Chem Soc Rev

REVIEW ARTICLE

Cyclometalated [Cp*M(C^X)] (M = Ir, Rh; X = N, C, O, P) complexes†

Cite this: DOI: 10.1039/c3cs60343a

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Half-sandwich Cp*Ir and Cp*Rh metalacycles have been successfully applied in traditional domains encompassing organic transformations and catalysis in recent years, especially the catalytic activation of C–H bonds. Cyclometalation has proven to be a highly attractive and versatile synthetic method for the formation of organometallic metalacycles. This review intends to describe isolated and well-defined cyclometalated iridium–rhodium complexes that contain a Cp*M–C (M = Ir, Rh) bond stabilised by the intramolecular coordination of neutral donor atoms (N, C, O or P). The formation of metalamacrocycles and cages employing cyclometalated approaches is discussed. In focusing on selected mechanistic insights garnered from iridium/rhodium-catalysed functionalisation of C–H bonds involving cyclometalated complexes, a limited number of substrates will be discussed, but a broad range of mechanistic features is highlighted.

Received 30th September 2013

DOI: 10.1039/c3cs60343a

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1. Introduction

Exploring the chemistry and uses of half-sandwich cyclometalated complexes has become one of the most active and exciting areas of organometallic chemistry, because of the useful catalytic reactivity that these ligands impart on complexes.[1–8] Half-sandwich iridium and rhodium complexes containing at least one metal–carbon bond intramolecularly stabilised by at least one donor atom (such as N, C, O, P), termed cyclometalated [Cp*M(C^X)] (M = Ir, Rh) complexes, are two of the most popular classes of organometallic derivatives.[4–14] The two metalacycle skeletons are often encountered as intermediate species in carbon–carbon or carbon–heteroatom bond-forming reactions promoted by $[Cp^*MCl_2]_2$ (M = Ir, Rh) complexes.[12–14] During the past ten years, the formation of cyclometalated [Cp*M(C^X)] complexes has garnered much attention due to

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† Dedicated to Prof. Quanxin Xin on the occasion of his 80th Birthday.

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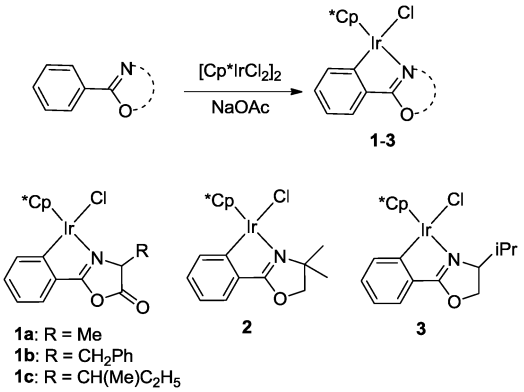
their facile accessibility through sodium-acetate-promoted C–H activation using $[Cp^*MCl_2]_2$ (M = Ir, Rh) as precursors.[10] Moreover, the successful isolation of cyclometalated intermediate complexes, a key step for detailed mechanistic investigations, has also been achieved recently.[5–8,10,12–14]

This review will concentrate on isolated and well-defined complexes that contain a Cp*M–C (M = Ir, Rh) bond stabilised by the intramolecular coordination of neutral donor atoms (N, C, O or P). It does not attempt to be comprehensive, it merely attempts to allow the reader to comprehend cyclometalated half-sandwich iridium and rhodium chemistry in terms of complex formation and reactivity, which will hopefully provide a platform for in-depth mechanistic investigations of transition-metal-catalysed C–H bond functionalisation reactions in the future. There are excellent specialised reviews on the application of half-sandwich iridium and rhodium complexes in both organic synthesis and organometallic catalysis. However, the synthesis and reactivity aspects of cyclometalated Cp*Ir and Cp*Rh complexes, as well as their applications as supramolecular building blocks, have only been marginally treated thus far. During the last three years, the applicability of half-sandwich cyclometalated iridium and rhodium complexes as connectors in supramolecular chemistry has increased exponentially.

Among the several methods for the generation of cyclometalated Cp*M (M = Ir, Rh) complexes, the direct chelation-assisted activation of C–H bonds is the most simple and direct method. An efficient sodium-acetate-promoted C–H activation was developed by the Davies group using $[Cp^*MCl_2]_2$ (M = Ir, Rh).[15] In the presence of sodium acetate acting as both catalyst and base, the C–H bonds were cleaved for certain substrates at room temperature and the expected cyclometalated complexes were formed almost stoichiometrically. The effective C–H bond activation is a heteroatom-assisted process. Thus, three sections of this review are divided between the classical donors in this process, such as N and C (from carbenes) and P (Sections 2 to 4). Section 5 describes in detail examples of the formation of metalamacrocycles and cages employing cyclometalated approaches. Complexes of the form [Cp*M(C^O)], in which oxygen serves as the donor atom, will be discussed in this section. Selected examples of catalytic processes *via* cyclometalated complexes are summarised in Section 6.

2. Cyclometalated [Cp*M(C^N)] complexes

In 1998, an initial study of cyclometalation reactions with iridium in the presence of sodium acetate was reported by Beck and co-workers. The reaction of $[Cp^*IrCl_2]_2$ with substituted 2-phenyl-4-*R*-5(4*H*)-oxazolones gave the cyclometalated complexes **1a–c**.[16] The substituted oxazoline ligands 4,4′-dimethyl-2-oxazolinylbenzene[15] and 4(*S*)-isopropyl-2-oxazolinylbenzene[17] are easily cyclometalated by $[Cp^*IrCl_2]_2$ in the presence sodium acetate (Scheme 1). In complexes **2** and **3**, the existence of two diastereomers was proven by NMR spectra.

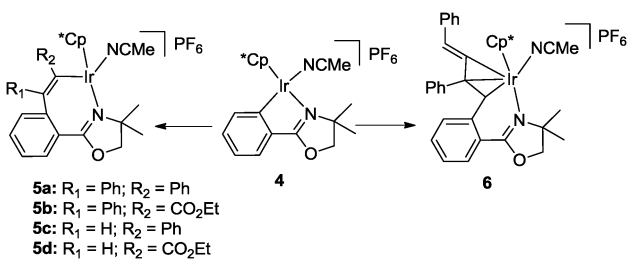


Scheme 1

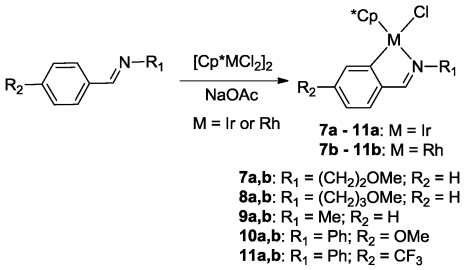
In complexes **2** and **3**, two sets of signals corresponding to the Cp* rings were observed in different ratios.

Davies and co-workers reported their results on the reactivity of acetonitrile-coordinated cationic complex **4**, which was synthesized from the half-sandwich cyclometalated phenyl oxazoline complex **2**, with different alkynes (Scheme 2).[18] They found that both internal and terminal alkynes can insert into the Ir–C bond of complex **4**. The reactions of internal alkynes such as PhC≡CPh and PhC≡CCO_2Et gave only the monoinsertion products **5a** and **5b**, respectively. When PhC≡CCO_2Et was used, a regioselective insertion occurred. In complex **5b**, the ester group was found on the carbon atom adjacent to the metal, with the phenyl group attached to the carbon atom adjacent to the phenyl oxazoline. Reactions of terminal alkynes such as PhC≡CH or HC≡CCO_2Et with **4** in a 1 : 1 ratio in CH_2Cl_2 led to the monoinsertion complexes **5c** and **5d**, in 86% and 82% yields, respectively. Given that the regioselectivity for HC≡CCO_2Et was the same as that for PhC≡CCO_2Et, the authors suggested that electronic factors are important in the insertion reaction process. When complex **4** was treated with two equivalents of PhC≡CH in CH_2Cl_2 solution, the insertion of two molecules of alkyne into the Ir–C bond took place to afford the di-insertion product **6** in an 89% yield. The structure of complex **6** was determined by single-crystal X-ray diffraction.

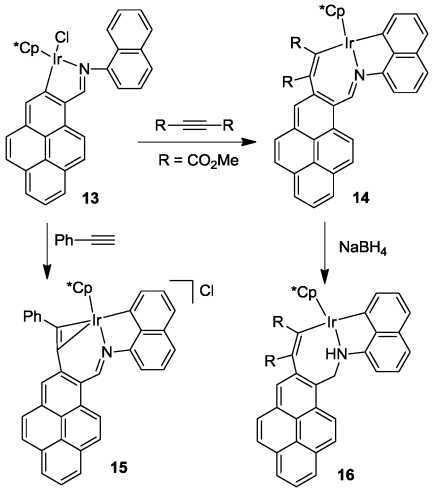
The acetate-promoted cyclometalation of $[Cp^*MCl_2]_2$ (M = Ir, Rh) with aldimine ligands was first studied by Davies and co-workers in 2003,[15] and then by Jones and others (Scheme 3).[19–21] A series of *para*-substituted phenylimines has been



Scheme 2



Scheme 3



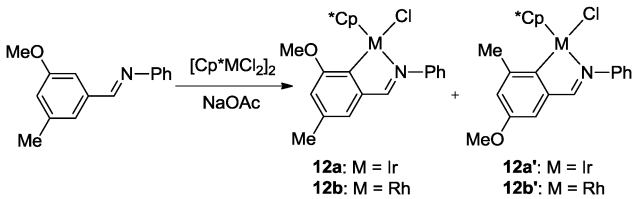
Scheme 5

investigated by Jones and co-workers in order to probe how electronic factors affect C–H activation.[20] Using a series of *para*-substituted phenylimines as substrates, complexes **7–11** were synthesised in good yields. They found that the reaction with a substrate bearing an electron-donating substituent (such as *p*-OMe) is faster than the reaction with a substrate bearing an electron-withdrawing substrate (such as *p*-CF_3) under otherwise identical conditions. It was also observed that, for the same substituent, the reaction with $[Cp^*IrCl_2]_2$ is faster than the reaction with $[Cp^*RhCl_2]_2$. In addition, the regioselectivity of the C–H activation was extremely sensitive to steric effects. In contrast to *meta*-R (R = Me, CF_3 or COOMe) groups that lead to only one regioisomer, two regioisomers were obtained when different *meta*-R-substituted (R = OMe, F or CN) phenylimines were applied. For example, the highly regioselective C–H bond activation of 3-methoxy-5-methylbenzylidene-benzenamine was found to preferentially generate the regioisomers **12a,b** (Scheme 4).[20]

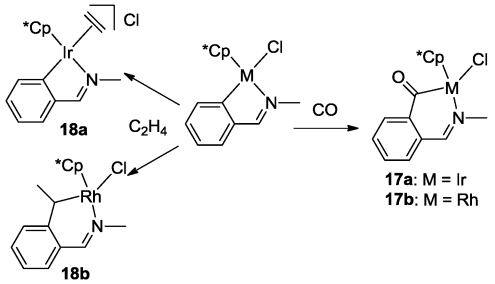
The insertion of alkynes into the Ir–C bond of complex **13**, inducing the regiospecific *peri*-$C8'_{naphthyl}$–H bond activation under very mild conditions, was reported by Jin and co-workers.[22] As shown in Scheme 5, the *ortho*-$(C2_{pyrene})$ C–H activation was first promoted by sodium acetate with $[Cp^*IrCl_2]_2$ in CH_2Cl_2 at room temperature to form the cyclometalated complex **13**. The cycloiridation reaction took place at the 2-position of the pyrene group with the formation of a five-membered metalacycle. Reactions of dimethylacetylenedicarboxylate (DMAD) and PhC≡CH with complex **13** at 40 °C in CH_2Cl_2 gave the air- and thermally-stable complexes **14** and **15** in good yields, respectively. The molecular structure of complex **14** showed a distorted seven-membered metalacycle, and a newly formed five-membered iridacycle through *peri*-$(C8'_{naphthyl})$ C–H activation. Unlike that of complex **14**, in complex **15**, the metal center is coordinated with the inserted alkyne through a π-bonding mode. It is interesting that the newly formed Ir–$C8'_{naphthyl}$ bond is stable and free from further insertion even in the presence of an excess of alkyne. Complex **16** can be obtained in high yields from the reduction of the C=N group of complex **13** with an excess of sodium borohydride. All of the cyclometalated complexes **13–16** were characterised by single crystal X-ray diffraction.

A detailed study of the reactivity of five-membered iridium and rhodium cyclometalated complexes with a variety of unsaturated molecules was reported by Jones and co-workers.[23] The reactions with carbon monoxide showed the clean M–C bond insertion product **17**, while ethylene and acetylene formed different products depending on the metal centre. Instead of a single coordination product, **18a** was obtained from the reaction of ethylene with the iridium cyclometalated complex and the inserted product **18b** was isolated from the reaction of the rhodium cyclometalated complex (Scheme 6).

