** and 31% of bisarylated **4aa** formed (Table 1, entry 1). We then replaced $Pd(PPh_3)_4$ with $Pd(dba)_2$ and (*S*)-BINAP (**L1**), but under these conditions no reactivity was observed (entry 2). We had previously observed that the use of the highly hindered amine TMP (2,2,6,6-tetramethylpiperidine) as an additive enhances the reactivity of η^6-coordinated arenes toward C−H arylation.[29] Gratifyingly, the use of this additive promoted the reaction, forming monoarylated chromium complex **3aa** in 28% yield and a low but promising enantioselectivity (38:62 *er*) (entry 3). A screen of Pd(II) sources revealed that $Pd(CH_3CN)_4(BF_4)_2$ gave similar yield to $Pd(dba)_2$ with a slightly higher enantiomeric ratio (entry 4). Given that the carboxylic acid is involved in the C−H activation step, we expected the enantioselectivity of the process to be heavily influenced by the nature of the carboxylate. Indeed, carboxylic acid screening showed that dicyclohexylacetic acid enhanced both the reactivity and, importantly, the enantioselectivity (*er*: 18:82−16:84, entries 5 and 6). Conversely, reaction in the absence of the carboxylic acid gave a low yield of arylation and the enantiomeric ratio dropped to 55:45 (entry 7). Reactivity was completely shut down in the absence of silver carbonate (entry 8), whereas in the absence of K_2CO_3 a slightly lower yield and enantioselectivity were obtained (entry 9).[30] Unreacted starting material was observed in all reactions. In some cases, free arene(s) was detected due to decomplexation

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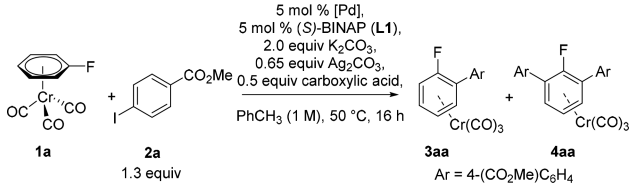
Table 1. Optimization of the Asymmetric C−H Arylation of Complex 1a with 2a



Entry	Conditions	Yield **3aa** (%)[a]	*er* **3aa**[b]	Yield **4aa** (%)[a]
1[c]	$Pd(PPh_3)_4$, 1-$AdCO_2H$	41	–	31
2	$Pd(dba)_2$, 1-$AdCO_2H$	0	–	0
3	$Pd(dba)_2$, 1-$AdCO_2H$, 2 equiv TMP	28	38:62	9
4	$Pd(CH_3CN)_4(BF_4)_2$, 1-$AdCO_2H$, 2 equiv TMP	28	36:64	7
5	$Pd(CH_3CN)_4(BF_4)_2$, Cy_2CHCO_2H, 2 equiv TMP	39	18:82	33
6[d]	$Pd(CH_3CN)_4(BF_4)_2$, Cy_2CHCO_2H, 2 equiv TMP	43	16:84	39
7[d]	$Pd(CH_3CN)_4(BF_4)_2$, 2 equiv TMP	24	55:45	2
8[d,e]	$Pd(CH_3CN)_4(BF_4)_2$, Cy_2CHCO_2H, 2 equiv TMP	0	–	0
9[d,f]	$Pd(CH_3CN)_4(BF_4)_2$, Cy_2CHCO_2H, 2 equiv TMP	40	19:81	27

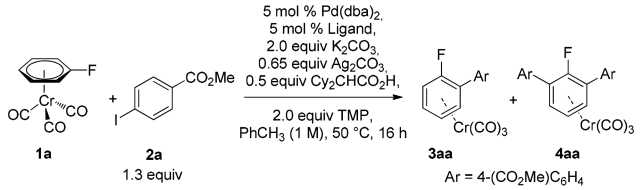
[a]Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b]Determined by HPLC (Chiralpak IB hexane/isopropyl alcohol). [c]Reaction carried out without **L1**. [d]Reactions carried out with 2 equiv of ArI. [e]Reaction carried out without Ag_2CO_3. [f]Reaction carried out without K_2CO_3.

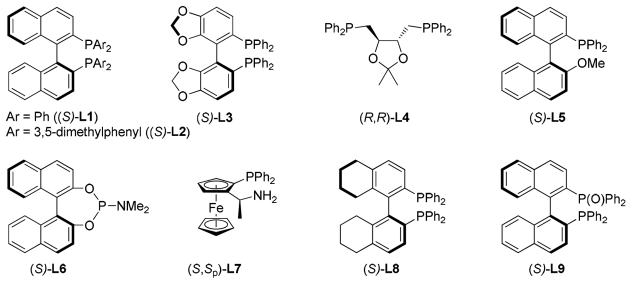
of starting material and/or product and/or bisarylated byproduct.

