Asymmetric Catalysis

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# Chiral Cyclopentadienyl Iridium(III) Complexes Promote Enantioselective Cycloisomerizations Giving Fused Cyclopropanes

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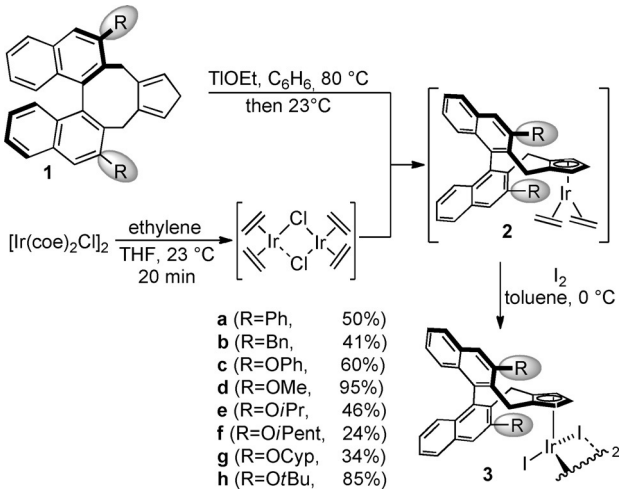
***Abstract:*** *The cyclopentadienyl (Cp) group is a very important ligand for many transition-metal complexes which have been applied in catalysis. The availability of chiral cyclopentadienyl ligands ($Cp^x$) lags behind other ligand classes, thus hampering the investigation of enantioselective processes. We report a library of chiral $Cp^xIr^{III}$ complexes equipped with an atropchiral Cp scaffold. A robust complexation procedure reliably provides $Cp^xIr^{III}$ complexes with tunable counterions. In a proof-of-concept application, the iodide-bearing members are shown to be highly selective for enyne cycloisomerization reactions. The dehydropiperidine-fused cyclopropane products are formed in good yields and enantioselectivities.*

The design of new ligand systems for transition-metal complexes is important to expand current reactivity boundaries in catalysis. In this respect, cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp*) are essential ligands for many complexes with numerous applications in catalysis.[1] The limited availability of chiral versions of Cp ligands ($Cp^x$)[2] and their corresponding metal complexes[3] has hampered progress in asymmetric catalysis with this ligand type. We recently introduced two classes of chiral $Cp^x$ ligands.[4] Their disubstituted nature places them intermediate between Cp and Cp* in terms of their electronic and steric properties. For the most part, the use of these ligand series in asymmetric catalysis has been limited to rhodium-catalyzed C–H bond functionalizations.[4,5] The exploitation of chiral $Cp^x$ ligands in conjunction with other important and frequently used transition metals is an important and highly promising task. However, unlike phosphine ligands, for example, which often can be simply used by in situ formation procedures to form the required complexes, Cp metal complexes have to be preassembled prior to their use in catalysis.[6] Therefore, of primary importance is the development of robust complexation and purification techniques for each specific transition metal. Herein, we report a set of chiral $Cp^xIr^{III}$ complexes and demonstrate their potential in enantioselective cycloisomerization reactions as a proof-of-principle application.

First, a reliable method to prepare the desired iridium complexes was developed. Unfortunately, direct complexation between a chiral cyclopentadiene **1** and simple $Ir^{III}$ starting materials, in analogy to the well-established reactions of Cp*H and $IrCl_3$, failed to provide any clean complexes.[7] We therefore adapted a procedure previously established for the $[Cp^xRh(C_2H_4)_2]$ complexes.[4] Optimally, the useful but rather labile species $[\{Ir(C_2H_4)_2Cl\}_2]$ is generated transiently by briefly bubbling ethylene into a solution of $[\{Ir(coe)_2Cl\}_2]$ (Scheme 1; coe = cyclooctene). The solution containing




***Scheme 1.*** Synthesis of the chiral $[\{Cp^xIrI_2\}_2]$ complexes.

formed $[\{Ir(C_2H_4)_2Cl\}_2]$ was directly added to the cyclopentadienyl anion at ambient temperature yielding $Cp^xIr^I$ complexes **2a**–**2h**. To access the corresponding $Ir^{III}$ complexes, a suitable oxidation method was needed. In contrast to the corresponding $Cp^xRh^I$ complexes which fail to react with molecular iodine, the more easily oxidizable $Cp^xIr^I$ complexes **2** smoothly provide $[\{Cp^xIrI_2\}_2]$ dimers **3a**–**3h**.[8] The dark-red and completely air-stable powders **3** are versatile intermediates to which any other desired counterion can be readily introduced by simple halide-abstraction methods.