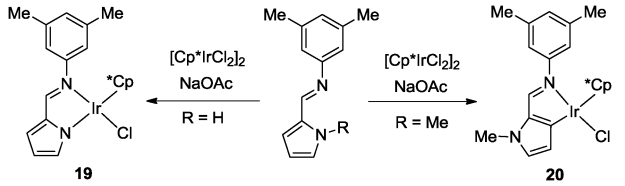
Davies and co-workers reported the cyclometalation of pyrrole imines with $[Cp^*IrCl_2]_2$/NaOAc (Scheme 7).[24] The competition between N–H activation and C–H activation of the pyrrole imine was observed. The reaction of the pyrrole imine with $[Cp^*IrCl_2]_2$/NaOAc gave the *N*,*N* chelating product **19**, suggesting that N–H activation is preferred to C–H activation at the pyrrole in this process. However, the reaction of the *N*-



Scheme 4



Scheme 6

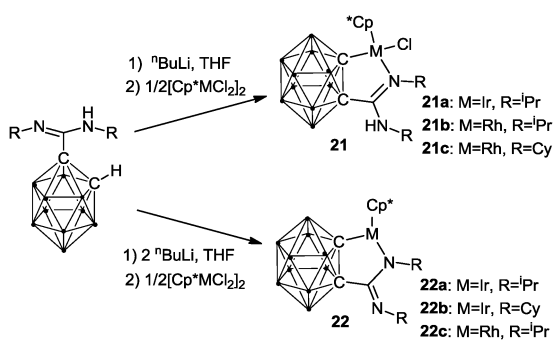


Scheme 7

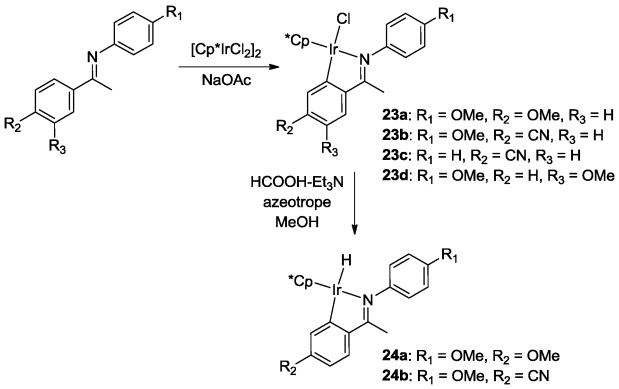
methylated ligand gave the C–H activated product **20** in good yield.

Jin and co-workers reported the synthesis of a series of 18- and 16-electron carboranylamidinate-based five-membered cyclometalated iridium and rhodium complexes.[25] As illustrated in Scheme 8, the 18-electron half-sandwich iridium complexes **21a–c** were prepared in a one-pot reaction by the *in situ* formation of a *C*-lithio-carboranylamidinate ligand, followed by the addition of $[Cp^*MCl_2]_2$ (M = Ir, Rh) in THF at room temperature. In these processes, carboranylamidinate produced an unexpected *C,N*-coordination mode, rather than the ordinary *N,N*-mode. However, unsaturated 16-electron complexes **22a–c** were formed when excess *n*-BuLi was used. The formed five-membered ring showed a resemblance of the structures to the related 16-electron "*pseudo-aromatic*" complexes $Cp^*MS_2[C_2B_{10}H_{10}]$ (M = Co, Rh, Ir). The carboranylamidinate iridium complex **21a** showed good catalytic activity for the polymerisation of norbornene.

The cyclometalation of ketimine ligands with $[Cp^*IrCl_2]_2$ has been documented by Xiao and co-workers.[26–28] They found that ketimines reacted equally as well as aldimines. The reaction of one equivalent of $[Cp^*IrCl_2]_2$ with 2.2 equivalents of ketimine in the presence of NaOAc in dichloromethane afforded cyclometalated Cp*Ir complexes in good yields. It is interesting that the reaction still proceeds well in MeOH without any base additive.[27] The cyclometalated iridium complexes **23a** and **23b** have been identified as excellent catalysts, allowing the efficient reductive amination of a wide variety of carbonyl compounds with a diverse range of amines and formate. The iridium hydride complexes **24**, key intermediates in hydrogenation, could be isolated by treatment of **23a** and **23b** with four equivalents of a HCOOH–Et_3N azeotrope in MeOH.[27] Complexes **23a–c** can be "switched on" to function as excellent



Scheme 8



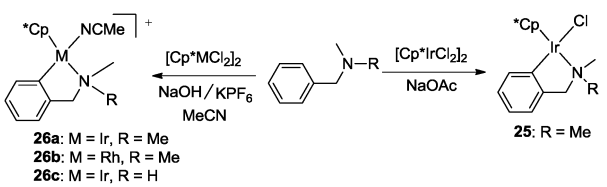
Scheme 9

catalysts for transfer hydrogenation of carbonyl compounds in water, with no need for organic solvents.[28] Recently, the same group developed catalyst **23d** for the oxidant-free, acceptorless catalytic dehydrogenation of various benzofused N-heterocycles (Scheme 9).[29]

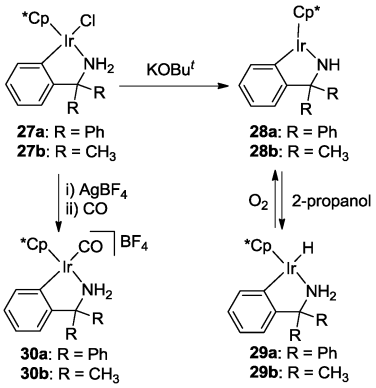
A series of cyclometalated imino-N-heterocyclic carbene (NHC)-based iridium complexes, prepared *in situ* by transmetalation from the corresponding silver complexes of acyclic imino-functionalised imidazolium chlorides, was reported by Hou and co-workers (Scheme 10).[30]

The reaction of imines with $[Cp^*MCl_2]_2$ (M = Ir, Rh) in the presence of a base under the same conditions used for the amines also generates cyclometalated complexes containing M–C bonds. *N,N*-Dimethylbenzylamine underwent cyclometalation to form complex **25** with $[Cp^*IrCl_2]_2$ when treated with NaOAc in dichloromethane at room temperature, however, the reaction of $[Cp^*RhCl_2]_2$ in the presence of NaOAc led to a mixture.[18] Barloy, Pfeffer and co-workers showed that the metalation of *N,N*-dimethylbenzylamine and $[Cp^*MCl_2]_2$ (M = Ir, Rh) with NaOH/KPF_6, resulted in the cationic complexes **26**.[31] Similar activation chemistry using a secondary amine led to the corresponding iridacycle **26c**.[32,33] However, the reaction of chiral (2*R*,5*R*)-2,5-diphenylpyrrolidine resulted in a mixture.[34]

Several examples of the cyclometalation of primary amine ligands have been published.[31,35–38] This process was described by Ikariya and co-workers, wherein the chloride complexes **27** bearing C–N chelate primary ligands could be prepared from the reaction of $[Cp^*IrCl_2]_2$ and primary benzylamines. Notably, the cyclometalation step was also markedly accelerated in the presence of sodium acetate. Complexes **27** were shown to be



Scheme 10

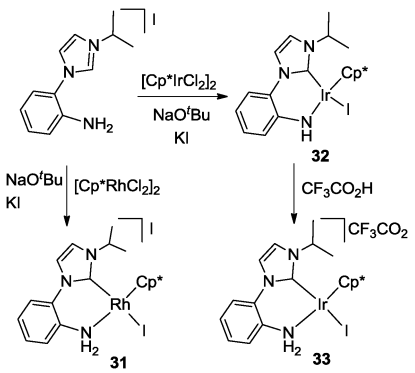


Scheme 11

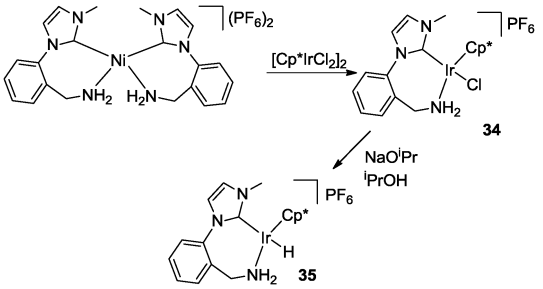
susceptible to the formation of the 16-electron Cp*Ir amido complexes **28** with a loss of H_2. As summarised in Scheme 11, complexes **28** were found to react readily with 2-propanol, leading to the 18-electron hydrido(amine) complexes **29**. The reaction of complexes **28** with acetic acid, dimethyl malonate and acetone also gave the corresponding acetato(amine) and alkyl(amine) complexes, respectively. The cationic carbonyl complexes **30** have been prepared from the reaction of **27** with an equimolar amount of $AgBF_4$ in CH_3CN, followed by exposure to CO at atmospheric pressure in CH_2Cl_2.[35,36] The reactions of **28** and **29** are reversible. The amido complexes **28** can be accessed from the amine-hydrido complexes **29** in the presence of oxygen.[37] The coordinatively unsaturated amidoiridium complexes **28** were found to serve as racemisation catalysts for secondary alcohols under mild and base-free conditions.[38]

Cross and co-workers reported the reactions of $[Cp^*MCl_2]_2$ (M = Ir, Rh) with a primary-amine-functionalised imidazolium salt, which resulted in different products under the same conditions.[39] Whereas the reaction of imidazolium salt with $[Cp^*RhCl_2]_2$ and NaO^{t}Bu/KI gave the amine-N-heterocyclic carbene (NHC) salt **31**, the analogous reaction with $[Cp^*IrCl_2]_2$ gave the amido-NHC complex **32** (Scheme 12). Treating **32** with trifluoroacetic acid gave the amine-NHC complex **33** in nearly quantitative conversion.

Using the transmetalation method, complex **34** containing an NHC ligand with a tethered primary amine donor was



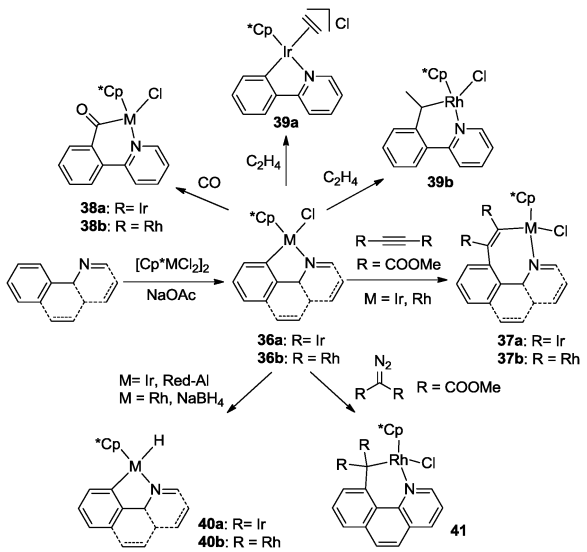
Scheme 12



Scheme 13

synthesised by Morris and co-workers.[40] The air-stable complex **34** was prepared by a transmetalation reaction of bis[1-(2-aminomethylphenyl)-3-methylimidazol-2-ylidene] nickel(II) hexafluorophosphate and $[Cp^*IrCl_2]_2$ in refluxing acetonitrile. The hydride-amine complex **35** was prepared from a warm 2-propanol solution of **34** containing three equiv. of sodium isopropoxide (Scheme 13). Complex **34** can catalyse the hydrogenation of acetophenone and benzophenone in the presence of an alkoxide base. It is of note that an N–H group is required by the chloride complex **34** for catalysis.

N-heterocycles such as pyridine are frequently utilised in *half*-sandwich metal chemistry. Such N-heterocycles are capable of cyclometalative C–H bond reactions involving iridium and rhodium. By analogy to Davies's work, the expected cyclometalated [Cp*M(C^N)Cl] complexes **36** were also easily obtained through cyclometalation with phenylpyridine and its analogue benzo[*h*]quinoline (Scheme 14). An efficient low-temperature method for polycyclic isoquinoline salt synthesis *via* C–H activation with $[Cp^*MCl_2]_2$ (M = Ir, Rh) was developed by Jones and co-workers in 2008.[19] For the same substituent, the regioselectivity for the reactions with 2-phenylpyridines is not as good as with *meta*-substituted phenyl-imines under similar reaction



Scheme 14

conditions. The authors attribute this to the slightly reduced bulk of the pyridyl group compared to the phenyl imines.[20]

The unsaturated DMAD molecule was found to insert into the metal–carbon bonds of **36** *via* a clean monoinsertion, leading to **37**. In addition, the rhodium-based insertion compounds were oxidatively cleaved from the metal using anhydrous $CuCl_2$ at room temperature to obtain the expected isoquinoline salt in high yields.[19] As observed in related imine complexes,[23] the reactions of **36** with carbon monoxide showed clean M–C bond insertion products in both cases, resulting in complexes **38**. Only coordination product **39a** was obtained for the reaction of ethylene with iridium complex **36a**, while the inserted and rearranged product **39b** was isolated from the reaction with the rhodium complex **36b**. In contrast to the single insertion of acetylene, the insertion of two equivalents of phenyl-acetylene was observed. Results with a series of internal unsymmetrical alkynes revealed that the regioselectivity was controlled by both steric and electronic factors, favouring products with an electron-withdrawing group on the carbon adjacent to the metal.[23]

Alternatively, the insertion of a nitrene group into the metal–carbon bond can be achieved through the reaction of cationic complex $[Cp^*Ir(2\text{-phenylpyridine})(MeCN)]^+$ with PhINTs (Ts = tosyl).[41] Treating Cp*M(2-phenylpyridine)Cl and Cp*M-(benzo[*h*]quinoline)Cl (M = Ir, Rh) with the appropriate group 13 hydrides, the corresponding hydride complexes **40** were formed.[42]

Yu and co-workers developed a mild Rh(III)-catalysed carbenoid *ortho* C–H cross-coupling reaction with diazomalonates. They found that the σ-alkyl–Rh(III) complex **41** can be separated from the reaction of the cyclometalated Rh(III) complex with diazomalonate in a 69% yield. Its structure was determined by X-ray crystallography.[43]

Owing to their rigid structures, phenylpyridine and its derivatives are frequently utilised in detailed mechanistic investigations.[44,45] This will be discussed in Section 6. Accordingly, it has been well documented that such ligands can enable the isolation of intermediates in Rh(III)-catalysed imine arylation and styrene oxidative coupling reactions.