We then set out to explore a variety of chiral ligands (Table 2). In comparison with BINAP (**L1**), the more sterically hindered 3,5-xylyl-BINAP (**L2**) gave a similar arylation yield but significantly lower enantioselectivity (Table 2, entries 1 and 2). On exploring the effect of the bite angle, we found that SegPhos (**L3**), with its smaller bite angle than **L1**, decreased the enantiomeric ratio while keeping similar reactivity; DIOP (**L4**), which has a larger bite angle than **L1**, also gave very low enantioselectivity (entries 3 and 4), suggesting that bite angles similar to that of **L1** were ideal for this transformation. Good conversion but low *er* was observed when the monophosphine MeO-MOP (**L5**) was used (entry 5). Phosphoramidite MonoPhos (**L6**) and the P,N-ligand PPFA (**L7**) both completely inhibited the reaction (entries 6 and 7), while H_8-BINAP (**L8**) led to similar reactivity to its unsaturated counterpart BINAP (**L1**) but with slightly higher *er* (entry 8). Finally, we tested BINAP(O) (**L9**), a ligand that has been rarely used in asymmetric catalysis,[31] which contains both a strong and a weak donor atom, providing it the ability to act as a di- or monodentate ligand. Interestingly, in the presence of this hemilabile ligand, the yield and enantioselectivity of the process increased up to 47% and 14:86 *er*, respectively (entry 9).

2.2. Synthesis and Reactivity of H_8-BINAP(O) and H_8-BINAP Derivatives. As the best results of reactivity and selectivity were found when H_8-BINAP (**L8**) and BINAP(O) (**L9**) were used as chiral ligands, we decided to synthesize H_8-BINAP(O) and other partially hydrogenated BINAP variants to test them as chiral ligands in the C−H asymmetric arylation of chromium complexes.

Table 2. Screening of Chiral Ligands in the Asymmetric C−H Arylation of Complex 1a with 2a



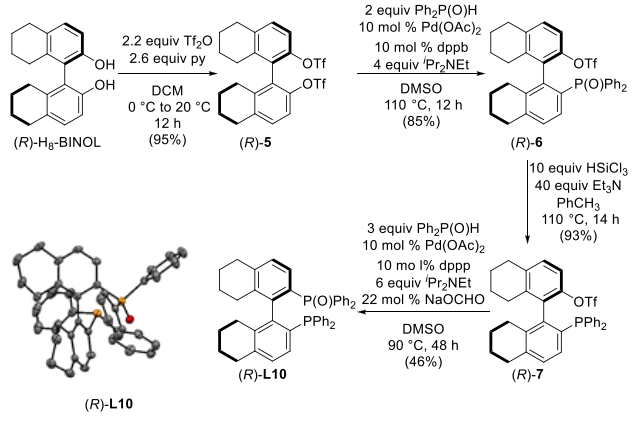


Entry	Ligand	Yield **3aa** (%)[a]	*er* **3aa**[b]	Yield **4aa** (%)[a]
1	(*S*)-**L1**	42	18:82	31
2	(*S*)-**L2**	40	32:68	26
3	(*S*)-**L3**	45	25:75	28
4	(*R,R*)-**L4**	39	51:49	29
5	(*S*)-**L5**	46	46:54	34
6	(*S*)-**L6**[c]	0	–	0
7	(S,S_p)-**L7**[c]	0	–	0
8	(*S*)-**L8**	40	16:84	31
9	(*S*)-**L9**	47	14:86	25

[a]Determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b]Determined by HPLC (Chiralpak IB hexane/isopropyl alcohol). [c]Reactions carried out with 10 mol % of ligand.

(*R*)-(2′-(Diphenylphosphanyl)-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalen]-2-yl)diphenylphosphine oxide ((*R*)-H_8-BINAP(O), (*R*)-**L10**)[32] was prepared in four steps following a methodology similar to that used for the synthesis of its unsaturated analogue BINAP(O) (Scheme 3).[33] The preparation of (*R*)-**L10** from commercially available (*R*)-H_8-BINOL was accomplished by sequential substitution of the homotopic triflate groups of (*R*)-**5** by diphenylphosphine oxide.[34,35] The absolute configuration of the final product (*R*)-**L10** was

Scheme 3. Synthesis and ORTEP Plot of (*R*)-H_8-BINAP(O) Ligand (*R*)-L10[a]



[a]All hydrogen atoms are omitted for clarity.

