Communication

Lewis Acid Activation of Carbodicarbene Catalysts for Rh-Catalyzed Hydroarylation of Dienes.

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J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 11 May 2015

Lewis Acid Activation of Carbodicarbene Catalysts for Rh-Catalyzed Hydroarylation of Dienes.

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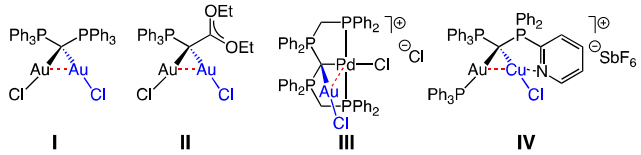
Supporting Information Placeholder

ABSTRACT: The activation of carbodicarbene-Rh(I) pincer complexes by secondary binding of metal salts is reported for the catalytic site-selective hydro-heteroarylation of dienes (up to 98% yield and >98:2 γ:α). Reactions are promoted by 5 mol % of a readily available tridentate carbodicarbene-Rh complex in the presence of an inexpensive lithium salt. The reaction is compatible with a variety of terminal and internal dienes and tolerant of esters, alkyl halides, and vinyl boron functional groups. X-ray data and mechanistic experiments provide support for the role of the metal salts on catalyst activation and shed light on the reaction mechanism. The increased efficiency (120 to 22 °C) made available by catalytic amounts of metal salts to catalysts containing C(0) donors is a significant aspect of the disclosed studies.

Development of catalytic methods that directly employ readily available unsaturated hydrocarbons represents an important objective in chemical synthesis. A subgroup of these reaction types is catalytic intermolecular hydroarylation, a highly atom-economical process involving the net C–H addition across an unsaturated C–C bond.[1,2,3] Metal π-acid catalysts are effective promoters for such transformations, wherein the C=C bond is rendered electrophilic and susceptible to addition by arene nucleophiles.[4] Reactions typically proceed at elevated temperatures (70–135 °C) in the presence of a cationic Pt,[4d-f] or Au[4e-i] catalyst with electron-rich alkenes, and are generally inhibited by Lewis-basic functionality,[4i] a problem also common to catalytic hydroamination.[5] To address some of these limitations we initiated a program to develop new catalysts and catalytic methods that enable the addition of nucleophiles to C–C double bonds. We previously developed Rh(I) complexes supported by pincer carbodicarbene (CDC) ligands that efficiently catalyze the hydroamination of 1,3-dienes with aryl and alkyl amines (35–120 °C).[6]

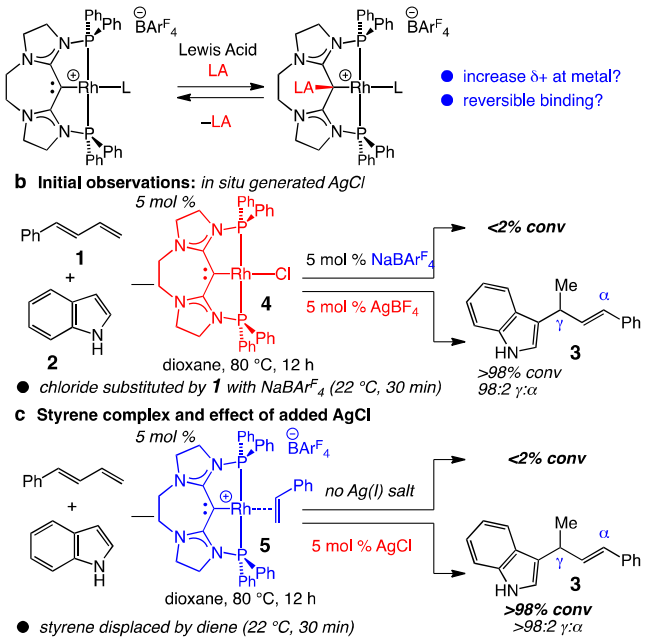
Divalent carbon(0) compounds, such as CDCs and carbodiphosphoranes (CDPs), represent an emerging area in ligand development for transition metal catalysis and provide strategies to access new modes of reactivity.[7] Principal to their reactivity is a divalent carbon(0) supported by two L-type donor groups.[8] Unlike their carbon(II) analogs, N-heterocyclic carbenes (NHCs), the reactivity profile of carbon(0) ligands is centered around two lone-pairs of electrons that are available for binding to Lewis acids. Homo- and heterobimetallic transition metal complexes of carbon(0) have been reported, and primarily employ CDP ligand frameworks and coinage metals (**I**–**IV** Chart 1).[9] Strong electron donor properties paired with the ability to form dinuclear species provides a framework to electronically and sterically modify catalyst reactivity profiles through binding of a second Lewis acid to the carbon(0) either temporarily or permanently. The use of carbon(0) bimetallic complexes as catalysts, or the application of Lewis acids to alter catalyst reactivity by secondary binding to carbon(0) ligands in catalysts, has not been reported.[10,11]

