

Phenyl vs. Ferrocenyl Cyclometallation Selectivity: Diastereoselective Synthesis of an Enantiopure Iridacycle

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This paper is dedicated to the memory of Sarah R. Delf. Friend, colleague and chemist.

Abstract: Ferrocenyl (Fc) and phenyl (Ph) containing imines FcCH=NCH(R)Ph and FcCH(R)N=CHPh (R = H and Me) were cycloiridated using [Cp*IrCl₂]₂ with NaOAc in CH₂Cl₂. All resulted in the formation of neutral chloride ligated half-sandwich iridacycles as a result of *ortho*-phenyl and not α -ferrocenyl C-H activation. The complexes derived from FcCH=NCH(R)Ph (R = H, Me) were obtained as a mixture of *E* and *Z* imine isomers, and with R = Me the product obtained from the (*S*)-imine was isolated by recrystallisation as a single diastereoisomer. The configuration was determined by an X-ray crystal structure analysis as *S_c,R_{ir},E*.

Introduction

Several recent publications have described the synthesis of neutral or cationic iridium(III) half-sandwich metallacycles of general structure **1**¹ (Figure 1), with many of these investigations being directed towards application of the resulting complexes in catalysed organic transformations.² In addition, a number of chiral non-racemic examples are known for which a key issue is configurational control of the iridium-based stereogenic centre.³ To this end we recently reported the synthesis of ferrocene-based planar-chiral iridacycle **2**, synthesised as a single diastereoisomer from a precursor ferrocenylimine by α C-H bond activation. Extension of this reaction to a chiral non-racemic ferrocenyloxazoline substrate resulted in highly diastereoselective α C-H bond activation and isolation of iridacycle **3**. In both **2** and **3** the iridium-centred chirality is controlled by the planar chirality *via* Fe-Ir mediated stereoelectronic control of ligand substitution.⁴

In a related approach to obtain imine-based complexes we chose to investigate the cycloiridation of *N*-benzylimines **4** and isomeric *N*-ferrocenylmethylimines **5**. These substrates, in addition to being readily accessible, are set up to determine the *exo* vs. *endo* or phenyl vs. ferrocenyl selectivity arising from α or *ortho* C-H bond activation. Furthermore, with substrates **4b** and **5b** there is the potential for the carbon-based stereogenic centre to control the iridium-based stereogenic centre of the resulting metallacycle, either with or without the

generation of a new element of planar chirality.

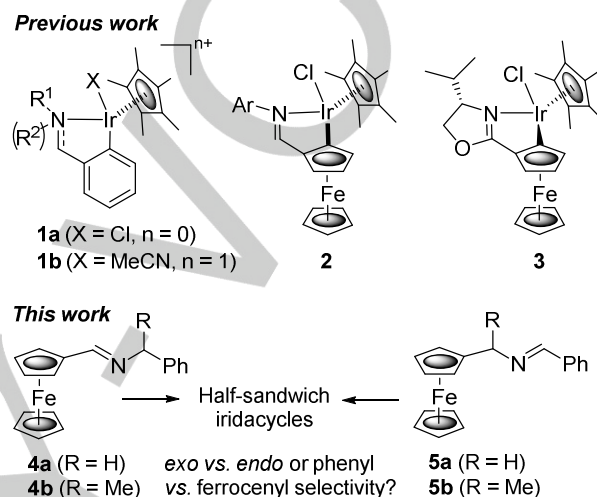


Figure 1. Half-sandwich Iridacycles **1-3** and potential routes to related complexes from **4** and **5**.

