Application of Transmetallation to the Synthesis of Planar Chiral and Chiral-at-Metal Iridacycles

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ABSTRACT: Diastereoselective lithiation of (S)-2-ferrocenyl-4-(1-methylethyl)oxazoline followed by addition of HgCl₂ resulted in the formation by transmetallation of an (SSR₁,R₂)-configured mercury substituted complex. Addition of this to [Cp²IrCl₂]₂ and tetrabutylammonium chloride resulted in a second transmetallation reaction and formation of an (SSR₂,S₃)-configured chloride-substituted half-sandwich iridacycle as exclusively a single diastereoisomer. By reversing the diastereoselectivity by use of a deuterium blocking group an alternative (SSR₂,S₃)-configured iridacycle was synthesised similarly. Use of (R)-Ugil’s amine as a substrate in the lithiation/double transmetallation sequence gave a (RRS₂,S₃)-configured half-sandwich iridacycle, complexes of this type being previously unavailable by direct cycloiridation. Lithium to gold transmetallation was also demonstrated with the synthesis of an (SSR₂,S₃)-configured Au(I) ferrocenylloxazoline derivative. Use of the (SSR₂,S₃)-iridacycle as a catalyst for the formation of a chiral product by reductive amination with azeotropic HCO₂H/NEt₃ resulted in a racemate.

INTRODUCTION

Metallacycles derived from late transition metals have been studied extensively as catalysts and pre-catalysts for use in synthesis.¹ Much of this work has focused on non-racemic metallacycles displaying planar chirality, including examples that have found application in asymmetric catalysis.² The element of planar chirality is typically generated with relative ease by diastereoselective ortho-C-H activation mediated by a chiral auxiliary attached to a suitable substrate, such as ferrocene (Scheme 1 - (a)).³ Transmetallation has also been used for the synthesis of metallacycles,⁴ this providing an alternative approach where direct access by C-H activation is not possible. However, the use of transmetallation for the synthesis of planar chiral metallacycles is rare (Scheme 1 - (b)).⁵

Scheme 1. General approaches to the synthesis of planar chiral ferrocene-based metallacycles.

We recently reported the synthesis of planar-chiral iridacycles by diastereoselective C-H activation of ferrocenylazolines.⁶ In addition to a new element of planar chirality, this also results in an iridium-based stereogenic center, the configuration of the former controlling the configuration of the latter as exemplified by the formation of (SSR₂,S₃)-² from (S)-¹ (Scheme 2). This methodology was subsequently extended to planar-chiral iridacycles containing a bulky cobalt-based sandwich complex.⁷ Although successful, C-H activation in this way does limit the structure of the iridacycle with respect to relative stereochemistry of the product, and the identity of the auxiliary employed. Therefore, as a potentially more versatile approach, transmetallation was investigated for the synthesis of planar-chiral iridacycles. The results of this investigation are reported in this Article.

Scheme 2. Diastereoselective cycloiridation of ferrocenylloxazoline (S)-¹.⁷

RESULTS AND DISCUSSION

Transmetallation typically involves the transfer of an alkyl or aryl group from an electropositive metal to a metal with an electronegativity closer to the value for carbon. Simultaneous formation of a more polar by-product, typically a halide salt, from the electropositive metal provides the driving force for the transmetalation process.
force for the reaction. Use of lithium as the electropositive metal is attractive given the ubiquity of lithiation as a method of C-H activation, albeit that the use of organolithiums in this way may alternatively result in reduction of the transmetallation partner. As conditions have been reported for the highly diastereoselective lithiation of ferrocenyl oxazoline (S)-1, this reaction was repeated followed by the addition of [Cp*IrCl2]2 in an attempted transmetallation reaction. No iridacycle was observed and the starting material (S)-1 was recovered from the reaction. In contrast, diastereoselective lithiation followed by the addition of HgCl2 did lead to transmetallation and isolation of mercury substituted ferrocenyl oxazoline (SSe)-3 (Scheme 3). The structure of this complex was confirmed by an X-ray crystallographic analysis (Figure 1). A small quantity of a second product was also isolated (16% yield) resulting from double transmetallation of HgCl2 with two equivalents of lithiated ferrocenyl oxazoline (see supporting information).