Chart 1. Bimetallic Complexes of Carbon(0) Ligands



Herein, we report the remarkable increase in catalyst reactivity (120 °C to 22 °C) of (CDC)-Rh(I) complexes in intermolecular hydroarylations caused by catalytic amounts of metal salt additives. Reactions proceed in the presence of 5 mol % of a readily available Rh(I) complex with terminal and 1,4-disubstituted dienes and a variety of N-heterocyclic arenes.[12] Mechanistic evidence is provided through protonation studies that show secondary binding to the carbon(0) donor results in a more electron deficient Rh center and increased positive charge at a bound alkene. An outline of the activation strategy for our studies is shown in Scheme 1a. Reversible binding of a Lewis acid to a (CDC)-Rh(I) complex will result in decreased electron density at Rh(I) when a Lewis

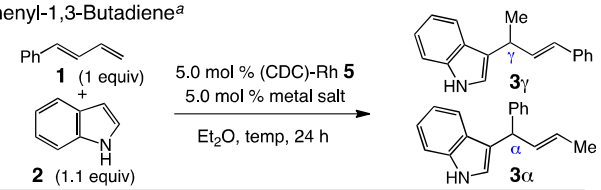
Scheme 1. Pincer (CDC)-Rh-Catalyzed Electrophilic C=C Activation



acid is bound, rendering the Rh(I) more activating towards π acids.

We began our investigations with Rh–Cl complex **4** (Scheme 1b). Treatment of indole and diene **1** with 5 mol % **4** and 5 mol % $NaBAr^F_4$ in dioxane at 80 °C resulted <2% conversion to product; chloride is efficiently substituted by diene **1** in the presence of $NaBAr^F_4$. Use of 5 mol % $AgBF_4$ in place of $NaBAr^F_4$ as a halide scavenger (in situ generation of AgCl) delivers **3** in >98% conversion (>98:2 γ:α). In order to determine if AgCl was responsible for the increased catalyst reactivity, cationic Rh(I)-styrene complex **5** was synthesized.[13] Hydroarylation in the presence of 5 mol % styrene complex **5** in dioxane at 80 °C for 12 h affords <2% conversion to **3**; styrene in **5** is displaced by diene **1** at 22 °C in 30 min (Scheme 1c). Use of 5 mol % **5** and 5 mol % AgCl under identical conditions affords **3** in >98% conversion and >98:2 γ:α. These initial observations demonstrate the ability of AgCl as an additive to increase the activity of the (CDC)-Rh complexes for hydroarylation.

Table 1. Additive Effect in (CDC)-Rh-Catalyzed Addition of Indole to Phenyl-1,3-Butadiene[a]

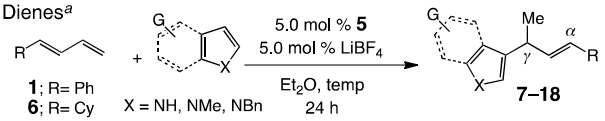


entry	metal salt	temp (°C)	conv (%);[b] γ:α	yield (%)[c]
1[d]	-	**120**	6; -	-
2	CuCl	50	>98; 90:10	91
3	AgCl	50	92; 95:5	89
4	AuCl	50	>98; 85:15	96
5	$LiBAr^F_4$•OEt_2	50	87; >98:2	76
6	$LiBF_4$	50	>98; 97:3	94
7	$NaBAr^F_4$	50	<2; -	-
8	CuCl	22	<2; -	-
9	AgCl	22	<2; -	-
10	AuCl	22	60; 81:19	53
11	$LiBF_4$	22	>98; 85:15	98
12[e]	$LiBF_4$, 2,6-di-*t*-Bu-pyridine	50	>98; 94:6	74

[a]See SI for experimental details; all reactions performed under N_2 atm. [b]Conversion to product; values determined by analysis of 400 or 600 MHz ^{1}H NMR spectra of unpurified mixtures with DMF as an internal standard. [c]Yields of purified products are an average of two runs. [d]Dioxane as solvent. [e]10 mol % 2,6-di-*t*-Bu-pyridine.

