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Notes

Enantioselective Preparation of a Chiral-at-Metal Cp*Ir(NHC) Complex and Its Application in the Catalytic Diboration of Olefins

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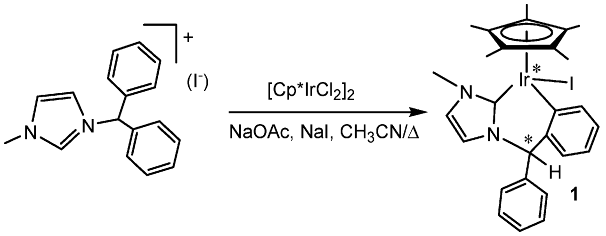
*Summary: The reaction of (S,S)-1,3-di(methylbenzyl)imidazolium chloride with [Cp*IrCl$_2$]$_2$ in the presence of NaOAc affords the diastereoselective formation of a Cp*Ir(NHC) complex with a chelating ligand coordinated through the carbene and the ortho-position of one of the phenyl groups. The crystal structure of this new enantiomerically pure compound is described. The complex has been used in the catalytic diboration of olefins, providing high efficiencies and chemoselectivities on the organodiboronate products.*

1. Introduction

It is now considered that the incorporation of N-heterocyclic carbenes (NHCs) to metal complexes represents one of the most significant achievements of homogeneous catalysis. The easy access to NHCs has also allowed the preparation of many examples of chiral compounds, which help to satisfy the increasing demand for enantiopure species that can be potentially applied in asymmetric catalysis.[1] Among chiral complexes, those with the asymmetric center at the reacting metal atom are particularly interesting because, in principle, they can provide higher asymmetric efficiencies on the reaction products. Typically, chiral-at-metal complexes are pseudooctahedral[2] or half-sandwich pseudotetrahedral species with η^5-Cp or η^6-C$_6$H$_6$ ligands,[3] whose syntheses often require many reaction steps with consequent reduced isolated yields. In this sense, we find that the search for simple synthetic protocols to provide enantiopure metal-centered chiral complexes in high yields is an important issue that is potentially desirable to many research groups. In the case of half-sandwich NHC-based complexes with metal-centered chirality, only a few recent examples have been reported in the literature.[4]

We recently reported a series of Cp*Ir(NHC) complexes that showed high-activity in CH bond activation processes, such as the catalytic deuteration of organic molecules[5] and the intramolecular activation of aliphatic and aromatic C−H bonds.[6] The metalation of 1-diphenylmethyl-3-methylimidazolium iodide to [Cp*IrCl$_2$]$_2$ afforded compound **1**, with two stereogenic centers at the metal and at the C(H)(Ph) group of the bridging ligand (Scheme 1). Since none of these chiral centers are fixed, we obtained a mixture of four isomers, or two pairs of diastereomers. Interestingly, the synthetic procedure was diastereoselective, providing a mixture of the two diastereomers in a 5:1 molar ratio, which were easily separated by column chromatography.

Scheme 1



On the basis of these results, we decided to use a chiral imidazolium salt to provide the diastereoselective synthesis of a chelating Cp*Ir(NHC) complex, in which the NHC is a chelating imidazolylidene-phenyl ligand. The initial idea is to fix the stereogenic center at the ligand, so that we could easily separate the resulting diastereomers, now being enantiopure species. In this work we describe our results on the diastereoselective preparation and full characterization of a new Cp*Ir(NHC) chiral compound and its use in the catalytic diboration of olefins, which in fact represents the first example of Ir-mediated B−B addition to alkenes.

Results and Discussion

The reaction of (*S*,*S*)-1,3-di(methylbenzyl)imidazolium chloride[7] with [Cp*IrCl$_2$]$_2$ in acetonitrile in the presence of NaOAc afforded compound **2** in high yield (63%). The coordination of the NHC ligand, together with the orthometalation of the phenyl ring, provides the chelating coordination of the ligand. Due to the pseudotetrahedral arrangement of the ligands, a stereogenic center at the metal is created, leading to the existence of two diastereomers, due to the presence of the chiral ligand. From the ^{1}HNMR spectrum of the reaction mixture, only one of the