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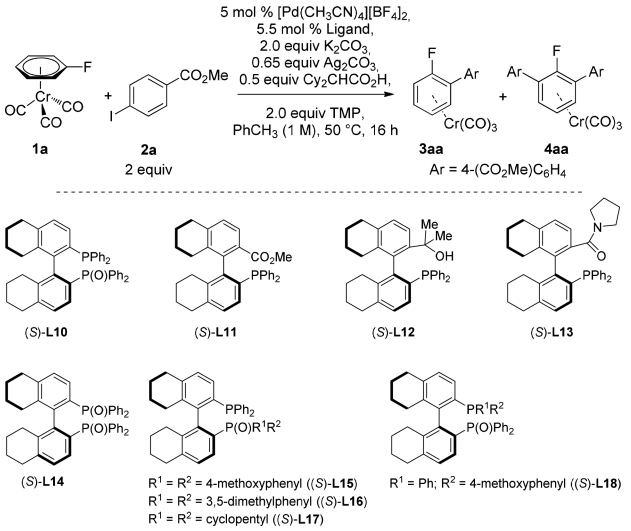
confirmed by X-ray diffraction analysis (Scheme 3). With the aim of investigating the influence on the modification of electronic and steric properties of the H_8-BINAP(O) ligand on the reactivity and enantioselectivity of the reaction, we synthesized a range of H_8-BINAP derivatives (**L11**−**L18**) following similar experimental procedures to those reported for their BINAP analogues (see Supporting Information).[36]

Gratifyingly, when H_8-BINAP(O) (**L10**) was tested as the ligand, high reactivity and enantioselectivity were observed for the arylation of **1a** (Table 3, entry 1). We then tested ligands

Table 3. Screening of H_8-BINAP Derivatives in the Asymmetric C−H Arylation of Complex 1a with 2a



Entry	Ligand	Yield **3aa** (%)[a]	*er* **3aa**[b]	Yield **4aa** (%)[a]
1	(*S*)-**L10**	42	7:93	27
2	(*S*)-**L11**	33	46:54	16
3	(*S*)-**L12**	27	46:54	7
4	(*S*)-**L13**	37	27:73	22
5	(*S*)-**L14**	33	50:50	19
6	(*S*)-**L15**	46	10:90	24
7	(*S*)-**L16**	37	20:80	20
8	(*S*)-**L17**	37	27:73	22
9	(*S*)-**L18**	40	18:82	22

[a]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [b]Determined by HPLC (Chiralpak IB hexane/isopropyl alcohol).

in which the weaker donor atom of the mono-oxidized H_8-BINAP(O) was substituted by different functional groups. When the chiral ligand contained an ester group (**L11**) reactivity decreased while the product obtained was almost racemic (entry 2). A similar result was observed with a ligand bearing an alcohol substituent (**L12**) (entry 3). Interestingly, the more coordinating amide-derivative (**L13**) yielded 37% of product **3aa** with a moderate 27:73 *er* (entry 4). These results demonstrate that the oxidized phosphine is essential to achieve high enantioselectivity. To evaluate the influence of the phosphine fragment, we tested the bis-oxidized H_8-BINAP ligand (**L14**). This led to a racemic product in similar yield to that obtained in the absence of chiral ligand (29% of **3aa** and 12% of **4aa**), indicating that the phosphine moiety is necessary for coordination to the metal center. Once we had established that the combination of phosphine−phosphine oxide is the most adequate for achieving high reactivity and enantioselectivity, we decided to investigate the influence of the substituents in both of these groups. A ligand containing the P(O)(4-methoxyphenyl)$_2$ fragment (**L15**) gave analogous results to H_8-BINAP(O) ligand (**L10**) in terms of both reactivity and *er* (entry 6). However, when the phenyl groups were replaced by 3,5-dimethylphenyl groups (**L16**), both reactivity and enantioselectivity decreased (entry 7). The same scenario, but with even lower *er*, was observed when the aryl groups of the oxidized phosphine were replaced by alkylic cyclopentyl fragments (**L17**) (entry 8). Finally, replacing the phenyl groups in the PPh_2 fragment with the more electron-donating 4-methoxyphenyl substituents (**L18**), led to only a moderate enantiomeric ratio (entry 9).

2.3. Enantioselective C−H Activation of (η^6-Fluoroarene)Cr(CO)$_3$ Complexes. With the optimized conditions for the asymmetric arylation reaction, we set out to explore the generality of the methodology with respect to the fluoroarene chromium complex (Scheme 4a). Unsubstituted fluoroarene chromium derivatives showed good reactivity and *er* (**3aa**,**ab**). The presence of a methyl substituent on the fluoroarene did not produce a significant difference in terms of yield or enantiomeric ratio (**3bb**); however, when the substituent was an ester or a methoxy group a slight decrease in the enantiomeric ratio was observed (**3cb**,**db**). Interestingly, when the fluoroarene core contains a masked aldehyde in the form of a 1,3-dioxane group, the enantioenriched product was obtained in a 97:3 enantiomeric ratio (**3eb**). Different protecting groups for the aldehyde gave similar results of yield and enantioselectivity to 1,3-dioxane (**3fb**,**gb**,**fc**). The absolute configuration of the planar-chiral products could be unambiguously confirmed by X-ray diffraction analysis of a monocrystal of enantioenriched **3aa**, showing that when (*R*)-**L10** is used as a chiral ligand, the major isomer obtained is (S_p)-**3aa** (Figure 2)