As illustrated in Scheme 15, acetate-promoted 2-acetylpyridine sp^3 C–H activation with rhodium occurred cleanly to form C,N chelate complex **42b**, while the similar reaction with iridium gave inseparable mixtures. Notably, in the absence of acetate, the reaction of 2-acetylpyridine with $[Cp^*IrCl_2]_2$ in the presence of KPF_6 generated an equilibrium mixture of the starting material and a N,O chelate complex **43**, however, no reaction of $[Cp^*RhCl_2]_2$ was observed. The cyclometalated products **42a** and **42b** can be prepared from the lithium enolates of 2-acetylpyridine.[46]

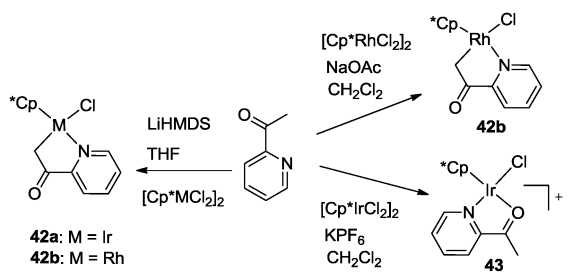
The first example of *N*-functionalised *o*-carboranyl cyclometalated *half*-sandwich iridium complex **44**, which exhibited activity toward the polymerisation of ethylene, was reported by Jin and co-workers.[47] The *C*,*N*-chelated metal complex **44** was prepared by the reaction of $[Cp^*IrCl_2]_2$ with two equivalents of a 1-(2′-picolyl)-*ortho*-carborane lithium salt (Scheme 16). Preliminary experiments indicated that complex **44** can be activated by treatment with MAO to polymerise ethylene. Notably, the spherical morphology of polyethylene obtained from the reaction catalysed by the homogeneous catalyst **44** is different from the sponge-like morphology obtained when other homogeneous catalysts are used.

The six-membered cyclometalated iridium complexes **45** and **46** could be formed in high yields through the reactions of $[Cp^*IrCl_2]_2$ with 2-benzylpyridine and 2-benzoylpyridine, respectively (Scheme 17).[17]

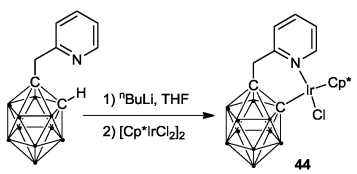
The chelating NHC pyrimidine iridium complexes **47a** and **47b** were prepared *via in situ* transmetalation from the silver carbene complexes of the imidazolium salts (Scheme 18).[48] Treatment with Ag_2O under light-free conditions in CH_2Cl_2 at room temperature formed the presumed silver carbenes, which subsequently reacted with $[Cp^*IrCl_2]_2$ and KPF_6 to yield the yellow-orange solids **47a** and **47b** in good yields.

In order to control the chirality around a metal center in chiral-at-metal complexes, Nishioka and co-workers reported an example of a diastereoselective synthesis induced by the anomeric isomerism of sugar units into the ligands of metal complexes.[49] By using chelate-type NHC ligands with α- and β-glucopyranosyl units, *S* and *R* configurations of chiral-at-metal half-sandwich Cp*M (M = Ir, Rh) complexes **48** can be diastereoselectively obtained. In these complexes, the configuration of the metal center was affected by the conformation of the glucopyranosyl group (Scheme 19).

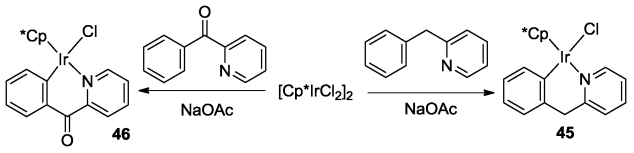
The reactivity of a set of prototypical (η^6-arene)tricarbonylchromium complexes bearing amino, oxazolyl, and pyridyl ancillary ligands with $[Cp^*MCl_2]_2$ (M = Ir, Rh) has been investigated by Djukic and co-workers (Scheme 20).[50–52] Although the cyclometalation of 2-phenylpyridine chromium complexes with $[Cp^*MCl_2]_2$ (M = Ir, Rh) was efficient, a lack of reactivity of the *N*,*N*-dimethylbenzylamine and 2-phenyl-2-oxazoline chromium complexes was observed. The authors attributed this to the $Cr(CO)_3$ moiety sterically inhibiting the



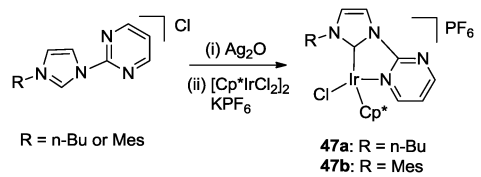
Scheme 15



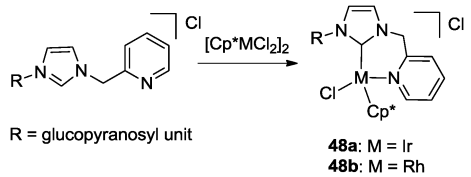
Scheme 16



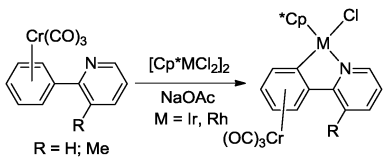
Scheme 17



Scheme 18



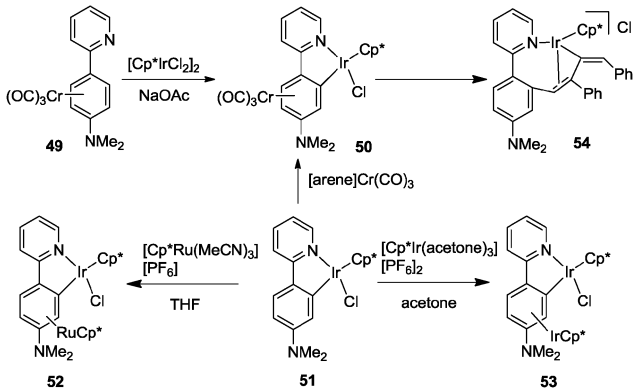
Scheme 19



Scheme 20

coordination of the pendant amino and oxazolyl ligands to the metal centre. The most notable feature of the cyclometalation of 2-phenylpyridine chromium complexes with $[Cp^*MCl_2]_2$ (M = Ir, Rh) is their high stereoselectivity. Only one diastereomer was formed, that in which the Rh- and Ir-bound chloro ligand is located *trans* with respect to the $Cr(CO)_3$.

Djukic and co-workers provided evidence of the capability of cycloiridated 2-phenylpyridines to undergo π-coordination with cationic metal moieties containing one or two positive charges.[53] The $Cr(CO)_3$-containing complex **50** can not only be synthesised by the cycloiridation of ligands **49**, but also by the quantitative ligand-exchange reaction of tricarbonyl(η^6-naphthalene)chromium with complex **51**. Alternatively, the reactions of complex **51** with $[Cp^*Ru(MeCN)_3]PF_6$ and $[Cp^*Ir(acetone)_3][PF_6]_2$ at room temperature for over 24 h led to the unique products **52** and **53**, respectively (Scheme 21). In contrast, 2-phenylpyridine remained unreacted under the same conditions, suggesting that the presence of a donor substituent such as NMe_2 was necessary for the formation of these complexes. Theoretical investigations showed that the electron-donating amino group, which operates by the transfer of electron density from its lone pair to the arene ligand through two channels, can contribute to the stability of the complexes. The reaction of complex **50** with a terminal alkyne in MeOH–H_2O produced complex **54** as a major product through double insertion, and an iridium–acyl byproduct.[54] The $Cr(CO)_3$-bound iridacycle **54** can readily promote the tandem hydro-amination and hydrosilation–protodesilation transformation of terminal alkynes into racemic amines.

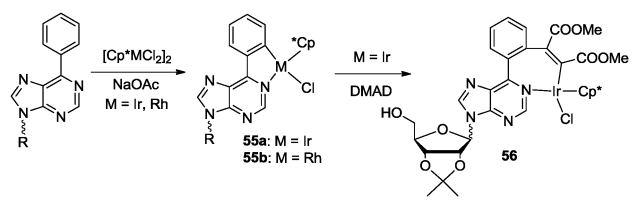


Scheme 21

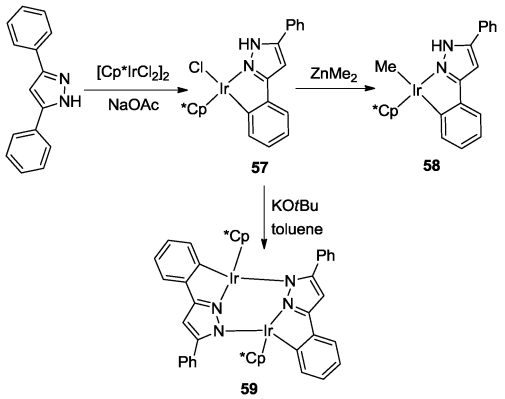
The efficient preparation of purine-derived metal-arylpurine nucleosides, metal-arylpurine nucleotides, and metal-arylpurine dinucleotides, has been reported.[55] As illustrated in Scheme 22, treatment of N9-protected 6-phenylpurine nucleosides with $[Cp^*MCl_2]_2$/NaOAc (M = Ir, Rh) afforded the corresponding cyclometalated derivatives **55**. The cyclometalated complex **56** was obtained in an 81% yield by the insertion of one molecule of DMAD into the Ir–C bond.

Pyrazole ligands have proven popular for use in cyclometalation chemistry. The ligand involves two adjacent nitrogen centres, and allows the reversible deprotonation of the β-NH group. Protic pyrazole complexes bearing an ionisable proton at the β-position to the metal are considered as potentially more accessible β-protic bifunctional catalysts.[56]

The protic pyrazole complex **57** was obtained through the reaction of $[Cp^*IrCl_2]_2$ with 3,5-diphenylpyrazole in the presence of sodium acetate. The reaction of complex **57** with 0.5 equiv. of dimethylzinc resulted in the formation of the pyrazole-methyl complex **58**. Treatment of complex **57** with an equivalent amount of a base in toluene generated the pyrazolato-bridged dimer **59** (Scheme 23). The dehydrochlorinated pyrazolato dimer **59** proved able to promote the



Scheme 22

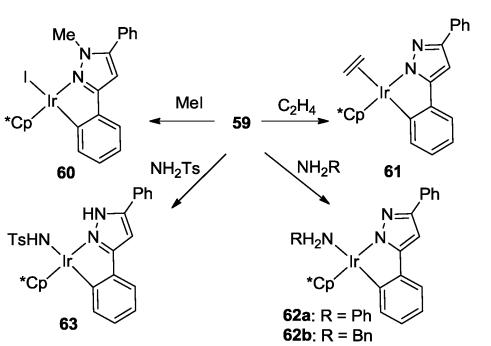


Scheme 23

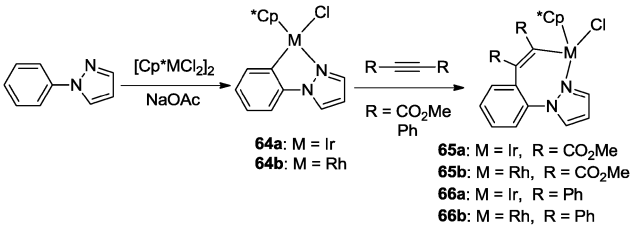
intramolecular hydroamination of the ω-alkenic primary amine to give the cyclisation product.[57] Based on computational studies, kinetic analysis and stoichiometric reactions, a metal–ligand cooperating mechanism was proposed in which cyclisation occurs through *syn* addition of the amino group to the coordinated olefin bond with the aid of the Brønsted-basic pyrazolato ligand.[58,59]

Scheme 24 illustrates the stoichiometric reactions of pyrazole complex **59**.[58] The reaction of complex **59** with iodomethane gave the *N*-methylpyrazole complex **60**. Exposure of a dichloromethane solution of complex **59** to an ethylene atmosphere resulted in the formation of the pyrazolato-ethylene complex **61**. When **59** was treated with aniline and benzylamine, the corresponding amine complexes **62** were obtained. In contrast, treatment of **59** with *p*-toluenesulfonamide led to the formation of the sulfonamidato-pyrazole complex **63**, which indicated a facile proton shift between the amine substrate and the cooperating pyrazolato ligand.

Complexes **64** were prepared by the acetate-assisted cyclometalation of 2-phenylpyrazole with $[Cp^*MCl_2]_2$ (M Ir, Rh).[17] Reactions of **64** with DMAD or PhC≡CPh in MeOH led to the monoinsertion products **65** or **66** in good yields. The structure of the monoinsertion product indicated that the alkyne inserted into the M–C bond rather than the M–N bond to form a seven-membered ring (Scheme 25).[60] These cyclometalated



Scheme 24



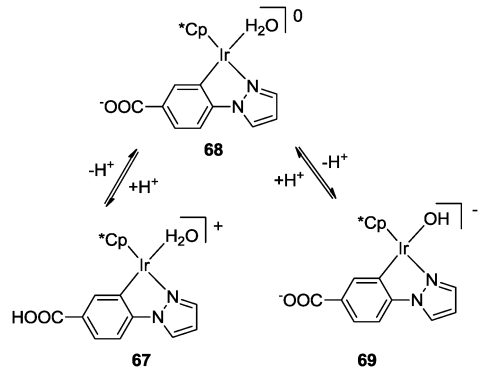
Scheme 25

complexes are proposed to be intermediates in known catalytic reactions.

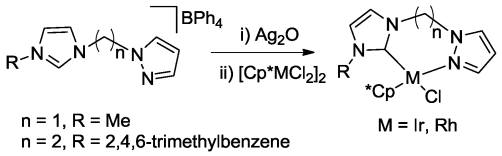
The water-soluble mononuclear [C,N]-cyclometalated *half*-sandwich iridium complex **67** was reported by Fukuzumi and co-workers.[61] The deprotonation equilibrium (pK_{a1} = 4.0 and pK_{a2} = 9.5) demonstrated that complex **67** forms the aqua complex **68** and the hydroxo complex **69** in water, depending on pH (Scheme 26). In the presence of a catalytic amount of complex **67**, the regioselective hydrogenation of the oxidised form β-nicotinamide adenine dinucleotide (NAD^+) was catalytically reduced by H_2 to produce the reduced form 1,4-NADH selectively in a high yield under neutral and slightly basic conditions in the presence of a catalytic amount of the aqua complex **68**.

As illustrated in Scheme 27, the synthesis of iridium and rhodium complexes containing pyrazolyl-N-heterocyclic carbene donor ligands was achieved *via* the transmetalation of the carbene from an *in situ*-generated silver complex.[62] These complexes were shown to yield active hydroamination catalysts upon the *in situ* abstraction of the chloride co-ligand using $AgBF_4$. Compared with diimine-containing complexes, chelating ligand groups containing a strongly coordinating N-heterocyclic carbene donor exhibited better catalytic activities. For the same donor ligand, the Ir(III) complexes are far superior catalysts for the hydroamination of both aliphatic amines and anilines compared to the Rh(III) complexes.