In the X-ray crystal structure, the $Ir^I$ ethylene complex **2d** (Figure 1a) shows identical bond lengths and geometries as its $Rh^I$ congener (Figure 1b),[4b] suggesting that complex **2d** and its analogues might be promising candidates in asymmetric transformations.[9]

As a proof-of-concept application for the chiral $Cp^xIr^{III}$ complexes, we selected the cycloisomerization of enynes to form cyclopropanes [Eq. (1)] reported by Malacria, Fensterbank, and co-workers.[10]

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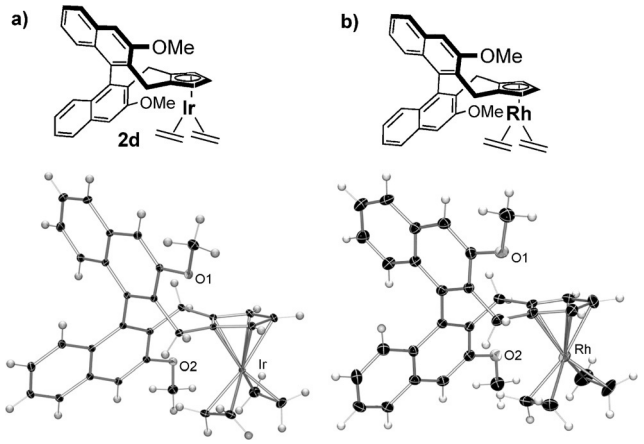
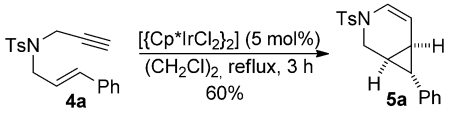



*Figure 1.* X-ray crystal structure of the $Cp^xIr^I$ complex **2d** and its $Cp^xRh^I$ analogue.

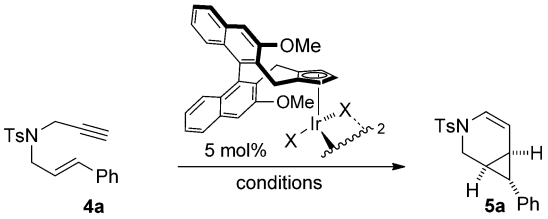



(1)

Cyclization reactions of this type are induced by an activation of the alkyne rendering it more electrophilic,[11] a reaction for which carbophilic π-acidic metals, such as Au and Pt, are typically employed.[12–14] Related asymmetric versions of the reaction were reported first with $Ir^I$ complexes[15] and recently using gold(I),[16] platinum(II),[17] and rhodium(I/II)[18] catalysts. However, to our knowledge, no chiral catalytic system efficiently accommodates terminal alkyne substrates,[19] making this transformation a challenging and complementary application for the $Cp^xIr^{III}$ system. First, the key contributing reaction parameters of the cyclization to form cyclopropane **5a** were evaluated using the parent ligand **1d** (Table 1), focusing, in this case, on the critical influence of the counterion on both reactivity and selectivity. The reactivity of the $Ir^{III}$ complexes increased substantially by changing from chloride to heavier halides (Table 1, entries 1–3). Moreover, the iodide complex provided a product with an increased enantioselectivity. A cationic or carboxylate bearing complex was not suitable, leading to unspecific decomposition or recovered starting material (Table 1, entries 4–5). The reaction proceeds well with the iodide complex at ambient temperature in $CHCl_3$ with an increased e.r. value of 85:15 (Table 1, entry 8). Other solvents were significantly less efficient (Table 1, entries 6–11).

