Available online at www.sciencedirect.com
ScienceDirect
Coordination Chemistry Reviews 252 (2008) 782–809
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

Half-sandwich iridium complexes—Synthesis and applications in catalysis

Jianke Liu *[,1], Xiaofeng Wu, Jon A. Iggo, Jianliang Xiao *

Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

Received 8 August 2007; accepted 17 January 2008
Available online 26 January 2008

Contents

Abstract

A brief summary of the organometallic chemistry of half-sandwich iridium complexes accomplished in the last a few years is given, with emphasis on chiral-at-metal complexes, the synthetic protocols employed and the stereochemistry involved in relevant transformations. The applications of these complexes in catalysis are highlighted by selected examples.

Keywords: Iridium; Half-sandwich complexes; Chiral complexes; Synthesis; Catalysis

* Corresponding authors. Tel.: +44 151 7942937; fax: +44 151 7943589.
E-mail addresses: liu@liv.ac.uk (J. Liu), j.xiao@liv.ac.uk (J. Xiao).
[1] Present address: Key Laboratory of Applied Surface and Colloid Chemistry of the Ministry of Education, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, People's Republic of China.

0010-8545/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2008.01.015

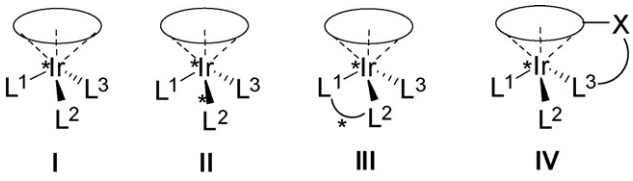
1. Introduction

Chiral organometallic chemistry has received a lot of attention from both academia and industry as a result of intensive studies of asymmetric catalysis in the last four decades or so. In particular, chiral-at-metal half-sandwich compounds, the most popular chiral organometallics, have been extensively studied since the very early stage of transition metal chemistry. Optically active organometallic compounds with chiral metal atoms were reviewed by Brunner in 1999 [1]; the synthesis/separation strategies to prepare chiral-at-metal compounds and their configurational stability has been discussed by Brunner [2] and Ganter [3]. These excellent reviews offer a broad view of chiral organometallic chemistry of various transition metals. Chiral half-sandwich complexes of d^6 transition metals are of particular interest due to their wide applications in organic transformations and catalysis. However, compared with the wealthy ruthenium and rhodium chemistry with chiral half-sandwich scaffolds, the iridium counterparts have been investigated to a much lesser degree. On the other hand, iridium catalysts have been shown to deliver superior performance for a range of reactions. For example, a Cp*-Ir(III) catalyst containing a diamine ligand gave a higher activity in transfer hydrogenation of aldehydes than its ruthenium and rhodium analogues [4]. Similarly, higher catalytic activities and enantioselectivities were obtained in the asymmetric transfer hydrogenation of ketones with an iridium catalyst containing a β-amino alcohol ligand than the corresponding Ru(II) and Rh(III) catalysts [5], highlighting the great potential of half-sandwich iridium complexes in catalysis [6]. Herein we focus attention on half-sandwich iridium complexes containing the Cp* and Cp ligands, especially on those with chirality at the metal and on the advances made from 2000 onwards. Other structurally related complexes are known but fewer in numbers and will not be covered here [7–12]. Rather than a comprehensive summary of half-sandwich iridium complexes reported in the literature, we attempt to highlight the progress made in their synthesis, especially the novel approaches developed recently. The applications of these complexes are briefly addressed toward the end.

It is noted that many of these half-sandwich complexes are often prepared as a racemic or diastereomeric mixture. Thus, although they possess stereogenic and chirotopic iridium centers, they may not display any optical activity. These complexes are included here because they are chiral-at-iridium and they are potential catalysts in synthesis. The absolute configuration of the complexes will only be specified where enantiomerically or diastereomerically pure forms are identified.

2. Classification of chiral half-sandwich iridium complexes

The concept of chiral organometallics was raised by analogy to chiral organic compounds, i.e., a transition metal tetrahedrally coordinated by four different ligands should be chiral. Although organometallic Ir(III) complexes generally possess an octahedral structure, the Cp ring of half-sandwich iridium complexes occupies one face of the octahedron and can be treated as one ligand, thus forming a pseudo-tetrahedral structure. If different L^1, L^2, L^3 ligands are present in the three-leg piano stool, chiral half-sandwich iridium complexes result.



Scheme 1.

These complexes can be categorized into four groups according to the nature of ligands (Scheme 1). Group I is defined as chiral-at-metal iridium compounds, with the absolute configuration at the metal atom, R_{Ir} or S_{Ir}, determined by the priority sequence of ligands L^1, L^2, L^3 and the Cp ring. Although the majority of group I complexes exist as a racemic mixture in solution due to poor configurational stability, the absolute metal configuration of both *R* and *S* enantiomers has been determined in the solid state by X-ray crystallography in many cases [1,2].

Group II complexes have chiral centers on both the metal and ligand, and can thus exist as a mixture of diastereomers. For complexes having two chiral centers, in principle there are four diastereomers, which can exist in equilibrium in solution. However, certain diastereomers are often formed preferentially over others due to a relatively higher kinetic or thermodynamic stability. Diastereomers can be separated by column chromatography or fractional crystallization; this allows resolution and isolation of group II chiral iridium complexes in diastereomerically pure form.

Group III complexes are essentially a subgroup of group II complexes, formed by replacing the monodentate ligands with chiral bidentate analogues. The chelating effect significantly enhances the configurational stability of the complexes, allowing many complexes of this group to be isolated and characterized in a single diastereomeric form. Furthermore, the great variety in the architectural design of chiral chelating skeletons makes this group of complexes easily tuneable, and hence has enabled their extensive applications in enantioselective catalysis.

Group IV complexes are the so-called tether complexes, in which a linker X is introduced to bridge the Cp ring and a coordinated ligand. However, although a number of successful tether catalysts based on half-sandwich ruthenium, zirconium, and titanium complexes have been reported, analogous iridium catalysts are fewer in the literature.

3. Synthesis of half-sandwich iridium complexes

The synthetic chemistry of half-sandwich complexes of transition metals is well established [1]. Many synthetic protocols developed for other transition metals, such as ligand substitution, cyclometallation, and oxidative addition, have general applicability for iridium complexes. Outlined below are important synthetic methodologies and the continuing efforts to control the configurational stability of resulting complexes, with emphasis

on chiral half-sandwich iridium complexes of synthetic importance.

3.1. Chiral-at-metal-only half-sandwich iridium complexes

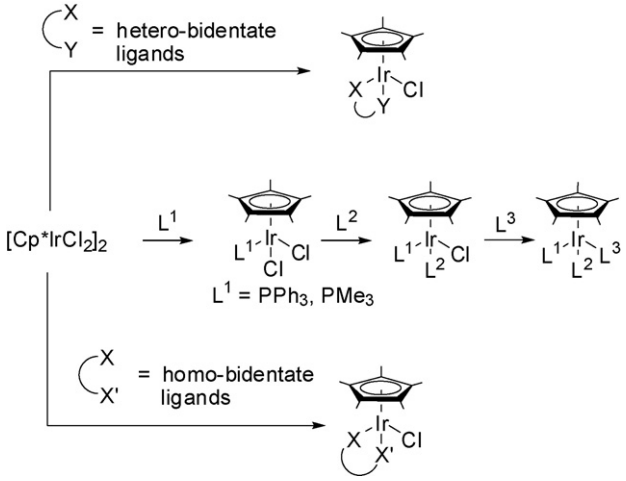
Half-sandwich iridium complexes with only one chiral center at the metal, i.e., the group I complexes, are usually prepared as racemic mixtures. The absolute configuration of the metal center has been determined by X-ray crystallography for most chiral-at-metal complexes reported so far. However, these iridium complexes are configurationally labile in solution. Therefore, the configuration of the metal center will not be specified in the following discussion.

3.1.1. Synthesis by ligand substitution

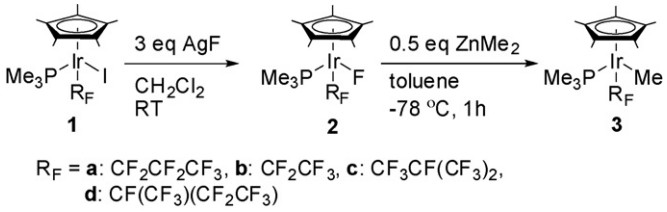
Structurally well-defined, optically active group I iridium complexes are rare in the literature. The synthetic protocols developed usually lead to racemic $Cp^*IrL^1L^2L^3$ complexes, which could, however, be extended to the synthesis of chiral iridium complexes when using appropriate substrates. The dimeric $[Cp^*IrCl_2]_2$ is the mostly used precursor to synthesize this group of iridium(III) complexes through chloride bridge cleavage and ligand substitution with monodentate or bidentate ligands, in the absence or presence of metathesis reagents such as NH_4PF_6, $NaPF_6$ and $AgBF_4$ (Scheme 2). Monomeric $Cp^*Ir(PR_3)Cl_2$ (R = aryl, alkyl) complexes are now commercially available, and have been used to prepare the chiral-at-metal complexes $Cp^*Ir(L^1,L^2,L^3)$ more directly.

Iridium precursors other than $[Cp^*IrCl_2]_2$ and its derivatives are also described in the literature. For example, a family of iridium fluoro compounds, **2**, has been prepared from their iodo analogues **1** by reaction with AgF in the dark. Subsequent methylation at low temperature leads to the iridium methyl complexes **3** (Scheme 3) [13]. Up to now, this appears to be the only way reported to synthesize half-sandwich iridium complexes with perfluoroalkyl groups.

3.1.1.1. Iridium complexes with hetero-bidentate ligands. Chiral-at-metal iridium complexes having bidentate ligands



Scheme 2.



Scheme 3.

can be directly accessed by substitution at two legs of the piano stool with heterobifunctional ligands. For example, the complexes **4** and **5** were synthesized by the reaction of $[Cp^*IrCl_2]_2$ with the monosulphide or monoselenide of bis(diphenylphosphino)amine in an acetone/dichloromethane mixture followed by chloride abstraction with $AgBF_4$ (Table 1, entries 1 and 2) [14].

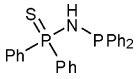
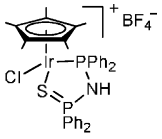
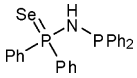
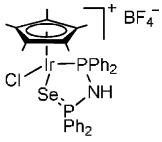
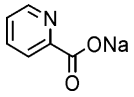
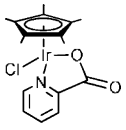
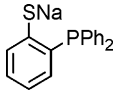
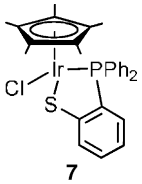
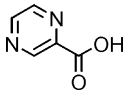
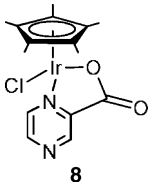
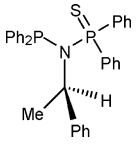
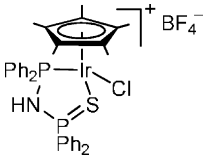
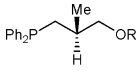
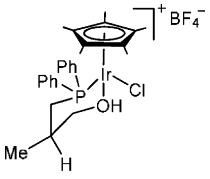
The sodium salts of anionic bidentate ligands can act as both incoming ligand and metathesis reagent. Thus, reaction of $[Cp^*IrCl_2]_2$ with sodium pyridine-2-carboxylate or sodium 2-(diphenylphosphanyl)thiophenolate afforded the corresponding iridium η^2-(N,O) and η^2-(S,P) half-sandwich complexes **6** and **7** (Table 1, entries 3, 4) [15]. The structurally similar iridium carboxylato pyrazine complex **8** was prepared from $[Cp^*IrCl_2]_2$ and pyrazine-2-carboxylic acid in the presence of sodium methoxide (Table 1, entry 5) [16].

Ligands containing a chiral center close to the donor atoms have also been used. An example is the reaction of $[Cp^*IrCl_2]_2$ with the chiral sulphur diphosphazane *S*-$Ph_2PN(CHMePh)P(S)Ph_2$ in the presence of $AgBF_4$. The reaction did not give the expected η^2-(P,S) diastereomer, however. Instead, **9** was generated in which the chiral – CHMePh moiety was lost as a result of C–N bond cleavage (Table 1, entry 6) [17]. More promising results were obtained from the reaction of $[Cp^*IrCl_2]_2$ with a chiral phosphino alcohol in the presence of $TlBF_4$. The chiral moiety remained in the cationic iridium product **10**; but no diastereo-induction was observed due to the chiral element being too remote from the iridium center (Table 1, entry 7) [18].

3.1.1.2. Iridium complexes with unsymmetrical homo-bidentate ligands. When the Cp*-Ir(III) precursor is complexed with an unsymmetrical homo-bidentate ligands, a chiral iridium complex can also be constructed due to the difference in the coordinating groups. For example, the reaction of $[Cp^*IrCl_2]_2$ with the 2-(2′-pyridyl)imidazole ligands resulted in the formation of racemic, cationic complexes **11** and **12** in the presence of NH_4PF_6 (Table 2, entries 1 and 2) [19].

Similar reactions with polypyridyl ligands have also been reported. Thus, treatment of $[Cp^*IrCl_2]_2$ with 2,3-di(2-pyridyl)pyrazine (dpp) or 2,4,6-tri(2-pyridyl)-1,3,5-triazine (tptz) afforded the complexes **13** and **14** (Table 2, entries 3 and 4) [20]. Due to the presence of uncoordinated donor sites, these complexes can be easily functionalized and potentially used as building blocks for supramolecular assembly through C–H···X

Table 1
Synthesis of half-sandwich iridium complexes from $[Cp^*IrCl_2]_2$ and bidentate ligands

Entry	Ligand	Metathesis reagent	Conditions	Ir complex formed	Yield	Reference
1		$AgBF_4$	Acetone/CH_2Cl_2	 **4**	63%	[14]
2		$AgBF_4$	Acetone/CH_2Cl_2	 **5**	70%	[14]
3		N/A	CH_3OH	 **6**	89%	[15]
4		N/A	THF	 **7**	72%	[15]
5		NaOMe	MeOH	 **8**	75%	[16]
6		$AgBF_4$	Acetone/$CHCl_3$	 **9**	N/A	[17]
7	 R = H, OMe, SO_2Me	$TlBF_4$	THF	 **10**	N/A	[18]

(X=N, F, Cl and π bond) interactions. Similarly, complex **15** was prepared in the presence of $NaBF_4$ in refluxing methanol (Table 2, entry 5) [21].

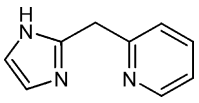
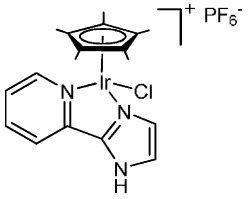
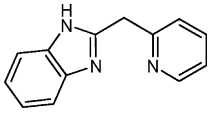
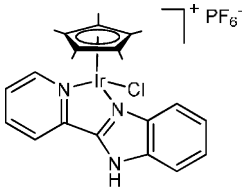
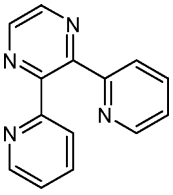
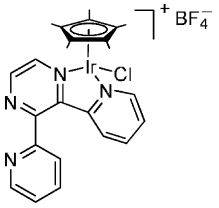
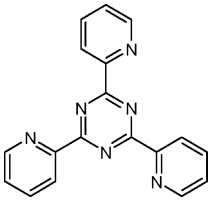
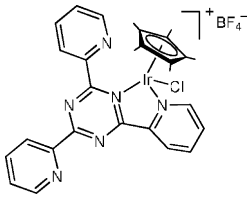
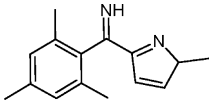
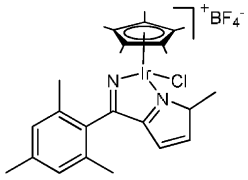
Another group of important iridium complexes of the same category is half-sandwich iridium complexes containing monotosylated diamine ligands. These complexes were prepared in racemic form from achiral tosyl diamines (**16**–**20**) (Scheme 4) [4]. The closely related chiral variants will be addressed in Section 3.3.2. The tosyl group is crucial for efficient transfer hydrogenation.

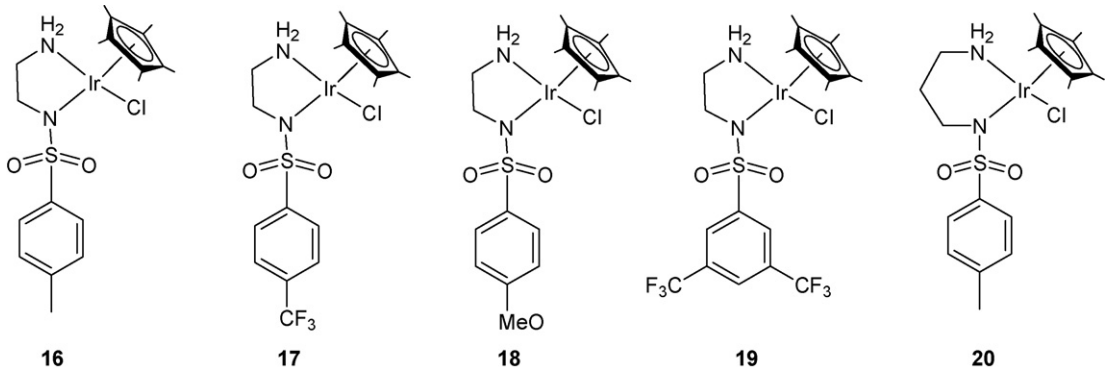
3.1.2. Synthesis by nucleophilic displacement

Besides ligand substitution, other synthetic methodologies have been applied with high efficiency and yield. Some examples are given below.