Scheme 3. Diastereoselective lithiation of (S)-1 and transmetallation with HgCl2.

Figure 1. A representation of the X-ray structure of (SSe)-3 (hydrogen atoms omitted for clarity). Principal bond lengths [Å] include: Hg(1)-C(1) = 2.032(6), Hg(1)-N(1) = 2.948(6), Hg(1)-Cl(1) = 2.295(2). Principal bond angles [°] include: N(1)-Hg(1)-C(1) = 71.63(2), Cl(1)-Hg(1)-C(1) = 178.1(2), Cl(1)-Hg(1)-N(1) = 108.23(11). Thermal ellipsoids are drawn at the 50% probability level. Flack parameter = -0.014(4).

Scheme 4. Mercurcation of (S)-1 by direct C-H activation.

Direct cyclomercuration of (S)-1 was investigated with Hg(OAc)2: followed by acetate/chloride ligand exchange, or by the use of HgCl2 in the presence of excess NaOAc (Scheme 4). Both reactions resulted in mercury substituted complexes with no, or very low, diastereoselectivity. Use of cesium pivalate in place of sodium acetate resulted in a 1:1 ratio of diastereoisomers. The formation of both diastereoisomers by C-H activation was used to confirm, using 1H NMR spectroscopy, the absence of (SSe)-4 in the product of the lithiation/transmetallation procedure. For this, the formation of only (SSe)-3 confirms that transmetallation results in no erosion of diastereoselectivity following highly selective lithiation.

Scheme 5. Synthesis of iridacycles by transmetallation of (SSe)-5.

Addition of [Cp*IrCl2]2 to (SSe)-3 with either dichloromethane or acetone as solvent resulted only in the recovery of starting material (SSe)-3. However, when tetrabutylammonium chloride (TBAC) was included, the reaction in acetone resulted in clean transmetallation (Scheme 5). The broad 1H NMR spectrum of the product matched that of chloride ligated iridacycle (SSe,Rh)-5 synthesized previously. The selectivity of iridacycle formation was determined following addition of KPF6 in acetonitrile and isolation of (SSe,Rh)-2. No other diastereoisomers were observed in the sharp 1H NMR spectrum obtained from this compound. As ligand substitution reactions in these iridacycles have previously been shown to be stereospecific, proceeding with retention of configuration, this outcome confirms that only a single diastereoisomer of (SSe,Rh)-5 was formed on transmetallation. The cationic complex (SSe,Rh)-2 may alternatively be formed, again as a single diastereoisomer, directly by performing the transmetallation reaction in acetonitrile in the presence of KPF6. We also investigated the mercurcation of (η4-2,4-methylenecyclopentadienyl)(η4-tetraphenylcyclobutadiene)cobalt (a
cobalt sandwich complex analogue of (S)-1, which gave a 2:1 ratio of α-HgCl substituted complexes. Mercury to iridium transmetalation was found to proceed in low yield giving a 2:1 ratio of iridacycles (see supporting information).


Unlike direct cycloiridation, the lithiation-transmetalation sequence provides (S,S,S,S)-2 free of small quantities of the planar chiral diastereoisomer (S,R,R,R)-7, as well as avoiding the formation of iridocenium cations. We then chose to selectively synthesize this alternative isomer by utilizing a deuteration blocking group to reverse the diastereoselectivity of ferrocenylaxazoline lithiation (ky/k0 ~ 20). Accordingly, (S)-1 was first lithiated as before followed by the addition of MeOH to give (S,R)-2-d-1 (Scheme 6). Use of this in a second lithiation reaction with n-BuLi in THF, followed by the addition of HgCl2, resulted predominantly in the formation of (S,R)-5-d-4 (d.r. = 10:1). The pure diastereoisomer was obtained readily by recrystallisation, and the identity confirmed by X-ray crystallographic analysis (Figure 2). The X-ray structures of both mercury containing complexes reveal an essentially linear coordination about this metal [C(1)-Hg(1)-Cl = 178.1(2)° in (S,S)-3 and 177.1(2)° in (S,R)-5-d-4]. In both structures the nitrogen is oriented towards mercury such that the distance between this metal and nitrogen [2.948(6) Å in (S,S)-3 and 2.927(5) Å in (S,R)-5-d-4] is less than the estimated sum of their van der Waals radii (~3.6 Å). As such these complexes are designated as mercuracycles, albeit with a weak and labile Hg---N bond as determined for related complexes. This is supported by the similarity of the oxazoline C=N stretch in (S)-1 and (S,S)-3 (1657 and 1645 cm⁻¹ respectively).