Then, we turned our attention to the effect of substitution at the iodoarene coupling partner (Scheme 4b). A variety of functional groups at the *para*- and *meta*-positions of iodoarenes, including electron-donating and electron-withdrawing substituents, were tolerated, affording the corresponding chiral biaryl chromium complexes **3** in moderate yield and high enantioselectivities. The reaction is compatible with carbonyl functionalities such as ester, ketone, and aldehydes (**3ea**,**ek**,**el**). Nitrogen-containing substituents, such as nitro (**3ed**) and cyano (**3ec**), can be present on the iodoarene. The reaction is also compatible with Br and Cl substituents (**3eg**,**em**), which would allow for further functionalization via cross-couplings, CF_3 substituents (**3ef**) and 3,5-disubstituted iodoarenes (**3eo**). For *p*-substituted iodoarenes, higher *er* values are obtained with electron-poor arenes (**3ea**−**3eg**) than with electron-rich derivatives (**3ei**). However, similar enantioselectivities were observed for *m*-substituted iodoarenes regardless of their electronic properties (**3ek**−**3en**). On the other hand, *ortho*-substituted iodoarenes showed low reactivity (**3ap**,**aq**).

Analysis over time of the reaction of **1e** with **2b** shows that at low conversions the product **3eb** is formed in 92:8 *er*. However, the *er* increases steadily throughout the reaction, in parallel to the formation of bisarylation product **4eb**, with *er* reaching 98:2 when 27% of bisarylated **4eb** has been formed (see SI). This suggests that the observed *er* values in Scheme 4 are the result of an asymmetric C−H arylation step compounded with a kinetic resolution of the product.

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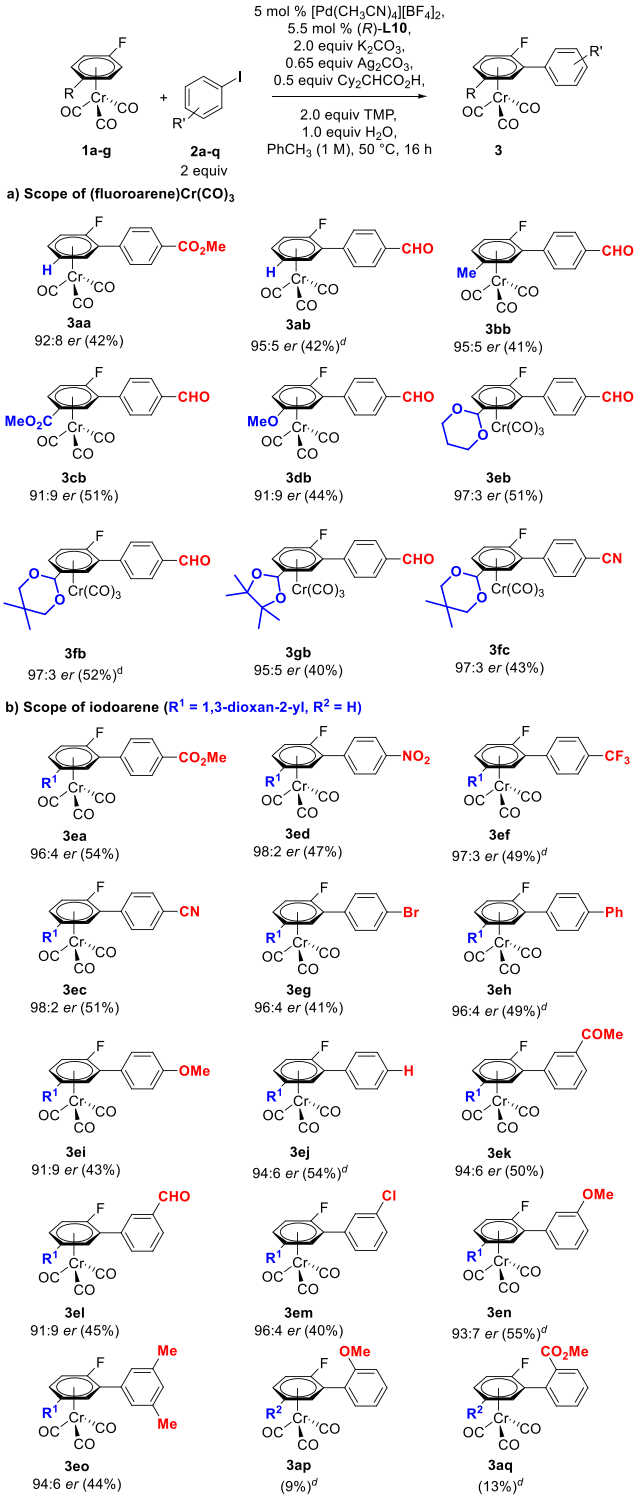
Scheme 4. Scope of the Asymmetric Arylation of (Fluoroarene)Cr(CO)$_3$ 1a−g with Iodoarenes 2a−q[a,b,c]