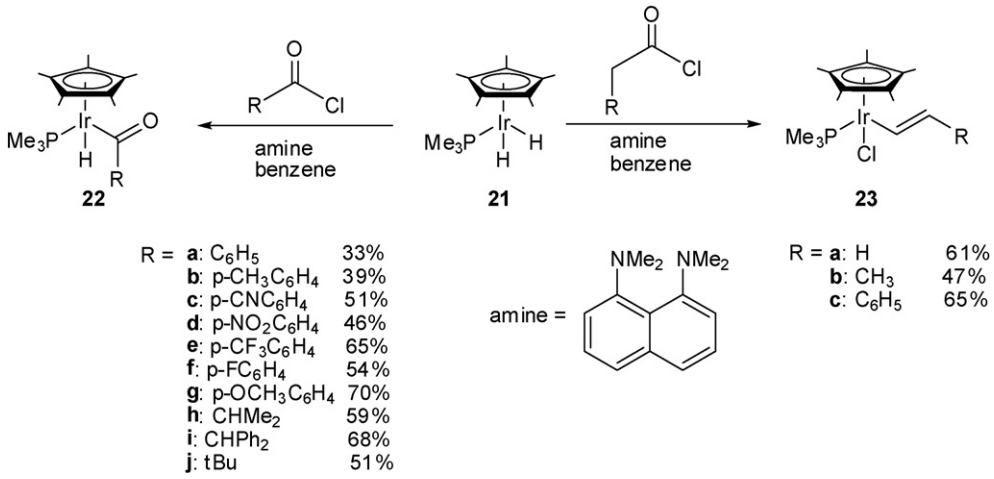
As with $Cp^*(PR_3)IrCl_2$, the iridium dihydride $Cp^*(PMe_3)IrH_2$ **21** is also a good precursor. Its reaction with a variety of aromatic and hindered aliphatic acid chlorides RC(O)Cl afforded various Ir(III) acyl hydride complexes **22a–j** in moderate yields (Scheme 5) in the presence of proton sponge [22]. Precipitation of the resulting ammonium salt promotes the

Table 2
Synthesis of half-sandwich iridium complexes from $[Cp^*IrCl_2]_2$ and unsymmetrical bidentate ligands

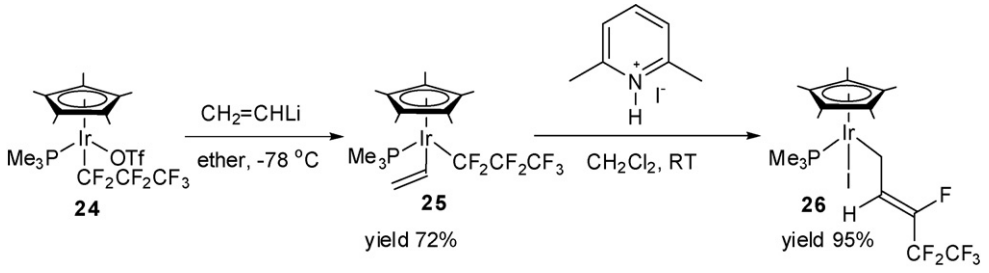
Entry	Ligand	Reagent	Ir complex formed	Reference
1		NH_4PF_6 MeOH	 **11**	[19]
2		NH_4PF_6 MeOH	 **12**	[19]
3		N/A	 **13**	[20]
4		N/A	 **14**	[20]
5		$NaBF_4$ MeOH	 **15**	[21]



Scheme 4.



Scheme 5.



Scheme 6.

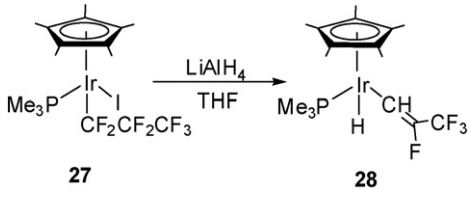
reaction. Other bases, e.g., (−)-sparteine and triethylamine, led to similar yields. The reaction mechanism is different from the ligand substitution described above. Kinetic studies revealed that this reaction proceeds via nucleophilic attack of the iridium center at the carbon atom of the acyl chloride [22]. When the same synthetic procedure was applied to the $RCH_2C(O)Cl$ type acetyl chlorides (R=H, CH_3, C_6H_5) under otherwise identical conditions, vinyl iridium chloride complexes **23a–c** were obtained (Scheme 5) [22]. It was suggested that, for these substrates, an α-hydrogen of the acyl group is abstracted after nucleophilic attack of the metal center, yielding a vinyl enolate intermediate. This vinyl enolate then rearranges to an enol and then a vinylidene intermediate. Re-addition of HCl to the vinylidene leads ultimately to the observed product.

An iridium(perfluoropropyl)(vinyl) complex **25** was prepared from the reaction of the iridium triflate **24** with vinyl lithium at low temperature. The preferred conformation of **25** in solution has been determined by $^{19}F\{^1H\}$-HOESY spectrum, which is the same as that in the solid state. **25** reacts with the weak acid lutidinium iodide to give the η^1-allylic complex **26** in high yield (Scheme 6) [23].

The reaction of the analogous iridium perfluoroalkyl iodide complex **27** with $LiAlH_4$ afforded an iridium hydride with a fluoroalkenyl group, **28**, instead of the saturated iridium fluoroalkyl-hydrido complex. Apparently α-CF bond activation takes place in both the reactions of **25** and **27**, presumably followed by elimination of HF (Scheme 7) [24].

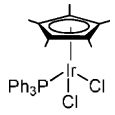
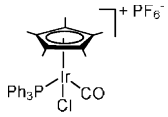
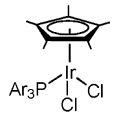
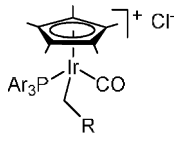
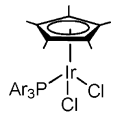
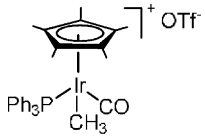
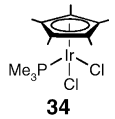
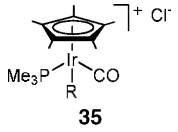
3.1.3. Synthesis of iridium carbonyls by C–C bond cleavage

Half-sandwich iridium carbonyl complexes can be accessed by a novel reaction involving C–C bond cleavage. Thus the complex $Cp^*Ir(PPh_3)Cl_2$, **29**, reacted with a terminal alkyne and H_2O in the presence of KPF_6, affording the carbonyl **30** (Table 3, entry 1) [25,26]. The reaction possibly involves C–C triple bond cleavage with H_2O, as indicated by the formation of toluene. The metathesis reagent $NaPF_6$ is not necessary when the water soluble iridium precursor $Cp^*Ir(PAr_3)Cl_2$ **31** ($PAr_3 = P(m\text{-}C_6H_4SO_3Na)_3$) is used, $[Cp^*Ir(PAr_3)(CH_2R)(CO)]^+Cl^-$ **32** being obtained in good yield (80–91%) (Table 3, entry 2) [27]. Mechanistically importantly, $[Cp^*Ir(PAr_3)(CD_2R)(CO)]^+Cl^-$ or $[Cp^*Ir(PAr_3)(CH_2R)(C^{18}O)]^+Cl^-$ isotopomers were obtained when the reactions were carried out in D_2O or $H_2{}^{18}O$, respectively. It is apparent that the hydrogen atoms on the α-carbon of alkyl and oxygen atom of carbonyl come from water.



Scheme 7.

Table 3
Synthesis of chiral half-sandwich iridium complexes by C–C bond cleavage

Entry	Ir precursor	Organic reactants	Metathesis reagent	Conditions	Ir complex formed	Reference
1	 **29**	HC≡CPh	$NaPF_6$	H_2O	 **30**	[25,26]
2	 **31**	RC≡CH R=Ph,CH_2Ph, $C(CH_3)_3$, *p*-$C_6H_4CH_3$	N/A	H_2O 25 °C	 **32**	[27]
3	 **31**	ethylene	AgOTf	H_2O	 **33**	[27]
4	 **34**	RCH_2OH R=Et,Ph,Me	N/A	D_2O 135 °C 40 h	 **35**	[28]

The same methodology also works for alkenes. In the reaction of **31** with ethylene, the C=C bond cleavage with H_2O in the presence of a silver salt afforded **33** in water, possibly via a reactive aqua iridium intermediate (Table 3, entry 3) [27]. Mechanistic studies show that the reaction involves steps similar to the Wacker process, followed by oxidative addition of aldehydic C–H to iridium to form an iridium acyl complex and finally CO deinsertion from the coordinated acyl group gives the iridium alkyl carbonyl product. Primary alcohols undergo similar reactions; the formation of **35** from **34** have been reported to take place under harsher conditions (135 °C, 40 h, Table 3, entry 4) [28].The reaction appears to be general for terminal alkynes. Additional examples are found in the synthesis of **36a–h**, with varying yields under mild conditions (Scheme 8) [29]. All these reactions probably involve the formation of aldehyde intermediates.

R =	**a**: Ph	85%
	b: p-BrC_6H_4	81%
	c: Cy	89%
	d: ^tBu	17%
	e: ^nBu	91%
	f: Fc	71%
	g: $(CH_2)_4CCH$	85%
	h: 3-SC_4H_3	80%

Scheme 8.

3.1.4. Synthesis by oxidative addition

3.1.4.1. Oxidative addition of Ir(I) complexes. All the examples given above use a Cp*Ir(III) dimeric or monomeric complex as substrates. Ir(I) complexes are also excellent precursors for half-sandwich iridium complex synthesis. Thus, oxidative addition of perfluoroalkyl iodides to the Ir(I) complexes $Cp^*Ir(CO)_2$ **37** gives the Ir(III) complexes **38** in good yield (Table 4, entry 1) [30]. Subsequent substitution of CO with trimethylphosphine affords $Cp^*Ir(R_F)(PMe_3)I$.

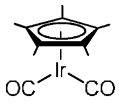
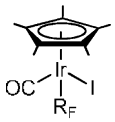
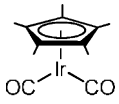
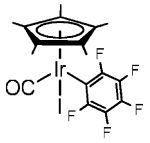
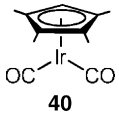
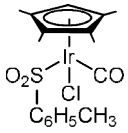
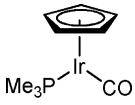
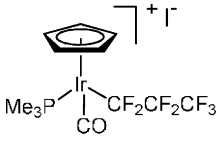
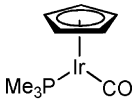
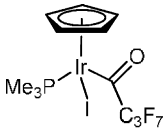
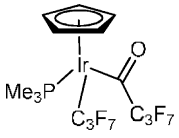
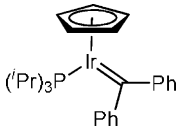
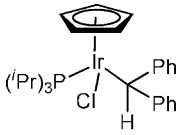
A similar transformation with a perfluoroaryl iodide gives the complex **39** (Table 4, entry 2), which can be further derivatized to $Cp^*Ir(C_6F_5)(PMe_3)I$, $[Cp^*Ir(C_6F_5)(H_2O)]OTf$ or $Cp^*Ir(C_6F_5)(H)I$ through ligand substitution [31]. These can serve as intermediates, from which other complexes have been synthesized [35]. Iridium complexes capped with other Cp derivatives can also be prepared in the same way. For instance, the oxidative addition of tosylchloride to **40** affords the compound **41** (Table 4, entry 3), which readily eliminates one molecule SO_2 to give $[(\eta^5\text{-}C_5HMe_4)Ir(C_6H_4CH_3)(CO)]Cl$ as final product [32].

In contrast to the clean reaction of **37**, where a single racemic product is formed, oxidation addition of $CF_3CF_2CF_2I$ to **42** is temperature dependent (Table 4, entries 4 and 5) [33]. At low temperature (−78 °C), the cationic complex **43** was the sole product. At room temperature, however, direct fluoroalkylation of coordinated CO was observed, giving rise to a mixture of iridium fluoroacyl compounds **44** and **45** (Table 4, entry 5).

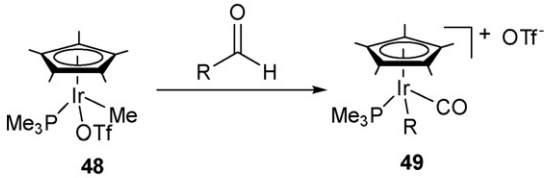
A twist to these reactions is the oxidative addition of HCl to the Ir=C bond of an Ir(I) carbene complex **46**, affording the Ir(III) alkyl chloride **47** quantitatively (Table 4, entry 6) [34].

C–H activation is another type of important oxidative addition reaction. An example is seen in the complex **48**, which

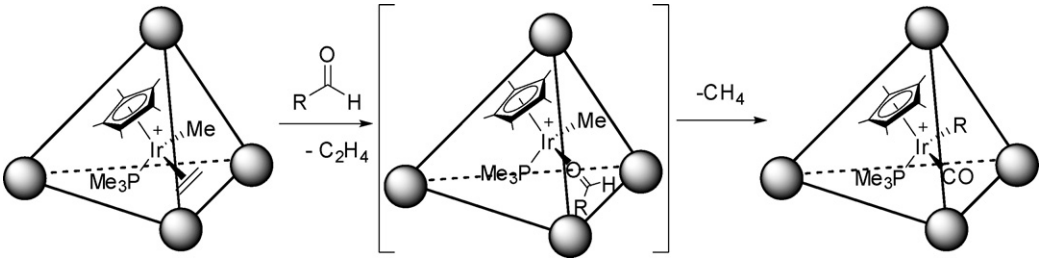
Table 4
Synthesis of half-sandwich iridium complexes by oxidative addition of Ir(I) complexes

Entry	Ir precursor	Organic reactants	Conditions	Ir complex formed	Reference
1	 **37**	R_FI R_F=CF_2CF_3 $CF_2CF_2CF_3$ $CF_2C_6F_5$ $CF(CF_3)_2$	CH_2Cl_2	 **38**	[30]
2	 **37**	C_6F_5I	N/A	 **39**	[31]
3	 **40**		N/A	 **41**	[32]
4	 **42**	$CF_3CF_2CF_2I$	−78 °C	 **43**	[33]
5	 **42**	$CF_3CF_2CF_2I$	20 °C	 **44** 24%	[33]
				 **45** 34%	
6	 **46**	HCl	N/A	 **47**	[34]

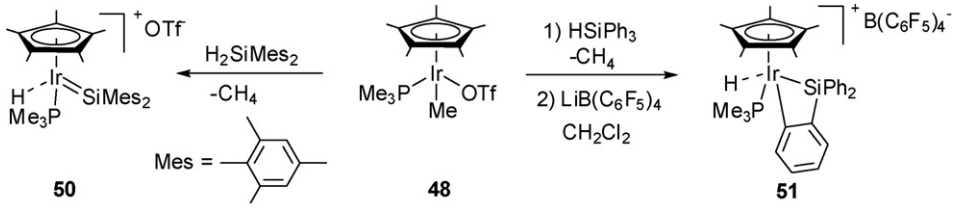
has been extensively studied by Bergman and co-workers [36]. A variety of cationic iridium alkyl carbonyl complexes **49** were prepared as racemic mixtures by the tandem C–H bond activation and decarbonylation reactions of aldehydes over the iridium center (Scheme 9). A similar reaction of aldehydes with [Cp*(PMe_3)Ir(Me)(C_2H_4)]OTf was demonstrated in the supramolecular tetrahedral assembly $Na_{12}[Ga_4L_6]$ (L = naphthalene-based catecholamide) (Scheme 10), affording host–guest products diastereoselectively due to the confinement effect of the chiral host [37]. The diastereomeric ratio (dr) of products formed increases from 60:40 for acetaldehyde to 70:30 for butyraldehyde. The shape of substrates also matters here, a lower dr being obtained for isobutyraldehyde (55:45). The enrichment of a specific isomer may result from a transition



Scheme 9.



Scheme 10.



Scheme 11.

state or a product selective process occurring in the host–guest nanoreactor.

3.1.4.2. Oxidative addition of Ir(III) precursors. Oxidative addition of Ir(III) complexes to form Ir(V) is less common than the Ir(I) to Ir(III) transformation; but it is important for C–H and Si–H activation reactions, especially from a mechanistic point of view. The first example of Si–H oxidative addition proceeding from Ir(III) to Ir(V) was observed in the reaction of **48** with the secondary silane H_2SiMes_2; an iridium silylene complex **50** was obtained, which proved to be an excellent intermediate for further transformations (Scheme 11) [38]. The reaction was facilitated by reductive elimination of CH_4. A slightly different reaction was observed for tertiary silanes. In the presence of the less coordinating $B(C_6F_5)_4^-$ anion, consecutive Si–H activation of $HSiPh_3$ and C–H activation at the *ortho* position of one benzene ring in the silane afforded a cationic iridium hydride **51** as final product (Scheme 11).