Subsequently, we explored the influence of substituents on the chiral $Cp^x$ structure on the progress of the reaction (Table 2). Although a phenyl or benzyl R group at the 3,3′-position instead of the methoxy group conserved mostly the selectivity, conversion and yield dropped (Table 2, entries 1–3). Therefore, we focused on different ether groups. Typically, bulkier ethers gave rise to better enantioselectivities and improved the yield (Table 2, entries 4–7). The highest selectivity was achieved with complex **3h** containing a *tert*-butoxy ligand giving **5a** in 93.5:6.5 e.r. (Table 2, entry 8). Finally,

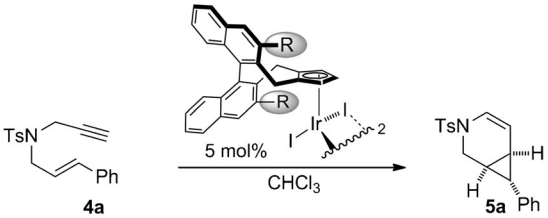
***Table 1:*** Initial optimization of the $Cp^xIr^{III}$-catalyzed cyclopropanation.[a]




| Entry | X | Solvent | *T* [°C] | Conv. [%][b] | **5a** [%][b] | e.r.[c] |
|---|---|---|---|---|---|---|
| 1 | Cl | $CHCl_3$ | 60 | 40 | 20 | 75:25 |
| 2 | Br | $CHCl_3$ | 60 | 100 | 43 | 80:20 |
| 3 | I | $CHCl_3$ | 60 | 100 | 40 | 82:18 |
| 4 | OBz | $CHCl_3$ | 60 | 0 | 0 | – |
| 5 | $SbF_6$ | $CHCl_3$ | 23 | 100 | 0 | – |
| 6 | I | $(CH_2Cl)_2$ | 23 | 83 | 32 | 81:19 |
| 7 | I | $CH_2Cl_2$ | 23 | 100 | 36 | 82:18 |
| 8 | I | $CHCl_3$ | 23 | 100 | 50 | 85:15 |
| 9 | I | toluene | 23 | 74 | 19 | 83:17 |
| 10 | I | THF | 23 | 70 | 16 | 79:21 |
| 11 | I | $CH_3CN$ | 23 | 53 | 6 | 76:23 |

[a] Conditions: **4a** (25 μmol), **3d** (1.25 μmol), 0.1 M in the indicated solvent, 24 h. [b] Determined by $^1$H NMR spectroscopy using an internal standard. [c] Determined by HPLC on a chiral stationary phase. Bz = benzoyl.

***Table 2:*** Screening of different $Cp^xIr^{III}$ catalysts **3**.[a]



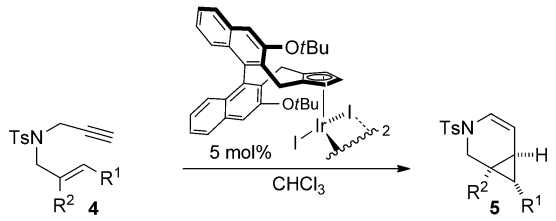

| Entry | **3** | R | *T* [°C] | Conv. [%][b] | **5a** [%][b] | e.r.[c] |
|---|---|---|---|---|---|---|
| 1 | **3a** | Ph | 23 | 72 | 11 | 75:25 |
| 2 | **3b** | Bn | 23 | 66 | 11 | 85:15 |
| 3 | **3d** | MeO | 23 | 100 | 50 | 85:15 |
| 4 | **3c** | PhO | 23 | 76 | 38 | 82.5:17.5 |
| 5 | **3e** | *i*PrO | 23 | 100 | 61 | 90:10 |
| 6 | **3f** | *i*PentO | 23 | 70 | 44 | 89:11 |
| 7 | **3g** | CypO | 23 | 100 | 43 | 88:12 |
| 8 | **3h** | *t*BuO | 23 | 100 | 64 | 93.5:6.5 |
| 9[d] | **3h** | *t*BuO | 0 | 100 | 76 | 96:4 |

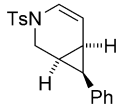
[a] Conditions: **4a** (25 μmol), **3** (1.25 μmol), 0.1 M in $CHCl_3$, 24 h. [b] Determined by $^1$H NMR spectroscopy using an internal standard. [c] Determined by HPLC on a chiral stationary phase. [d] 120 h. Bn = benzyl; Cyp = cyclopentyl.

lowering the reaction temperature to 0 °C increased the selectivity to 96:4 e.r. (Table 2, entry 9).