[a]Reactions performed at 0.1 mmol scale. [b]*er* determined by chiral HPLC. [c]Isolated yields in brackets. [d]Yield determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

2.4. Mechanistic Studies. *2.4.1. Role of Ag(I) Salts in Asymmetric Arylation of (Fluoroarene)Cr(CO)$_3$ Complexes.* Recent studies by our group on Pd-catalyzed direct functionalization of aryl C−H bonds in the presence of silver salts revealed that phosphine ligated silver carboxylate can metalate the C−H bonds in arenes bound to a Cr(CO)$_3$ fragment;[27] the resulting arylsilver(I) complex is then proposed to transfer its aryl moiety to a palladium intermediate. Similar conclusions were also drawn by Sanford[37] and Hartwig,[38] in the case of thiophenes and (poly)fluoroarenes, and we have recently exploited this activation mode to develop the first direct *α*−arylation of benzo[*b*]thiophenes and thiophenes at room temperature.[39]

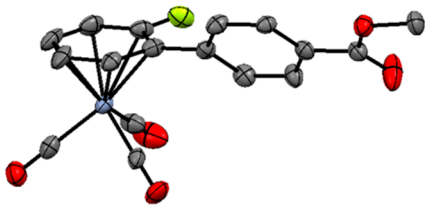
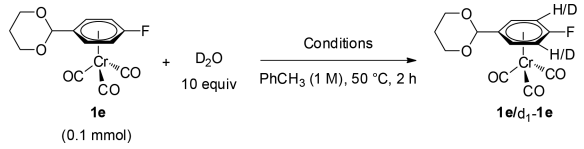


Figure 2. ORTEP plot of the major enantiomer of **3aa**, obtained using (*R*)-**L10** ligand. All hydrogen atoms are omitted for clarity.

As this reaction did not proceed in the absence of silver (Table 1, entry 8), we hypothesized that in this case the silver salt would also be involved in the C−H bond cleavage step. To test this hypothesis, we studied the H/D exchange of **1e** with 10 equiv of D_2O in the presence of different combinations of additives (Table 4). No deuteration was observed when **1e** was submitted to the standard reaction conditions in the absence of the silver salt (Table 4, entry 1). Deuterated complex d$_1$-**1e** was not detected when the reaction was carried out only in the presence of Ag_2CO_3 (entry 2), or in combination with the chiral ligand **L10** with or without the carboxylic acid (entries 3−4). Importantly, in entries 2−4, the silver salt was appreciably insoluble in toluene. On the other hand, addition of TMP to Ag_2CO_3 led to formation of 32% of d$_1$-**1e** (entry 5). This is consistent with a higher solubility of the Ag-salt either through coordination or increased solvent polarity. Addition of 5.5 mol % of **L10** led to an increased H/D exchange of 54% (entry 6), consistent with an enhanced rate of C−H activation of the **Ag-L10** complex. Similarly enhanced H/D exchange was obtained when both **L10** and the carboxylate were added in the presence of TMP (entry 7). Interestingly, ^{1}H and ^{31}P NMR analysis of the reaction mixture in entry 7 revealed the presence of a **Ag-L10** complex. These results are consistent

Table 4. H/D Exchange Experiments of 1e[a]



Entry	Conditions	d$_1$-**1e** (%)[a]
1	Standard conditions without Ag_2CO_3	0
2	0.65 equiv Ag_2CO_3	0
3	0.65 equiv Ag_2CO_3, 5.5 mol % (*R*)-**L10**	0
4	0.65 equiv Ag_2CO_3, 5.5 mol % (*R*)-**L10**, 0.5 equiv Cy_2CHCO_2H	0
5	0.65 equiv Ag_2CO_3, 2 equiv TMP	32
6	0.65 equiv Ag_2CO_3, 5.5 mol % (*R*)-**L10**, 2 equiv TMP	54
7	0.65 equiv Ag_2CO_3, 5.5 mol % (*R*)-**L10**, 0.5 equiv Cy_2CHCO_2H, 2 equiv TMP	48

[a]Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

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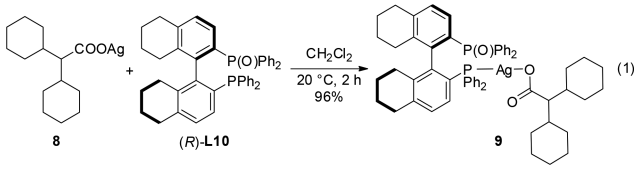
with a silver(I)-mediated C−H activation step in operation under the present reaction conditions that likely involves a coordinated **L10** ligand.