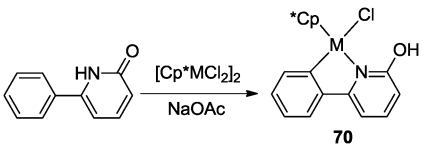
One catalytic system for the dehydrogenative oxidation of alcohols using complex **70** has been reported by Yamaguchi and co-workers.[63] Complex **70** was readily obtained by the acetate-promoted cyclometalation of 6-phenyl-2-pyridone (Scheme 28). This complex exhibited a high activity for the



Scheme 26



Scheme 27



Scheme 28

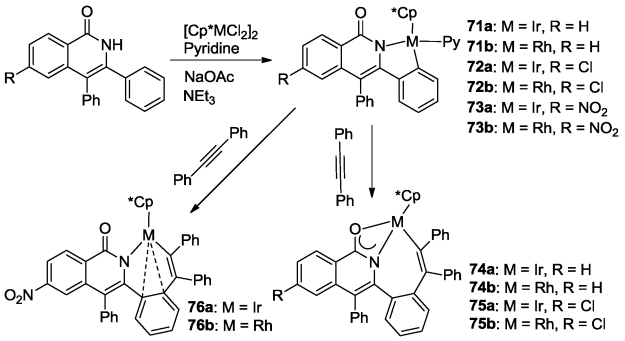
dehydrogenative oxidation of both primary and secondary alcohols. Under this catalytic system, both primary and secondary alcohols were efficiently converted to aldehydes or ketones, respectively, accompanied by the release of hydrogen gas.

Recently, a detailed investigation and comparison of the mechanistic steps in the iridium and rhodium-catalysed oxidative annulation of isoquinolones and alkynes by isolating the relevant intermediate compounds, was published by Wang and co-workers.[64] The cyclometalation of isoquinolone with stoichiometric quantities of $[Cp^*MPyCl_2]$ (Py = pyridine) promoted by NaOAc and Et_3N afforded complexes **71–73**. However, the formation of a cyclometalated complex failed in the absence of pyridine. As expected, the alkyne-inserted complexes **74–76** could be formed in good-to-excellent yields from the reactions between the cyclometalated complexes and PhC≡CPh. Two different molecular structures have been observed in the solid state. In complexes **76**, a phenyl group of the isoquinolone moiety was found to be η^2-coordinated to the metal. In contrast, an M–O bond was observed in complexes **74** and **75**. The final organic products, dibenzo [*a*,*g*]quinolizin-8-one derivatives, were isolated in high yields upon heating complexes **75b** and **76b** with the oxidant $Cu(OAc)_2$ in *o*-xylene. However the iridium complexes **75a** and **76a** were found to be inactive under the same conditions.

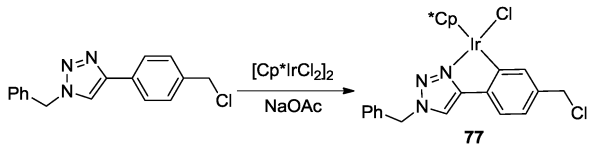
When the substrate 1-benzyl-4-(4-chloro-benzyl)-1*H*-1,2,3-triazole was treated with $[Cp^*IrCl_2]_2$, two possible isomers (five-membered or six-membered ring complexes) may be obtained if different nitrogen atoms act as the directing atom. As shown in Scheme 30, the five-membered ring complex **77** was isolated as a single product. In complex **77**, the N3 atom of the 1,2,3-triazole is a good directing group for acetate-assisted aromatic C–H activation.[17]

Similarly, the reaction of a related heterocyclic imidazole 2-phenylimidazole with $[Cp^*IrCl_2]_2$ in dichloromethane in the presence of NaOAc gave **78** in a moderate yield (Scheme 31).[17]

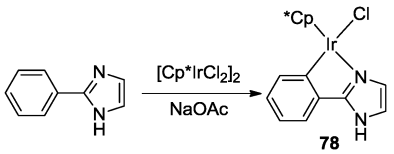
Ikariya and co-workers reported that the cyclometalation of the 16-electron iridium amide complex **79** in the presence of an acidic alcohol afforded complex **80** as a single diastereomer in a high yield through intramolecular C–H bond activation of the aromatic group on the diamine ligand. Complex **80** can also be conveniently obtained by the reaction of complex **81** with PhONa in good yields (Scheme 32).[65]



Scheme 29



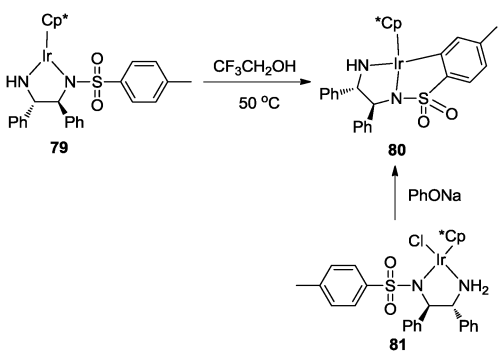
Scheme 30



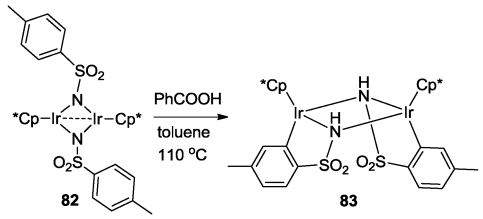
Scheme 31

The sulfonylimido-bridged diiridium complex **82** undergoes intramolecular cyclometalation in the presence of a weak acid, affording the dinuclear cyclometalated iridium complex **83** (Scheme 33).[66]

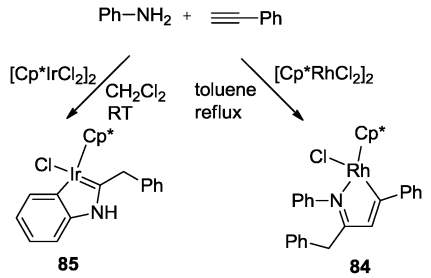
As demonstrated in Scheme 34, the synthesis of N-containing cyclometalated rhodium complex **84** using a one-



Scheme 32



Scheme 33



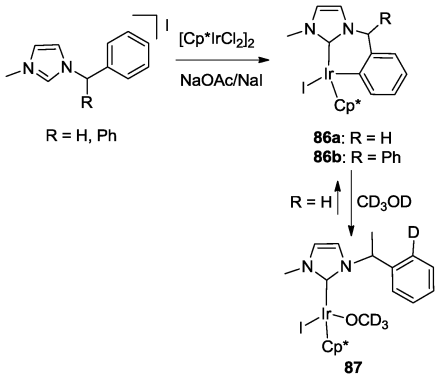
Scheme 34

pot reaction involving $[Cp^*RhCl_2]_2$, an aniline, and a terminal alkyne was realised by Leong and co-workers.[67,68] They found that both electron-donating and electron-withdrawing substituents on the alkyne and the aniline are tolerated. The reaction proceeded smoothly with aliphatic amines in refluxing toluene solution. During this process, an excess of alkyne is required due to alkyne hydroamination and insertion. However, N-containing cyclometalated rhodium complexes could not be obtained when aliphatic alkynes and internal alkynes served as substrates. For the analogous reaction where $[Cp^*RhCl_2]_2$ is replaced by $[Cp^*IrCl_2]_2$, a different type of product, the cyclometalated amino-carbene derivative **85**, was formed. The authors proposed that the reason for the difference between the formation of the iridium and rhodium products lies in the reduced tendency for rhodium to orthometalate *via* a Rh(v) species.

3. Cyclometalated [Cp*M(C^C)] complexes

N-heterocyclic carbene (NHC) ligands are known for binding tightly to metal centres and for their high donor abilities relative to phosphines. Additionally, the relatively strong σ-donor power of the ligand assists in stabilising high-valent metal complexes. Recently, a series of Cp*Ir(NHC) complexes that undergo facile intramolecular aromatic C–H activation to form cyclometalated [Cp*M(C^C)Cl] complexes have been described.

Peris and co-workers observed the iridation of a benzyl-functionalised imidazolium salt with $[Cp^*IrCl_2]_2$ in the presence of NaOAc–NaI, yielding the cyclometalated complex **86a**.[69] Thereby, a dynamic metalation–demetalation equilibrium process was confirmed. The reaction of **86a** in refluxing CD_3OD afforded complex **87** quantitatively through deuteration of the *ortho*-position of the metalated phenyl group. This type of complex using an N-heterocyclic carbene as an anchoring group provides an effective catalyst for the H/D exchange of a wide range of organic molecules in CD_3OD (Scheme 35).

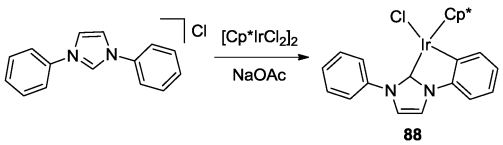


Scheme 35

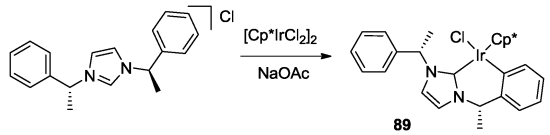
Alternatively, the reaction of 1-diphenylmethyl-3-methylimidazolium iodide with $[Cp^*IrCl_2]_2$ in the presence of NaOAc–NaI afforded complex **86b**. In complex **86b**, a mixture of the two diastereomers in a 5 : 1 molar ratio suggested that the synthetic procedure was diastereoselective.[70]

Crabtree and co-workers showed that treatment of *N*,*N*′-diphenylimidazolium chloride with $[Cp^*IrCl_2]_2$ in the presence of a base led to the generation of complex **88**.[71] As confirmed by single-crystal X-ray diffraction, complex **88** contains a Cp* and a κ^2C^2,$C^{2\prime}$-1,3-diphenylimidazol-2-ylidene ligand. The complex is a C–C chelate, where one C donor is an NHC ligand and the other is a cyclometalated *N*-phenyl wingtip group (Scheme 36). This complex was found to serve as a precursor to a catalyst that can oxidise water to dioxygen.

In a further study, Peris and co-workers described the diastereoselective preparation of a chiral Cp*Ir(NHC) complex with a stereogenic centre at the metal atom by using a chiral imidazolium salt. As shown in Scheme 37, the metalation of (*S*,*S*)-1,3-di(methylbenzyl)imidazolium chloride with $[Cp^*IrCl_2]_2$ afforded complex **89**, with a stereogenic center at the metal due to the *pseudo*-tetrahedral arrangement of the ligand.[72] In complex **89**, coordination of the NHC ligand, together with the orthometalation of the phenyl ring, provides the chelating coordination of the ligand. Its molecular structure revealed that the orthometalation of one of the phenyl substituents of the carbene ligand had occurred, with the formation of a six-



Scheme 36



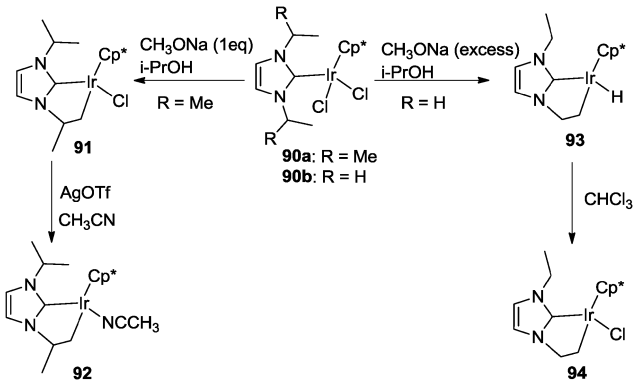
Scheme 37

membered iridacycle in a distorted boat conformation. Complex **89** has been used in the catalytic diboration of olefins, providing high efficiency and chemoselectivity for organodiboronate production.

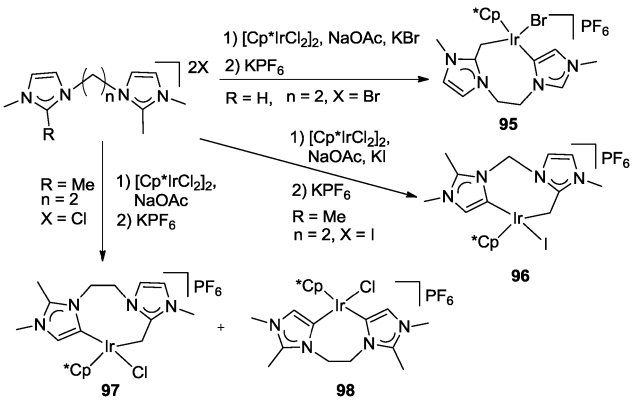
A few reports have demonstrated that highly electron-donating NHC ligands are not always inert; several interesting reactions have been published involving the formation of cyclometalated [Cp*M(C^C)Cl] complexes through the activation of the C–H bond in NHC ligands. For example, Herrmann and co-workers reported the first intramolecular alkyl C–H bond activation reaction of the alkyl complex $Cp^*Ir(ICy)(Me)_2$ (ICy = 1,3-dicyclohexylimidazol-2-ylidene) induced by the addition of trifluoromethanesulfonic acid.[73]

Yamaguchi and co-workers also disclosed the facile aliphatic C–H activation of N-heterocyclic carbenes induced by a base such as MeONa (Scheme 38).[74,75] The reaction of **90a** with MeONa (1 equiv.) gave the cyclometalated carbene complex **91** in a nearly quantitative yield through an intramolecular C–H bond activation reaction. By treatment with AgOTf in the presence of acetonitrile, complex **91** can be converted into the unstable cyclometalated complex **92**.[74] The reaction of **90b** with an excess of MeONa also gave the similar cyclometalated complex **93** in a 94% yield. Complex **93** was readily converted into the chloride complex **94** upon dissolution in chloroform.[75]