We next examined the effect of other Lewis acid additives on catalyst activity, the results of these studies are shown in Table 1. Control reaction with Rh(I)-styrene complex **5** at 120 °C in dioxane, leads to only 6% conversion to **3** (entry 1). As illustrated in entries 2–4, reaction of 5 mol % **5** with an equimolar amount of Cu-, Ag-, or Au chloride in Et_2O at 50 °C for 24 h affords indole **3** in high yield (up to 96%) and selectivity (up to 95:5 γ:α). Lithium salts were also found to promote catalytic hydroarylation with similar efficiency (entries 5–6); 5 mol % $LiBAr^F_4$-OEt_2 and $LiBF_4$ deliver **3** in 76% and 94% yield and >98:2 and 97:3 γ:α, respectively.[7c,14] Notably, sodium salts are not effective at increasing catalyst reactivity, likely due to the decreased Lewis acidity of sodium compared to lithium (entry 7, Table 1). Decreasing the reaction temperature to 22 °C results in <2% conversion to **3** except in the case of AuCl (60%, 81:19 γ:α, entry 10), and $LiBF_4$ (>98%, 85:15 γ:α, entry 11). To achieve both high conversion and site-selectivity in further studies, optimal reaction conditions were chosen that employ cost effective $LiBF_4$ at 50 °C. Of note, catalytic hydroarylation in the presence of 10 mol % 2,6-di-*t*-Bu-pyridine as a Brønsted acid scavenger does not inhibit the reaction (entry 12, Table 1).[15]

Table 2. (CDC)-Rh-Catalyzed Addition of *N*-Heteroarenes to 1,3-Dienes[a]



entry	heterocycle; product	diene	temp (°C)	yield (%);[b] γ:α
1	N-Me-indole; **7**	**1**	40	63; >98:2
2	7-Cl-indole; **8**	**1**	50	71; 96:4
3[c]	2,4-Me-pyrrole; **9**	**1**	22	88; >98:2
4	6-NO_2-indole; **10**	**1**	60	57; 91:9
5	3-Me-indole; **11**	**1**	60	33; 92:8
6	N-TIPS-pyrrole; **12**	**1**	70	38; >98:2[d]
7	indole; **13**	**6**	50	85; >98:2
8	6-MeO-indole; **14**	**6**	50	91; 98:2
9	N-Me-indole; **15**	**6**	50	66; >98:2
10	2-Me-indole; **16**	**6**	50	66; >98:2
11[e]	2,4-Me-pyrrole; **17**	**6**	22	53; >98:2
12[f]	N-Bn-indole; **18**	**6**	60	85; 87:13

[a]See SI for experimental details. [b]Yields of purified products are an average of two runs. [c]91:9 C2:C3 site-selectivity on pyrrole. [e]^{1}H NMR yield; determined by analysis of 400 or 600 MHz ^{1}H NMR spectra of unpurified mixtures with DMF as an internal standard. [e]85:15 C2:C3 site-selectivity on pyrrole. [f]48 h reaction.