Figure 2. A representation of the X-ray structure of (S,S)-5-d-4 (hydrogen and deuterium atoms omitted for clarity). Principal bond lengths [Å] include: Hg(1)-Cl(1) = 2.030(6), Hg(1)-N(1) = 2.927(5), Hg(1)-Cl(1) = 2.303(2). Principal bond angles [°] include: N(1)-Hg(1)-C(1) = 71.7(2), Cl(1)-Hg(1)-C(1) = 177.1(2), Cl(3)-Hg(1)-N(1) = 107.88(11). Thermal ellipsoids are drawn at the 50% probability level. Flack parameter = 0.015(4).

Transmetalation of (S,R)-5-d-4 with [Cp*IrCl2] in the presence of KPF6 gave iridacycle (S,R,R)-5-d-7 as a single diastereoisomer. The identity of this compound was confirmed by comparison of its ¹H NMR spectrum to that of the minor diastereoisomer formed on cycloiridation of (S)-1. The only difference was the absence of a cyclopentadienyl proton signal at 4.85 ppm due to the presence of deuterium. In addition, a NOESY spectrum revealed an NOE between the Cp and Cp* moieties in support of the RR configuration. Transmetalation of (S,R)-5-d-4 with [Cp*IrCl2] in the presence of TBAC gave the neutral chloride ligated complex (S,R,R)-5-d-6. As observed before with chloride ligated iridacycles, the ¹H NMR spectrum of this compound was very broad, so its identity and stereo-chemical integrity were confirmed by conversion into (S,R,R)-5-d-7.

Scheme 7. Synthesis of planar chiral Au(I) complex (S,S)-8.

An advantage of using mercuracycles as the transmetalation intermediate in these reactions is the air and water stability of these complexes, such that they may be purified readily to give a single diastereoisomer. A disadvantage is the toxicity of mercury, and this led us to briefly investigate the use of gold as an alternative metal. Accordingly, diastereoselective lithiation of (S)-1 as before followed by the addition of CIAuPh3 gave (S,S)-8, the ¹H NMR spectrum of...
which displayed three cyclopentadienyl hydrogen signals for the disubstituted ring at 4.89, 4.42 and 4.23 ppm, in addition to characteristic signals for a triphenylphosphine ligand. A related synthesis of planar chiral Au(I) and Au(II) species derived from ferrocenylimidazoline (S)-1 was reported recently.\textsuperscript{15} Attempted transmetallation with [Cp\textsuperscript{+}IrCl\textsubscript{3}]\textsubscript{2} was unsuccessful, and outcome that is likely due to the preference for halogen ligands to be present in both transmetallation partners.

Ugi’s amine 9 is the most widely used starting material for the synthesis of planar chiral ferrocene derivatives,\textsuperscript{16} but a previous attempt by us to use this as a substrate for cycloridation with [Cp\textsuperscript{+}IrCl\textsubscript{3}]\textsubscript{2} was unsuccessful.\textsuperscript{7} These reactions led only to the isolation of ferrocene derivatives formed as a result of \( \alpha \)-substitution, \( \alpha \)-oxidation or elimination. Transmetallation was therefore investigated as an alternative approach starting with the synthesis of (\( R_{3}S_{3} \)-10 (Scheme 8).\textsuperscript{17} This was obtained with a small quantity of the alternative \( R_{3}R_{3} \) isomer, and the 10:1 ratio of diastereoisomers obtained is similar to the ratio of diastereoisomers resulting initially from lithiation under the conditions used (14:1).\textsuperscript{18} Transmetallation of (\( R_{3}S_{3} \)-10 in the presence of excess TBAC proceeded to give a new complex that was purified by recrystallisation. That a new iridacycle had been formed was supported by its \( ^{1} \)H NMR spectrum containing three cyclopentadienyl hydrogen signals for the disubstituted ring (4.20, 4.12 and 3.76 ppm), and a singlet integrating to 15 hydrogen for the Cp\textsuperscript{+} group at 1.71 ppm. Confirmation of the product as (\( R_{3}S_{3} \)-11 was achieved by an X-ray crystallographic analysis (Figure 3).