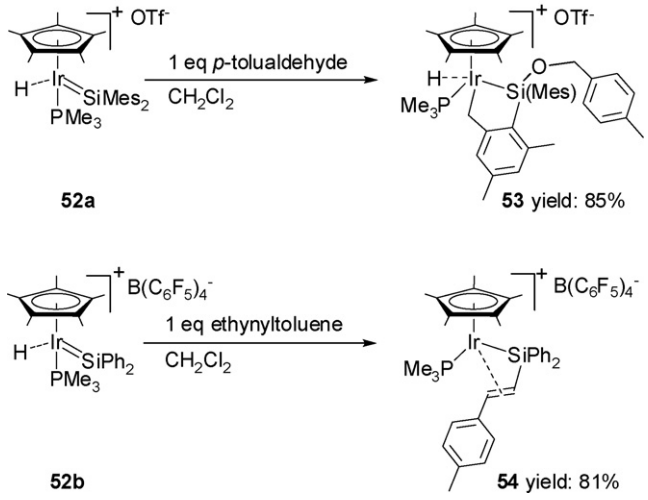
The resulting Ir(V) complexes are reactive towards a number of unsaturated substrates due to the highly electron-deficient nature of the metal center. This makes them suitable precursors for the preparation of new half-sandwich iridium complexes. In particular, the iridium(V) silylene complexes **52a** and **52b** are reactive towards a number of unsaturated substrates, such as *p*-tolualdehyde and 4-ethynyltoluene, which generated the Ir(V) silyl complexes **53** and **54** respectively [39]. The reactivity of **52** increases as the size of substituents on the silicon atom decreases from R=Mes (**52a**) to Ph (**52b**) (Scheme 12).

3.1.5. Synthesis by cyclometallation

Cyclometallation through C–H activation is a well-established method for the synthesis of transition metal complexes with η^2-C,X bidentate ligands. For instance, the cyclometallation of aromatic amines, imines and oxazolines with $[Cp^*IrCl_2]_2$ occurred at room temperature, affording the metallacycles **55**, **56** and **57** in good yields (Table 5, entries 1–3) [40]. The reaction takes place via C–H activation in the phenyl groups, presumably directed by nitrogen coordination to iridium.

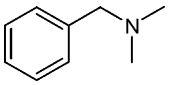
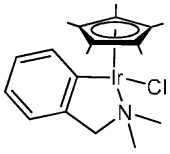
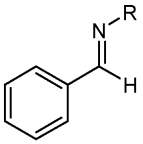
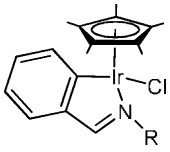
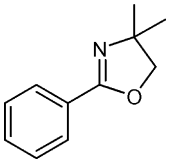
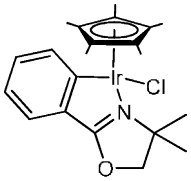
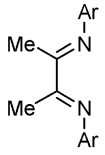
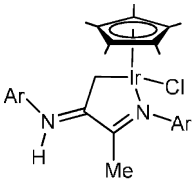
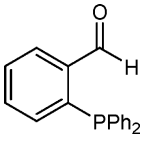
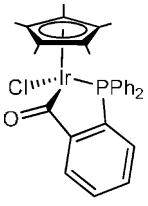
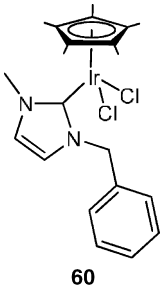
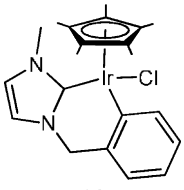
Cyclometallation may also proceed via C–H activation of alkyl groups. Thus, the reaction of $[Cp^*IrCl_2]_2$ with aryl-substituted diazabutadienes in methanol led to the η^2-C,N iridium complexes **58** through C–H activation of the methyl group on the ethylene bridge of the diimine (Table 5, entry 4); the anticipated $Cp^*Ir(\eta^2$-*N*,*N*-diimine) complex was not formed [41]. Reaction of 2-diphenylphosphinobenzaldehyde and $[Cp^*IrCl_2]_2$ resulted in a neutral acyl complex **59**, through C–H activation of the aldehyde (Table 5, entry 5) [42]. Elimination of HCl occurred readily in this transformation.

N-Heterocyclic carbenes (NHC) may also facilitate cyclometallation. An example is seen in **60**, which was obtained in the reaction of 1-methyl-3-benzylimidazolylidene with $[Cp^*IrCl_2]_2$ in CH_2Cl_2. This reaction occurs via transmetallation of the corresponding silver NHC to $[Cp^*IrCl_2]_2$. **60** was not stable at room temperature, resulting in the intramolecular



Scheme 12.

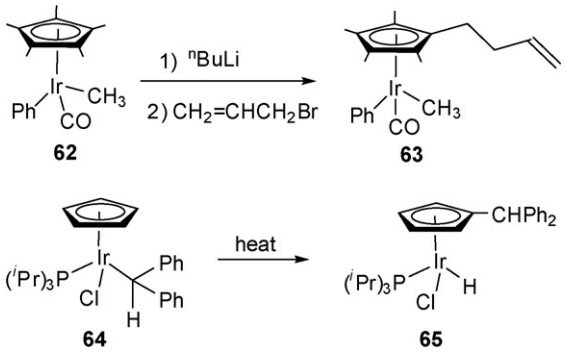
Table 5
Synthesis of half-sandwich iridium complexes by cyclometallation

Entry	Ligand	Reagent	Ir complex formed	Reference
1		NaOAc	 **55**	[40]
2	 R=Ph,$(CH_2)_3OMe$, $(CH_2)_4OMe$	NaOAc	 **56**	[40]
3		NaOAc	 **57**	[40]
4	 Ar=2,6-$Me_2C_6H_3$ 2,6-$^{i}Pr_2C_6H_3$ 2,4,6-$Me_3C_6H_2$	MeOH	 **58**	[41]
5		None	 **59**	[42]
6	 **60**	CH_2Cl_2 5 h	 **61**	[43]

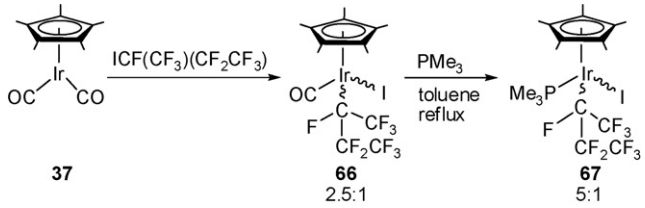
orthometallation of the benzene ring to afford the racemic **61** (Table 5, entry 6) [43]. However, a mixture of diastereomers in 5:1 ratio was obtained with imidazolium salt containing one chiral center [44], and the same reaction of an imidazolium salt with two chiral centers resulted in a diastereomerically pure complex [45], showing that chiral chelating ligands are crucial for stereoselective synthesis of iridium complexes. A fuller treatment of this subject is given in Section 3.2.

3.1.6. Synthesis by functionalization of Cp rings

The majority of half-sandwich iridium complexes have Cp*, or Cp in some cases, occupying the fac position of an octa-



Scheme 13.



Scheme 14.

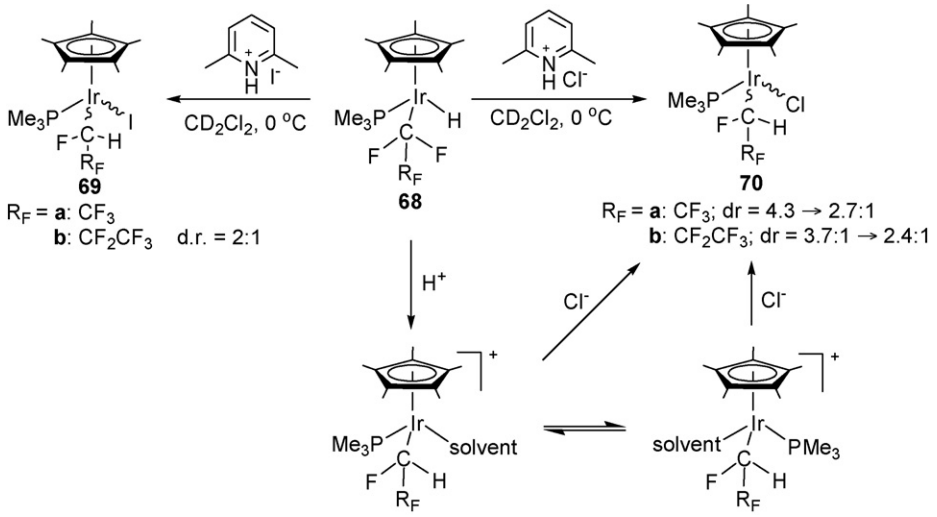
hedron to form the piano stool structure. Derivatization of the Cp/Cp* ring introduces new features into the half-sandwich complexes. This can be accomplished by preparation of appropriate cyclopentadienyl derivatives at an early stage of the synthesis or by functionalization of the coordinated Cp ring. The first route has been used in the synthesis of tethered half-sandwich iridium complexes, which will be described separately later. An example of the second route is given in Scheme 13. As with other metallocenes, the protons of the Cp ring in half-sandwich iridium complexes are weakly acidic, which can therefore be lithiated and then coupled with alkyl halides to introduce an alkyl chain on the Cp* ring (**62** → **63**, Scheme 13) [46]. The terminal C=C bond in **63** has been used for further reactions. Functionalization of the Cp* ring can also be performed intramolecularly. For example, when **64** was heated, the benzyl group migrated from the metal center to the Cp ring via C–H activation, affording the iridium hydride complex **65** [34].

3.2. Half-sandwich iridium complexes containing monodentate chiral ligands

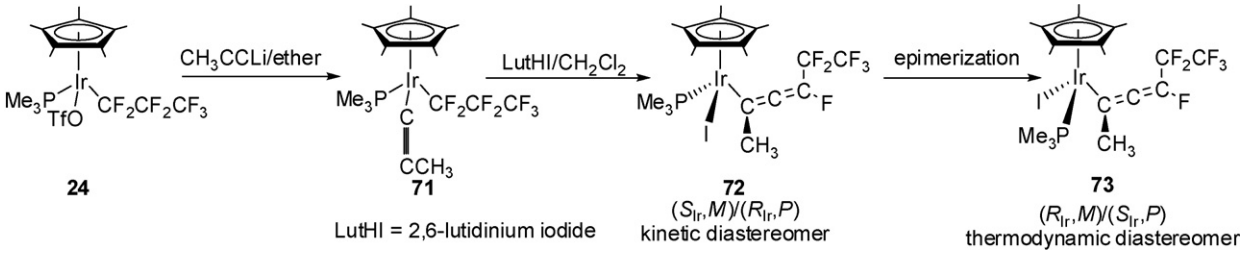
In contrast to the use of achiral ligands, when a chiral ligand is placed on the leg of half-sandwich piano stool, a mixture of two diastereomers results. The diastereoselectivity depends on a number of factors, such as the relative proximity of chiral centers in the complexes, the structural rigidity of ligands, and steric and/or electronic interactions between ligands.

Steric hindrance can be exploited to aid the diastereoselectivity of synthesis. Examples are seen in iridium fluoroalkyl complexes. Thus, oxidative addition of perfluoroalkyl iodide to **37** afforded the complex **66** with a dr of 2.5:1 due to the steric constraint on the rotation about the Ir–C bond. The dr increased to 5:1 in complex **67** on substitution of CO by the bulkier PMe_3 at iridium, suggesting that the iridium center is configurationally labile (Scheme 14). For the major diastereomers of both complexes, a (S_{Ir},S_C) or (R_{Ir},R_C) configuration was determined by using $^{19}F\{^1H\}$ HOESY and X-ray structural analysis [47].

However, the stereochemical control by size of the neighbouring group can be overridden by other factors such as kinetics and ligand dissociation. For example, a slightly better diastereomeric differentiation was achieved in the reaction of **68** with 2,6-dimethylpyridine hydrochloride rather than the corresponding hydroiodide (dr = 2.4 for **70b** versus 2.0 for **69b**, Scheme 15). In this example, the bulky nature of the iodide might be offset by its ready dissociation from the metal center. The initial dr of **70a** and **70b** was higher, however. Its decrease over the reaction time can be attributed to a two-step process: first, diastereoselective protonation takes place to give a cationic intermediate, which can then be irreversibly trapped by chloride to form the kinetic isomer, or undergo an epimerization at iridium followed by chloride trapping to form the thermodynamic isomer as illustrated in Scheme 15 [48]. The cationic intermediate is also shown to catalyze the kinetic and thermodynamic epimer-



Scheme 15.



Scheme 16.

ization by forming a chloride-bridged dimer with the kinetic product.

The interplay between kinetic and thermodynamic control over the iridium configuration is also manifest in other examples. The reaction of **71**, formed from **24**, with lutidinium iodide gave an unexpected iridium allenyl complex **72** as a single diastereomer, with a (S_{Ir},*M*)/(R_{Ir},*P*) configuration at the iridium and the helical allenyl ligand (Scheme 16). The reaction is believed to occur via a α-CF bond activation and propynyl migration to the carbon. The diastereoselectivity of the reaction is in fact under kinetic control; the (S_{Ir},*M*)/(R_{Ir},*P*) diastereomer formed initially slowly epimerized to the thermodynamically more stable (R_{Ir},*M*)/(S_{Ir},*P*) diastereomer **73** on standing in the solution [49].

The reaction of Cp*Ir(PMe_3)Cl_2 **34** and lithium phosphoranide in THF resulted in a diastereomeric mixture of the chiral-at-metal phosphoranide complex **74** (Scheme 17) [50]. This non-diastereoselective transformation illustrates the difficulty of controlling the configuration of iridium by using a monodentate ligand alone. Better stereochemical control is achieved via chelation. Thus, a single ($R_{Ir}S_P$)/($S_{Ir}R_P$) diastereomer of the metallaphosphacyclo **75** was obtained through rearrangement of **74** at 150 °C.

3.3. Half-sandwich iridium complexes containing bidentate chiral ligands

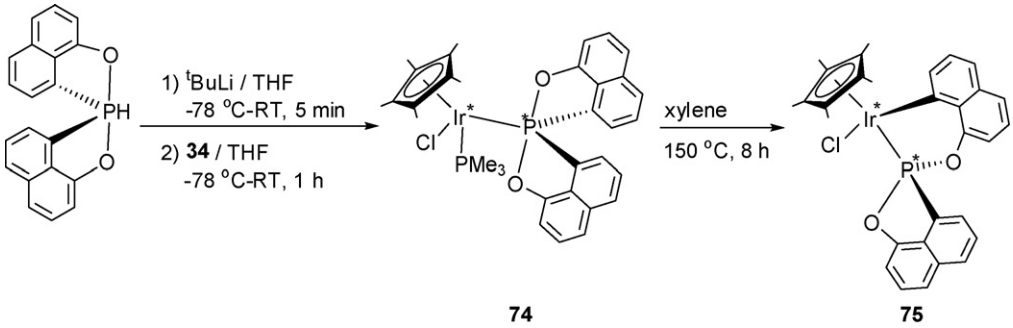
As aforementioned, half-sandwich iridium complexes incorporating monodentate ligands are generally configurationally labile. Iridium complexes containing chiral bidentate ligands offer better stereocontrol due to the chelating effect of the ligand, as demonstrated by the example of **75**.

3.3.1. Iridium complexes with hetero-bidentate chiral ligands

The introduction of resolved hetero-bidentate ligands to the piano stool could in principle generate diastereopure half-sandwich iridium complexes. In practice, the nature of bidentate ligand plays a crucial role in affecting the diastereoselectivity. Thus reaction of enantiopure benzylamines with [Cp*$IrCl_2$]$_2$ in the presence of NaOH and KPF_6 afforded the cationic cyclometallated complex **76** with no diastereomeric excess (de) (Table 6, entry 1) [51]. The diastereomers inter-converted quickly at room temperature, as indicated by NMR analysis, which is likely to be triggered by the dissociation of CH_3CN.

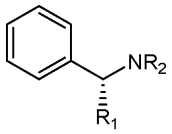
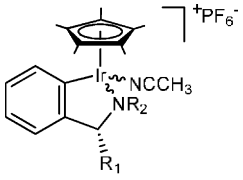
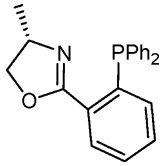
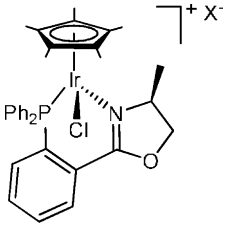
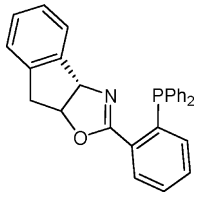
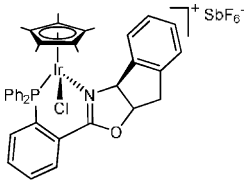
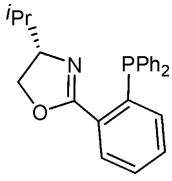
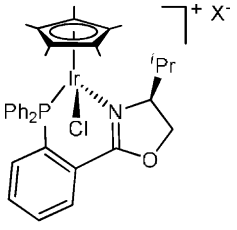
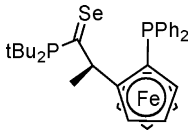
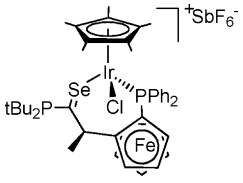
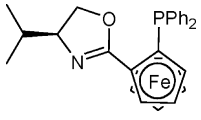
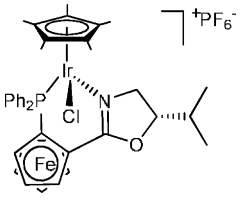
Under similar conditions, the reaction of [Cp*$IrCl_2$]$_2$ with chiral phosphinooxazolines also resulted in a mixture of two diastereomers (S_{Ir},S_C) and (R_{Ir},S_C); the dr varied with the substituents on the oxazoline ring and with the metathesis reagent used (**77–79**, Table 6, entries 2–4) [52]. However, single diastereomers of **77**, **78** and **79** (>98% by ^{1}H NMR) were obtained by fractional crystallization from methanol.