In cases where both aliphatic and aromatic C–H activations are possible, as summarised in Scheme 39, electronic and steric factors govern the selectivity of the reaction.[76] The reaction of 1,1′-ethylene-2,3,3′-trimethylbis(1*H*-imidazolium) dibromide with $[Cp^*IrCl_2]_2$ in the presence of NaOAc in refluxing acetonitrile allowed the preparation of complex **95**. In complex **95**, the chelating biscarbene ligand is coordinated through both abnormal and normal modes. The metalation of a series of C2-Me-substituted bisimidazolium salts with $[Cp^*IrCl_2]_2$ was also



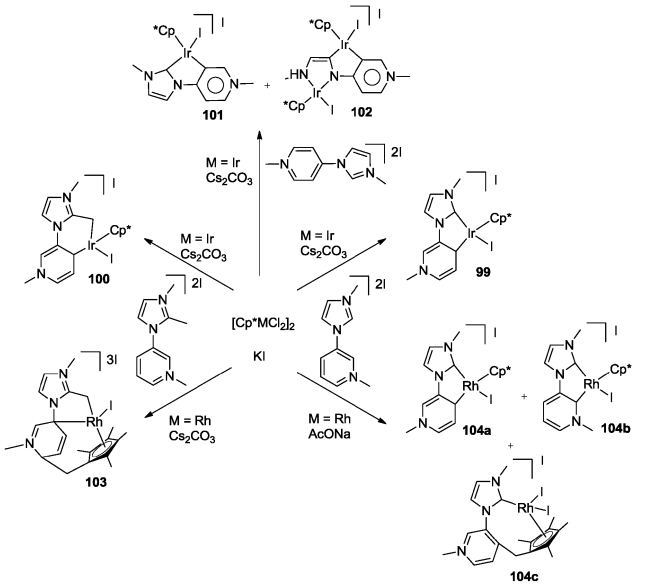
Scheme 38



Scheme 39

described. Small changes in the linker length between the two azolium rings provided great changes in the outcome of the reaction, hence leading to different products. When the methylene-linked bisimidazolium salt was used, only complex **96** was obtained. This complex shows an unusual type of coordination in which the chelating ligand is coordinated through an abnormal NHC and a methylene group resulting from the C–H activation of the C2-Me group. The reaction with an ethylene-linked bisimidazolium salt provided three different complexes: the chelating C2-Me-activated complex **97**, the chelating-bis-abnormal-NHC product **98**, and a neutral species with a 1,2-dimethylimidazole ligand. The experimental observations with DFT calculations suggested an irreversible C–H activation had taken place *via* weak base assistance. Although the calculations could not discriminate between direct deprotonation of the ligand by the base and metalation through C–H activation at Ir as the nature of the first metalation, both cases point to a kinetic preference for initial metalation at the aliphatic position and the second metalation process at the aromatic position.

Recently, the reactivity of a series of imidazolylidene pyridylidene ligands in Cp*M (M = Ir, Rh) was disclosed by Peris and co-workers (Scheme 40).[77] Different reaction outcomes were observed depending upon the nature of the metal. For one imidazolium pyridinium salt, the reaction with $[Cp^*IrCl_2]_2$ in refluxing acetonitrile in the presence of Cs_2CO_3 and KI afforded complex **99**, in which the pyridylidene coordinates to the metal through the *para*-carbon atom. Under similar conditions, another salt in which the C2 position of the imidazolium is blocked with one methyl group underwent C–H activation of the Me group at the C2 of the imidazolium ring to form complex **100**. When salt **99c** was used as a substrate, besides the expected complex **101**, a dimetallic species **102** was isolated through hydrolysis of the free carbene. It is interesting that the reaction of salt **99b** with $[Cp^*RhCl_2]_2$ led to the formation of complex **103** through the reductive coupling between the Cp* and the pyridinium rings, and the activation of the Me group at C2. For the reaction of **99a** with $[Cp^*RhCl_2]_2$ in refluxing acetonitrile in the presence of NaOAc and KI, together with two expected isomers in which the pyridylidene is bound to the

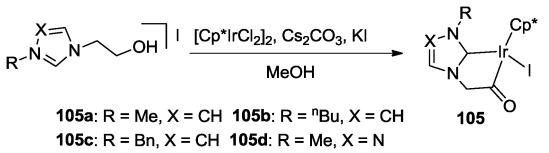


Scheme 40

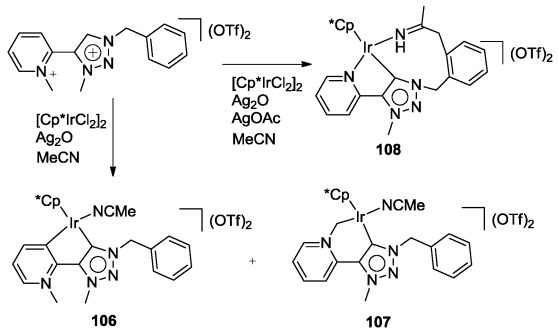
metal through the remote (**104a**, 38%) and normal (**104b**, 16%) coordination modes, a Cp* functionalized with a pendant imidazolylidene **104c** was also observed in a 25% yield.

The high tendency of the *N*-hydroxyethyl group to undergo oxidation and cyclometalation with $[Cp^*IrCl_2]_2$ in the presence of a weak base was also reported by Peris and co-workers.[78] Complexes **105a–c** were obtained by the direct reaction of the corresponding hydroxyethyl-substituted azolium salts with $[Cp^*IrCl_2]_2$ in refluxing methanol in the presence of Cs_2CO_3. Even when the less electron-donating triazolylidene ligand was used, the similar cyclometalated species **105d** could be formed (Scheme 41).

The transmetalation reaction is an interesting and often-used methodology for the generation of cyclometalated complexes. The formation of a series of iridium complexes containing carbene-type ligands through transmetalation was developed by Bernhard, Albrecht and co-workers (Scheme 42).[79] The metalation of a pyridinium-functionalised triazolium salt with $[Cp^*IrCl_2]_2$ in the presence of Ag_2O induced either pyridinium C–H bond activation or exocyclic C–H bond activation, giving the two C, C–bidentate complexes **106** and **107**. As confirmed by their single-crystal X-ray diffraction analyses, complex **106** was comprised of two different abnormally-bound N-heterocyclic ligands, a triazolylidene and a 3-pyridylidene, while complex **107** featured an ylidic bonding mode for the pyridinium ligand precursor, along with the



Scheme 41

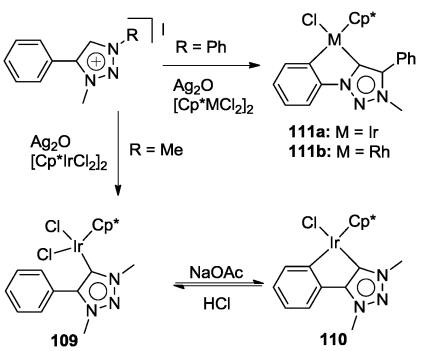


Scheme 42

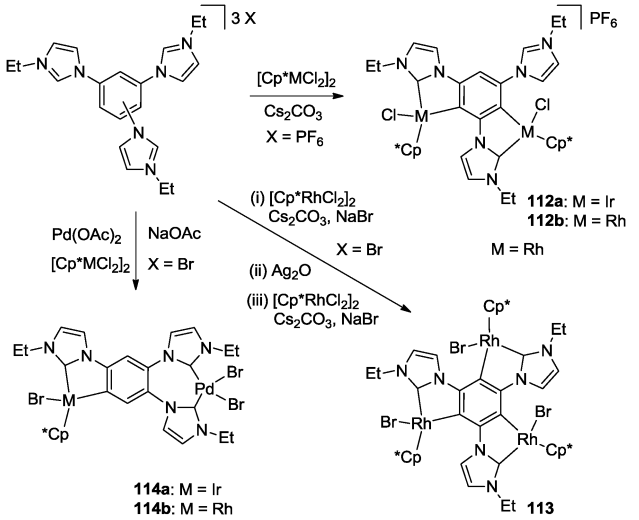
abnormal triazolylidene. However, if acetate was added to the reaction mixture, the pyridinium-functionalised triazolium salt underwent a N_{py}–CH_3 bond activation process affording complex **108** which comprises a tridentate trizaolylidene ligand with chelating pyridine and imine donor groups.[80] Notably, complexes **106** and **107** seemed to have the same monodentate triazolylidene iridium intermediate, as supported by NMR spectroscopy, which may undergo $C(sp^2)$–H or $C(sp^3)$–H bond activation and cyclometalation in different conditions. These cyclometalated iridium complexes were shown to exhibit excellent activity in electrochemically-induced water oxidation.

Complex **109** was obtained in a one pot procedure from a 1,3-dimethyl-4-phenyl-1,2,3-triazolium salt *via* Ag_2O-mediated proton abstraction and *in situ* metalation with $[Cp^*IrCl_2]_2$. Under basic conditions, such as the addition of NaOAc to the solution of complex **109**, the C-bound phenyl group readily cyclometalated yielding complex **110**, while under acidic conditions (HCl), cyclometalation is reversed (Scheme 43).[81] Transmetalation of the 1,4-diphenyl-substituted 1,2,3-trizaolylidene silver complex with $[Cp^*MCl_2]_2$ (M = Ir, Rh), induced spontaneous C–H bond activation of one phenyl substituent and afforded the cyclometalated complexes **111a** and **111b**. In these cases, the selective aromatic C–H bond activation of the *N*-bound phenyl wingtip group of the triazolylidene was established.[82]

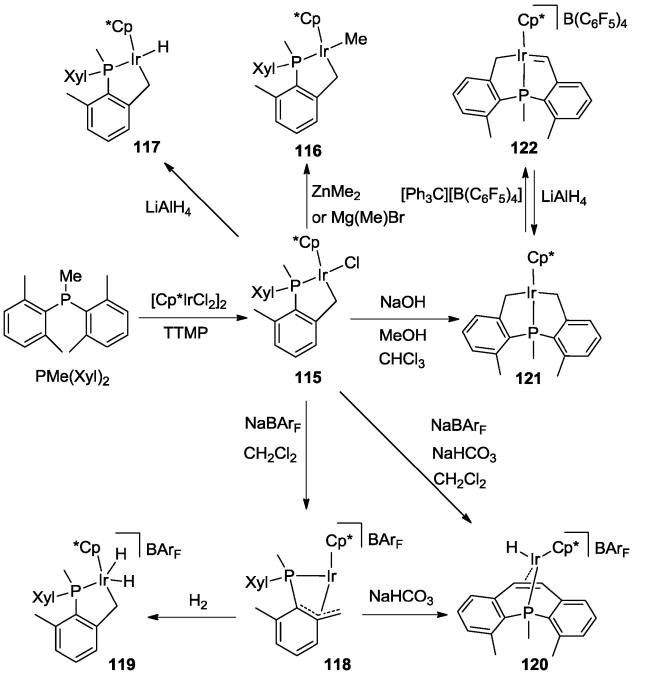
The reaction of a 1,3,5-triimidazolium-substituted benzene trication with $[Cp^*MCl_2]_2$ (M = Ir, Rh) gave the dinuclear complexes **112**, where each metal center is coordinated by an



Scheme 43



Scheme 44



Scheme 45

NHC donor and orthometalates the central phenyl ring. The trinuclear triply-orthometalated complex **113**, featuring three five-membered rhodacycles fused to the central phenylene ring, can be formed *in situ*. A dinuclear complex similar to that mentioned above is thought to be involved. The third imidazolium group could be metalated with $[Cp^*RhCl_2]_2$ with the help of its silver intermediate (Scheme 44).[83] Interestingly, Hahn and co-workers found that the one-pot reaction of a 1,2,4-tris(imidazolium) NHC precursor with $Pd(OAc)_2$ and $[Cp^*MCl_2]_2$ (M = Ir, Rh) with regioselective metalation of the two different coordination sites resulted in the heterobimetallic complexes **114** (Scheme 44). In complexes **114**, the palladium ion is chelated by two NHC donors in *ortho* positions at the central aryl ring of the ligand, while the remaining NHC donor coordinates to the iridium or rhodium with concurrent orthometalation of the central aryl ring.

Leong and co-workers reported a facile synthetic route to orthometalated iridium amino-carbene complexes from the reaction of anilines and terminal alkynes with $[Cp^*IrCl_2]_2$ *via* hydroamination and orthometalation (Scheme 29).[67] Deuterium labeling and computational studies suggest that the reaction pathway is very similar to that followed in the C≡C triple bond cleavage reaction with water and involves a hydroamination step.