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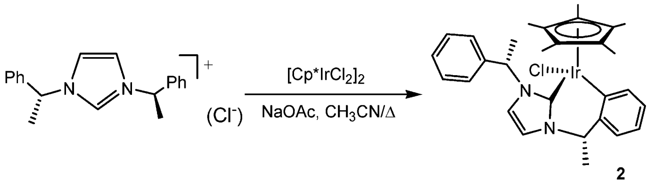
10.1021/om7004639 CCC: $37.00

Scheme 2



two possible diastereomers is observed, so we estimate a diastomeric excess (de) higher than 95% for this reaction. The ^{1}HNMR spectrum of a solution of **2** in $CDCl_3$ did not change after 1 week; thus epimerization to the other diastereomer did not take place. The $^{13}C\{^1H\}$ NMR spectrum of **2** reveals that the orthometalation has ocurred. A signal at 144.3 ppm is due to the metalated phenyl carbon, while the resonance corresponding to the carbene-carbon appears at 159 ppm, in the region of previously reported Cp*Ir(NHC) complexes.[5,6,8]

The molecular structure of **2** was determined by means of X-diffraction studies. Figure 1 shows the molecular diagram of **2** and the more relevant bond distances and angles.

The crystal structure of **2** confirms that only one enantiomer is present in the crystal. The absolute configuration about the metal center is *S*, which together with the configuration of the two chiral carbon centers reveals that the (S_{Ir},S_C,S_C)-**2** diastereomer was the only one obtained. The structure reveals that the orthometalation of one of the phenyl substituents of the carbene ligand has occurred, with the formation of a six-membered iridacycle in a distorted boat conformation. The Cp* ring and a chlorine ligand complete the coordination sphere about the Ir center. The chelate bite angle is 87.7°, similar to that shown for other cyclometalated complexes reported by us.[5,6] The Ir−$C_{carbene}$ distance of 1.990 Å lies in the expected range for other similar complexes.[5,8] The Ir−C bond distance for the cyclometalated phenyl ring is 2.043 Å.

We have been recently interested in the catalytic B-addition across unsaturated carbon−carbon bonds, to provide easy access to organoborane compounds, in particular, the catalytic hydroboration[9] and diboration[10] reactions. While many efforts have been focused on metal−phosphine complexes, we recently described a series of NHC-based metal complexes that cleanly performed B−H and B−B addition to alkenes.[10] The potential use of Ir−NHC complexes in this type of reaction is very attractive, because this metal has offered significant benefits in terms of increased stability of metal intermediates[11] toward catalytic hydroboration[12] and C−H borylation.[13] To the best of our knowledge there is no previously reported work on the catalytic diboration reaction with Ir complexes. The presence of the stereogenic center at the metal in (S_{Ir},S_C,S_C)-**2**, provides additional interest since we can evaluate the asymmetric induction of the reaction products of the catalytic reaction.

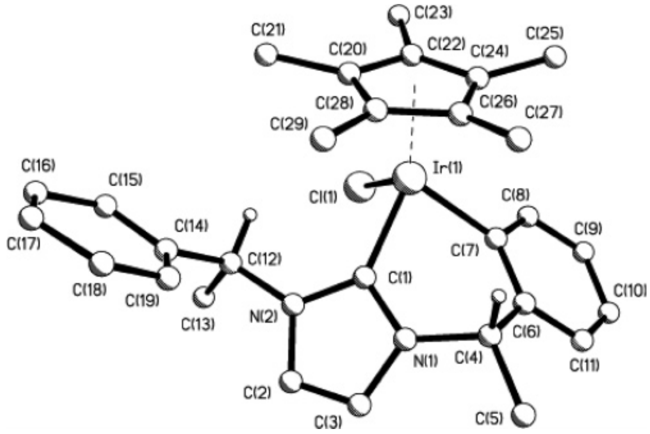
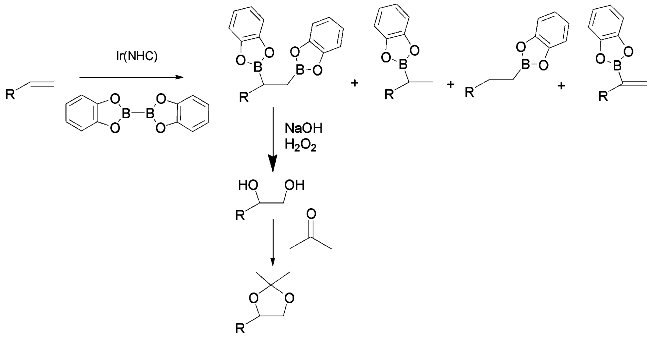