Next, the enantioselective cycloisomerization was applied to different enyne substrates. A variety of aromatic substituents $R^1$ are well tolerated and give cyclopropanes **5** in high enantioselectivity (Table 3, entries 1–10). Electron-rich arenes display a significantly higher reactivity, suggesting the importance of stabilization of positive charge during the reaction. Electron-poor arenes such as *p*-nitrophenyl need a slightly higher reaction temperature of 23 °C (Table 3,

***Table 3:*** Reaction scope for the synthesis of cyclopropanes **5**.[a]



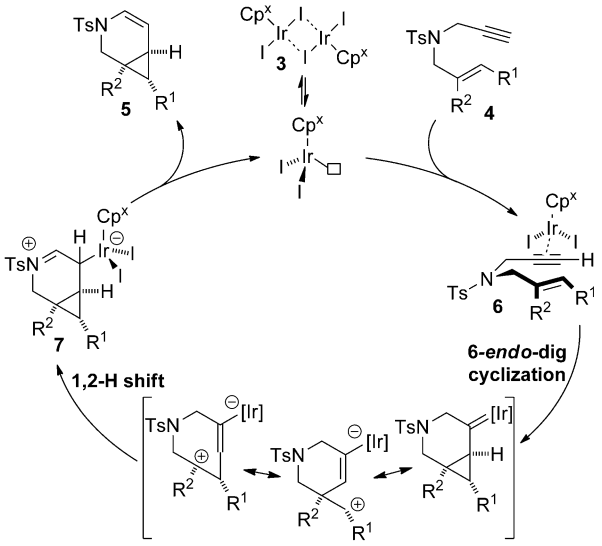

| Entry | 4 | 5 | | Yield [%][b] | e.r.[c] |
|---|---|---|---|---|---|
| 1 | **4a** | **5a** | $R^1$ = Ph, $R^2$ = H | 76 | 96:4 |
| 2 | **4b** | **5b** | $R^1$ = 4-$MeOC_6H_4$, $R^2$ = H | 52 | 96.5:3.5 |
| 3 | **4c** | **5c** | $R^1$ = 4-$(F_3CO)C_6H_4$, $R^2$ = H | 72 | 96.5:3.5 |
| 4 | **4d** | **5d** | $R^1$ = 5-benzo[*d*][1,3]dioxolyl, $R^2$ = H | 66 | 96:4 |
| 5 | **4e** | **5e** | $R^1$ = 4-$MeC_6H_4$, $R^2$ = H | 65 | 94:6 |
| 6 | **4f** | **5f** | $R^1$ = 3,5-$MeC_6H_3$, $R^2$ = H | 58 | 93.5:6.5 |
| 7 | **4g** | **5g** | $R^1$ = 4-$BrC_6H_4$, $R^2$ = H | 80 | 97:3 |
| 8 | **4h** | **5h** | $R^1$ = 3-$ClC_6H_4$, $R^2$ = H | 58 | 95:5 |
| 9 | **4i** | **5i** | $R^1$ = 2-naphthyl, $R^2$ = H | 67 | 92.5:7.5 |
| 10[d] | **4j** | **5j** | $R^1$ = 4-$NO_2C_6H_4$, $R^2$ = H | 70 | 94:6 |
| 11 | **4k** | **5k** | $R^1$ = 2-thienyl, $R^2$ = H | 47 | 94:6 |
| 12 | **4l** | **5l** | $R^1$ = 2-benzothienyl, $R^2$ = H | 79 | 97:3 |
| 13 | **4m** | **5m** | $R^1$ = 2-benzofuryl, $R^2$ = H | 87 | 96.5:3.5 |
| 14[e] | **4n** | **5n** | $R^1$ = 3-furyl, $R^2$ = H | 67 | 94:6 |
| 15[d] | **4o** | **5o** | $R^1$ = $CH_2OBn$, $R^2$ = H | 86 | 91:9 |
| 16 | **4p** | **5p** | $R^1$ = Ph, $R^2$ = Me | 87 | 91:9 |
| 17[f] | **4q** | **5q** | $R^1$ = H, $R^2$ = Ph | 78 | 91:9 |
| 18[f] | **4r** | **5r** | $R^1$ = H, $R^2$ = 5-benzo[*d*]-[1,3]dioxolyl | 45 | 89:11 |
| 19[f] | **4s** | **5s** | $R^1$ = H, $R^2$ = Me | 87 | 81.5:18.5 |
| 20 | *cis*-**4a** | *epi*-**5a** |  | 0 | – |