4. Cyclometalated [Cp*M(C^P)] complexes

An alternative approach to forming cyclometalated half-sandwich iridium and rhodium complexes is to employ a phosphorus ligand. Phosphorus-containing cyclometalated complexes have often been identified in C–H activation studies with Cp*M (M = Rh, Ir) complexes.[85–87] In 2004, Saunders and co-workers found that the reaction of 2-diphenylphosphinobenzaldehyde and $[Cp^*IrCl_2]_2$ resulted in a neutral acyl complex through C–H activation of the aldehyde. Elimination of HCl occurred readily in this transformation.[88]

Inspired by the pioneering work of Bergman and co-workers on electrophilic Ir(III) complexes such as $[Cp^*Ir(Me)(PMe_3)(ClCH_2Cl)]^+$ and related species,[85] some results based on the cyclometalation of bis(xylyl)phosphine $PMe(Xyl)_2$ by $[Cp^*MCl_2]_2$ (M = Ir, Rh), and the subsequent functionalisation of the resulting complexes, have been performed by Carmona and co-workers.[89–92]

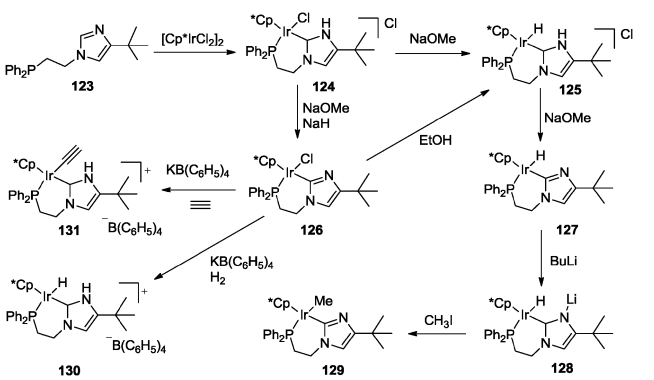
As shown in Scheme 45, in the presence of the weakly coordinating base 2,2,6,6-tetramethylpiperidine (TTMP), reaction of $[Cp^*IrCl_2]_2$ with $PMe(Xyl)_2$ in a CH_2Cl_2–MeOH mixed solution at 40 °C gave the major product **115** in a 90% yield. Treatment with dimethylzinc or methyl Grignard reagents yielded the methyl derivative complex **116**. The iridium hydride **117** was synthesised by reacting **115** with $LiAlH_4$. Similarly, the related halide (or *pseudo*-halide) complexes can be isolated by the metathesis reactions of **115** with LiBr, MgI_2 or NH_4SCN, respectively.[89,90]

When complex **115** was treated with 1 equiv. of $NaBAr_F$ [BAr_F = $B(3,5\text{-}C_6H_3(CF_3)_2)_4$] in CH_2Cl_2 solution, a cationic cyclometalated complex **118** that contains a bis(aryl) phosphine ligand was isolated as its BAr_F salt. Reactions of **118** with Lewis bases such as MeCN, pyridine, NH_3, CO and PMe_3 in a CH_2Cl_2 solution provided its corresponding adducts in nearly quantitative yields. The formation of the cationic bis(hydride) complex **119** was obtained in a quantitative yield by exposure of a dichloromethane solution of **118** to 1 bar of H_2 at 20 °C. However when the reaction of **115** and $NaBAr_F$ was performed in the presence of a base ($NaHCO_3$, piperidinium–piperidine), a mixture of **119** and **120** was generated. Complex **120** could be

isolated in a high yield under optimal conditions. In contrast, a strongly basic catalyst such as NaOH also gave rise to the neutral hydride **117** as a result of fast deprotonation of **119**. As determined by the single-crystal X-ray study of **120**, the new ligand is coordinated to iridium in a bidentate fashion through the phosphorus atom and the C=C bond.[91]

The synthesis of complex **121**, which contains two metalated xylyl groups, was realised by treatment of **115** with excess MeONa in a 1:1 solvent mixture of MeOH and $CHCl_3$. In the structure of **121**, the phosphepine ligand acts as a tridentate ligand and is coordinated to iridium through the phosphorus atom and two metalated carbon atoms, one from each of the original xylyl groups. A hydride abstraction reaction that converts **121** into the metalacyclic alkylidene **122** was also realised. Complex **122** was prepared by the reaction of **121** and $[Ph_3C][B(C_6F_5)_4]$ in CH_2Cl_2 solution at a low temperature (−60 °C). Complex **121** was successfully generated by the reaction of **122** and $LiAlH_4$ at −40 °C. The conversion of **122** to **120** has also been reported by the authors. They found that the hydride phosphepine **120** was formed in essentially a quantitative yield upon warming to room temperature a freshly prepared solution of **122** in CD_2Cl_2 at −60 °C, which experienced migration of the iridium–alkyl onto the iridium–alkylidene, accompanied by β-H elimination. Based on their observations, the authors suggested that cationic Ir(III) alkylidenes are key intermediates in the C–H bond activation and C–C bond-forming reactions. The synthesis and reactivity of a rhodium analogue that efficiently catalyses hydrogen isotope exchange in hydrosilanes has been reported by the same group.[92]

In 2008, the synthesis of a new series of imidazol-2-yl complexes of Cp*Ir and their bifunctional behaviour as ambident reactants was reported by Grotjahn and co-workers (Scheme 46).[93] The reaction of ligand **123** with $[Cp^*IrCl_2]_2$ afforded a mononuclear iridium complex that can be converted to the yellow carbene complex **124** through the tautomerisation of the imidazole. The NH group of **124** could be deprotonated by a base to give **126**. Not only could the carbene hydride **125** be obtained in a stoichiometric reaction of **126** with ethanol in CD_2Cl_2, but it can also be synthesised in a one pot procedure from **124** using NaOMe in ethanol. The reaction of **125** with NaOMe afforded the hydride complex **127**, which when treated further with 1 equiv. of BuLi led to complex **128**. Alkylation of **128** with MeI occurred at the metal centre to give **129**. In the presence of $KB(C_6F_5)_4$, chloride abstraction from **126** was realised easily, which could then react with hydrogen or acetylene, leading to heterolysis of the latter and formation of complexes **130** and **131**, respectively.



Scheme 46

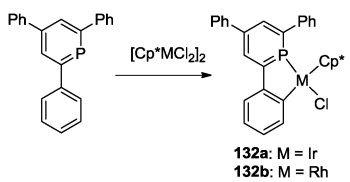
Müller and co-workers demonstrated the synthesis of cyclometalated [Cp*M(P^C)] (M = Ir, Rh) complexes from the C–H activation of 2,4,6-triphenylphosphinine by the half-sandwich Cp*M (M = Ir, Rh) precursors **132** (Scheme 47).[94,95] Complexes **132**, which were characterised by single-crystal X-ray crystallography, are stable under the applied reaction conditions. The authors assumed that the additional phenyl group in the 2-position of the phosphorus heterocycle contributes significantly to a kinetic stabilisation of the metal complex. Compared to its phosphorus counterpart, the analogous reaction of 2,4,6-triphenylpyridine does not show any *ortho*-metalation. These results conclusively demonstrate the difference in reactivity between related phosphorus and pyridine heterocycles.

5. Supramolecular architectures

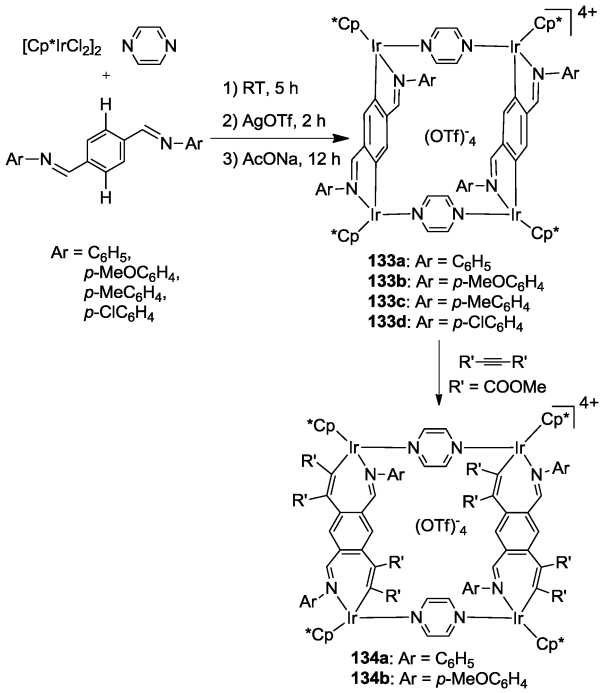
As illustrated above with many examples, intramolecular cyclometalative C–H bond activation is a fairly common phenomenon among half-sandwich iridium and rhodium complexes. However, using this process in a controlled manner to construct molecular macrocycles and cages has not been explored until recently. The incorporation of imine ligands or benzoic acid and bipyridine linking subunits into a macrocycle by cyclometalation-driven self-assembly was accomplished by Jin *et al.*[96–104]

5.1 Supramolecular architectures from the cyclometalation of imine ligands

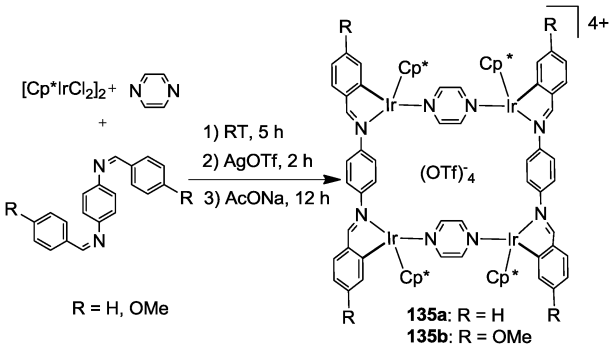
As shown in Scheme 48, the designed organometallic macrocycles **133** could be obtained in good yield from a one-pot procedure in which all of the commercially available starting materials were mixed at room temperature.[96–98] The tremendous separation problems and product loss that occur in stepwise formation were avoided. During these processes, the formation of half-sandwich cyclometalated iridium corners played an important role, in which all imine moieties were cyclometalated by Cp*Ir fragments in the *ortho*-position with respect to the imine groups. All of these molecular rectangles were isolated in good yields as robust, air-stable, microcrystalline solids. The core structure of **133a–c** bearing four Cp*Ir-



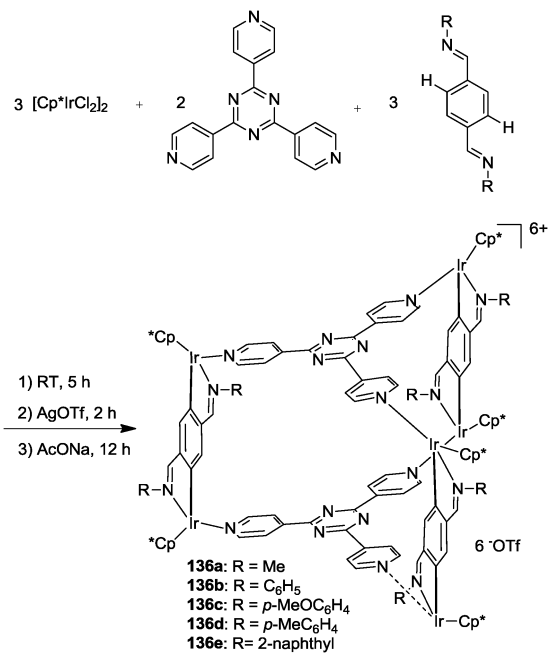
Scheme 47



Scheme 48



Scheme 49



Scheme 50

based five-membered metalacycles and two pyrazine ligands has been established by X-ray crystallographic studies. Alternatively, the macrocycle could be prepared by a ''C–H activation before self-assembly'' stepwise synthetic pathway, by firstly creating the stable bimetallic edges using two-site aromatic C–H activation in double-Schiff-base ligands with $[Cp^*IrCl_2]_2$, and then reaction with pyrazine or bipyridine in the presence of AgOTf. The dimension of these discrete organometallic macrocycles could be expanded through the insertion of unsaturated molecules into the Ir–C bond of the five-membered cyclometalation corners, leading to a new series of complexes, **134**.[96]

A similar approach can be applied for the rational design of the molecular macrocycles **135**. When *N*,*N*′-bisbenzylidenebenzene-1,4-diamine ligands were used instead of terephthal-bis-imine ligands, the molecular macrocycles **135** were obtained. The cation of complex **135** has a rectangular cavity with dimensions of 8.4 and 7.0 Å, with respect to the Ir···Ir separations, as determined by single crystal X-ray diffraction analysis. It is worth noting that the cavity of **135a** exhibits a remarkable ability to encapsulate triflate anions (Scheme 49).[96,98]

A novel approach toward the construction of organometallic trigonal prisms was recently demonstrated by the same group from a three-component reaction of imine and pyridyl donor ligands with a half-sandwich iridium complex. Such a multicomponent reaction, driven by C–H activation-directed self-assembly, as shown in Scheme 50, represents a unique assembly process in which multiple, varying components can selectively recognise and combine to generate one discrete structure. A series of organometallic cages **136** were obtained from the reaction of $[Cp^*IrCl_2]_2$ and 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) with terephthal-bis-aromatic imine ligands in the presence of AgOTf (Scheme 50).[99,100]

The resulting supramolecular assemblies were obtained as a racemate of the *P* and *M* forms. In the solid state structure of complexes **136**, the two central triazine units are very close, and the centroid···centroid distance between the two triazine moieties is only 3.3 Å.[99] The transformation of such a host molecule from the ''closed'' form to the ''open'' form could be realized by the introduction of an aromatic guest, thus this host molecule forms complexes with a wide variety of guest substrates, including $Pt(acac)_2$, pyrene and coronene.[99,100] The transannular separation between the centres of the triazine rings in the host–guest complex is enlarged to approximately 6.66 Å. The preparation of host–guest systems in a one-pot procedure was also accomplished.[100] A 1 : 1 complexation between the guest and host was confirmed by ^1H NMR, elemental analyses and single-crystal X-ray diffraction analyses.

Without other additional ligands, pyrazine can also be utilised as a precursor to construct multinuclear metalamacrocycles through C–H activation and metal–metal bond formation under mild conditions.[101]

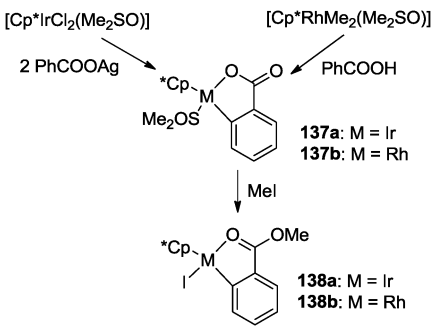
5.2 Supramolecular architectures from the cyclometalation of benzoic acids

Although several catalytic coupling reactions of benzoic acids with alkenes or alkynes *via* iridium- and rhodium-catalysed directed C–H bond cleavage have successfully been developed,[105] the isolation of cyclometalated [Cp*M(C^O)] intermediates is quite rare.

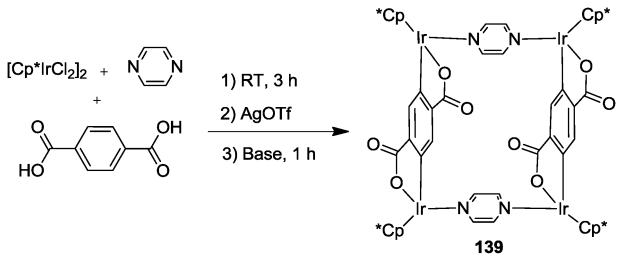
An early example of the cyclometalation of benzoic acid in iridium and rhodium complexes was reported by Maitlis and co-workers (Scheme 51).[106] The reaction of [Cp*RhMe$_2$(Me$_2$SO)] with one equivalent of benzoic acid led to cyclometalation and the formation of complex **137a**, while the similar complex **137b** was obtained by the reaction of [Cp*IrCl$_2$(Me$_2$SO)] with two equivalents of silver benzoate. Complexes **137** reacted with methyl iodide to give complexes **138** where the Me$_2$SO was replaced by iodide and the methyl was added to the benzoate oxygen.