Reaction of silver carboxylate **8** with 1 equiv of (*R*)-H_8-BINAP(O) ((*R*)-**L10**) in CH_2Cl_2 at room temperature afforded the phosphine-ligated Ag(I) carboxylate **9** in 96% yield (eq 1). Its structure was confirmed by X-ray diffraction



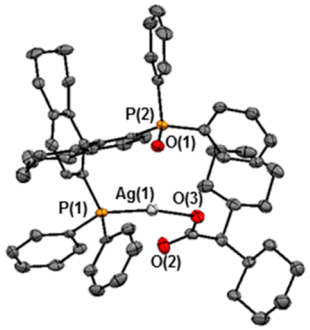


Figure 3. ORTEP plot of (*R*)-H_8-BINAP(O)-ligated silver carboxylate **9**. Selected bonds and angles: P(1)−Ag(1), 2.330(2) Å; P(2)−Ag(1), 3.463(2) Å; O(1)−Ag(1), 3.270 (4) Å; O(2)−Ag(1), 2.797 (5) Å; O(3)−Ag(1), 2.107 (5) Å; O(3)−Ag(1)−P(1), 123.35°. All hydrogen atoms omitted for clarity.

analysis (Figure 3). ^{1}H and ^{31}P NMR analysis of **9** matched with those observed in the reaction mixture of Table 4, entry 7, confirming the presence of the **Ag-L10** complex.[38,40] Furthermore, ^{31}P NMR analysis of the reaction of **1e** with **2i** under our standard conditions, after 2 h (Figure 4a), clearly showed resonances corresponding to the (*R*)-H_8-BINAP(O)-ligated silver carboxylate **9**, strongly suggesting its participation in the catalytic cycle (Figure 4b).

Interestingly, another smaller set of signals, presumably corresponding to a PdL* compound, were present in the ^{31}P NMR spectrum of the reaction mixture (Figure 4a). We speculated that these could correspond to Pd-complexes **11** or **12** (Scheme 5). Complex **11** was synthesized via the Buchwald-type palladium derivative **10**,[41] which underwent smooth oxidative addition with 4-iodoanisole to give **11** (Scheme 5). The structure of **11** was confirmed by single-crystal X-ray diffraction analysis (Figure 5). **12** was prepared from **11** by reaction with AgO_2CCHCy_2 (**8**). Comparison of the ^{31}P NMR of both **11** and **12** with those observed in the analysis of the catalytic reaction mixture, revealed that the small set of signals in the latter corresponded to **12** (Figure 4c). This analysis highlights that the ligand **L10** can coordinate to both Ag and Pd in the reaction. While qualitative analysis suggests that the majority of **L10** would be coordinated to Ag, it cannot be discarded that it also plays a role in the reactivity of the Pd-species.

2.4.2. Proposed Catalytic Cycle. From the experiments above and previous work in the field,[27] we propose the bimetallic catalytic cycle outlined in Scheme 6 to be in

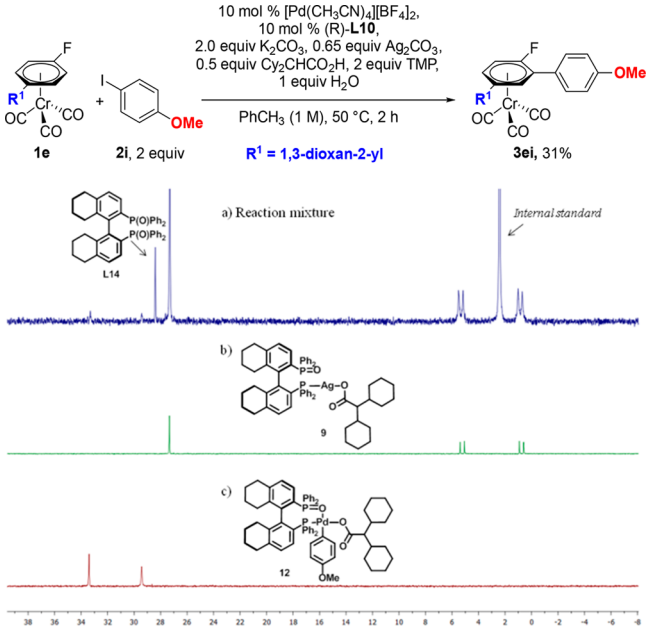
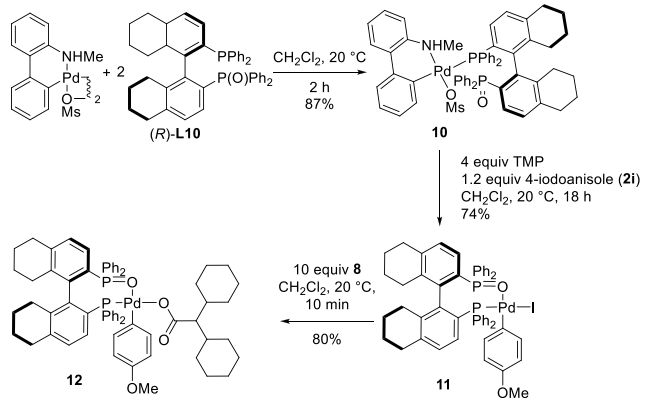