### Scheme 8. Synthesis of iridacycle (\( R_{3}S_{3} \)-11 via mercurated complex (\( R_{3}S_{3} \)-10.

**Figure 3.** A representation of the X-ray structure of (\( R_{3}S_{3} \)-11 (hydrogen atoms omitted for clarity). Principal bond lengths [Å] include: Ir(1)-C(1) = 2.039(4), Ir(1)-N(1) = 2.220(3), Ir(1)-Cl(1) = 2.4257(10), Ir(1)-Cp\textsuperscript{+} (centre of mass) = 1.822. Principal bond angles [°] include: N(1)-Ir(1)-C(1) = 76.90(17), Cl(1)-Ir(1)-C(2) = 92.42(13), Cl(1)-Ir(1)-N(1) = 85.82(14), N(1)-Ir(1)-Cp\textsuperscript{+} = 134.05, C(1)-Ir(1)-Cp\textsuperscript{+} = 132.06. Thermal ellipsoids are drawn at the 50% probability level. Flack parameter = -0.024(4).

\[
\begin{align*}
\text{Ph} & \text{Ph} & \text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} & \text{Ph} & \text{Ph} \\
\text{NMMe}_2 & \\
\text{10 eq. sBuLi, EtO, 40 °C, 5h} \\
\text{11 eq. HgCl, EtO, 40 °C, 0.5h} & (28\% d.r. = >99\%:1) \\
\text{Ph} & \text{Ph} & \text{Ph} & \text{Ph} \\
\text{NMMe}_2 & \\
\end{align*}
\]

In an attempt to extend this methodology we also investigated the ligated and subsequent transmetallation of \((R)\)-12, a bulky cobalt sandwich complex analogue of Ugi’s amine (Scheme 9).\(^9\)\(^\text{16}\) As was found with its ferrocene-based equivalent, \((R)\)-12 underwent \(\alpha\)-substitution, \(\alpha\)-oxidation or elimination on attempted direct cycloiridation (see supporting information). Thus, following highly diastereoselective ligiation of \((R)\)-12 \((\phi > 99\%:1)\), addition of excess \(\text{HgCl}_2\) led to the isolation by chromatography of \((R,S)_9\)-13 together with recovered \((R)\)-12. The \(^1\text{H}\) NMR spectrum of the new compound displayed a single set of three characteristic cyclopentadienyl hydrogen signals at 4.79, 4.64 and 4.27 ppm. Attempted transmetallation of \((R,S)_9\)-13 with \([\text{CP}^*\text{IrCl}_2]\), under the room temperature conditions used previously, or on heating at reflux, was unsuccessful and resulted only in the recovery of starting material \((R,S)_9\)-13. The low reactivity of bulky cobalt-based sandwich complexes in related metallation reactions has been noted previously.\(^{21}\)

Scheme 10. Iridacycle catalysed reductive amination.

\[
\begin{align*}
\text{Ph} & \text{Ph} & \text{Ph} & \text{Ph} \\
\text{Ph} & \text{Ph} & \text{Ph} & \text{Ph} \\
\text{HN} & \text{Ph} & \text{HN} & \text{Ph} \\
\text{1 mol\% (S,R,S)_{5-d}} & \text{MeOH} & \\
\text{52 HCCH} & \text{52 HCCH} & \\
\text{52 HCCH} & \text{52 HCCH} & \\
\text{80 °C, 16h} & \text{80 °C, 16h} & \\
\end{align*}
\]