Based on the successful construction of supramolecular architectures by the cyclometalation of imine ligands, a number of neutral rectangle assemblies containing rigid linking subunits, such as pyrazine, 4,4′-bipyridine (bpy), or *trans*-1,2-bis(4-pyridyl)ethylene (bpe), combined with cyclometalated benzoic acids, have also been reported by Jin and co-workers.[102] This methodology has proven to be an effective method for the formation and isolation of cyclometalated [Cp*M(C^O)] complexes from benzoic acids. For example, the molecular rectangle **139** was made by the cyclometalative C–H bond activation of benzoic acid (Scheme 52). The molecular structures of the complexes, consisting of neutral rectangular structures with Ir···Ir edges, were determined by X-ray diffraction studies. In addition, related dicarboxylic acids, such as 2,6-naphthalenedicarboxylic acid, biphenyl-4,4′-dicarboxylic acid and 4,4′-(diazene-1,2-diyl)dibenzoic acid were successfully used to build macrocyclic architectures.

The versatility of this cyclometalation-driven self-assembly strategy allows for the synthesis of organometallic macrocycles that contain reactive functionalities. For example, the formed



Scheme 51



Scheme 52

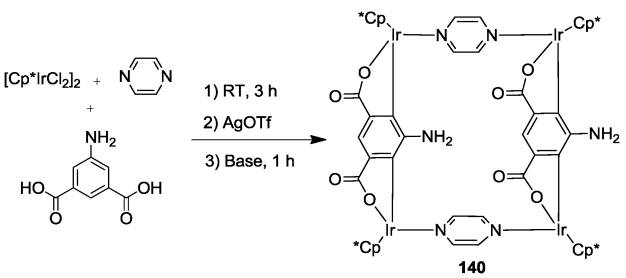
macrocycle **140**, which was obtained by the cyclometalative C–H bond activation of 5-amino-1,3-benzenedicarboxylic acid (Scheme 53), may undergo further transformation at the free amino groups.[103]

Jin and co-workers have also extensively investigated the formation of molecular rectangles through the C–H activation of fumaric acid. Bimetallic edges, obtained from a Cp*Ir salt and pyrazine, 4,4′-bipyridine or *trans*-1,2-bis(4-pyridyl)ethylene (bpe) linkers, were converted to neutral molecular rectangles by combination with fumaric acid. The formed rectangle **141** containing bpe linkers was shown to undergo postsynthetic modification *via* a UV irradiation-initiated [2+2] cycloaddition reaction to yield the cyclobutane-bridged complex **142** (Scheme 54).[104]

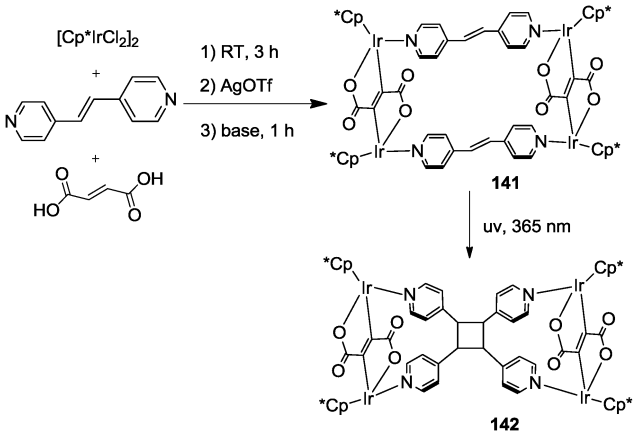
6. Hypothetical intermediates

Since most of the mechanistically-distinct reaction pathways that have been proposed in recent years involve the application of half-sandwich cyclometalated complexes,[12–14] we herein attempt to summarise the key examples of catalytic processes *via* cyclometalated complexes.

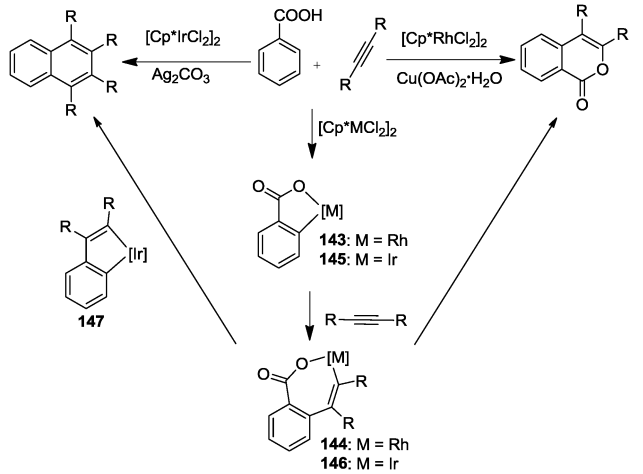
Miura and co-workers reported the direct oxidative coupling of carboxylic acids with alkynes in the presence of a [Cp*RhCl$_2$]$_2$/Cu(OAc)$_2$ catalytic system.[107–112] From the reactions of a series of benzoic and naphthoic acids, as well as heteroarene carboxylic acids and aromatic diacids, with alkynes, the corresponding isocoumarin derivatives were synthesised. A plausible mechanism for this reaction was investigated. As illustrated in Scheme 55, a rhodium benzoate is formed through coordination of the carboxylate oxygen to the metal center, which then gives the five-membered rhodacycle intermediate **143** *via ortho* rhodation, subsequent alkyne



Scheme 53



Scheme 54



Scheme 55

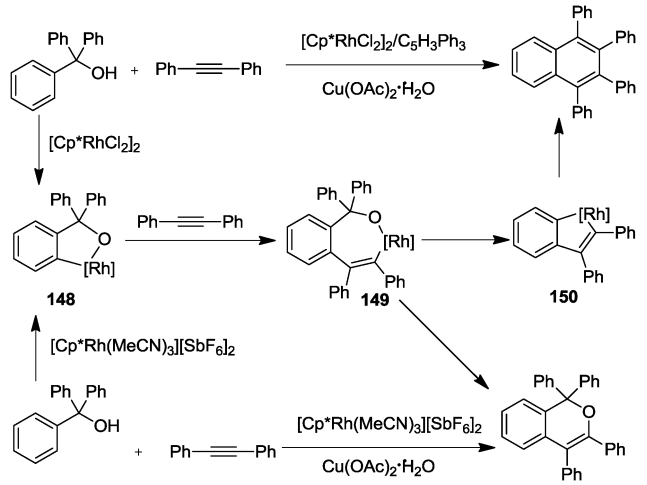
insertion to form the seven-membered rhodacycle **144**, and reductive elimination occurs to produce an isocoumarin. The resulting Cp*Rh(I) species may be oxidised in the presence of the copper cocatalyst to regenerate Cp*Rh(III). In addition, the rhodium-catalysed oxidative coupling of substituted acrylic acids with alkynes proceeds efficiently *via* vinylic C–H bond cleavage to give the corresponding R-pyrone derivatives.[110] On the other hand, by using $[Cp^*IrCl_2]_2/Ag_2CO_3$ in place of $[Cp^*RhCl_2]_2/Cu(OAc)_2$, the same substrates undergo a 1:2 coupling accompanied by decarboxylation to afford naphthalene derivatives, exclusively.[109] In this reaction, a seven-membered iridacycle intermediate **146** appears to be generated from the five-membered iridacycle **145**, followed by the formation of a five-membered iridacycle intermediate **147** through decarboxylation of **146**. Subsequently, the insertion and reductive elimination of the second alkyne occurs to give the naphthalene product. The minor naphthalene product in the rhodium-catalysed system could be explained using this plausible mechanism.

The same group also found that benzoic acid reacted with alkenes such as acrylates smoothly *via* rhodium catalysis to afford 7-vinylphthalides selectively.[107,108] The authors suggested that the rhodacycle intermediate **143** may undergo alkene insertion and successive β-hydride elimination to form the *ortho*-monovinylated benzoic acid, then the second vinylation takes place before the nucleophilic cyclisation to lead to the divinylated product. As a result, disubstitution at both the *ortho* positions occurred to afford 7-vinylphthalides, along with a minor amount of dehydrogenated derivatives. This methodology has also proven to be an effective method to synthesise buthenolide derivatives.[110] It is notable that the cyclisation exclusively occurred after the first vinylation when *N*,*N*-dimethylacrylamide and acrylonitrile were used as substrates.[107]

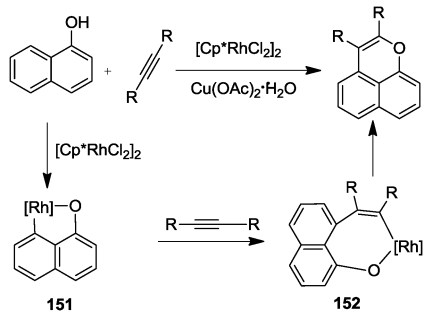
The rhodium-catalysed oxidative coupling of alcohols with internal alkynes has also been investigated by Miura and co-workers.[113–115] With a catalyst system consisting of $[Cp^*RhCl_2]_2/C_5H_3Ph_3/Cu(OAc)_2\cdot H_2O$ ($C_5H_3Ph_3$ = 1,2,4-triphenyl-1,3-cyclopentadiene), the reactions of triarylmethanols and alkynes effectively proceed in a 1:2 manner *via* cleavage of C–H and C–C bonds to produce the corresponding naphthalene derivatives. The authors proposed a catalytic cycle involving the initial formation of rhodacycle intermediate **148**, subsequent alkyne insertion afforded the seven-membered rhodacycle intermediate **149**, as illustrated in Scheme 55, which underwent β-carbon elimination to produce an important five-membered rhodacycle **150** after liberation of Ph_2CO. The corresponding naphthalene was obtained through a second alkyne insertion and reductive elimination.[113,115] However, from the same reaction, an isochromene product can be exclusively produced by using $[Cp^*Rh(MeCN)_3][SbF_6]_2$ and $Cu(OAc)_2\cdot H_2O$ as the catalyst and oxidant, respectively. The initiation of this catalytic cycle is similar to that observed in the former reaction. However, in this case, the reductive elimination of the seven-membered rhodacycle intermediate **150** predominated over the β-carbon elimination pathway. These results illustrate the sensitivity of these types of reactions to the nature of the catalyst (Scheme 56).[114]

Miura and co-workers reported an oxidative coupling of 1-naphthol with internal alkynes to naphtho[1,8-*bc*]pyran derivatives using a $[Cp^*RhCl_2]_2/Cu(OAc)_2\cdot H_2O$ catalyst system. In these annulation reactions, the hydroxy groups effectively act as the key functionality for the regioselective C–H bond cleavage at the *peri* position.[116] The proposed mechanism included directed C–H rhodation to form the rhodacycle intermediate **151** from a rhodium naphtholate, which can transfer to the rhodacycle intermediate **152** by alkyne insertion, followed by reductive elimination to form a naphthopyran (Scheme 57). However, treatment of equimolar amounts of 2-phenylphenol, diphenylacetylene, $Cu(OAc)_2\cdot H_2O$, and KI in the presence of $[Cp^*RhCl_2]_2$ selectively gave 5-(2-hydroxyphenyl)-1,2,3,4-tetraphenylnaphthalene in a good yield. The results indicate the existence of different intermediates.

Glorius and co-workers developed an efficient method for the synthesis of functionalised indenols and fulvenes through

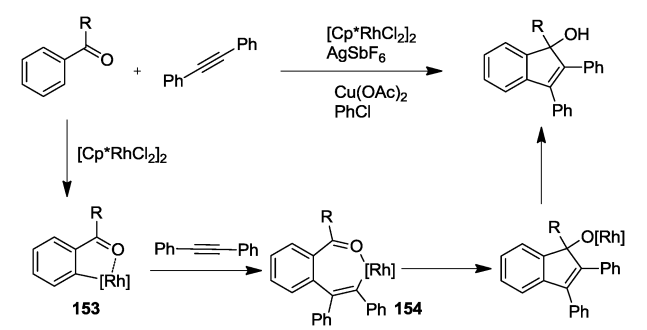


Scheme 56



Scheme 57

the Rh-catalysed C–H bond activation of a representative set of phenone derivatives and subsequent coupling with internal alkynes.[117] The reaction of pivalphenone with 1,2-diphenylethyne under optimised conditions (0.5 mol% $[Cp^*RhCl_2]_2$, 2 mol% $AgSbF_6$ and 2.1 equiv. of $Cu(OAc)_2$, PhCl) afforded an indenol product in a 99% isolated yield. The authors proposed that the first step of the reaction was a cyclometalation (**153**), followed by an alkyne insertion (**154**) and subsequent intramolecular electrophilic attack of the carbonyl moiety (Scheme 58).



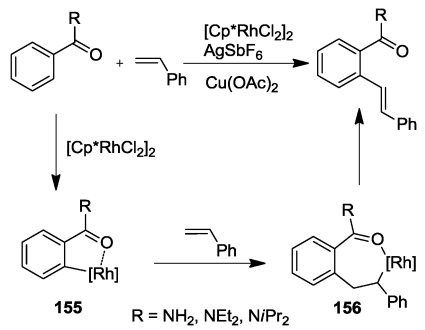
Scheme 58

The rhodium-catalysed annulation between benzimides and alkynes was developed by Shi and co-workers for the synthesis of indenones.[118] This work showed that the directing ability and electrophilicity of the imide group can provide a handle for the annulation with concomitant C–H and C–N cleavage. A preliminary mechanism including similar five- and seven-membered rhodacycles (**153**, **154**) was proposed. The formed seven-membered intermediate may undergo an intramolecular insertion of the carbonyl group into the vinyl–Rh bond, the formation of products and regeneration of the catalyst could then be realised by transmetalation between copper acetate and the rhodium alkoxide.