Results and Discussion

Imines **4a** (81%), (*S*)-**4b** (93%), **5a** (74%) and **5b** (74%) were synthesised from the corresponding aldehyde and amine by heating these at reflux in toluene in the presence of a catalytic quantity of potassium carbonate. Water was removed from the reaction by use of a Dean and Stark apparatus and 4 Å molecular sieves. Cycloiridation of phenyl compounds containing an *ortho* directing group with [Cp*IrCl₂]₂ and NaOAc in CH₂Cl₂ has resulted in a number of neutral half-sandwich iridacycles of general structure **1a**.³⁹ This cycloiridation method was also used for the synthesis of complexes **2** and **3**.⁴ Application of these conditions to **4a** resulted in the isolation of an inseparable mixture of two iridacycles in a 1 : 0.45 ratio (Scheme 1). That both had arisen from phenyl *ortho* C-H activation was apparent from the two sets of four aromatic proton signals in the ¹H NMR spectrum. This, together with there being two corresponding sets of nine ferrocenyl proton signals, led to the identification of these complexes as (*Z*)-**6a** and (*E*)-**6a**. The latter was assigned on the basis of the high chemical shift of one of the two diastereotopic α -proton signals observed at 6.23 ppm due to the proximity of this hydrogen to the iridium-chlorine bond (*vide infra*). Following isolation, no change was observed in the solution ratio of (*Z*)-**6a**/*E*-**6a** over a period of 24 hours suggesting that following isolation imine isomerisation does not occur.⁵

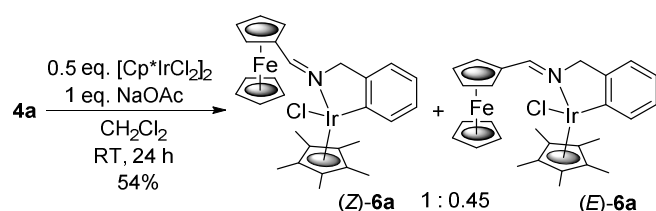
This observed preference for cycloiridation of the phenyl group, and thus *exo* over *endo* selectivity, is in marked contrast

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to the outcome of palladation of **4a** which results exclusively in ferrocenyl alpha C-H activation and formation of an *endo* palladacycle.⁶ The preference for *endo* selective cyclopalladation has been noted elsewhere,⁷ including the cyclopalladation of **5a** which results in a 3 : 2 ratio of *endo* : *exo* palladacycles.⁸ In this example *endo* selectivity partly overcomes the preference for ferrocenyl over phenyl cyclopalladation, an outcome rationalised by the significantly greater susceptibility of the former moiety to electrophilic aromatic substitution.⁹ In contrast, cycloiridation of **5a** resulted only in phenyl C-H activation and formation of **7a**, the ¹H NMR spectrum of the product again containing four distinct aromatic proton signals (Scheme 2). In this instance the endocyclic imine functionality dictates a single double bond configuration.

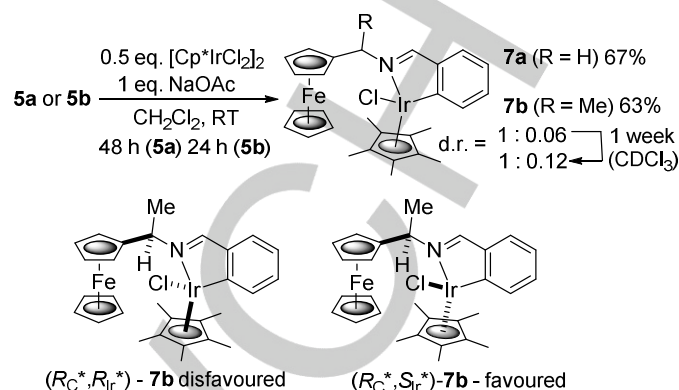


Scheme 1. Phenyl (*exo*) selective cycloiridation of imine **4a**.

The participation of an iridium-coordinated acetate in a concerted metallation deprotonation pathway has been studied in depth,¹⁰ and compared to cyclopalladation, DFT calculations point to there being stronger electrophilic character in C-H bond activation with Ir(III) complexes.¹¹ In agreement with this, a cycloiridation study with a series of *meta*-substituted phenylimines using $[\text{Cp}^*\text{IrCl}_2]_2$ and NaOAc revealed that substrates with electron donating substituents reacted significantly faster than those with electron withdrawing substituents.¹² In contrast, the exclusivity of phenyl over ferrocenyl C-H activation does not result from the relative susceptibility of these moieties to electrophilic substitution, assuming that the reactions are under kinetic control. Examination by ¹H NMR spectroscopy of the cycloiridation reaction mixtures in the early stages of the reaction revealed no evidence of initial ferrocenyl C-H activation.