Ferrocenyl ligands with planar chirality have been used in the construction of chiral-at-metal half-sandwich iridium complexes. For example, reaction of [Cp*$IrCl_2$]$_2$ with enantiopure bisphosphine monoselenide in the presence of $NaSbF_6$ afforded the diastereopure cationic complex **80** in 78% yield (Table 6, entry 5) [53]. The thermodynamic preference for *R*-configuration at the metal may result from the dominant steric interaction of the ferrocenyl moiety with Cp*. Using (*S*)-2-[2-(diphenylphosphino)ferrocenyl]-4-isopropyl oxazoline, an air-stable complex **81** resulted, with a de of 98% (Table 6, entry 6) [54]. The absolute configuration of this complex was determined to be *S* at the metal by X-ray crystallography. The complex has a high configurational stability, epimerization being



Scheme 17.

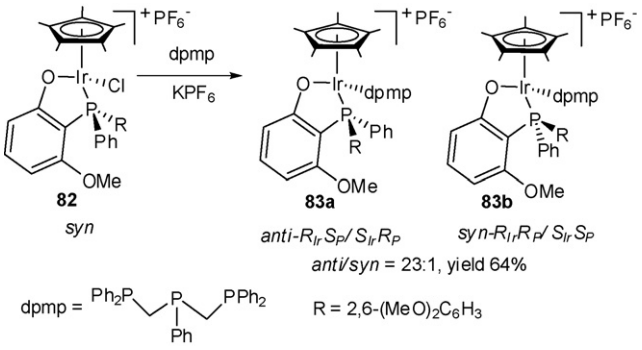
Table 6
Synthesis of chiral half-sandwich iridium complexes with chiral bidentate ligands

Entry	Ligand	Reagent	Ir complex formed	Configuration of metal	Reference
1	 R_1=H,Me R_2=Me,H	KPF_6 NaOH CH_3CN	 **76**	Not defined	[51]
2		NaX (X=SbF_6 or BF_4)	 **77**	R_{Ir}:S_{Ir} = 57:43 (X=SbF_6) R_{Ir}:S_{Ir} = 45:55 (X=BF_4)	[52]
3		$NaSbF_6$ MeOH	 **78**	R_{Ir}:S_{Ir} = 40:60	[52]
4		NaX (X=SbF_6 or BF_4)	 **79**	R_{Ir}:S_{Ir} = 79:21 (X=SbF_6) R_{Ir}:S_{Ir} = 59:41 (X=BF_4)	[52]
5		$NaSbF_6$ CH_2Cl_2	 **80**	R_{Ir}	[53]
6		KPF_6 MeOH	 **81**	S_{Ir}	[54]

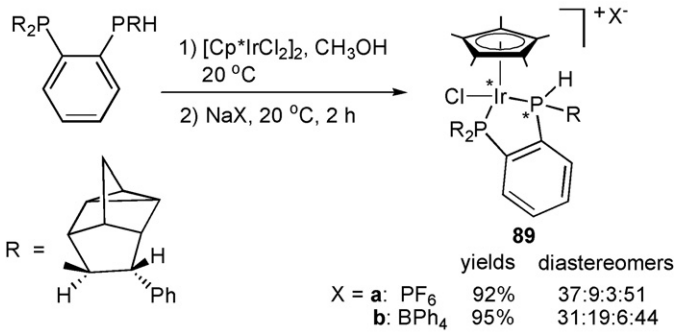
slow with the de decreasing to 80% after 20 days at room temperature.

Replacement of halide inherited from the iridium precursor by a bulky coordinating ligand can significantly impact on the de. Thus, the reaction of **82** with dpmp afforded **83a** with a high selectivity (Scheme 18). The *syn*- and *anti*-form refers to the R group and Cl/dpmp occupying the same or the opposite side. The relative stereoconfiguration at iridium and phosphorus of the P,O-chelate was determined to be $R_{Ir}S_P/S_{Ir}R_P$ by X-ray crystallography [55]. Thus the reaction proceeds preferentially with stereochemical inversion.

Half-sandwich iridium complexes of aminocarboxylates can be readily prepared from $[Cp^*IrCl_2]_2$ and the corresponding aminocarboxylate salts (Scheme 19, **84–87**) and have been used



Scheme 18.



Scheme 20.

as enantioselective hydrogen transfer catalysts [56]. Similarly these complexes can be accessed from α-amino acids or their derivatives [57–60].

The de values of these complexes vary with the ligands used and they are configurationally labile. For instance, the complex **84** existed as a 1:1 mixture of two diastereomers in the solid state; but a 90% de was measured in solution. The halide can be replaced with other ligands, e.g. phosphines. The resulting complexes are again configurationally labile. Kinetic measurements of the epimerization processes revealed an activation enthalpy of ca 20 kcal/mol [56]. The epimerization occurs probably via ligand dissociation, generating a 16-electron species; re-addition of the ligand may take place on both sides of the plane, thus leading to two chiral Ir(III) centers (Scheme 19) [56]. DFT calculations on closely related Ru(II) and Fe(II) complexes suggest that the 16-electron species may adopt a planar or pyramidal configuration at the metal on the ground state. However, the barrier for inter-conversion is low, ranging from being almost flat to ca 6 kcal/mol in the case of the Ru(II) complexes [61].

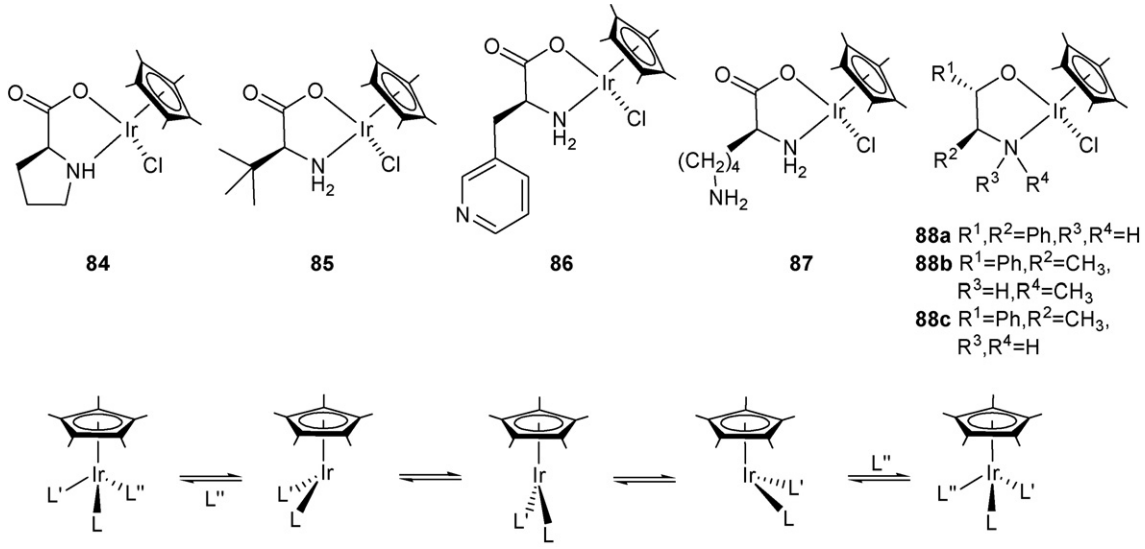
Amino alcohols reacted with $[Cp^*IrCl_2]_2$ in a similar manner. The resulting complexes show varying activities and enantioselectivities in asymmetric transfer hydrogenations of ketones [5]. The complexes **88a–c** were believed to be formed as catalyst precursors under the catalytic conditions (Scheme 19).

3.3.2. Iridium complexes with homo-bidentate chiral ligands

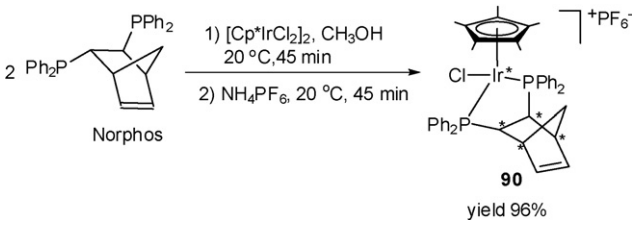
Diphosphine ligands with chiral backbones or substituents have found extensive applications in organometallic chemistry and catalytic synthesis; their half-sandwich iridium complexes have also been widely studied. Reaction of $[Cp^*IrCl_2]_2$ with an unsymmetrical chelating chiral phosphine in the presence of sodium salt gave the cationic complexes **89a** or **89b** in high yield (Scheme 20). The diastereomer composition obtained again depends on the counter-ion used, underlining the importance of anions in this type of synthesis. The major diastereomer (51%) of **89a** was crystallized from *n*-hexane/acetone and its configuration determined as (S_{Ir},S_P) by X-ray crystallography [62].

In a related reaction of $[Cp^*IrCl_2]_2$ with (+)-Norphos, complex **90** was obtained in high yield as a mixture of S_{Ir} and R_{Ir} diastereomers in a ratio of 42:58. Apparently, the ligand substitution is not very diastereoselective (Scheme 21) [62].

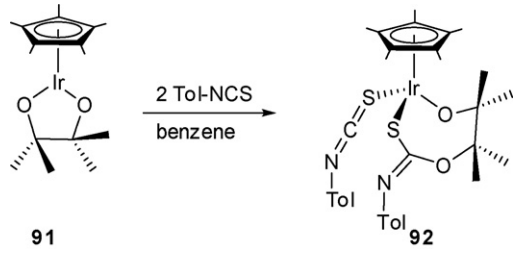
Half-sandwich iridium complexes with chiral diols have also been reported. An example is the iridium pinacolate complex **91**, which reacts with excess TolNCS to afford a new complex



Scheme 19.



Scheme 21.



Scheme 22.

92 (Scheme 22). The ring expansion might result from insertion of TolNCS; the 7-membered metallacycle was then trapped by a second equivalent of isothiocyanate [63].

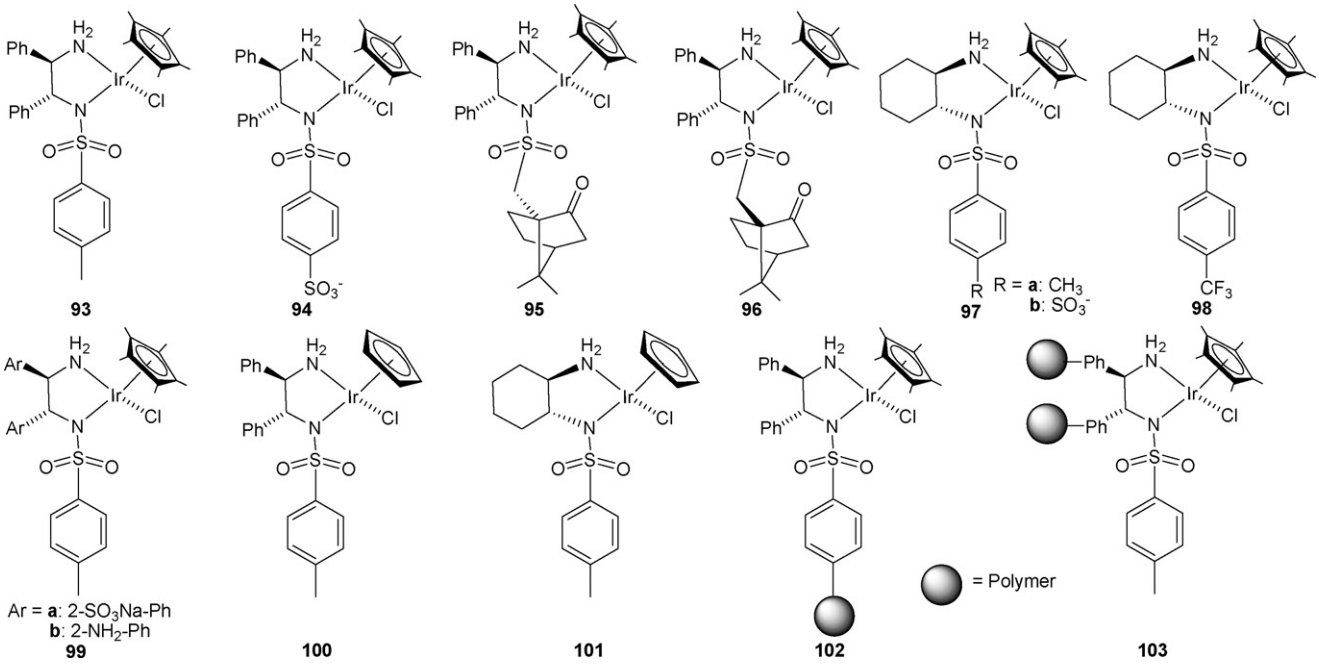
A number of half-sandwich iridium-(η^2-*N*,*N*-ligand) complexes have been prepared. Representative examples are shown in Scheme 23 [4,64–69]. The complexes **93**–**101** were generated by reacting the appropriate ligand with $[Cp^*IrCl_2]_2$ and base in an organic solvent, or in water without base. In both solution and solid states, these complexes appear to exist as a single diastereomer. The structures of analogous Rh(III) complexes have been determined, with (*R*,*R*)-diamines conferring *S* configuration on the metal [68–70]. This is in contrast to the configurational lability of the related amino acid complexes discussed above.

These complexes have been used as metal-ligand bifunctional catalysts in asymmetric transfer hydrogenation reactions of ketones. The acidic NH protons activate the substrate by hydrogen bonding to the carbonyl oxygen atom. Some of these catalysts have been heterogenized on polymer supports (**102** and **103**), showing reasonable recyclability [71].

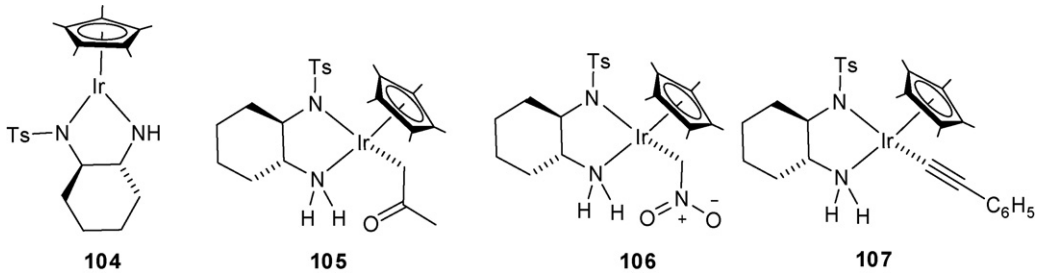
The iridium amido complex **104** and its analogues are coordinatively unsaturated. However, their electron-deficiency is alleviated by the amido nitrogen sharing its lone pair with an iridium d orbital [61,69]. Nonetheless, **104** reacts with nucleophiles bearing acidic protons, such as nitromethane, acetone and phenylacetylene, to give new chiral iridium complexes in quantitative yields (**105–107**, Scheme 24). The C–H activation proceeds through deprotonation of the acidic substrates by the basic amido group [72]. This results in protonation of the amido nitrogen, thus rendering the nitrogen lone pair unavailable to share with iridium; consequently, the reaction enhances the Lewis acidity of Ir(III) and so facilitates the nucleophilic attack to give **105**–**107**. It is noted that although achiral at iridium, **104** reacted with the nucleophiles to form only one diastereomer in solution, indicating the attack to be highly face-selective. Again, an *S* configuration at the metal was found for the (*R,R*)-diamine as revealed in **106**.

The 16-electron iridium amide complex **108** undergoes intramolecular cyclometallation in the presence of an acidic alcohol, affording the iridium complex **109** (Scheme 25) [73]. This complex can also be accessed from the chloride complex **93** in the presence of a strong base.

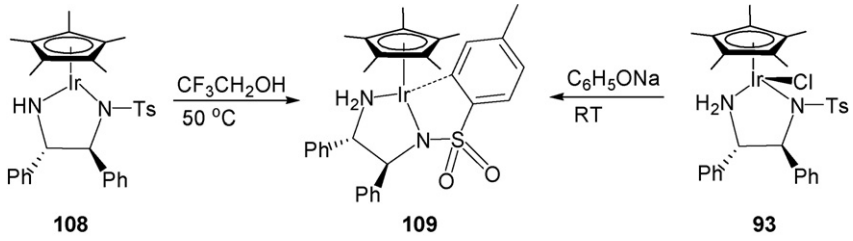
Coordinatively and electronically unsaturated Cp*Ir(III) complexes can also be prepared from diamides. The reaction of $[Cp^*IrCl_2]_2$ with a potassium salt of *N*-acetyldipeptide ester led to **110** (Scheme 26) [74]. As may be expected, this 16-electron iridium complex, in which the Cp* plane is almost perpendicular to that consisting of NCCN, does not display chirality on the



Scheme 23.