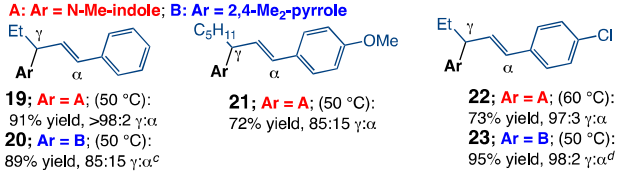
The scope of $LiBF_4$ as an additive was investigated for a range of N-heterocycles to phenyl and cyclohexyl 1,3-dienes **1** and **6**. As shown in Table 2, phenyl substituted 1,3-diene undergoes site-selective hydroarylation with N-Me and 7-Cl indole at 50 °C (entries 1–2) to afford **7** (63%, >98:2 γ:α) and **8** (71%, 96:4 γ:α). More nucleophilic 2,4-dimethylpyrrole reacts at 22 °C in the presence of 5 mol % Rh(I) **5** and $LiBF_4$ to deliver **9** in 88% yield, >98:2 γ:α, and 91:9 C2:C3 site-selectivity on the pyrrole ring. Indoles bearing electron-withdrawing groups require a slightly higher temperature (60 °C) to achieve good conversion; treatment of 6-NO_2 indole with **1** in the presence of **5** and $LiBF_4$ reacts to generate **10** in 57% yield and 91:9 γ:α (entry 4). 3-Methyl indole directs the diene addition to the 2-position of indole (entry 5) to afford **11** in 33 % yield and 92:8 selectivity. Similarly, increasing the sterics and decreasing the nucleophilicity of the N-hetereoarene results in a less efficient reaction; TIPS-pyrrole undergoes catalytic hydroarylation at 70 °C to yield **12** in 38% yield and >98:2 γ:α (entry 6, Table 1). The reaction does not improve if >5.0 mol % $LiBF_4$ is used. Alkyl dienes are equally effective reaction partners for Rh-catalyzed hydroarylation as illustrated by the reactions of cyclohexyl-1,3-diene **6** with a variety of substituted indoles (entries 7–10, Table 2); reactions proceed efficiently with catalytic $LiBF_4$ (5 mol %) at 50 °C and deliver the alkylated indoles (**13**–**16**) in good yields (66–91%) and excellent site-selectivity (>98:2 γ:α). 2,4-Dimethyl pyrrole affords 2-substituted pyrrole **17** in 53% yield and >98:2 diene γ:α selectivity (entry 11) at 22 °C in 24 h. Again, alkyl 1,3-dienes react more sluggishly with indoles bearing larger groups on nitrogen and require longer reaction times and higher temperatures; 60 °C for 48 h is required to generate substituted N-Bn indole **18** in 85% yield and 87:13 γ:α site-selectivity.

We next extended the utility of the Rh(I)-catalyzed protocol to more challenging site-selective additions to internal

dienes.[16] Products delivered through these catalytic reactions afford functionalized differentially allyl substituted heterocycles (Scheme 2). Reactions proceed with <2% conversion to product at 120 °C for 24 h without $LiBF_4$. 1,4-Aryl-alkyl substituted dienes undergo catalytic hydro-heteroarylation with indole and 2,4-dimethyl pyrrole to deliver functionalized heterocycles (**19**–**21**) in good yield but with a slight diminution in diene site-selectivity (>98:2–85:15 γ:α). The Rh-catalyzed synthesis of *p*-chorostyrene derivatives **22** and **23** is notable as such electron deficient dienes are not compatible with Au-catalyzed methods;[4c] 5 mol % **5** and 5 mol % $LiBF_4$ at 60 °C delivers **22** and **23** in 73% and 95% yield. The reaction demonstrates good functional group tolerance to alkyl halides (**24**), boronate esters (**25**), and esters (**26**). Addition of indole to symmetrical hexa-2,4-diene at 22 °C affords **27** in 64% yield in 67:33 β:α selectivity.

Scheme 2. (CDC)-Rh-Catalyzed Hydroheteroarylation of 1,4-Disubstituted Dienes[a–b]

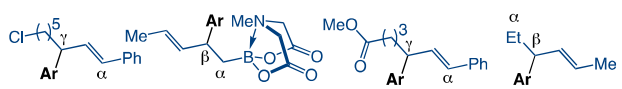
A: Ar = N-Me-indole; B: Ar = 2,4-Me$_2$-pyrrole



19; Ar = A; (50 °C): 91% yield, >98:2 γ:α
20; Ar = B; (50 °C): 89% yield, 85:15 γ:α[c]

21; Ar = A; (50 °C): 72% yield, 85:15 γ:α

22; Ar = A; (60 °C): 73% yield, 97:3 γ:α
23; Ar = B; (50 °C): 95% yield, 98:2 γ:α[d]