Extension of cycloiridation to substrate **5b**, containing a carbon-based stereogenic centre, also resulted exclusively in phenyl C-H activation and formation of a predominant diastereoisomer for which the percentage of the minor isomer (6%) did not change on standing in CDCl_3 for 24 hours. After 1 week the percentage of the minor isomer had increased to 12% (Scheme 2). For the major isomer an NOE interaction is observed between the imine C-H and the methyl group (Figure 2). Based on this conformational preference, with respect to C-N bond rotation, the largest group attached to the stereogenic centre, *i.e.* the ferrocenyl moiety, is oriented towards the bulky Cp^* group in the $R_{\text{C}}^*, R_{\text{Ir}}^*$ diastereoisomer. That this is avoided in the $R_{\text{C}}^*, S_{\text{Ir}}^*$ isomer is the basis of this relative configuration being assigned tentatively to **7b**, this being supported by an

NOE interaction between the methine of the carbon-based stereogenic centre and the Cp^* group.



Scheme 2. Phenyl (*endo*) selective cycloiridation of imines **5a/b** and suggested relative configuration of Iridacycle **7b**.

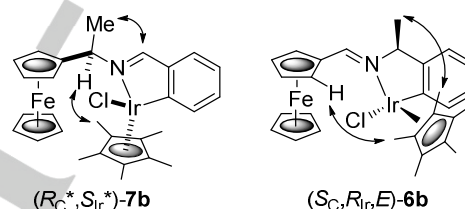
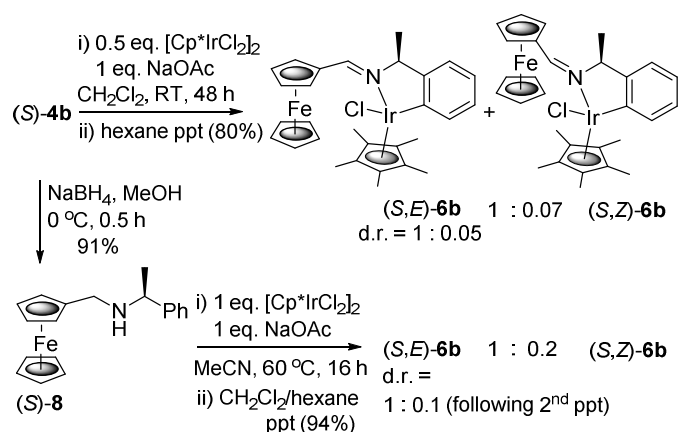


Figure 2. Significant NOE interactions observed for $(R_{\text{C}}^*, S_{\text{Ir}}^*)$ -**7b** and $(S_{\text{C}}, R_{\text{Ir}}, E)$ -**6b**.

In contrast to imine **5b**, enantiopure imine **4b** is readily synthesised due the commercial availability of both enantiomers of the precursor, α -methylbenzylamine. In addition to this impetus, it was reasoned that phenyl-selective C-H activation would place the carbon-based stereogenic centre within the resultant Iridacycle, possibly leading to control of the iridium-based stereogenic centre. Reaction of *(S)*-**4b** with $[\text{Cp}^*\text{IrCl}_2]_2$ and NaOAc in CH_2Cl_2 , and analysis of the reaction mixture after 48 h, revealed the formation of two major Iridacycles in a 1 : 0.4 ratio. Following filtration through Celite and precipitation with hexane this ratio had changed to 1 : 0.07 (Scheme 3). Recrystallisation from CH_2Cl_2 /hexane enabled confirmation of the identity of the complex as an Iridacycle by an X-ray crystal structure analysis, which also revealed the configuration as $S_{\text{C}}, R_{\text{Ir}}, E$ (Figure 3).¹³ That this is also the configuration of the major isomer found in solution was confirmed by the NOE interaction between Cp^*/Me and also between $\text{Cp}^*/\text{Fc-H}$ (Figure 2). For the latter pair, the chemical shift of this ferrocenyl hydrogen which is proximate to the iridium-chlorine bond is 6.23 ppm. By comparison this confirms the identity of *(E)*-**6a** (*vide supra*). The similarity of the spectral data of *(Z)*-**6a** to that of the other cycloiridation product confirms it to be imine stereoisomer *(S,Z)*-**6b** (for which the Ir configuration was not determined).



Scheme 3. Diastereoselective syntheses of Iridacycle (S_C, R_{Ir}, E)-**6b**.