Scheme 24.



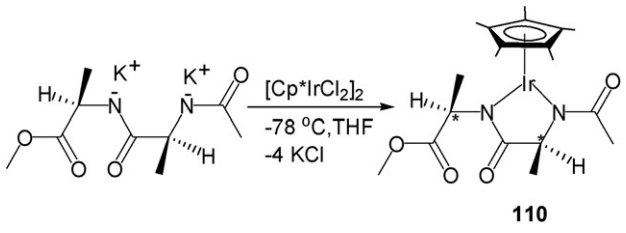
Scheme 25.

metal, although it has two chiral carbon centers on the peptide backbone.

Another interesting group of half-sandwich iridium complexes with bidentate nitrogen donors is the complexes **111–116**, which have been extensively investigated by Carmona et al. (Scheme 27) [75,76]. Using enantiopure imines, the reaction with $[Cp^*IrCl_2]_2$ in the presence of $NaSbF_6$ afforded the Ir(III)-imino complexes with dr in the range of 52:48 to 80:20, depending on the intramolecular interactions of chiral moiety and Cp* ring. The configuration of the major diastereomer in these complexes was determined to be $R_{Ir}S_C$ by either X-ray crystallography or NOEDIFF NMR spectroscopy [75].

The Ir(III)–pyridylamino complexes **117–121** were synthesized in a similar manner (Scheme 28) [76]. Whilst four diastereomers were observed for the complexes **117** and **119b**, only two were detected for the rest. It is noteworthy that only two diastereomers were observed for the iridium aqua complex **119b** in the ratio of 75:25; diastereomeric enrichment occurred on ligand exchange from **119a**. A slight increase in diastereomeric purity was also noticed for the aqua complex **118**. These results are interesting because the solvate complexes are real catalysts for enantioselective Diels–Alder reactions, whilst the corresponding chloride complexes are inactive due to chloride coordination.

The aqua analogues of **117**, **120** and **121** are unstable at room temperature. Diastereoselective cyclometallation via C–H bond activation of the phenyl or naphthyl ring took place cleanly, affording the diastereomerically pure complexes **123** and **124**. The complex **122** was obtained as a 96:4 mixture of two diastereomers. The configuration of the most favourable isomers of **122**, **123** and **124** were determined to be $S_{Ir}S_NR_C$ by NOESY spectroscopy (Scheme 29) [76].

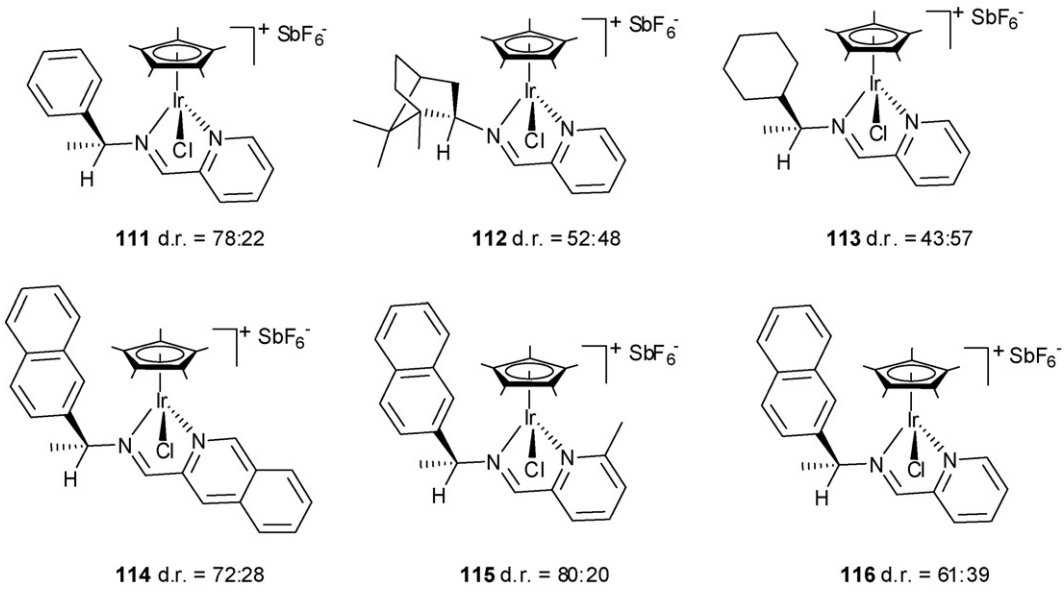


Scheme 26.

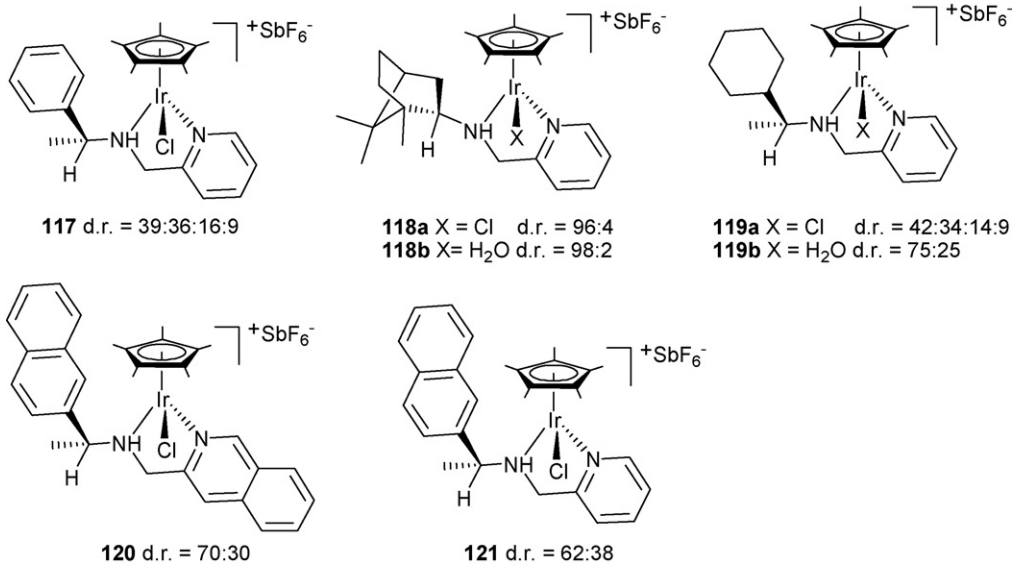
3.4. Tethered half-sandwich iridium complexes

Apart from using chelating bidentate ligands to stabilize the configuration of metal center, introducing a bridge between the Cp ring and a ligand of the piano stool is an efficient way to enhance the rigidity of resulting complexes. Such complexes are generally referred to as "tethered" half-sandwich compounds. "Tethered" ruthenium complexes have received a lot of attention; the analogous iridium complexes are fewer, however.

There are at least two routes to introduce suitable bridging linkers into half-sandwich metal complexes: (1) use of a functionalized Cp derivative with the pendent functional group acting as donor to iridium; (2) intramolecular ring closure between the Cp and ligands seated on the piano stool. The former route is more adopted since synthetic strategies of building functionalized Cp rings are well established. More importantly, substituted Cp rings could be used to construct planar chiral complexes. A number of chiral iridium complexes with Cp–phosphine ligands have been synthesized following this route. The cyclopentadienyl–phosphine ligands shown in Scheme 30 are accessible from optically active vicinal diols. Their reaction with $[Ir(COE)_2Cl]_2$ (COE = cyclooctene) afforded **125** and **126**, which were then oxidized by methyl iodide to give the chiral Ir(III) complexes **127** and **128** in moderate yields with high de of 95% and 80% respectively (Scheme 30) [77]. Greater stereochemical control is exerted on the metal center when the chiral moiety on the alkyl bridge is closer to the iridium atom. Furthermore, the cationic **127** and **128** are more



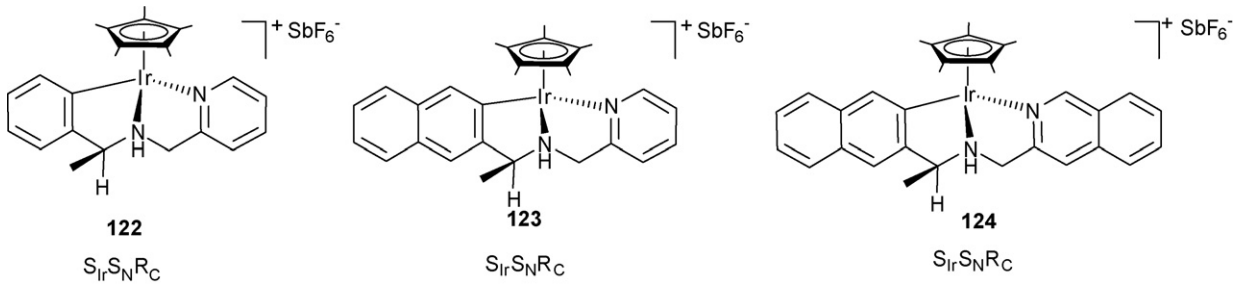
Scheme 27.



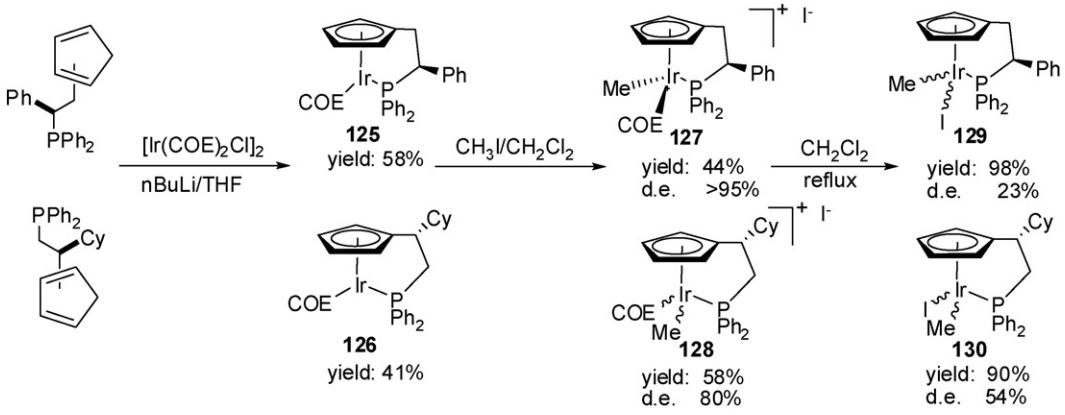
Scheme 28.

configurationally stable than their neutral counterparts, **129** and **130**.

In a similar manner, racemic iridium complexes have been synthesized from planar-chiral, phosphine-substituted cyclopentadienyl ligands (Scheme 31) [78]. One enantiomer of the diiodide complex **131** was kinetically resolved with binaphthol to afford complex **134** with 100% diastereoselectivity. The iridium dihydride **133** has been found to be an excellent catalyst for stereoselective C–H bond activation of benzene and cyclohexane [79]. Complexes **131** and **133**



Scheme 29.

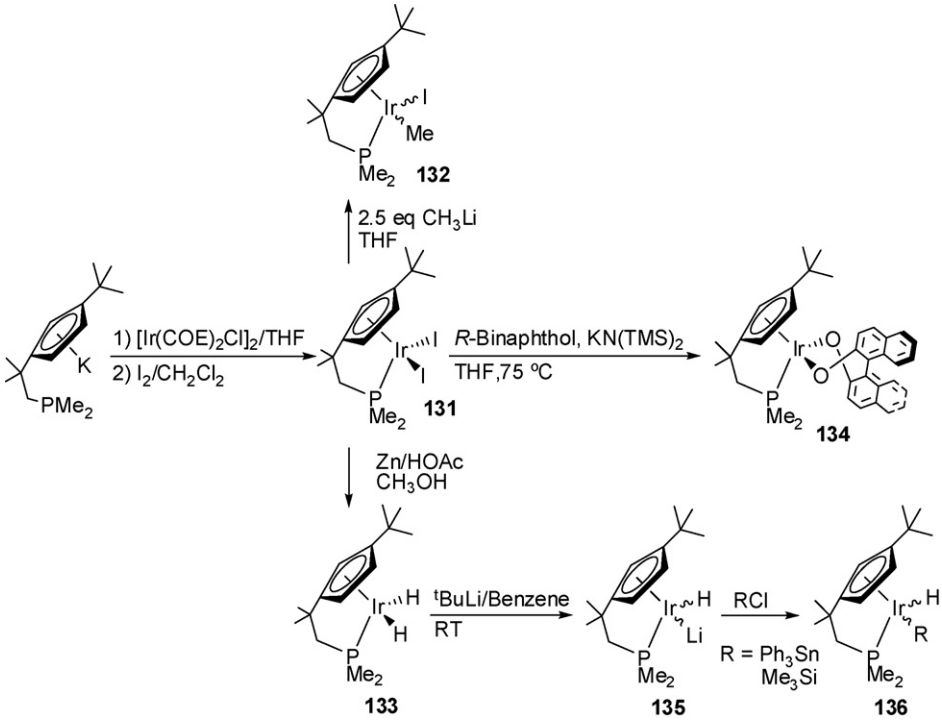


Scheme 30.

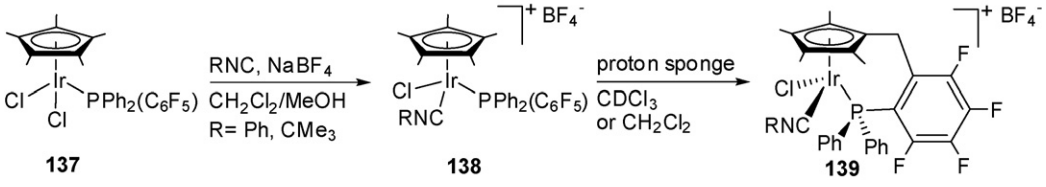
can be further converted into complexes such as **132**, **135** and **136**.

Using the second route, the cationic iridium complex **139** was prepared by intramolecular dehydrofluorinative coupling of Cp* and a pentafluorophenyl phosphine ligand in the complex **138**, which was made from **137** (Scheme 32) [80].

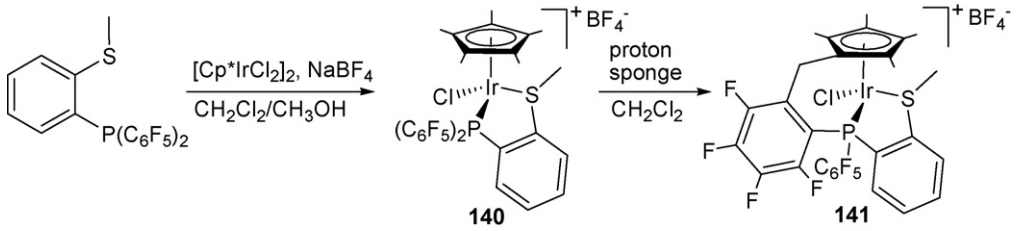
In a similar fashion, $[Cp^*IrCl_2]_2$ reacted with a phosphine thioether in the presence of $NaBF_4$ to give **140**, which, on treatment with proton sponge, afforded the tethered iridium complex **141** (Scheme 33). This compound has three chiral centers and most possibly exists as a pair of enantiomers with a $R_{Ir}R_SS_P/S_{Ir}S_SR_P$ configuration [80].



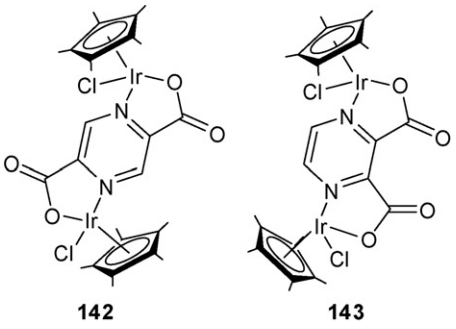
Scheme 31.



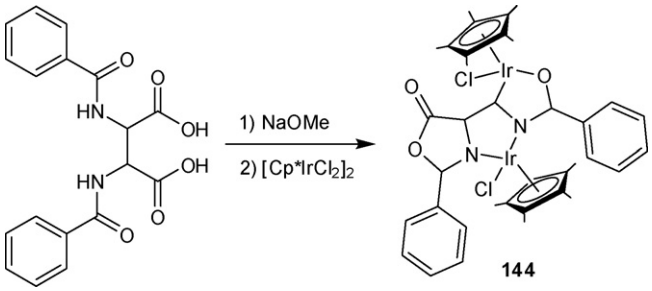
Scheme 32.



Scheme 33.



Scheme 34.



Scheme 35.

3.5. Multinuclear half-sandwich iridium complexes

Multinuclear iridium complexes are often generated when multi-dentate ligands are employed. For example, the reaction of $[Cp^*IrCl_2]_2$ with pyrazine-2,5-dicarboxylic acid or pyrazine-2,3-dicarboxylic acid afforded the dinuclear complexes **142** and **143**, shown in Scheme 34 [16].