In light of the extensive application of half-sandwich iridacycles derived from amines as catalysts for transfer hydrogenation,\(^{22}\) it was anticipated that the ferrocenyloxazoline derived iridacycles of this study could also be applied to such reactions. In a preliminary investigation, a mixture of acetophenone and benzylamine underwent reductive amination when heated with an azetrope mixture of formic acid and triethylamine in the presence of 1 mol\% \((S,R,S)_{5-d}\) (Scheme 10). Following acetylation (see supporting information), the product of this reaction was determined by chiral HPLC to be racemic. On the basis of an experimental and computational study, the mechanism of intermediate imine reduction is proposed to proceed by rate determining iridacycle hydride formation by outer-sphere hydride transfer to the imino bond.\(^{23}\) In light of this, it is notable that the use of a related chiral non-racemic iridacycle as a catalyst for reductive amination resulted in a complete absence of stereoinversion.\(^{24}\)

**CONCLUSION**

Transmetalation is a viable alternative to cycloiridation as a method for the synthesis of ferrocene-based planar chiral iridacycles. Although lithium to iridium transmetalation did not prove possible, lithium to mercury by mercury to iridium transmetalation reactions were successful. This process provided access to iridacycles that were previously unavailable by direct introduction of iridium by C-H activation. In the first example, the reversal of ferrocenyloxazonilium diastereoselectivity by use of a deuterium blocking group led to the exclusive synthesis of the minor diastereoisomer generated previously by cycloiridation. In the second example, the transmetalation approach gave access to an iridacycle derived from Ugi’s amine; whereas previously attempted cycloiridation had resulted in substrate degradation. The intermediate mercurycycles generated in this study are air and water stable, and may be purified to remove any minor diastereoisomer arising from incomplete selectivity on substrate lithiation. Gold was investigated as an alternative to mercury, transmetalation providing access to a planar chiral Au(l) species. A preliminary investigation into the use of an enantiomerically and diastereomerically pure iridacycle as a catalyst for reductive amination resulted in the formation of a racemic product.

**EXPERIMENTAL SECTION**

**General remarks. Caution!** All organo mercury compounds are highly toxic. Extreme care is necessary when handling all products and their solutions. Diethyl ether and THF were distilled over sodium and benzophenone ketyl. Acetonitrile and dichloromethane were dried by distillation from calcium hydride. Methanol was dried over 4 Å molecular sieves. All cyclorization reactions and reactions involving the use of dry solvents were carried out under an inert atmosphere of either nitrogen or argon. Silica gel (60 Å pore size, 40 – 63 μm technical grade) and neutral aluminum oxide (Brockmann I, 50 – 200 μm) were used for chromatography.

**Synthesis of \((S,S)_{5-d}\) -3 (51 g, 0.51 mmol) was added to a flame dried Schlenk tube under an atmosphere of argon and dissolved in dry diethyl ether (6.56 mL). TMEDA (0.10 mL, 0.66 mmol) was added and the subsequent orange solution was cooled to -78 °C and stirred for 5 minutes after which sec-butyl lithium (1.4 M in hexanes) (0.47 mL, 0.66 mmol) was added slowly. In a separate Schlenk tube mercury(II) chloride (0.2741 g, 1.01 mmol) was stirred by heating under high vacuum and allowed to cool. After the reaction had stirred for 2 hours the mixture was warmed to 0 °C and a partial suspension of mercury(II) chloride was added (using dry diethyl ether (6 mL)) to the reaction mixture and stirred for 10 minutes. The reaction was allowed to warm to room temperature, and after an additional 30 minutes, was quenched with saturated sodium hydrogen carbonate solution. The organics were separated with H₂O, washed with brine, dried over MgSO₄ and upon removal of the solvent in vacuo gave a crude product. Column chromatography (SiO₂, 10% EtOAc/hexane) yielded a yellow solid as a single diastereoisomer (0.1748 g, 65%). R₉ 0.51 (10% EtOAc in hexane).