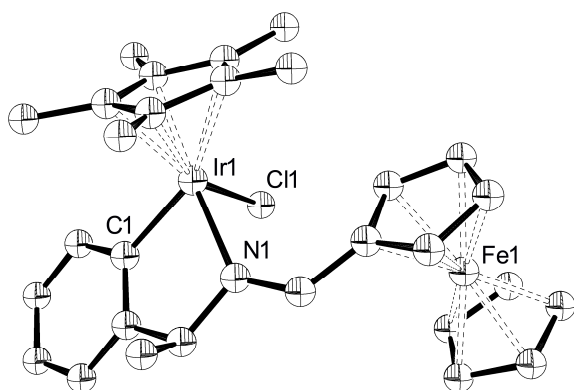


Figure 3. A representation of the X-ray structure of (S_C, R_{Ir}, E)-**6b** (hydrogen atoms omitted for clarity). Principal bond lengths [Å] include: Ir(1)-C(1) = 2.025(5), Ir(1)-N(1) = 2.095(4), Ir(1)-Cl(1) = 2.4093(12), Ir(1)-Cp* (centre of mass) = 1.837(2). Principal bond angles (°) include: N(1)-Ir(1)-C(1) = 78.77(19), Cl(1)-Ir(1)-C(1) = 85.47(14), Cl(1)-Ir(1)-N(1) = 89.36(12), N(1)-Ir(1)-Cp* = 133.44(14), C(1)-Ir(1)-Cp* = 128.97(15).

Closer inspection of the ^1H NMR spectrum of the material obtained by precipitation revealed a third Iridacycle product in a relative ratio of 0.05. A deshielded ferrocenyl hydrogen signal at 6.44 ppm is indicative of this complex being (S_C, S_{Ir}, E)-**6b**. This signal is absent in the spectrum of the recrystallised sample of (S_C, R_{Ir}, E)-**6b** (as are the signals for (S, Z)-**6b**). Re-recording the spectrum after the CDCl_3 solution had stood at room temperature for 24 hours revealed the reappearance of the minor signal arising from epimeric (S_C, S_{Ir}, E)-**6b**. The mother liquor resulting from the crystallisation of (S_C, R_{Ir}, E)-**6b** contained a 1:0.6 ratio of (S_C, R_{Ir}, E):(S_C, S_{Ir}, E)-**6b**. After the CDCl_3 solution of this mixture had stood at room temperature for 24 hours, re-recording the spectrum revealed that this had also equilibrated to a mixture containing approximately 5–10% of (S_C, S_{Ir}, E)-**6b** (and with no change in the relative ratio of (S, Z)-**6b**).

As a preliminary investigation into the substitution chemistry of this complex, a CDCl_3 solution of the precipitation product containing predominantly (S_C, R_{Ir}, E)-**6b** was shaken

sequentially with aqueous solutions of NaBr, NaI and KF, and the ^1H NMR spectrum recorded after each cycle. These showed the formation of the halide substitution products for which the imine C-H signal changes as F (8.51), Cl (8.48), Br (8.42) and I (8.34 ppm). The iridium centre undergoing substitution is gamma to the ferrocenyl group and is connected by the unsaturated C=N bond. This connectivity may facilitate halide ligand substitution by a dissociative mechanism, and explain the greater configurational lability of (S_C, R_{Ir}, E)-**6b** compared to (R_C^*, S_{Ir}^*)-**7b**.

Very few half-sandwich iridacycles derived from α -methylbenzylamine, N, N -dimethyl- α -methylbenzylamine and related compounds have been reported.^{3b,c,j} In contrast much more work has appeared on the synthesis and characterisation of corresponding half-sandwich rhodacycles and ruthenacycles which are generally obtained as a mixture of configurationally labile diastereoisomers.¹⁴ In common with a detailed analysis of some of these complexes,^{3b} the X-ray structure of (S_C, R_{Ir}, E)-**6b** reveals that the cycloiridated five-membered ring displays an envelope conformation containing an out of plane nitrogen and a pseudoaxial methyl substituent (δ conformation^{3b}). That this arises from the S_C, R_{Ir} stereogenic centres is in agreement with the usual $R_C, S_M/\delta$ (or $S_C, R_M/\delta$) association found with metallacycles derived from primary and secondary α -methylbenzylamines.¹⁵