[a] Conditions: **4** (0.1 mmol), **3h** (5.0 μmol), 0.1 M in $CHCl_3$, 5 days at 0 °C. [b] Yield of isolated product. [c] Determined by HPLC on a chiral stationary phase. [d] **3h** (10 μmol). [e] **3h** (7.5 μmol). [f] **3d** (5.0 μmol), 0 °C, 48 h.

entry 10). Electron-rich heterocycles also display good reactivities and high enantioselectivities (Table 3, entries 11–14). The cycloisomerization is not limited to arene groups and a functionalized alkyl substituent $R^1$ provides comparable results (Table 3, entry 15). Trisubstituted alkene **4p** ($R^1$ = Ph, $R^2$ = Me) cyclizes with slightly lower selectivity (Table 3, entry 16). 1,1-disubstitued olefins ($R^1$ = H) react more selectively with methoxy-substituted complex **3d** (Table 3, entries 17–19). In stark contrast, a *cis*-1,2-disubstituted olefin (*cis*-**4a**) is not suitable for the cyclization and is completely recovered (Table 3, entry 20). Related substrates that have the NTs group replaced by an oxygen atom or a malonate group react very sluggishly. The absolute configuration of the cyclopropane products was unambiguously established by X-ray crystallographic analysis of **5g** to be (*S*,*S*,*S*).[9]

In analogy to related reactions with Au and Pt catalysts,[13a,16c,d] the following catalytic cycle is proposed (Scheme 2). After initial dissociation of dimeric complex **3**, coordination




***Scheme 2.*** Proposed catalytic cycle for the cyclization.

to the terminal alkyne of **4** gives π-complex **6**. We believe that the orientation of the alkyne with respect to the chiral $Cp^x$ ligand is critical for the enantioselectivity. A 6-*endo*-dig cyclization would lead to cyclic structures represented in their different mesomeric forms. The carbocationic character of these intermediates provides a rationale for the detected increase in reaction rates with electron-rich arene substituents $R^1$. Finally, a 1,2-hydride shift yields **7**, which in turn releases product **5** and the $Ir^{III}$ complex, completing the catalytic cycle. Alternatively, a mechanism involving an iridium vinylidene intermediate[20] could be considered, although this pathway is less likely as an internal alkyne substrate also cyclizes.[21]

In summary, we report enantiopure cyclopentadienyl $Ir^{III}$ complexes drawing their chirality from an atropchiral $Cp^x$ ligand. A robust complexation using commercial [{Ir-(coe)$_2$Cl}$_2$] and iodine as oxidant provides [{$Cp^xIrI_2$}$_2$] dimers. As the first application of the obtained complexes in asymmetric catalysis, we developed cycloisomerization reactions of enynes to give fused cyclopropanes with high enantioselectivities. The discovered 3,3′-*tert*-butoxy $Cp^x$ ligand displayed superior selectivity. Importantly, complementary to asymmetric Au catalysis, the $Ir^{III}$-catalyzed process is well suited to terminal alkynes. Further work encompassing the application of $Cp^xIr^{III}$ complexes as catalysts, in particular for enantioselective C–H functionalization reactions, is ongoing.

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**Keywords:** asymmetric catalysis · cycloisomerization · cyclopentadienyl ligands · enantioselectivity · iridium

  

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