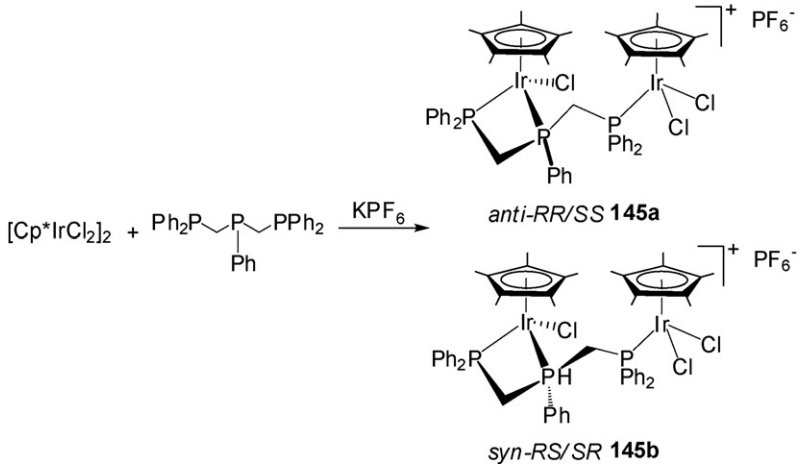
An unexpected dinuclear iridium complex containing a fused amino acid dimmer was obtained from the reaction of $[Cp^*IrCl_2]_2$ and a dimeric hippuric acid derivative in the presence of NaOMe. The reaction leading to **144** occurred by decarboxylation of one carboxylic group of the amino acid dimer and formation of an oxazoline ring (Scheme 35) [81].

The tridentate dpmp has been used to build a large family of mono- and poly-nuclear complexes. In its reaction with $[Cp^*IrCl_2]_2$ in the presence of KPF_6, a 1:1 mixture of two diastereomers, *anti-RR/SS* and *syn-RS/SR*, was formed (**145a** and **145b**, Scheme 36). The *syn*-diastereomer was formed kinetically; but the *anti*-diastereomer was thermodynamically more stable [55].

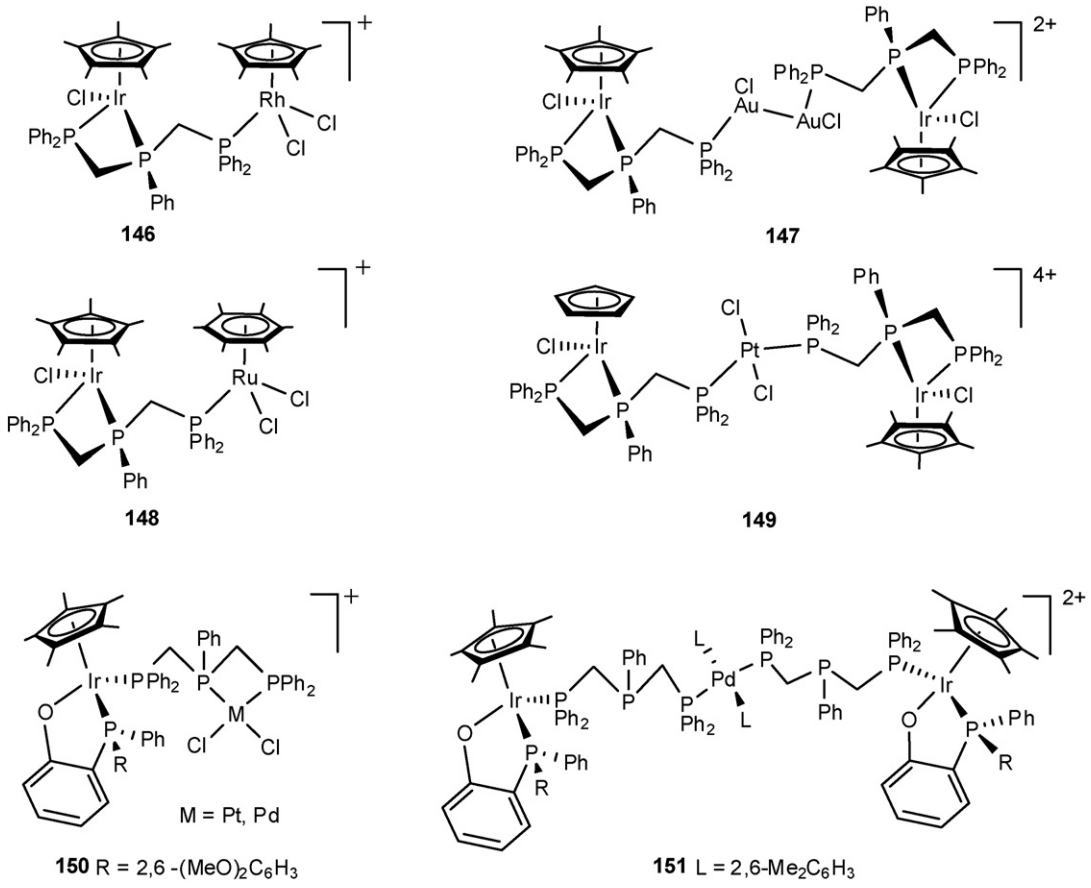
Closely related hetero-metallic multinuclear complexes can also be prepared, starting from suitable iridium precursors, e.g., $[Cp^*IrCl(\eta^2\text{-dpmp})]PF_6$. Some examples (**146–151**) are shown in Scheme 37 [55].

The multinuclear iridium complexes can be further functionalized. An example is the reaction of the binuclear complex **152** with phenylacetylene in water, resulting in a symmetrical dicarbonyl iridium complex **153** (Scheme 38) [26].

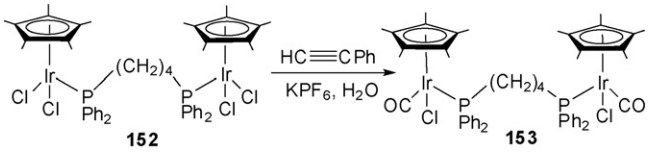
An unusual example of a heterobinuclear iridium complex is formed, in which a pendent olefin on the Cp ring acts as the bridge. Thus, $[PtI_2(Me_2phen)]$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline) reacted with **63** to afford a stable heterometallic binuclear complex **154** via coordination of the alkene to Pt(II) (Scheme 39) [46]. However, the spatial separation of the chiral iridium center from the prochiral olefin



Scheme 36.



Scheme 37.

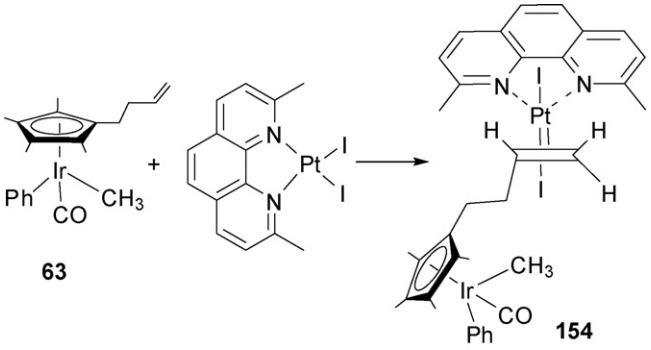


Scheme 38.

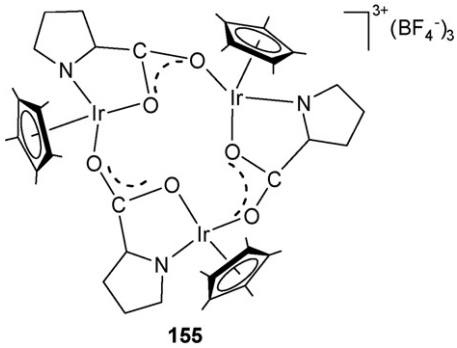
resulted in little chiral relay from the former to the latter on the formation of the prochiral η^2-olefin complex, thus resulting in an equilibrating mixture of diastereomers in the solution.

Mononuclear Ir–Cp* complexes may aggregate in solution through self-recognition. Thus, the mononuclear [Cp*Ir(η^2-*C,N*-D-proline)] self assembled in water to give a trinuclear complex [Cp*Ir(D-proline)]$_3$ **155**, which contains nine chiral centers (3Ir,3N,3α-C) of *R*-configuration (Scheme 40) [82]. Similarly, treatment of the mononuclear complex [Cp*Ir(α-aminoacidate)Cl] with $AgBF_4$ led to new chiral trimers [83]. Interestingly, the cationic trimers afforded similar activities and enantioselectivities to the mononuclear chloro complex in transfer hydrogenation of acetophenone in 2-propanol, suggesting disintegration of the trimer into monomer in solution.

As aforementioned (Section 3.1.4), $[M_4L_6]^{12-}$ (M = Ga(III), Al(III), Fe(III) has proven to be a robust chiral host, which



Scheme 39.



Scheme 40.

contains large cavities and can be used to encapsulate cationic guest molecules (Scheme 10). The cationic complexes $[Cp^*Ir(PMe_3)(Me)(propene)]^+$ and $[Cp^*Ir(PMe_3)(Me)(cis\text{-}2\text{-}butene)]^+$ were encapsulated into $Na_{12}[Ga_4L_6]$, forming guest-host assemblies with moderate diastereoselectivity, due to the chirality of the host and the chiral-at-metal iridium guests [84].

4. Application in catalysis

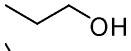
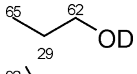
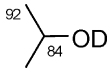
Although this review is focused on the preparation of chiral half-sandwich iridium complexes, a few selected examples of their applications in catalysis are presented below, aiming to highlight the potential of such complexes in catalyzing reactions of widely differing nature.

4.1. C–H activation

The application of C–H bond activation reactions in the synthesis of half-sandwich iridium complexes has already been summarized above. A number of half-sandwich iridium complexes are known to be active in catalyzing isotope labelling of organic molecules. Representative examples are given in Table 7. Deuteration of benzene has been used as a benchmark reaction to evaluate the performance of catalysts. It appears that the choice of iridium catalyst and deuterium sources is crucial for high catalytic performance. Thus, $Cp^*(PMe_3)IrCl_2$ is a catalyst for deuteration of benzene and alcohols with D_2O, with some regioselectivity in deuterium incorporation being observed (Table 7, entries 1–6) [28,85]. Extensive deuterium incorporation at unactivated C–H bond positions means this is an economic way to synthesize deuterium-labelled compounds.

With acetone-d_6 as isotopic source, the reaction time can be significantly reduced by employing the trihydride $Cp^*(PMe_3)Ir(H_3)OTf$ as catalyst; 99% deuteration of benzene was achieved in 20 h. In contrast, a 90% deuterium incorporation necessitated 5 days with $Cp^*(PMe_3)IrCl_2$ in D_2O (Table 7, entry 7) [86]. Under the same reaction conditions, good to excellent deuteration of the aryl rings of ferrocene and other aromatic substrates is also demonstrated (Table 7, entries 8–9). The Cp*Ir(III) complexes of NHC show good H/D exchange activity at a lower catalyst loading in the presence of AgOTf (Table 7, entries 10–13) [43]. It is interesting that the NHC complex **60** shows a higher H/D exchange activity than the cyclometallated complex **61**, suggesting that half-sandwich iridium complexes with monodentate ligand are preferable for selective deuteration of aromatic compounds. Highly selective deuteration of the olefinic positions of styrene with **61** is also notable (Table 7, entry 13), and this is in contrast to the non-selective deuteration observed when using **60**.

Table 7
H/D exchange reactions catalyzed by Cp*–Ir(III) complexes

Entry	Catalyst	Substrate	D-source	Temp	Time	% D_{inc}[a]	Reference
1	$Cp^*(PMe_3)IrCl_2$	C_6H_6	D_2O	135	5 d	90	[85]
2	$Cp^*(PMe_3)IrCl_2$	C_6H_6	D_2O/CD_3OD	135	2 d	97	[85]
3	$Cp^*(PMe_3)IrCl_2$	C_6H_6	CD_3OD	135	2 d	58	[85]
4	$Cp^*(PMe_3)IrCl_2$		D_2O	135	40 h		[28]
5	$Cp^*(PMe_3)IrCl_2$		D_2O	135	40 h		[28]
6	$Cp^*(PMe_3)IrCl_2$		D_2O	135	40 h		[28]
7	$Cp^*(PMe_3)Ir(H_3)OTf$	C_6H_6	Acetone-d_6	135	20 h	99	[86]
8	$Cp^*(PMe_3)Ir(H_3)OTf$	Ferrocene	Acetone-d_6	135	20 h	99	[86]
9	$Cp^*(PMe_3)Ir(H_3)OTf$		Acetone-d_6	135	20 h	*o*: 57[b] *m*: 98[b] *p*: 97[b] CH_3: 50	[86]
10	**60**	$(CH_3CH_2)_2O$	CD_3OD	100	12 h	CH_3,CH_2:[c] > 99	[43]
11	**61**	$(CH_3CH_2)_2O$	CD_3OD	100	12 h	CH_3: 45[c] CH_2: 65[c]	[43]
12	**60**	Styrene	CD_3OD	100	12 h	vinyl: > 99[d] *o*: > 99 *m*,p: 65	[43]
13	**61**	Styrene	CD_3OD	100	12 h	vinyl: > 99[d] *o*,*m*,*p*: 0	[43]

[a] Percentage of deuterium incorporation.
[b] The percentage of deuterium incorporation at the *ortho*-, *meta*-, *para*-position of aromatic ring.
[c] The percentage of deuterium incorporation at the CH_3 and CH_2 groups of diethyl ether.
[d] The percentage of deuterium incorporation at thevinyl group of styrene.

4.2. Hydrogen transfer reactions

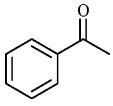
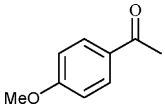
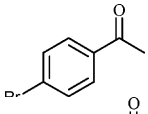
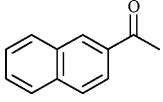
Half-sandwich iridium chloro, aminocarboxylate, amino alcohol, and diamine complexes are excellent catalysts for a range of hydrogen transfer reactions, including asymmetric transfer hydrogenation (ATH) in organic media or in water [5,69,70,87–93]. Described below are selected recent examples of alcohol oxidation, ATH of ketones, and dynamic kinetic resolution of imines and alcohols. The application of $[Cp^*IrCl_2]_2$ in hydrogen transfer reactions has been summarised by Fujita and Yamaguchi [6], and we recently reviewed the aqueous-phase asymmetric transfer hydrogenation reactions, including the use of half-sandwich iridium catalysts [64].

Pioneering work on ATH of ketones and imines with half-sandwich iridium complexes was carried out by the groups of Tani [69,70], Blacker [94], Ikariya [68], and Baker [95], and a significant development in the last a few years is the ATH in aqueous media [64]. As shown in Table 8, ATH of ketones with the catalysts **93–99** can be performed in either organic solvents or aqueous media. In general, the ATH reactions in water afford faster reaction rates than in isopropanol (Table 8, entries 4 versus 1, 8 versus 7, and 20 versus 19). The same is also true with the catalyst **88**. The reduction appears to be much slower in the azeotropic mixture of HCOOH-Et_3N with the iridium complexes, as reviewed by Wills [99–101]. The ATH of imines with **93** and **99** have also been demonstrated [95,98]. The reaction works efficiently for cyclic imines and iminium salts, affording good to excellent enantioselectivities. This is not the case for acyclic imines, however, where very low ee's were observed. A new bidentate monosulfonated diamine with an axially chiral biaryl backbone in combination with $[Cp^*IrCl_2]_2$ was recently reported for the ATH of ketones in isopropanol [102], affording moderate ee's.

The iridium–amido complexes **16–20**, especially **17**, have been disclosed as remarkably efficient and highly chemoselective catalysts for both hydrogenation and transfer hydrogenation of aldehydes in aqueous media [4,103]. Similar water-soluble phenanthroline complexes of iridium have also been applied to transfer hydrogenation of ketones in water [16,104,105]. It is worth noting that Cp*Ir–NHC complexes also serve as active catalysts for both hydrogenation and transfer hydrogenation reactions [106–113].

The $[Cp^*IrCl_2]_2$ dimer itself is an excellent catalyst for hydrogen transfer reactions, such as the Oppenauer-type oxidation of alcohols, *N*-alkylation of amines and alcohols, and transfer hydrogenation of quinolines [6,114–122]. Selected examples of these applications are given in Table 9 . The oxidation of alcohol proceeds under mild conditions (room temperature in acetone in the presence of K_2CO_3), with both primary and secondary alcohols being feasible substrates. The same oxidation can also be effected by half-sandwich Cp*Ir–NHC complexes [120,125–127]. In these reactions, acetone serves as hydrogen acceptor, being converted into isopropanol. However, acceptor-less oxidation has been demonstrated with a hydroxypyridine-substituted complex **156**, where hydrogen is released as H_2 (Scheme 41) [120]. The 2-substitued OH group is believed to play a critical role in the hydrogen generation; the analogous 3- and 4-OH complexes were much less active.