The success of imine cycloiridation prompted an attempt to perform the same reaction on a corresponding amine. Reduction of (S)-**4b** gave (S)-**8** with which cycloiridation was attempted by reaction with $[\text{Cp}^*\text{IrCl}_2]_2$ and NaOAc in MeCN (Scheme 3). The main iridacycles in the initial product mixture were identified as imine derivatives (S_C, R_{Ir}, E)-**6b** and (S, Z)-**6b** and in a 1 : 0.2 ratio. Following a second cycle of precipitation from CH_2Cl_2 /hexane this ratio increased to 1 : 0.05, the product also containing approximately 10% of the minor S_C, S_{Ir}, E isomer of **6b**. That this outcome is very similar to that obtained with imine (S)-**4b** points to amine oxidation occurring prior to cycloiridation. Concomitant secondary amine oxidation/cycloiridation has been observed previously,^{3e,16} and this result reinforces our previous observations that ferrocenylmethylamines, due to their propensity for oxidation, are unsuitable substrates for cycloiridation.⁴

Conclusions

Cycloiridation with $[\text{Cp}^*\text{IrCl}_2]_2$ and NaOAc in CH_2Cl_2 is selective for a phenyl group given the choice between this and a ferrocenyl group as the moiety undergoing C-H activation. Substrates $\text{FcCH}(\text{R})\text{N}=\text{CHPh}$ are *endo* selective, whereas substrates $\text{FcCH}=\text{NCH}(\text{R})\text{Ph}$ are *exo* selective, and also result in imine *E* and *Z* diastereoisomers. Both types of substrate, with $\text{R} = \text{Me}$, result in the isolation of predominantly one chiral-at-iridium diastereoisomer, the configuration of the major iridacycle derived from (S)- $\text{FcCH}=\text{NCH}(\text{Me})\text{Ph}$ being determined as S_C, R_{Ir}, E by an X-ray crystal structure analysis.

Experimental Section

Synthesis of (S_C, R_{ir}, E)-**6b**. Imine (S)-**4b** (0.080 g, 0.25 mmol), (pentamethylcyclopentadienyl)iridium(III) chloride dimer (0.100 g, 0.13 mmol) and sodium acetate (0.023 g, 0.28 mmol) were added to a flame dried Schlenk tube under an inert atmosphere. Dry dichloromethane (8 mL) was added and the resulting solution stirred at room temperature for 48 h. Upon completion (reaction progress monitored by ^1H NMR), the reaction mixture was filtered through Celite[®] using dichloromethane as the eluent, collecting a deep orange solution. The solvent was reduced *in vacuo* and hexane added to afford precipitation. The solid was collected by filtration to give an orange powder containing predominantly (S_C, R_{ir}, E)-**6b** with (S, Z)-**6b** and (S_C, S_{ir}, E)-**6b** (1 : 0.07 : 0.05 ratio, 0.14 g, 80 %). Pure (S_C, R_{ir}, E)-**6b** was obtained by recrystallisation from $\text{CH}_2\text{Cl}_2/\text{hexane}$. mp 210 - 211 °C (decomp.); $[\alpha]_D^{26}$ -1267 (c 0.12, CHCl_3); v_{max} (film)/ cm^{-1} 3103, 3048, 2982, 2910, 1617 (C=N); HRMS (AS) $[\text{M}-\text{Cl}]^+ \text{C}_{29}\text{H}_{33}\text{FeIrN}^+$, Calc. 644.1588, Obs. 644.1590; ^1H NMR (500 MHz, CDCl_3) 8.48 (1H, s, HC=N), 7.41 (1H, dd, $J = 7.5, 0.9$ Hz, Ph-H), 7.01 (1H, td, $J = 7.3, 1.3$ Hz, Ph-H), 6.96 (1H, dd, $J = 7.3, 1.0$ Hz, Ph-H), 6.87 (1H, td, $J = 7.3, 1.2$ Hz, Ph-H), 6.23 (1H, dt, $J = 2.4, 1.2$ Hz, Cp-H), 4.83 (1H, q, $J = 6.8$ Hz, CH), 4.54 (1H, dt, $J = 2.4, 1.2$ Hz, Cp-H), 4.51 (1H, dt, $J = 3.7, 1.9$ Hz, Cp-H), 4.48 (1H, dt, $J = 3.7, 1.9$ Hz, Cp-H), 4.24 (5H, s, CpH), 1.49 (15H, s, Cp*), 1.36 (3H, d, $J = 6.9$ Hz, CH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 167.3 (C=N), 152.0 (Ar-C), 150.6 (Ar-C), 136.5 (Ar-C), 127.1 (Ar-C), 122.6 (Ar-C), 119.2 (Ar-C), 87.8 (Cp*-C), 82.0 (CHMe), 78.9 (Fc-C), 73.7 (Fc-C), 71.9 (Fc-C), 71.8 (Fc-C), 70.5 (Fc-C), 70.1 (Fc-C), 26.7 (CH_3), 9.6 (Cp*-C).