Figure 4. ^{31}P NMR spectra in $CDCl_3$ of (a) reaction mixture of **1e** with **2i** under asymmetric catalytic conditions after 2 h; (b) (*R*)-H_8-BINAP(O)-ligated silver carboxylate **9**; (c) L*PdAr-carboxylate **12**.

Scheme 5. Synthesis of H_8-BINAP(O)-Ligated Palladium Complexes



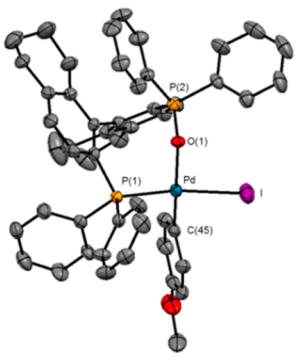


Figure 5. ORTEP plot of (*R*)-H_8-BINAP(O)-ligated IArPd complex **11**. Selected bonds and angles: I−Pd, 2.6352(9) Å; Pd−P(1), 2.282(2) Å; Pd−O(1), 2.234(6) Å; Pd−C(45), 1.980(10) Å; P(1)−Pd−I, 167.66(6)°; O(1)−Pd−I, 93.88(17)°; O(1)−Pd−P(1), 87.32(18)°; C(45)−Pd−I, 85.8(3)°; C(45)−Pd−P(1), 94.1(3)°; C(45)−Pd−O(1), 174.7(3)°. All hydrogen atoms are omitted for clarity.

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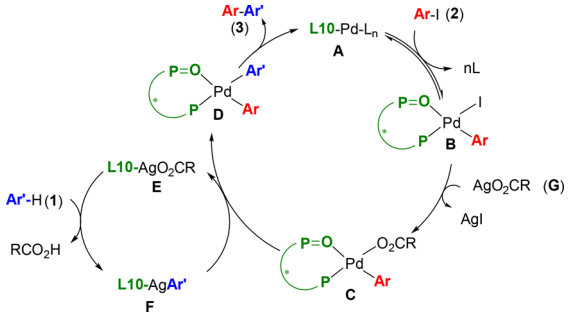
Scheme 6. Proposed Mechanism



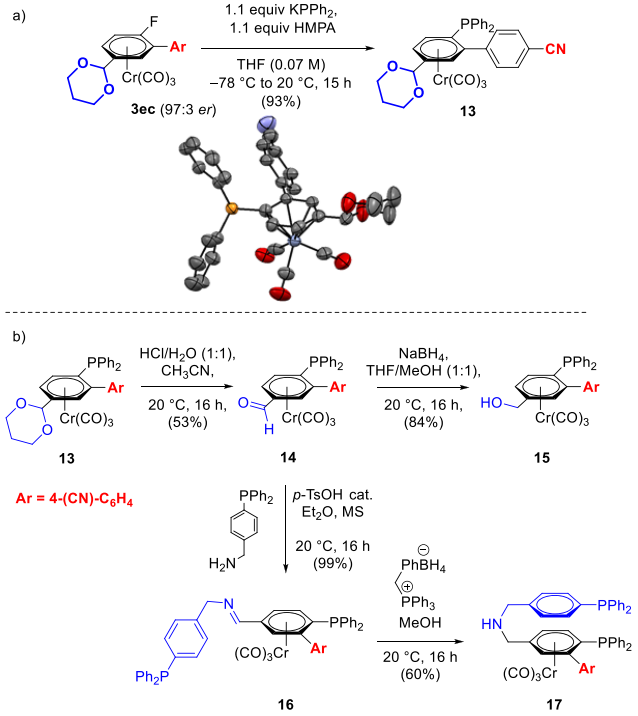
operation. In this mechanism, a Pd(0)-**L10** complex **A** undergoes oxidative addition to **B**, which after transmetalation affords arylcarboxylate-Pd derivative **C**, structurally related to complex **12**. In a parallel catalytic cycle, silver carboxylate **E** carries out C−H activation on η^6-coordinated arene **1** to form arylsilver intermediate **F**, presumably by a carboxylate assisted CMD mechanism.[37] Transmetalation from silver intermediate **F** to the palladium-arylcarboxylate **C**[38] would form **D**, which would in turn release the product **3** after reductive elimination. We propose that **L10** is coordinated to both Ag and Pd, throughout the process. Two possible enantiodetermining steps must thus be considered: an enantioselective C−H activation by complex **E**, followed by a fast transmetalation with **C**, or alternatively a fast reversible C−H activation, followed by a rate and enantioselectivity determining transmetalation. However, further experiments will be necessary to understand this process fully, which is further complicated by the low solubility of some of the species in toluene.