24; Ar = A; (50 °C): 79% yield, 83:17 γ:α

25; Ar = A; (60 °C): 62% yield,[e] >98:2 β:α

26; Ar = A; (50 °C): 91% yield, 76:24 γ:α

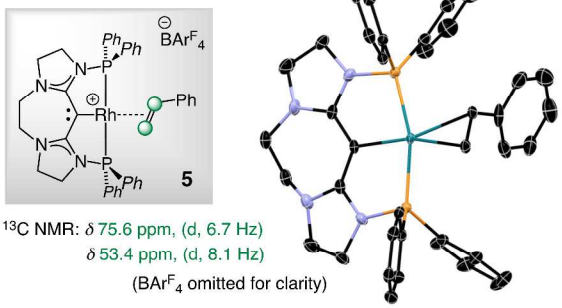
27; Ar = A; (22 °C): 64% yield, 67:33 β:α

[a–b]See Table 2. [c]85:15 C2:C3 site-selectivity on pyrrole. [d]98:2 C2:C3 site-selectivity on pyrrole. [e]^{1}H NMR yield; determined by analysis of 400 or 600 MHz ^{1}H NMR spectra of unpurified mixtures with DMF as an internal standard.

To gain insight into the catalyst structure and the effect of the metal salt additive, we obtained an X-ray structure of cationic (CDC)-Rh-styrene complex **5** (Scheme 3a). Complex **5** has a square-planar structure, with an sp^2 hybridized C(0) donor and a C(0)–Rh bond length of 2.07 Å. The styrene ligand exhibits significant metal–alkene π-back-donation demonstrated by an elongated styrene C=C bond (1.395 Å).[17] To investigate the electronic changes that occur to the Rh–alkene bond upon binding a second species to the carbon(0) donor, we attempted to analyze the ^{13}C NMR spectrum of the coordinated styrene in complex **5** in the presence of a Lewis acid additive (Scheme 3b). However, when complex **5** is treated with a metal salt, loss of styrene is observed; treatment of (CDC)-Rh(I)–styrene complex **5** with $LiBAr^F_4$, or AuCl in d_8-thf at 22 °C for 24 h leads to tetrahydrofuran bound **28** and free styrene (AuCl: 81% styrene, and $LiBAr^F_4$: 6% styrene (17% in 72 h)). No loss of styrene (<2%) is observed without any additive. These results indicate olefin substitution is facilitated by binding of a metal salt to the CDC, which destabilizes the olefin complex by decreasing π-back donation, leading to styrene substitution by a weakly donating tetrahydrofuran molecule. In addition, rapid substitution of styrene occurs when complex **5** is reacted with 1 equivalent of indole and $LiBF_4$ at 40 °C. No Rh–H signals are observed in the ^{1}H NMR spectrum, suggesting a C–H activation mechanism is unlikely, indicating an alkene activation pathway. To quantify the electronic changes that occur at Rh(I) upon binding to the carbon(0) donor, pincer (CDC)-Rh(I)–CO complex **29**[6] was treated with HBF_4-OEt_2 to cleanly yield **30** in >98% conversion (Scheme 3c). Protonation at C(0) leads to shortening of the CO bond length, indicated by an increase in the IR stretching frequency (ν_{CO} = 2016 cm^{-1}), representing a significant decrease in π-back donation and decrease in electron density at Rh. Tetrafluoroboric acid is a less effective activator, compared to $LiBF_4$, for diene hydroarylation.[18] This is likely due to ligand protonation being less reversible than binding $LiBF_4$, which would indicate the importance of a reversible interaction provided by Lewis acid additives such as AgCl and $LiBF_4$. Coinage metal salts also present the possibility of a bimetallic interaction,[9] although this is unlikely with lithium. Together, the enhanced ligand substitution and reactivity suggests that the metal additives bind to the C(0) of the olefin complex promoting ligand substitution (styrene by THF) and also addition of a nucleophile to the bound C=C bond.[19] Further analysis of the catalytic reaction mechanism with $LiBF_4$ through deuterium labeling studies with C-3 deuterium labeled N-Me-indole results in formation of d_1-**7** with >95% deuterium transfer (Scheme 3d).