Acknowledgements

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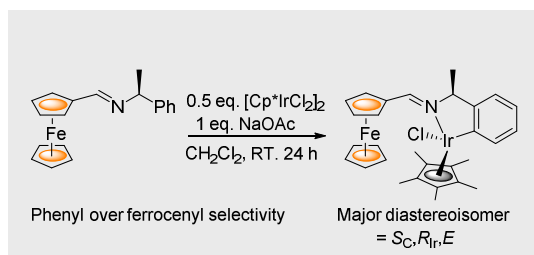
Keywords: Iridacycle • ferrocene • regioselectivity • diastereoselectivity • enantiopure

- [1] Y.-F. Han, G.-X. Jin, *Chem. Soc. Rev.* **2014**, *43*, 2799.
 [2] Selected examples: a) J. F. Hull, D. Balcells, J. D. Blakemore, C. D. Incarvito, O. Eisenstein, G. W. Brudvig, R. H. Crabtree, *J. Am. Chem. Soc.* **2009**, *131*, 8730. b) Y. Kashiwame, S. Kuwata, T. Ikariya, *Chem. Eur. J.* **2010**, *16*, 766. c) T. Jerphagnon, R. Haak, F. Berthiol, A. J. A. Gayet, V. Ritleng, A. Holuigue, N. Pannetier, M. Pfeffer, A. Voelklin, L. Lefort, G. Verzijl, C. Tarabiono, D. B. Janssen, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *Top. Catal.* **2010**, *53*, 1002. d) C. Wang, A. Pettman, J. Bacsa, J. Xiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 7548. e) M. Watanabe, Y. Kashiwame, S. Kuwata, T. Ikariya, *Eur. J. Inorg. Chem.* **2012**, 504. f) J. Wu, D. Talwar, S. Johnston, M. Yan, J. Xiao, *Angew. Chem. Int. Ed.* **2013**, *52*, 6983. g) D. Talwar, N. P. Salguero, C. M. Robertson, J. Xiao, *Chem. Eur. J.* **2014**, *20*, 245.
 [3] a) W. Bauer, M. Prem, K. Polborn, K. Sünkel, W. Steglich, W. Beck, *Eur. J. Inorg. Chem.* **1998**, 485. b) J.-B. Sortais, N. Pannetier, A. Holuigue, L. Barloy, C. Sirlin, M. Pfeffer, N. Kyritsakas, *Organometallics* **2007**, *26*, 1856. c) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Organometallics* **2008**, *27*, 2795. d) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Angew. Chem. Int. Ed.* **2008**, *47*, 2447. e) L. Barloy, J.-T. Issenhuth, M. G. Weaver, N. Pannetier, C. Sirlin, M. Pfeffer, *Organometallics* **2011**, *30*, 1168. f) N. Pannetier, J.-B. Sortais, J.-T. Issenhuth, L. Barloy, C. Sirlin, A. Holuigue, L. Lefort, L. Panella, J. G. de Vries, M. Pfeffer, *Adv. Synth. Catal.* **2011**, *353*, 2844. g) Y. Boutadla, D. L. Davies, R. C. Jones, K. Singh, *Chem. Eur. J.* **2011**, *17*, 3438. h) J. H. Barnard, C. Wang, N. G. Berry, J. Xiao, *Chem. Sci.* **2013**, *4*, 1234. i) E. Féghali, L. Barloy, J.-T. Issenhuth, L.