Figure 1. Molecular diagram of compound (S_{Ir},S_C,S_C)-**2**. Hydrogen atoms (except at chiral centers) and crystallization solvent (tetrahydrofuran) have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−C(1) 1.990(11), Ir(1)−Cl(1) 2.412(3), Ir(1)−C(7) 2.043(10), Ir(1)−$Cp^*_{centroid}$ 1.85, C(1)−Ir(1)−C(7) 83.8(4), C(1)−Ir(1)−Cl(1) 89.4(3), C(7)−Ir(1)−Cl(1) 87.7(3), $Cp^*_{centroid}$−Ir(1)−C(1) 133.1, $Cp^*_{centroid}$−Ir(1)−C(7) 126.9, $Cp^*_{centroid}$ −Ir(1)−Cl(1) 121.9.

Scheme 3



Compound (S_{Ir},S_C,S_C)-**2** was initially tested in the diboration of styrene (Scheme 3), but it did not lead to the formation of any diboronate esters when bis(catecholato)diboron, (B_2cat_2), was added to a solution of the catalyst (5 mol %) and styrene in THF under argon (Table 1, entry 1). Addition of $AgBF_4$ for the *in situ* generation of cationic species did not provide any catalytic performance toward the desired product (Table 1, entry 2). However, addition of NaOAc and an excess of diboron reagent afforded an almost quantitative conversion of the styrene, providing an extraordinarily high chemoselectivity on the diborated product, with values up to 99.2% (Table 1, entry 3). Other neutral and cationic Ir(I) complexes modified with (*S*)-Quinap were not active under such conditions (Table 1, entries 4 and 5), despite the effectiveness of their Rh analogue complexes.[14] The specific effectiveness of the NHC ligands toward the high chemoselectivities on the diboronate product has been shown in the comparative diboration reaction catalyzed by $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$ and $Cp^*Ir(I^{Me})(Cl)_2$ (I^{Me} = 1,3-dimethylimidazolylidene) (Table 1, entries 6 and 7). Also, high chemoselectivities were observed for the diboration of *p*(F)PhCH═CH_2 and *p*(MeO)PhCH═CH_2 with complex **2** (Table 1, entries 8 and 9), although conversions dropped significantly for these substituted vinylarenes. We also studied the catalytic B−B addition to the aliphatic 1-alkene substrates vinylcyclohexane and 3,3-dimethyl-1-butene (Table 1, entry 10 and 11). In both

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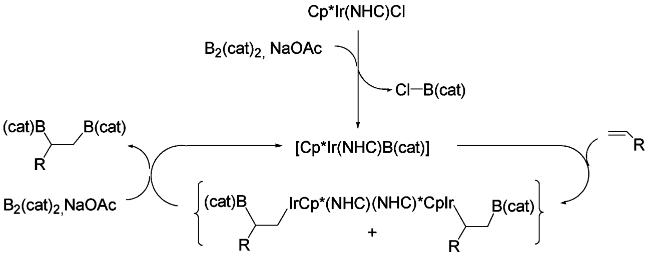
Table 1. 1,2-Diboration/Oxidation of Alkenes with Ir(III)−NHC and $B_2(cat)_2$[a]

entry	substrate	catalytic system	additive	conv (%)[b]	diol (%)[b]	byproducts (%)[b]
1	$PhCH{=}CH_2$	Ir(III)−NHC		60		100 (vinyl ester)
2	$PhCH{=}CH_2$	Ir(III)−NHC/ $AgBF_4$				
3[c]	$PhCH{=}CH_2$	Ir(III)−NHC	NaOAc	91	99.2	0.8 (br)
4[c]	$PhCH{=}CH_2$	$[Ir(\mu\text{-}Cl)(COD)]_2$/(*S*)-Quinap	NaOAc	100		100 (l)
5[c]	$PhCH{=}CH_2$	$[Ir(COD)_2]BF_4$/(*S*)-Quinap	NaOAc	40		100 (l)
6[c]	$PhCH{=}CH_2$	$[Cp^*Ir(\mu\text{-}Cl)Cl]_2$	NaOAc	87	97	3 (vinyl ester)
7[c]	$PhCH{=}CH_2$	$Cp^*Ir(NHC)(Cl)_2$	NaOAc	95	99.9	
8[c]	$p(F)PhCH{=}CH_2$	Ir(III)−NHC	NaOAc	79	91	9 (br)
9[c]	$p(MeO)PhCH{=}CH_2$	Ir(III)−NHC	NaOAc	43	93	7 (br)
10[c]	$CyCH{=}CH_2$	Ir(III)−NHC	NaOAc	100	92	8 (l)
11[c]	$^tBuCH{=}CH_2$	Ir(III)−NHC	NaOAc	100	99.9	
12[c]	$PhCH{=}CH_2$	Ir(III)−NHC/$AgBF_4$	NaOAc	100	82 (ee = 10%)[d]	11 (br) 7 (l)