Table 8
ATH of ketones with half-sandwich iridium complexes

Entry	Substrate	Catalyst	Solvent[a] & [H]	Temperature (°C)	Time/h	Conv. (%)	ee (%)	Reference
1		**93**	IPA	30	12	36	96	[68]
2			Azeotrope	40	16	No[b]	–	[96]
3			Azeotrope/H_2O	40	24	39	83	[96]
4			H_2O/HCOONa	40	3	99	93	[96]
5		**94**	IPA/H_2O	22	140	90	82	[94]
6		**95**	H_2O/HCOONa	40	0.7	98	97	[90]
7		**97a**	IPA	30	12	36	96	[68]
8			H_2O/HCOONa	40	1	99	93	[89]
9		**97b**	IPA/H_2O	22	26	88	96	[94]
10		**99a**	H_2O/HCOONa	40	24	10	58	[97]
11		**99b**	H_2O/HCOONa	28	0.5	29	94	[98]
12		**93**	H_2O/HCOONa	40	24	97	91	[96]
13		**94**	IPA/H_2O	22	150	22	78	[94]
14		**95**	H_2O/HCOONa	40	22	94	97	[90]
15		**97b**	IPA/H_2O	22	141	80	95	[94]
16		**94**	IPA/H_2O	22	91	93	76	[94]
17		**95**	H_2O/HCOONa	40	1.8	97	95	[90]
18		**97b**	IPA/H_2O	22	20	99	95	[94]
19		**93**	IPA	r.t.	48	67	81	[70]
20		**93**	H_2O/HCOONa	40	3	100	80	[96]
21		**94**	IPA/H_2O	22	139	77	73	[94]
22		**95**	H_2O/HCOONa	40	4	>99	97	[90]
23		**97b**	IPA/H_2O	22	45	96	96	[94]

[a] Azeotrope refers to the azeotropic mixture of HCOOH-NEt_3; IPA is isopropanol.
[b] No = no reaction.

Table 9
Hydrogen transfer reactions catalyzed by $[Cp^*IrCl_2]_2$

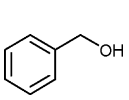
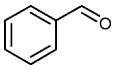
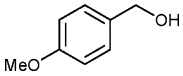
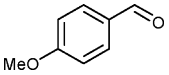
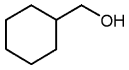
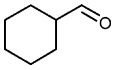
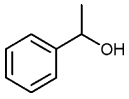
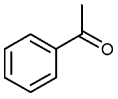
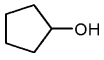
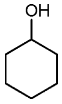
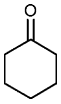
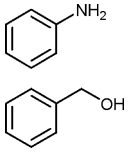
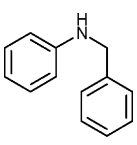
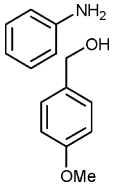
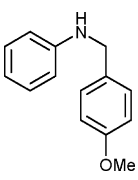
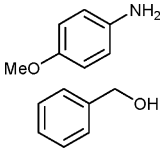
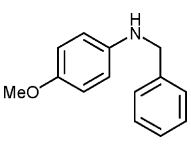
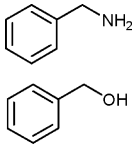
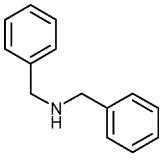
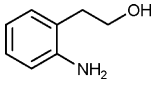
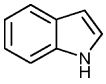
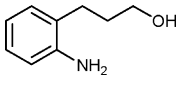
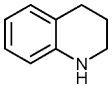
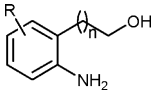
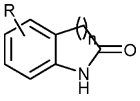
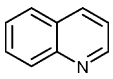
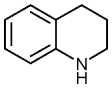
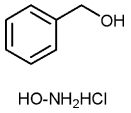
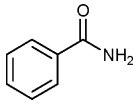
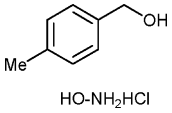
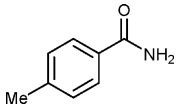
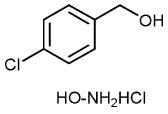
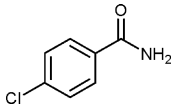
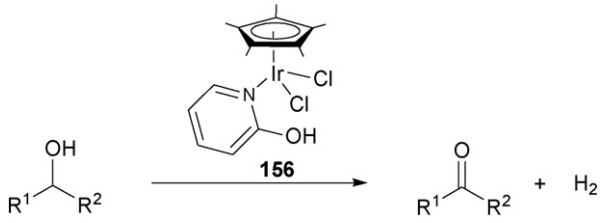
Entry	Substrate	Product	Solvent	Temperature (°C)	Time (h)	Conv. (%[a])	Reference
1			Acetone	r.t.	6	87	[6,122,123]
2			Toluene	110	24	100	[124]
3			Acetone	r.t.	6	99	[6,122,123]
4			Acetone	r.t.	6	47	[6,122,123]
5			Acetone	r.t.	6	100	[6,122,123]
6			Acetone	r.t.	6	100	[6,122,123]
7			Acetone	r.t.	6	79	[6,122,123]
8			Toluene	110	17	(88)	[6,117]
9			Toluene	110	17	(95)	[6,117]
10			Toluene	110	17	(93)	[6,117]
11			Toluene	110	17	(67)	[6,117]
12			Toluene	110	17	(80)	[6,121]
13			Toluene	110	17	(96)	[6,121]
14			Acetone	100	20	N/A	[6,119]
15			IPA/H_2O	Reflux	17	(93)	[6,116]

Table 9 (*Continued*)

Entry	Substrate	Product	Solvent	Temperature (°C)	Time (h)	Conv. (%[a])	Reference
16			Toluene	Reflux	24/16	(87)	[124]
17			Toluene	Reflux	24/16	(90)	[124]
18			Toluene	Reflux	30/16	(83)	[124]

[a] The number in bracket refers to the isolated yield.



Scheme 41.

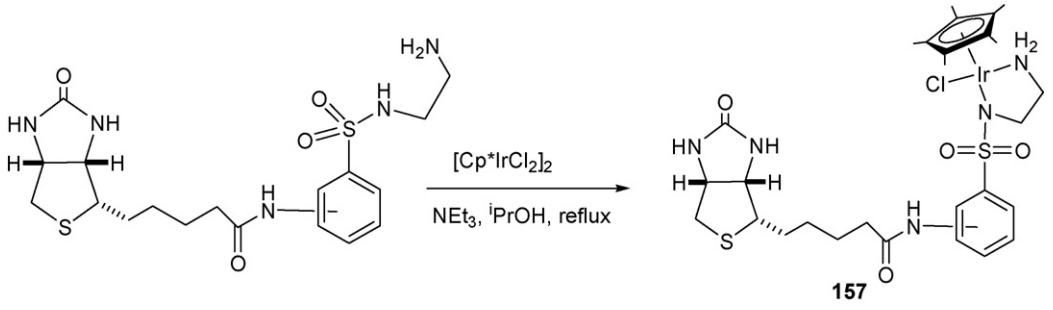
The iridium dimer has also been used as catalyst for the conversion of alcohols into amines via a process of dehydrogenation of the alcohol, condensation to form an imine, and finally hydrogenation to afford the amine (Table 9, entries 8–15). It is noted that this "borrowing hydrogen" strategy has also been applied to the formation of C–C bond from alcohols via alkene and aldehydes derived from dehydrogenation of the alcohols [128–132]. Very recently, the application of $[Cp^*IrCl_2]_2$ in catalysis has been extended to a one-pot synthesis of amides from alcohols via oximes (Table 9, entries 16–18) [124].

Half-sandwich iridium complexes have also shown promise in metallo-enzymatic catalysis, thanks to the recent development in Biotin–Avidin technology, allowing organometallic catalysts to be integrated with protein/peptide hosts. An excellent example is the docking of the biotinylated, racemic Cp*Ir–diamine complexes **157** into a variety of protein and DNA hosts to afford artificial metalloenzymes, which catalyze enantioselective transfer hydrogenation of ketones (Scheme 42) [133,134]. The configuration of the iridium complex is influenced by the host protein; a more stable one can be readily achieved by chloride dissociation. This epimerization can lead to optically active catalyst, and as might be expected, the enantioselectivity of the ATH is shown to vary significantly with the host structure.

Dynamic kinetic resolution (DKR) takes advantage of both resolution and racemisation, and is a most efficient approach to prepare enantiomerically pure compounds. The Ir–TsDPEN complex **93** catalyzed the DKR of α-substituted cyclic ketimines, using $HCOOH/Et_3N$ as the hydrogen source (Table 10, entries 1–3) [65]. The achiral half-sandwich iridium complex **60** has been combined with an enzyme for DKR; excellent conversions and enantioselectivity were obtained in the one-pot chemoenzymatic DKR of secondary alcohols (Table 10, entries 4–6) [135]. In the first example, the catalyst selectively reduces one of the racemic ketimines, with inter-conversion between the pair being triggered presumably by protonation of the imine. The success of the second example hinges on the efficient racemization of the alcohol by **60** through a process of dehydrogenation and hydrogenation.

4.3. Asymmetric Diels–Alder reaction

A variety of iridium complexes are known to be active for the Diels–Alder (DA) reactions. Table 11 shows the asymmetric DA reaction of methacrolein with cyclopentadiene using half-sandwich iridium catalysts. The chloride complexes are generally inactive, the active catalyst being iridium solvate complexes generated in situ. Evidently, the DA reaction is catalyzed



Scheme 42.

Table 10
DKR catalyzed by half-sandwich iridium complexes

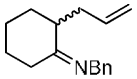
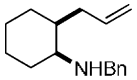
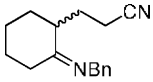
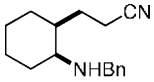
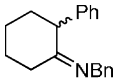
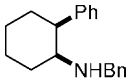
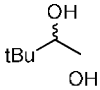
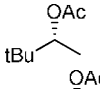
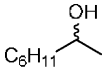
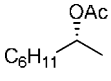
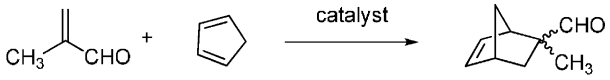
Entry	Catalyst	Substrate	S/C	Time	Product	Yield (%)	ee (%)	Reference
1	(*S*,*S*)-**93**		500	1 d		75	63	[65]
2	(*S*,*S*)-**93**		500	6 d		60	72	[65]
3	(*S*,*S*)-**93**		500	1 d		55	50	[65]
4	**60**/Novozyme 435		1000	18 h		93	97	[135]
5	**60**/Novozyme 435		1000	18 h		89	99	[135]
6	**60**/Novozyme 435		1000	8 h		>99	99	[135]

Table 11
Enantioselective DA reactions catalyzed by chiral half-sandwich iridium complexes 

Entry	Catalyst (R_{Ir}:S_{Ir} ratio)	Solvent	Temperature (°C)	Time (h)	Yield (%)	Isomeric ratio (*exo*:*endo*)	ee (%) (*exo*)	Reference
1	**79** (79:21)	CH_2Cl_2	r.t.	0.1	96	91:9	51	[52]
2	**77** (57:43)	CH_2Cl_2	r.t.	0.1	95	91:9	58	[52]
3	**81** (0:100)	CH_2Cl_2	r.t.	1	94	87:13	8	[54]
4	**111** (32:68)	CH_2Cl_2/acetone	r.t.	0.9	91	90:10	7	[75]
5	**111** (98:2)	CH_2Cl_2/acetone	r.t.	1.5	94	90:10	5	[75]
6	**111** (98:2)	CH_2Cl_2/acetone	−50	94	48	93:7	32	[75]
7	**116** (98:2)	CH_2Cl_2/acetone	r.t.	1.6	89	90:10	14	[75]
8	**114** (98:2)	CH_2Cl_2/acetone	r.t.	2	94	85:15	0	[75]
9	**112** (50:50)	CH_2Cl_2/acetone	r.t.	0.3	100	90:10	20	[75]
10	**120** (70:30)	CH_2Cl_2	r.t.	2	96	85:15	0	[76]
11	**120** (70:30)	CH_2Cl_2	−80	72	97	98:2	70	[76]
12	**119** (75:25)	CH_2Cl_2	r.t.	0.17	94	91:9	16	[76]
13	**119** (75:25)	CH_2Cl_2	−80	72	95	98:2	72	[76]

by half-sandwich iridium complexes containing diverse ligands. However, the enantioselectivity is low. The *exo* adduct is obtained preferentially, with higher enantioselectivities obtained at lower temperatures.

There appears to be no correlation between the optical purity/diastereomeric composition of the catalyst and the enantioselectivity of the reaction. For example, the diastereomerically pure **81** gave a poor enantioselectivity of 7% ee [54], and little significant change was observed in ee's when the diastereoselectivity of **111** was varied [75]. As aforementioned, the configuration of the iridium center can change on displacement of the chloride with a solvent molecule; this leads to variation in the diastereomeric purity of the catalyst (e.g. **119a** versus **119b**, Scheme 28). Such diastereoisomerization of catalysts under reaction conditions is expected to impact on the enantioselectivities of the catalyzed reactions. However, this configurational lability of the metal center also prevents a clear structure–selectivity relationship from being established.

5. Conclusions

Three-legged piano stool half-sandwich iridium complexes can be accessed by a number of means. The group I complexes can be readily prepared from suitable Cp*/Cp-Ir precursors by ligand substitution. Alternative synthetic protocols have also been established, which include: (1) C–X (X=C, H) bond cleavage of terminal alkynes, alkenes, aldehydes and alcohols, affording "one pot" syntheses of half-sandwich iridium carbonyl complexes; (2) oxidative addition of alkyl/fluoroalkyl halides to iridium(I) and iridium(III) complexes; (3) cyclometallation through C–H bond activation to afford Cp*Ir(η^2-C,X) complexes (X=P, S, O, N). In most cases, these complexes are obtained as racemic mixtures, although a specific configuration at the iridium can be enriched through diastereoselective guest-host interactions. This group of complexes has been mostly studied in stoichiometric transformations; however, their success in catalytic synthesis has also been demonstrated, e.g.,

the selective deuteration of organic substrates catalyzed by Cp*Ir(PMe_3)(Me)(R)X, affording isotopically labelled compounds.

Half-sandwich chiral-at-metal iridium complexes with more than one chiral center, viz the groups II and III complexes, can be prepared by the complexation of an iridium precursor with ligands containing chiral elements. The diastereoselectivity of these reactions depends on the steric and electronic interactions between the stereogenic centers involved. For chiral monodentate ligands, moderate diastereoselectivity has been obtained under both kinetic and thermodynamic control. Highly diastereoselective synthesis of iridium complexes is achieved when chiral bidentate ligands are employed. In some cases, a single diastereomer has been observed in both solution and the solid state. These features confer advantages on chiral half-sandwich iridium as potential catalysts for highly enantioselective synthesis. A good example is seen in the Cp*Ir–TsDPEN type complexes, which display high rates and enantioselectivities in ATH reactions. Analogous complexes have also found applications in enantioselective Diels–Alder reactions. However, in many other cases, configurational lability at iridium is observed when a chiral bidentate ligand is employed, and for catalysis, a clear relationship between the chirality of catalysts, particularly that at the metal, and the enantioselectivity of reactions is yet to be established.

The group IV, tethered half-sandwich iridium complexes can relay chirality from the bridge to iridium. Configurational change at iridium through ligand dissociation could also be minimised by the chelating effect. Whilst the potential of these complexes in catalysis remains to be explored, analogous Ru(II) complexes have shown excellent performance in asymmetric hydrogen transfer reactions [136].

Half-sandwich iridium complexes have shown applications in a number of highly interesting chemical reactions. However, their use in catalysis appears to be still limited thus far, with the most notable examples being found in hydrogen transfer reactions. Given the rich chemistry displayed by these complexes, we believe that it will only be a matter of time before their full potential in catalysis is exploited.

Acknowledgement

The financial support of EPSRC (EP/C005643) (JK Liu) and the DTI MMI project (XF Wu) is gratefully acknowledged.