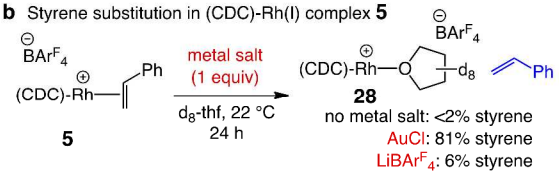
Scheme 3. Catalyst Structure and Additive Effect

a X-ray structure of (CDC)-Rh **5**



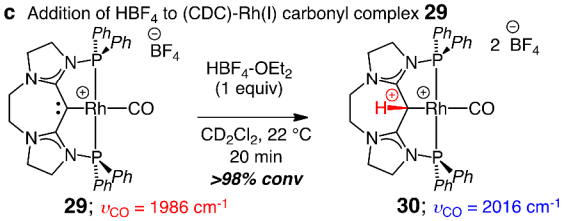
^{13}C NMR: δ 75.6 ppm, (d, 6.7 Hz)
δ 53.4 ppm, (d, 8.1 Hz)
(BAr^F_4 omitted for clarity)

b Styrene substitution in (CDC)-Rh(I) complex **5**



5
metal salt (1 equiv)
d_8-thf, 22 °C
24 h
28
no metal salt: <2% styrene
AuCl: 81% styrene
$LiBAr^F_4$: 6% styrene

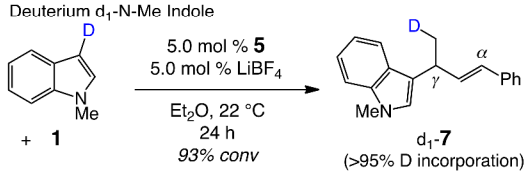
c Addition of HBF_4 to (CDC)-Rh(I) carbonyl complex **29**



HBF_4-OEt_2 (1 equiv)
CD_2Cl_2, 22 °C
20 min
>98% conv

29; ν_{CO} = 1986 cm^{-1}
30; ν_{CO} = 2016 cm^{-1}

d Deuterium d_1-N-Me Indole



+ **1**
5.0 mol % **5**
5.0 mol % $LiBF_4$
Et_2O, 22 °C
24 h
93% conv
d_1-**7**
(>95% D incorporation)

In summary, these studies describe a key attribute of carbon(0) donor ligands that expands their limited use in catalysis.[6,20] We show the potential for tuning ligand donation in CDCs through secondary binding of Lewis acids, which enables the use of cationic (CDC)-Rh-based complexes as catalysts for diene hydroarylation. Notably, simple lithium salts emerged as effective catalytic Lewis acids that promote reactions under mild conditions for a range of heteroarenes with terminal and internal dienes. Development of related reactions that utilize CDC catalyst activation, as well as enantioselective variants, are in progress.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectral and analytical data for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

Authors declare no competing financial interests.

ACKNOWLEDGMENT

Financial support was provided by the University of North Carolina at Chapel Hill, the Petroleum Research Fund of the American Chemical Society (52447-DNI1), and an Eli Lilly New Faculty Award. C.C.R. is an NSF graduate research fellow. We are grateful to M. Joannou (UNC) for helpful discussions and assistance solving the X-ray structure of Rh complex **5**.

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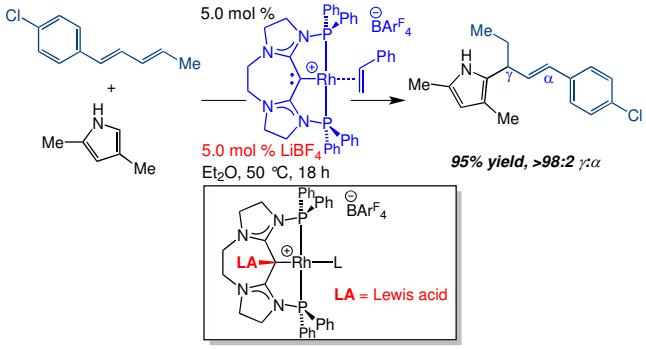
Cl
Me
+
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N
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5.0 mol %
Ph
Ph
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P
Ph
Ph
5.0 mol % LiBF$_4$
Et$_2$O, 50 °C, 18 h
Me
H
N
Me
γ
α
Cl
95% yield, >98:2 γ:α
LA
Rh
L
LA = Lewis acid