M.p: 149 - 152 °C. [α]D²⁵⁻²⁵⁻ = -312 (c 0.2, CHCl₃). IR (film): 3095, 2952, 2924, 2869, 1645 (CN); H NMR (500 MHz, CDCl₃): 4.84 (IH, dd, \(\delta_{J_{HH}} = 2.6\), \(\delta_{J_{HH}} = 1.1\) Hz, Cppf), 4.52 (IH, ap, \(\delta_{J_{HH}} = 2.4\) Hz, Cppf), 4.45 (IH, dd, \(\delta_{J_{HH}} = 9.6\), \(\delta_{J_{HH}} = 8.4\) Hz, Cppf), 4.31 (IH, dd, \(\delta_{J_{HH}} = 2.4\), \(\delta_{J_{HH}} = 1.1\) Hz, Cppf), 4.21 (5H, s, Cppf), 4.14 (1H, ap, \(\delta_{J_{HH}} = 0.2\) Hz, Cppf), 3.90 - 3.08 (1H, m, Cppf), 1.76 - 1.71 (1H, m, Cppf), 1.06 (3H, d, \(\delta_{J_{HH}} = 6.7\) Hz, Cppf), 1.02 (3H, d, \(\delta_{J_{HH}} = 6.7\) Hz, Cppf). ¹³C NMR (125 MHz, CDCl₃): 168.6 (C=O, 85.8 (Cp(C)), 75.5 (Cp(CH)), 74.5 (Cp(CH)), 73.0 (Cp(CH)), 72.0 (CH), 71.8 (CH), 70.2 (Cp(CH)), 70.1 (Cp(CH)), 33.0 (CH), 19.2 (CH₃), 18.8 (CH₃). High resolution MS (m/z, APCl):

In vacuo. 13C NMR (125 MHz, CDCl3): 168.5 (C=N), 86.4 (Cp), 75.5 (Cp), 72.4 (Cp), 72.3 (C=C), 70.2 (C=CH2), 33.3 (CH3), 19.1 (CH2). High resolution MS (m/z, ASAP): found for [M-H]+ = 505.0276, calcd for C32H37FeIrNO+H- = 505.0267.

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103.2 (d, Jο=122.6 Hz, C蓬P蓬)H), 73.8 (d, Jο=4.6 Hz, C蓬P蓬), 72.4 (CH), 72.1 (d, Jο=5.8 Hz, C蓬P蓬), 71.0 (d, Jο=5.1 Hz, C蓬P蓬), 69.0 (CH), 68.9 (CH), 32.5 (CH), 19.2 (CH), 17.9 (C蓬H蓬). 13C NMR (202 MHz, CDCl3): 44.06 (P蓬H蓬). High resolution MS (m/z, APCI-): found for [M+H]+=756.1390, calcd for C蓬H蓬11蓬AuFeNOP+H+=756.1397.

**Synthesis of (R蓬S蓬)-10.** [R蓬S蓬]-9 [0.2572 g, 1.00 mmol] was dissolved in diethyl ether (2 mL) in a flame dried Schlenk tube under an inert atmosphere. n-Butyllithium (0.86 mL, 1.20 mmol) was added dropwise and the solution stirred at room temperature for 2 h. In a separate dry vessel, mercury(II) chloride (0.407 g, 1.50 mmol) was heated under high vacuum to ensure it was completely dry and dissolved in the minimum quantity of diethyl ether once cool. After 2 h, the mercury(II) chloride solution was added rapidly to the reaction mixture which was then stirred at room temperature for 30 minutes. The resulting cloudy orange suspension was quenched with saturated sodium hydroxide solution and the mixture was filtered through Celite™ and dried with potassium carbonate followed by removal of the solvent in vacuo. The resulting pale yellow solid was recrystallized from ethyl acetate. The organic solvent was removed in vacuo and the residue was purified by column chromatography (SiO2, 1 % NEt3/ EtOAc) giving a red solid (0.171 g, 84 %). 1H and 13C NMR (CDCl3) were measured by thin-slice ω- and φ-scans. Data were processed using the Bruker Topspin 4.0 software. Spectral assignments were made using 1D and 2D homo- and heteronuclear correlation experiments. Crystal structure analyses -