[a] Standard conditions: 5 mol % of Ir(III)−NHC catalytic system, alkene/diboron = 1/1.1, T = 25 °C, reaction time 4 h, solvent THF. [b] Conversion and selectivity based on ^1H NMR (l: linear monoalcohol, br: branched monoalcohol). [c] Alkene/diboron = 1/3, NaOAc 1 equiv. [d] Enantiomeric excess determined by GC with chiral column, as derivated acetals.

Scheme 4



cases the conversion was complete and the chemoselectivity was quantitative toward the organodiboronate product. Under these reaction conditions, we were unable to obtain any asymmetric induction. However, when $AgBF_4$ was added to the reaction mixture to promote the removal of the halide from the Ir metal sphere, we found that the catalytic diboration was efficiently performed with total conversion and high chemoselectivity (Table 1, entry 10), in the presence of NaOAc. Under these conditons, enantiomeric excess values of around 10% were found for the corresponding acetal derivative in the catalytic diboration/oxidation protocol (Scheme 3).

Although further investigations are needed, we believe that the role of NaOAc may favor the heterolytic cleavage of B_2cat_2, thus justifying the formation of the Ir−B without need of oxidative addition of the diborane to the Ir(III) complex. This would imply that the metal remains in the same oxidation state (III) during the entire reaction process. Subsequent alkene coordination and migratory insertion into the Ir−B bond could provide the Ir−alkyboronate, which finally could transmetalate with B_2cat_2 to generate the diborated product (see Scheme 4). We recently performed a combined experimental and computational analysis of the same reaction using a Pd−NHC catalyst.[15] The theoretical calculations showed that, when NaOAc is added, this is the most likely mechanism.[15] From this reaction pathway, we also justify the experimental observation that an excess of $B_2(cat)_2$ is needed in order to afford full conversions, since only one B(cat) fragment is added to the alkene per molecule of $B_2(cat)_2$.

Conclusions

We have described the diastereoselective preparation of a chiral Cp*Ir(NHC) complex with a stereogenic center at the metal atom. The method is simple and provides a high yield in the desired compound. The complex has been tested in the catalytic diboration of olefins, providing high conversions and chemoselectivities on the organodiboronate products. Addition of $AgBF_4$ was needed to produce any asymmetric induction on the reaction, although this was low (10% ee). To our knowledge, this is the first example of an Ir compound tested in the catalytic diboration of olefins. Both the simplicity of the preparation of the catalyst and the good performances in the catalytic reactions make us believe that these results may constitute the beginning of a new series of Ir−NHC catalysts for the diboration of olefins. Further studies on the preparation of more sterically hindered Cp*Ir(NHC) chiral complexes are underway, and higher asymmetric performances may be envisaged.[16]

Experimental Section

General Procedures. $[Cp^*IrCl_2]_2$[16] and (*S*,*S*)-1,3-di(methylbenzyl)imidazolium chloride[7] were prepared according to literature procedures. All other reagents were used as received from commercial suppliers. NMR spectra were recorded on a Varian Innova 300 and 500 MHz, using $CDCl_3$ as solvent. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a EuroEA3000 Eurovector analyzer. Optical activity was measured on a DIP-1000 JASCO digital polarimeter with a sodium lamp and a 50 mm cell.