2.5. Synthesis and Derivatization of Enantioenriched Planar-Chiral (Arene)Chromium Tricarbonyl Phosphines. The presence of a C−F bond in the aromatic core of the chiral (arene)chromium complexes allows easy functionalization via a variety of nucleophilic aromatic substitutions,[42] including phosphination reactions, to obtain arylphosphine derivatives easily.

Nelson and co-workers investigated the effectiveness of optically active arylmonophosphine Cr-complexes as ligands in asymmetric catalysis in the Pd(II)-catalyzed alkylation of allylic acetates under Trost's conditions,[8b] thus demonstrating that chromium-complexed arylphosphines provide chiral equivalents of triarylphosphine ligands that are ubiquitous in late transition-metal chemistry and catalysis. To test the applicability of our approach for the synthesis of new planar-chiral phosphines we carried out the asymmetric arylation of **1e** with 4-iodobenzonitrile (**2c**) at 1 mmol scale under the standard catalytic conditions. Enantioenriched product **3ec** was obtained in 48% yield with 97:3 *er*. Reaction of **3ec** with potassium diphenylphosphide resulted in nucleophilic aromatic substitution to afford the chiral planar triarylphosphine (S_p)-**13** in 93% yield and 97:3 enantiomeric ratio. The structure and absolute stereochemistry of **13** was confirmed by X-ray diffraction analysis (Scheme 7a).

The protected aldehyde on **13** provides an ideal handle for further derivatization and tuning of electronic properties of this chiral phosphine. Accordingly, treatment of **13** under acidic conditions revealed the aldehyde to obtain **14**, which could then be reduced by $NaBH_4$ to the alcohol derivative **15** (Scheme 7b). Both the aldehyde in **14** and the alcohol in **15** could then be easily transformed into a variety of functionalities. Over the past few decades, chiral diphosphines

Scheme 7. (a) Synthesis and ORTEP Plot of 13[a]; (b) Derivatization of Planar-Chiral Monophosphines, and Synthesis of Novel Planar-Chiral Diphosphines



[a]All hydrogen atoms omitted for clarity.

have proven to be among the most useful and versatile ligands for metal-catalyzed asymmetric reactions and the design and preparation of such diphosphines remains as active an area of research as ever.[43] The synthesis of C_2-symmetric diphosphine ligands has long received the most attention, due perhaps to the relative ease of obtaining these molecules.[44] However, studies have showed that C_2 symmetry is not a necessary condition for attaining high enantioselectivity in catalysis.[45] Our functionalized planar chiral phosphines, such as **14** and **15**, are ideal starting points for the synthesis of novel classes of planar chiral diphosphines. Reaction of the aldehyde derivative **14** with *p*-(diphenylphosphino)benzylamine in the presence of a catalytic amount of acid afforded the diphosphine-imine derivative **16** in quantitative yield. This compound can be reduced by benzyltriphenylphosphonium tetrahydroborate to give the corresponding chiral amine-diphosphine derivative **17**, providing a novel class of bidentate chiral phosphines (Scheme 7b).

3. CONCLUSIONS

In conclusion, we have developed the first protocol for catalytic direct C−H asymmetric arylation of (η^6-arene)-chromiumtricarbonyl complexes to afford enantioenriched planar-chiral products in one step. The development of this methodology required the synthesis of a new family of H_8-BINAP derivatives, finding that H_8-BINAP(O) was the most suitable chiral ligand for the reaction. Optimized catalytic conditions were applied to a variety of iodoarenes and (fluoroarene)$Cr(CO)_3$ complexes affording the corresponding chiral products in good yield and excellent enantioselectivity. Mechanistic studies suggest that the reaction proceeds through a Pd/Ag bimetallic double catalytic cycle where the C−H

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activation is carried out by Ag. These enantioenriched aryl-complexes can be used for the synthesis of chiral planar monodentate phosphines and a new class of chiral planar bidentate phosphines. The application of these new chiral ligands to asymmetric catalysis is currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b00918.

Experimental procedures and characterization data (PDF)

Data for $C_{44}H_{40}OP_2$ (CIF)

Data for $C_{58}H_{63}AgO_3P_2$, $C_4H_{10}O$, $0.78(H_2O)$ (CIF)

Data for $C_{17}H_{11}CrFO_5$ (CIF)

Data for $C_{32}H_{24}CrNO_5P$, C_5H_{12} (CIF)

Data for $C_{51}H_{47}IO_2P_2Pd$, CH_2Cl_2 (CIF)

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Notes

The authors declare no competing financial interest.

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