References

[1] H. Brunner, Angew. Chem. Int. Ed. 38 (1999) 1195.
[2] H. Brunner, Eur. J. Inorg. Chem. 4 (2001) 905.
[3] C. Ganter, Chem. Soc. Rev. 32 (2003) 130.
[4] X.F. Wu, J.K. Liu, X.H. Li, A. Zanotti-Gerosa, F. Hancock, D. Vinci, J.W. Ruan, J.L. Xiao, Angew. Chem. Int. Ed. 45 (2006) 6718.
[5] X.F. Wu, X.H. Li, M. McConville, O. Saidi, J.L. Xiao, J. Mol. Catal. A: Chem. 247 (2006) 153.
[6] K. Fujita, R. Yamaguchi, Synlett (2005) 560.
[7] C. Slugovc, I. Padilla-Martinez, S. Sirol, E. Carmona, Coord. Chem. Rev. 213 (2001) 129.
[8] A. Pfaltz, J. Blankenstein, R. Hilgraf, E. Hormann, S. McIntyre, F. Menges, M. Schonleber, S.P. Smidt, B. Wustenberg, N. Zimmermann, Adv. Synth. Catal. 345 (2003) 33.
[9] J.B. Chen, R.J. Angelici, Coord. Chem. Rev. 206 (2000) 63.
[10] E. Carmona, M. Paneque, L.L. Santos, V. Salazar, Coord. Chem. Rev. 249 (2005) 1729.
[11] M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, Eur. J. Inorg. Chem. 1 (2004) 17.
[12] H. Werner, Organometallics 24 (2005) 1036.
[13] C.J. Bourgeois, S.A. Garratt, R.P. Hughes, R.B. Larichev, J.M. Smith, A.J. Ward, S. Willemsen, D. Zhang, A.G. DiPasquale, L.N. Zakharov, A.L. Rheingold, Organometallics 25 (2006) 3474.
[14] M. Valderrama, R. Contreras, P. Munoz, M. Pilar Lamata, D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, J. Organomet. Chem. 633 (2001) 182.
[15] M. Gorol, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Eur. J. Inorg. Chem. (2005) 4840.
[16] P. Govindaswamy, B. Therrien, G. Suss-Fink, P. Stepnicka, J. Ludvik, J. Organomet. Chem. 692 (2007) 1661.
[17] E. Simon-Manso, M. Valderrama, P. Gantzel, C.P. Kubiak, J. Organomet. Chem. 651 (2002) 90.
[18] O. Diaz, R. Contreras, M. Valderrama, J. Chil. Chem. Soc. 51 (2006) 875.
[19] K. Pachhunga, B. Therrien, K.A. Kreisel, G.P.A. Yap, M.R. Kollipara, Polyhedron 26 (2007) 3638.
[20] S.K. Singh, M. Chandra, S.K. Dubey, D.S. Pandey, Eur. J. Inorg. Chem. 19 (2006) 3954.
[21] D.F. Kennedy, B.A. Messerle, M.K. Smith, Eur. J. Inorg. Chem. 1 (2007) 80.
[22] S.N. Paisner, P. Burger, R.G. Bergman, Organometallics 19 (2000) 2073.
[23] R.P. Hughes, R.B. Laritchev, L.N. Zakharov, A.L. Rheingold, J. Am. Chem. Soc. 127 (2005) 6325.
[24] R.P. Hughes, I. Kovacik, D.C. Lindner, J.M. Smith, S. Willemsen, D. Zhang, I.A. Guzei, A.L. Rheingold, Organometallics 20 (2001) 3190.
[25] K. Ogata, K. Kuge, K. Tatsumi, Y. Yamamoto, Chem. Commun. (2002) 128.
[26] K. Ogata, J. Seta, K. Sugawara, N. Tsutsumi, Y. Yamamoto, K. Kuge, K. Tatsumi, Inorg. Chim. Acta 359 (2006) 1549.
[27] C.S. Chin, D. Chong, B. Maeng, J. Ryu, H. Kim, M. Kim, H. Lee, Organometallics 21 (2002) 1739.
[28] S.R. Klei, J.T. Golden, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 124 (2002) 2092.
[29] V.S. Sridevi, W.Y. Fan, W.K. Leong, Organometallics 26 (2007) 1173.
[30] R.P. Hughes, J.M. Smith, L.M. Liable-Sands, T.E. Concolino, K.C. Lam, C. Incarvito, A.L. Rheingold, Dalton Trans. (2000) 873.
[31] R.P. Hughes, A. Williamson, R.D. Sommer, A.L. Rheingold, J. Am. Chem. Soc. 123 (2001) 7443.
[32] A. Mahr, O. Nurnberg, H. Werner, Z. Anorg. Allgem. Chem. 629 (2003) 91.
[33] C.J. Bourgeois, R.P. Hughes, T.L. Husebo, J.M. Smith, I.M. Guzei, L.M. Liable-Sands, L.N. Zakharov, A.L. Rheingold, Organometallics 24 (2005) 6431.
[34] D.A. Ortmann, B. Weberndoerfer, K. Ilg, M. Laubender, H. Werner, Organometallics 21 (2002) 2369.
[35] R.P. Hughes, S. Willemsen, A. Williamson, D. Zhang, Organometallics 21 (2002) 3085.
[36] P.J. Alaimo, B.A. Arndtsen, R.G. Bergman, Organometallics 19 (2000) 2130.
[37] D.H. Leung, D. Fiedler, R.G. Bergman, K.N. Raymond, Angew. Chem. Int. Ed. 43 (2004) 963.
[38] S.R. Klei, T.D. Tilley, R.G. Bergman, J. Am. Chem. Soc. 122 (2000) 1816.
[39] S.R. Klei, T.D. Tilley, R.G. Bergman, Organometallics 21 (2002) 4648.
[40] D.L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S.T. Hilton, D.R. Russell, Dalton Trans. (2003) 4132.
[41] B.J. Wik, C. Romming, M. Tilset, J. Mol. Catal. A: Chem. 189 (2002) 23.
[42] M. Nieuwenhuyzen, G.C. Saunders, Inorg. Chim. Acta 357 (2004) 2870.
[43] R. Corberan, M. Sanau, E. Peris, J. Am. Chem. Soc. 128 (2006) 3974.
[44] R. Corberan, M. Sanau, E. Peris, Organometallics 25 (2006) 4002.

[45] R. Corberan, V. Lillo, J.A. Mata, E. Fernandez, E. Peris, Organometallics 26 (2007) 4350.
[46] P. Papadia, A. Ciccarese, J.A. Miguel-Garcia, P.M. Maitlis, F.P. Fanizzi, J. Organomet. Chem. 690 (2005) 2097.
[47] R.P. Hughes, D. Zhang, A.J. Ward, L.N. Zakharov, A.L. Rheingold, J. Am. Chem. Soc. 126 (2004) 6169.
[48] S.A. Garratt, R.P. Hughes, I. Kovacik, A.J. Ward, S. Willemsen, D. Zhang, J. Am. Chem. Soc. 127 (2005) 15585.
[49] R.P. Hughes, R.B. Larichev, L.N. Zakharov, A.L. Rheingold, Organometallics 25 (2006) 3943.
[50] K. Kajiyama, A. Nakamoto, S. Miyazawa, T.K. Miyamoto, Chem. Lett. 32 (2003) 332.
[51] J.B. Sortais, N. Pannetier, A. Holuigue, L. Barloy, C. Sirlin, M. Pfeffer, N. Kyritsakas, Organometallics 26 (2007) 1856.
[52] D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, M.P. Lamata, F. Viguri, F. Sanchez, S. Martinez, C. Cativiela, M.P. Lopez-Ram de Viu, Organometallics 21 (2002) 5100.
[53] S. Evans, J.W. Faller, J. Parr, J. Organomet. Chem. 674 (2003) 56.
[54] D. Carmona, R. Medrano, I.T. Dobrinovich, F.J. Lahoz, J. Ferrer, L.A. Oro, J. Organomet. Chem. 691 (2006) 5560.
[55] Y. Yamamoto, Y. Kosaka, Y. Tsutsumi, Y. Sunada, K. Tatsumi, T. Fumie, T. Shigetoshi, Dalton Trans. (2004) 2969.
[56] D. Carmona, M.P. Lamata, L.A. Oro, Eur. J. Inorg. Chem. 9 (2002) 2239.
[57] B. Kayser, W. Beck, Z. Naturforsch. B: Chem. Sci. 59 (2004) 1423.
[58] W. Hoffmuller, H. Dialer, W. Beck, Z. Naturforsch. B: Chem. Sci. 60 (2005) 1278.
[59] W. Ponikwar, W. Beck, Z. Naturforsch. B: Chem. Sci. 58 (2003) 318.
[60] W. Ponikwar, W. Beck, Z. Naturforsch. B: Chem. Sci. 58 (2003) 92.
[61] V.N. Sapunov, R. Schmid, K. Kirchner, H. Nagashima, Coord. Chem. Rev. 238 (2003) 363.
[62] H. Brunner, I. Grau, M. Zabel, Organometallics 23 (2004) 3788.
[63] A.W. Holland, R.G. Bergman, Inorg. Chim. Acta 341 (2002) 99.
[64] X.F. Wu, J.L. Xiao, Chem. Commun. (2007) 2449.
[65] A. Ros, A. Magriz, H. Dietrich, M. Ford, R. Fernandez, J.M. Lassaletta, Adv. Synth. Catal. 347 (2005) 1917.
[66] F. Wang, H. Liu, L. Cun, J. Zhu, J. Deng, Y. Jiang, J. Org. Chem. 70 (2005) 9424.
[67] G.R. Hodges, J. Martin, N.A. Hammil, I.N. Houson, WO2006067395, 2006.
[68] K. Murata, T. Ikariya, R. Noyori, J. Org. Chem. 64 (1999) 2186.
[69] K. Mashima, T. Abe, K. Tani, Chem. Lett. 27 (1998) 1201.
[70] K. Mashima, T. Abe, K. Tani, Chem. Lett. 27 (1998) 1199.
[71] X.G. Li, W.P. Chen, W. Hems, F. King, J.L. Xiao, Org. Lett. 5 (2003) 4559.
[72] K. Murata, H. Konishi, M. Ito, T. Ikariya, Organometallics 21 (2002) 253.
[73] T. Koike, T. Ikariya, Organometallics 24 (2005) 724.
[74] W. Ponikwar, P. Mayer, W. Beck, Eur. J. Inorg. Chem. 8 (2002) 1932.
[75] D. Carmona, F.J. Lahoz, S. Elipe, L.A. Oro, M.P. Lamata, F. Viguri, C. Mir, C. Cativiela, M.P. Lopez-Ram de Viu, Organometallics 17 (1998) 2986.
[76] D. Carmona, M.P. Lamata, F. Viguri, R. Rodriguez, F.J. Lahoz, I.T. Dobrinovitch, L.A. Oro, Dalton Trans. (2007) 1911.
[77] A. Doppiu, U. Englert, V. Peters, A. Salzer, Inorg. Chim. Acta 357 (2004) 1773.
[78] S.N. Paisner, G.G. Lavoie, R.G. Bergman, Inorg. Chim. Acta 334 (2002) 253.
[79] T.A. Mobley, R.G. Bergman, J. Am. Chem. Soc. 120 (1998) 3253.
[80] R.M. Bellabarba, G.C. Saunders, Polyhedron 23 (2004) 2659.
[81] H. Dialer, S. Schumann, K. Polborn, W. Steglich, W. Beck, Eur. J. Inorg. Chem. 7 (2001) 1675.
[82] T. Poth, H. Paulus, H. Elias, C. Ducker-Benfer, R. Van Eldik, Eur. J. Inorg. Chem. 5 (2001) 1361.
[83] D. Carmona, F.J. Lahoz, R. Atencio, L.A. Oro, M.P. Lamata, F. Viguri, E. San Jose, C. Vega, J. Reyes, F. Joo, A. Katho, Chem. Eur. J. 5 (1999) 1544.
[84] D.H. Leung, R.G. Bergman, K.N. Raymond, J. Am. Chem. Soc. 128 (2006) 9781.
[85] C.M. Yung, M.B. Skaddan, R.G. Bergman, J. Am. Chem. Soc. 126 (2004) 13033.
[86] M.B. Skaddan, C.M. Yung, R.G. Bergman, Org. Lett. 6 (2004) 11.
[87] K. Murata, T. Ikariya, J. Org. Chem. 64 (1999) 2186.
[88] T. Hamada, T. Torii, T. Onishi, K. Izawa, T. Ikariya, J. Org. Chem. 69 (2004) 7391.
[89] X.F. Wu, D. Vinci, T. Ikariya, J.L. Xiao, Chem. Commun. (2005) 4447.
[90] X.H. Li, J. Blacker, I. Houson, X.F. Wu, J.L. Xiao, Synlett 8 (2006) 1155.
[91] B.Z. Li, J.S. Chen, Z.R. Dong, Y.Y. Li, Q.B. Li, J.X. Gao, J. Mol. Catal. A: Chem. 258 (2006) 113.
[92] W.Y. Shen, H. Zhang, H.L. Zhang, J.X. Gao, Tetrahedron-Asymmetry 18 (2007) 729.
[93] Y. Xing, J.S. Chen, Z.R. Dong, Y.Y. Li, J.X. Gao, Tetrahedron Lett. 47 (2006) 4501.
[94] T. Thorpe, J. Blacker, S.M. Brown, C. Bubert, J. Crosby, S. Fitzjohn, J.P. Muxworthy, J.M.J. Williams, Tetrahedron Lett. 42 (2001) 4041.
[95] J.M. Mao, D.C. Baker, Org. Lett. 1 (1999) 841.
[96] X.F. Wu, X.H. Li, A. Zanotti-Gerosa, A. Pettman, J.K. Liu, A. Mills, J.L. Xiao, Chem. Eur. J. (2008), doi:10.1002/chem.200701258.
[97] Y.P. Ma, H. Liu, L. Chen, X. Cui, J. Zhu, J.E. Deng, Org. Lett. 5 (2003) 2103.
[98] L. Li, J.S. Wu, F. Wang, J. Liao, H. Zhang, C.X. Lian, J. Zhu, J.G. Deng, Green Chem. 9 (2007) 23.
[99] M.J. Palmer, M. Wills, Tetrahedron-Asymmetry 10 (1999) 2045.
[100] F.K. Cheung, A.M. Hayes, J. Hannedouche, A.S.Y. Yim, M. Wills, J. Org. Chem. 70 (2005) 3188.
[101] S. Gladiali, E. Alberico, Chem. Soc. Rev. 35 (2006) 226.
[102] M. Furegati, A.J. Rippert, Tetrahedron-Asymmetry 16 (2005) 3947.
[103] X.F. Wu, C. Corcoran, S.J. Yang, J.L. Xiao, ChemSuSChem. 1 (2008) doi:10.1002/cssc200700086.
[104] J. Canivet, G. Suss-Fink, P. Stepnicka, Eur. J. Inorg. Chem. 30 (2007) 4736.
[105] P. Govindaswamy, J. Canivet, B. Therrien, G. Suss-Fink, P. Stepnicka, J. Ludvik, J. Organomet. Chem. 692 (2007) 3664.
[106] R.H. Crabtree, Coord. Chem. Rev. 251 (2007) 595.
[107] E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.
[108] J.R. Miecznikowski, R.H. Crabtree, Organometallics 23 (2004) 629.
[109] J.R. Miecznikowski, R.H. Crabtree, Polyhedron 23 (2004) 2857.
[110] M. Vogt, V. Pons, D.M. Heinekey, Organometallics 24 (2005) 1832.
[111] M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, Organometallics 25 (2006) 3063.
[112] R. Corberan, M. Sanau, E. Peris, Organometallics 26 (2007) 3492.
[113] M. Viciano, M. Feliz, R. Corberan, J.A. Mata, E. Clot, E. Peris, Organometallics 26 (2007) 5304.
[114] K. Fujita, C. Asai, T. Yamaguchi, F. Hanasaka, R. Yamaguchi, Org. Lett. 7 (2005) 4017.
[115] K. Fujita, S. Furukawa, R. Yamaguchi, J. Organomet. Chem. 649 (2002) 289.
[116] K. Fujita, C. Kitatsuji, S. Furukawa, R. Yamaguchi, Tetrahedron Lett. 45 (2004) 3215.
[117] K. Fujita, Z.Z. Li, N. Ozeki, R. Yamaguchi, Tetrahedron Lett. 44 (2003) 2687.
[118] K. Fujita, M. Nonogawa, R. Yamaguchi, Chem. Commun. (2004) 1926.
[119] K. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, Org. Lett. 6 (2004) 2785.
[120] K. Fujita, N. Tanino, R. Yamaguchi, Org. Lett. 9 (2007) 109.
[121] K. Fujita, K. Yamamoto, R. Yamaguchi, Org. Lett. 4 (2002) 2691.
[122] K.I. Fujita, T. Fujii, R. Yamaguchi, Org. Lett. 6 (2004) 3525.
[123] F. Hanasaka, K.I. Fujita, R. Yamaguchi, Organometallics 23 (2004) 1490.
[124] N.A. Owston, A.J. Parker, J.M.J. Williams, Org. Lett. 9 (2007) 73.
[125] F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 24 (2005) 3422.
[126] F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 25 (2006) 4643.
[127] Y. Tanabe, F. Hanasaka, K. Fujita, R. Yamaguchi, Organometallics 26 (2007) 4618.
[128] M. Hamid, P.A. Slatford, J.M.J. Williams, Adv. Synth. Catal. 349 (2007) 1555.

[129] P.J. Black, M.G. Edwards, J.M.J. Williams, Eur. J. Org. Chem. 21 (2006) 4367.
[130] P.J. Black, G. Cami-Kobeci, M.G. Edwards, P.A. Slatford, M.K. Whittlesey, J.M.J. Williams, Org. Biomol. Chem. 4 (2006) 116.
[131] M.G. Edwards, R.F.R. Jazzar, B.M. Paine, D.J. Shermer, M.K. Whittlesey, J.M.J. Williams, D.D. Edney, Chem. Commun. (2004) 90.
[132] M.G. Edwards, J.M.J. Williams, Angew. Chem. Int. Ed. 41 (2002) 4740.
[133] C.M. Thomas, C. Letondor, N. Humbert, T.R. Ward, J. Organomet. Chem. 690 (2005) 4488.
[134] C. Letondor, A. Pordea, N. Humbert, A. Ivanova, S. Mazurek, M. Novic, T.R. Ward, J. Am. Chem. Soc. 128 (2006) 8320.
[135] A.C. Marr, C.L. Pollock, G.C. Saunders, Organometallics 26 (2007) 3283.
[136] D.J. Morris, A.M. Hayes, M. Wills, J. Org. Chem. 71 (2006) 7035.