Synthesis of 2. A mixture of $[Cp^*IrCl_2]_2$ (300 mg, 0.38 mmol), (*S*,*S*)-1,3-di(methylbenzyl)imidazolium chloride (234 mg, 0.75 mmol), and NaOAc (92 mg, 1.13 mmol) in CH_3CN was refluxed for 7 h. The solution was filtered through Celite, the solvent was evaporated, and the crude solid was purified by column chromatography. The pure compound **2** was eluted with hexanes/diethyl ether (7:3) and precipitated in hexanes to give a yellow solid. Yield: 301 mg (63%). $[\alpha]_D$ −46.9 (c 1.1, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, $^3J(H,H)$ = 7.5 Hz, 1H, Ph), 7.26 (m, 2H, Ph), 7.17 (t, $^3J(H,H)$ = 7.0 Hz, 1H, Ph), 7.07 (d, $^3J(H,H)$ = 2.0 Hz, 1H, C*H* imidazole), 7.03 (m, 3H, Ph), 6.96 (d, $^3J(H,H)$ = 2.0 Hz, 1H, C*H* imidazole), 6.89 (t, $^3J(H,H)$ = 7.3 Hz, 1H, Ph), 6.79 (t, $^3J(H,H)$ = 7.3 Hz, 1H, Ph), 6.53 (q, $^3J(H,H)$ = 7.0 Hz, 1H, N-C*H*(CH_3)-Ph), 4.72 (q, $^3J(H,H)$ = 7.0 Hz, 1H, N-C*H*(CH_3)-Ph), 1.94 (d, $^3J(H,H)$ = 7.0 Hz, 3H, N-CH(CH_3)-Ph), 1.74 (d, $^3J(H,H)$ = 7.0 Hz, 3H, N-CH(CH_3)-Ph), 1.38 (s, 15H, $C_5(CH_3)_5$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0 (C-Ir carbene), 148.41 (Ph), 144.32 (C−Ir Ph), 143.47 (Ph) 141.50 (Ph), 128.56 (Ph), 127.57 (Ph), 126.92 (Ph), 125.78 (Ph), 122.08 (Ph), 120.81 (Ph), 118.53 (*C*H imidazole), 116.52 (*C*H imidazole), 90.42 ($C_5(CH_3)_5$), 58.89 (N-*C*H(CH_3)-Ph), 58.20 (N-*C*H(CH_3)-Ph), 25.03 (N-*C*H(CH_3)-Ph), 16.06 (N-*C*H(CH_3)-Ph), 9.60 ($C_5(CH_3)_5$). Anal. Calcd for $C_{29}H_{34}$-

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Table 2. Crystallographic Data

empirical formula	$C_{33}H_{42}ClIrN_2O$
mol wt	710.34
radiation	Mo Kα (monochr); 0.71073 λ (Å)
T (K)	273
cryst syst	monoclinic
space group	$P2(1)$
a (Å)	8.5458(6)
b (Å)	15.2243(10)
c (Å)	23.9895(15)
α (deg)	90
β (deg)	90.042(2)
γ (deg)	90
V (Å^3)	3121.1(4)
Z	4
D_{calcd} (Mg m^{-3})	1.512
μ(Mo Kα) (mm^{-1})	4.390
total, unique no. of reflns	21 414, 11 495
R_{int}	0.0489
no. of params, restrictions	692, 1
R, R_w	0.0863, 0.1124
GOF	1.024
min., max. resid dens (e Å^{-3})	−1.210, 1.239

$ClIrN_2$: C, 54.57; H, 5.37; N, 4.39. Found: C, 54.71; H, 5.37; N, 4.38. Electrospray MS cone: 30 V. MS m/z (fragment): 603.3 $[Cp^*IrL]^+$.

X-ray Diffraction Studies. Single crystals of **2** were mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. Space group assignment was based on systematic absences, E statistics, and successful refinement of the structures. The structure was solved by direct methods with the aid of successive difference Fourier maps and was refined using the SHELXTL 6.1 software package.[17] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to ideal positions and refined using a riding model. Details of the data collection, cell dimensions, and structure refinement are given in Table 2. The diffraction frames were integrated using the SAINT package.[17,18]

Typical Catalytic Diboration of Styrene. Bis(catecholato)-diboron (1.5 mmol) was added to a solution of the catalyst (5 mol %, 0.025 mmol) and NaOAc (0.5 mmol) in THF (2 mL) under argon. The solution was stirred for 5 min, and styrene (0.5 mmol) was then added. The mixture was stirred for 4 h at room temperature. After that time, a solution aliquot was taken from the reaction mixture and monitored by ^{1}H NMR, from which the degree of conversion and the nature of the organoboron products formed in the reaction were obtained.

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Supporting Information Available: Crystallographic data of compound (S_{Ir},S_C,S_C)-**2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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