**Crystal structure analyses - (R蓬S蓬)-3 & (S蓬S蓬)-5-4** For each sample, a single crystal was mounted on a glass fiber and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur-3+Sapphire3-CCD diffractometer (at UEA). Intensity data were measured by thin-slice ω- and φ-scans. Data were processed using the CrystAlisPro-CCD and RED32 programs. The structures were determined by the intrinsic phasing routines in the SHELXT program and refined by full-matrix least-squares methods on F2, in SHELXL. The non-hydrogen atoms were refined with anisotropic displacement parameters. Water and then brine, dried over potassium carbonate, and the solvent removed in vacuo. Purification by column chromatography (SiO2, 50 % EtOAc/hexane) yielded the product as a yellow solid (0.035 g, 28 %). IR (film): 3053, 2971, 2928, 2879. 1H NMR (500 MHz, CDCl3): 7.49 - 7.45 (8H, m, ArH), 7.27 - 7.24 (12H, m, ArH), 4.79 (1H, dd, J=2.4, J=1.2 Hz, C蓬P蓬), 4.27 (1H, dd, J=2.4, J=1.2 Hz, C蓬P蓬), 4.64 (1H, apt, J=3.4, J=2.4 Hz, C蓬P蓬), 3.04 (1H, brq, J=6.7 Hz, CH), 1.96 (6H, s, N(C蓬H蓬)), 0.87 (3H, d, J=6.7 Hz, CH). 13C NMR (125 MHz, CDCl3): 136.2 (ArC蓬H蓬), 128.8 (ArC蓬H蓬), 128.5 (ArC蓬H蓬), 126.7 (ArC蓬H蓬), 104.7 (C蓬P蓬), 88.9 (C蓬P蓬), 84.5 (C蓬P蓬), 61.9 (C蓬P蓬), 75.3 (C蓬P蓬), 55.6 (CH), 39.1 (N(C蓬H蓬)), 9.8 (CH). High resolution MS (m/z, APPI-): [M-H]+=788.1413, calcd for C蓬H蓬16蓬C蓬6蓬C蓬2蓬H篷G篷可蓬H篷OnH蓬+H+=788.1414.

Iridacycle catalysed reductive amination. To a Schlenk tube was added acetonitrile (0.12 mL, 1.00 mmol), benzylamine (0.13 mL, 1.20 mmol) and (S蓬S蓬)-5-6 (0.007 g, 0.01 mmol) followed by dissolution in methanol (3 mL). A 5:2 mixture of formic acid and triethylamine (0.5 mL) was then added and the reaction heated to 80°C and stirred at this temperature overnight following sealing of the Schlenk tube. After cooling, the reaction was quenched with water, made basic with potassium hydroxide and extracted with ethyl acetate. The organic solvent was removed in vacuo and the residue purified by column chromatography (SiO2, 10 % EtOAc/hexane) yielding a colorless oil (0.068 g, 32 %, 0 % ee). Data as previously reported.6 The crystal structure solution program, SHELXL-97, was employed the structure solution and refinement process. The model was refined with version 2014/7 of ShelXL using Least Squares minimization.

**Crystal structure analysis of (S蓬S蓬)-11.** A suitable crystal (0.130×0.120×0.005) mm was selected and mounted on a MITIGEN holder in perfluoroether oil on a Rigaku FRE+ equipped with VHF Varimax confocal mirrors and an AFC12 goniometer and HyPix 6000 detector diffractometer. The crystal was kept at T=100 (2) K during data collection. Using Olex2,9 the structure was solved with the ShelXT-2016 structure solution program, using the Intrinsic Phasing solution method. The model was re-refined with version 2014/7 of ShelXL using Least Squares minimization.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website. Copies of the 1H, 13C, 31P NMR and X-ray crystallography details (PDF file). CCDC 1873232, 1873231 and 1862175 contain supplementary X-ray crystallographic data for (S蓬S蓬)-3, (S蓬S蓬)-5-4 and (R蓬S蓬)-11, respectively. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax(+44) 1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk.
REFERENCES