- Karmazin-Brelot, C. Bailly, M. Pfeffer, *Organometallics* **2013**, *32*, 6186. j) S. Sabater, M. Baya, J. A. Mata, *Organometallics* **2014**, *33*, 6830.
 [4] R. A. Arthurs, M. Ismail, C. C. Prior, V. O. Oganessian, P. N. Horton, S. J. Coles, C. J. Richards, *Chem. Eur. J.* **2016**, *22*, 3065.
 [5] It is frequently assumed that aldimines are *E*-configured, but a significant percentage of the *Z*-isomer can exist in solution. See: J. Bjørge, D. R. Boyd, C. G. Watson, W. B. Jennings, D. M. Jerina, *J. Chem. Soc., Perkin Trans. 2* **1974**, 1081.
 [6] C. López, J. Sales, X. Solans, R. Zquiak, *J. Chem. Soc., Dalton Trans.* **1992**, 2321.
 [7] R. Y. Mawo, S. Mustakim, V. G. Young Jr., M. R. Hoffmann, I. P. Smoliakova, *Organometallics* **2007**, *26*, 1801.
 [8] R. Bosque, C. López, J. Sales, *J. Organomet. Chem.* **1995**, *498*, 147.
 [9] A CMD type pathway has been proposed for acetate-assisted cyclopalladation for which the nucleophilicity of the carbon at which the new metal bond is formed is a factor determining regioselectivity. See a) A. D. Ryabov, I. K. Sakodinskaya, A. K. Yatsimirsky, *J. Chem. Soc., Dalton Trans.* **1985**, 2629. b) D. L. Davies, S. M. A. Donald and S. A. Macgregor, *J. Am. Chem. Soc.* **2005**, *127*, 13754. c) S. I. Gorelsky, D. Lapointe, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 10848.
 [10] (a) D. L. Davies, S. M. A. Donald, O. Al-Duaij, S. A. Macgregor, M. Pölleth, *J. Am. Chem. Soc.* **2006**, *128*, 4210. (b) J. Li, W. Hu, Y. Peng, Y. Zhang, J. Li, W. Zheng, *Organometallics* **2014**, *33*, 2150.
 [11] M. García-Melchor, S. I. Gorelsky, T. K. Woo, *Chem. Eur. J.* **2011**, *17*, 13847.
 [12] L. Li, W. W. Brennessel, W. D. Jones, *Organometallics* **2009**, *28*, 3492.
 [13] CCDC 1491981 contains the supplementary crystallographic data for this paper. This data is provided free of charge by The Cambridge Crystallographic Data Centre.
 [14] Examples include: (a) H. C. L. Abbenhuis, M. Pfeffer, J.-P. Sutter, A. de Cian, J. Fischer, H. L. Ji, J. H. Nelson, *Organometallics* **1993**, *12*, 4464. (b) S. Fernandez, M. Pfeffer, V. Ritleng, C. Sirlin, *Organometallics* **1999**, *18*, 2390. (c) M. Pfeffer, *Organometallics* **2000**, *19*, 2427. (d) H. D. Hansen, J. H. Nelson, *Organometallics* **2001**, *20*, 5257. (e) J.-B. Sortais, V. Ritleng, A. Voelklin, A. Holuigue, H. Small, L. Barloy, C. Sirlin, G. K. M. Verzijl, J. A. F. Boogers, A. H. M de Vries, J. G. de Vries, M. Pfeffer, *Org. Lett.* **2005**, *7*, 1247.
 [15] J.-B. Sortais, N. Pannetier, N. Clément, L. Barloy, C. Sirlin, M. Pfeffer, N. Kyritsakas, *Organometallics* **2007**, *26*, 1868.
 [16] T. Jerphagnon, A. J. A. Gayet, F. Berthiol, V. Ritleng, N. Mršić, A. Meetsma, M. Pfeffer, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *Chem. Eur. J.* **2009**, *15*, 12780.

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SHORT COMMUNICATION

**Chiral Iridacycles**

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**Phenyl vs. Ferrocenyl
Cyclometallation Selectivity:
Diastereoselective Synthesis of an
Enantiopure Iridacycle**

Imines containing both ferrocenyl and phenyl groups undergo selective phenyl C-H activation on cycloiridation with $[Cp^*IrCl_2]_2$ and NaOAc in CH_2Cl_2 . This was applied to the diastereoselective synthesis of an enantiopure iridacycle of configuration S_C, R_{Ir}, E .