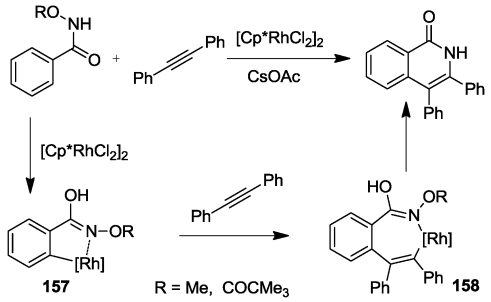
Unlike the synthesis of indenols from aryl ketones and alkynes *via* ketone-assisted C–H activation, in the case of rhodium-catalysed cascade oxidative annulation reactions of benzoylacetonitriles with alkynes, Wang and co-workers proposed a path of acetophenones with alkynes *via* C–H activation and subsequent annulation to afford six-membered carbocyclic products.[119] In this process, a five-membered rhodacycle intermediate may be formed in the first step through sequential cleavage of the $C(sp^3)$–H/$C(sp^2)$–H bond, annulation with an alkyne then leads to 1-naphthols as the intermediate product. Similar to Muria's work,[116] 1-naphthols react with alkynes by cleavage of $C(sp^2)$–H/O–H bonds, affording the 1 : 2 coupled naphtho[1,8-*bc*]pyran products.

The use of a series of acetophenones and benzamides as substrates for the selective rhodium-catalysed oxidative *ortho*-olefination reaction has been reported by Glouris and co-workers (Scheme 59).[120] They proposed that the oxidative cyclisation reaction proceeded through electrophilic activation of the olefin including C–H activation directed cyclometalation (**155**), olefin insertion and subsequent β-hydride elimination (**156**). Recently, a rhodium(III)-catalysed direct C–H allylation reaction using allyl carbonates as the allyl electrophile in a similar hypothesised reaction mechanism was reported by the same group.[121] In the case of the rhodium-catalysed dehydrogenative Heck reaction of salicylaldehyde with olefin, the formation of a five-membered rhodacycle is perhaps the key step in the production of 2-hydroxychalcone.

Guimond, Fagnou and co-workers developed an efficient approach to C–N bond formation from benzhydroxamic acid precursors.[122,123] It is worth noting that this redox-neutral



Scheme 59



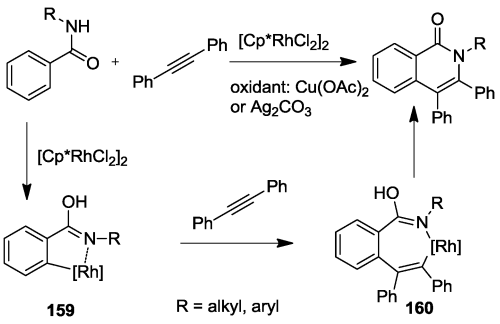
Scheme 60

isoquinolone synthesis does not require an external oxidant. The postulated mechanism is presented in Scheme 60, the five-membered intermediate **157** was formed through arene rhodation, and then alkyne insertion into the Rh–C bond provided the seven-membered complex **158**. The desired isoquinolone was obtained by stepwise C–N bond reductive elimination/N–O bond oxidative addition. The DFT calculations conducted support the proposed mechanism. Additionally, the importance of substrate deprotonation throughout the catalytic cycle was revealed by DFT calculations. A more reactive internal oxidant/directing group (N–$COCMe_3$) can promote the formation of a wide variety of isoquinolones under mild conditions even using lower catalyst loadings.

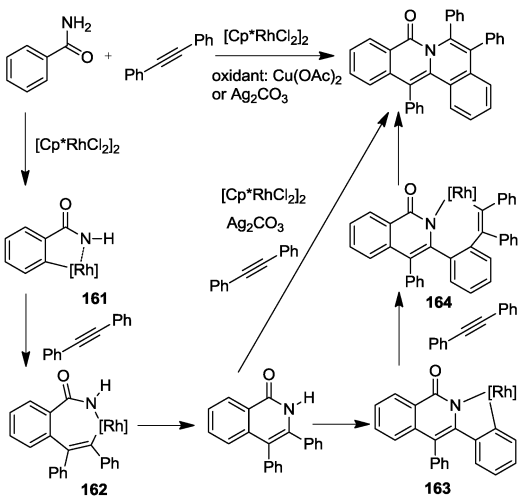
Meanwhile, the oxidative cycloaddition of *N*-alkyl and *N*-aryl secondary benzamides and alkynes using rhodium catalysts was developed by Miura,[124] Rovis,[125,126] Li[127] and their co-workers, respectively. As shown in Scheme 61, Rovis and co-workers proposed an acetate-promoted cyclometalation mechanistic model which indicated that the oxidative cycloaddition proceeds by N–H metalation of the amide followed by *ortho* C–H activation. The resultant five-membered rhodacycle **159**, accessed from *ortho* C–H/N–H activation, has an open coordination site, which can regioselectively and irreversibly insert an equivalent of alkyne to form the seven-membered rhodacycle **160** with an open coordination site. The authors also demonstrated that the alkyne insertion is largely governed by steric factors, and the alkyne coordination plays a central role in product selectivity. A rhodium-catalysed intramolecular annulation of alkyne-tethered hydroxamic esters involving similar five- and seven-membered rhodacycles for the synthesis of 3-hydroxyalkyl isoquinolones and 6-hydroxyalkyl-2-pyridones has also been reported by Park and co-workers.[128]

When the catalyst $[Cp^*RhCl_2]_2$ in the presence of a $Cu(OAc)_2$ or Ag_2CO_3 oxidant was used, the reaction of alkyne and primary benzamides underwent a 1 : 2 coupling leading to a series of tetracyclic dibenzoquinolizinone products *via* double C–H activation and N–H bond cleavage. The cyclometalated complexes **161–164**, as shown in Scheme 62, were presumably involved.[124] When N- and O-containing substituted 2-hydroxyisoquinolines were applied as substrates, formation of both N- and O-containing rhodacyclic intermediates were observed by Li and co-workers.[127]

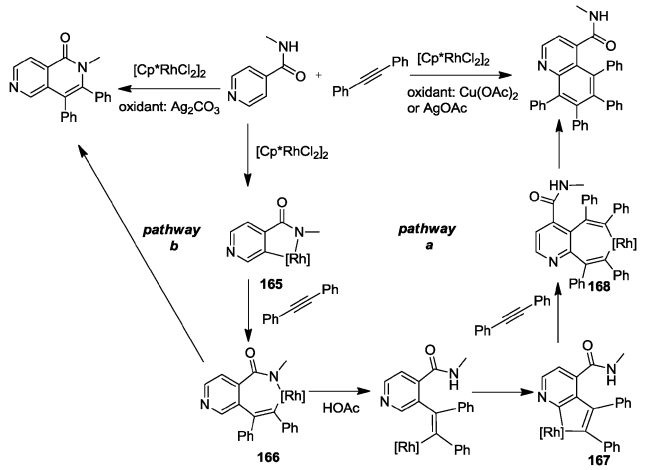
The oxidative annulation of pyridines with alkenes under Rh(III)-catalysed C–H activation conditions in the presence of an oxidant was reported by Li and co-workers.[129] They observed that the selectivity of this reaction is oxidant-dependent, particularly on the anion of the oxidant. As shown in Scheme 63, from the reaction of isonicotinamide and diphenylacetylene using $[Cp^*RhCl_2]_2$ as a catalyst and Ag_2CO_3 as an oxidant, an isoquinolone compound was obtained in a moderate yield. However, using $Cu(OAc)_2$ or AgOAc as an oxidant with the same catalyst, led to a quinoline compound in a high yield. A plausible catalytic cycle was proposed. Both reactions start with the reversible C–H activation and formation of five-membered rhodacycle **165**, as illustrated in Scheme 63, and then alkyne insertion into the Rh–C bond occurs regioselectively to afford the key seven-membered intermediate **166**. Following pathway a, the seven-membered intermediate **168**, which is derived from **167**, can undergo a protonolysis of the Rh–N bond to directly lead to a vinyl intermediate, while the quinoline product can be obtained after a second regioselective insertion of alkyne and subsequent reductive elimination. On the other hand, similar to the oxidative cycloaddition of *N*-alkyl and *N*-aryl secondary benzamides and alkynes, in the presence of Ag_2CO_3, the isoquinolone product was generated *via* C–N reductive elimination (pathway b).



Scheme 61

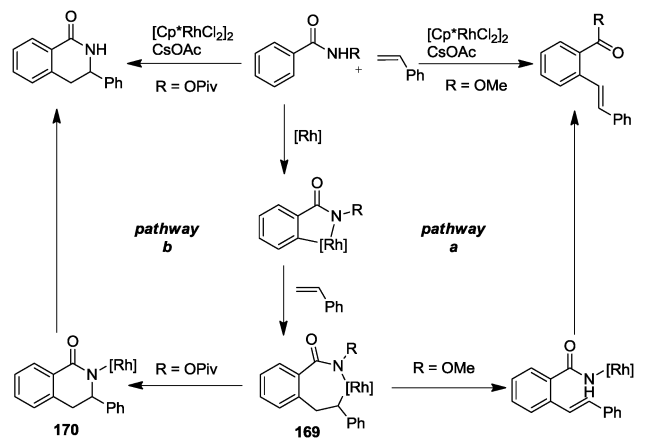


Scheme 62



Scheme 63

In the Rh(III)-catalysed functionalisation of aromatic C–H bonds with olefins, independent reports by the groups of Glorius,[130,131] Fagnou,[123] Li[132,133] and their co-workers, disclosed an interesting ability to control the reaction pathway by using different internal oxidants. The *N*-acyloxy benzamide led exclusively to a heterocyclic product, while for the *N*-methoxy benzamide, the olefinated product was obtained. According to the mechanism shown in Scheme 64, the similar seven-membered rhodacycles **169** form from the N–H deprotonation, C–H activation, and olefin insertion steps. However, the further reaction was controlled by the nature of the internal oxidant. When N–OMe is involved, the β-H elimination/reductive elimination is much more facile than the difficult C–N formation from the cyclic $C(sp^3)$–Rh(III)–$N(sp^3)$ unit, and leads to the olefination product exclusively. In contrast, the *N*-acyloxy-containing intermediate **170** could be stabilised by coordination of the pendant carbonyl oxygen of the *N*-acyloxy moiety; reductive elimination and N–O cleavage then became easier and formed the heterocyclic product. Very recently, an efficient method for the synthesis of azepinones utilising benzamides and α,β-unsaturated aldehydes and ketones as starting materials, involving tandem C–H activation, cyclisation, and condensation steps, has been developed by Glorius and co-workers.[134]

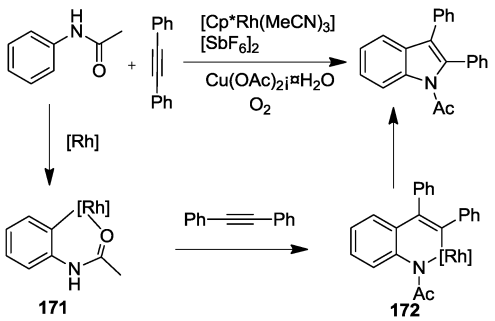


Scheme 64

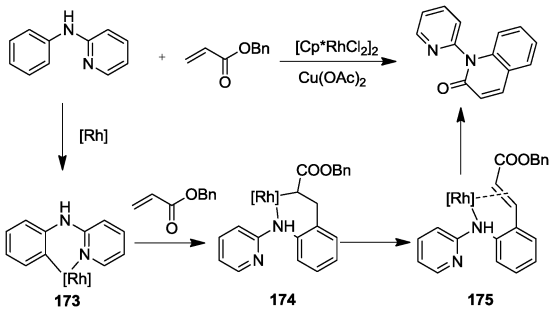
An efficient Rh(III)-catalysed *ortho* allylation of benzamide derivatives with polysubstituted allenes was reported by Ma and co-workers[135] and Glorius and Wang,[136] independently. For two reactions, a similar mechanism was proposed. The arene electrophilic rhodation of the substrate provided a five-membered rhodacycle intermediate, followed by coordination with the less-substituted C=C bond and mild insertion of this C=C bond to afford a seven-membered intermediate. Examples of vinylcarbenoids as three-carbon components in the rhodium catalysed C–H activation/[4+3] cycloaddition of benzamides was reported by Cui and co-workers recently.[137]

In 2008, Fagnou and co-workers reported that acetanilides oxidatively couple with alkynes with a Rh(III) catalyst and $Cu(OAc)_2 \cdot H_2O$ as the oxidant to afford *N*-acetylindoles.[138] As extended research, the same group discovered that this reaction can be carried out under mild conditions by introducing dicationic $[Cp^*Rh(MeCN)_3][SbF_6]_2$ as the catalyst and molecular oxygen as the terminal oxidant.[139] After a mechanistic investigation of the reaction including employing deuterium labeling experiments and kinetic analysis, a plausible mechanism was provided. As demonstrated in Scheme 65, the six-membered rhodacycle **171** should be involved after C–H bond cleavage, which then coordinates to an alkyne, followed by carborhodation to yield intermediate **172**. The desired indole product could be isolated through C–N bond reductive elimination of intermediate **172**. Along the same lines, Glorius and co-workers successfully synthesised multisubstituted pyrroles by the rhodium-catalysed oxidative combination of enamines and unactivated alkynes.[140] A methodology to achieve the direct *ortho* olefination and vinylation of acetanilides *via* a six-membered Rh(III) intermediate has also been proposed by Glorius and co-workers.[141] In the rhodium-catalysed direct intermolecular tandem C–H allylation and oxidative cyclisation of acetanilides with allyl carbonates, an intermediate similar to rhodacycle **171** may be involved.[142]

Incorporating a pyridyl directing group, Li and co-workers found that *N*-aryl-2-aminopyridines are suitable substrates for the syntheses of *N*-(2-pyridyl)indoles, through oxidative coupling with alkynes using $[Cp^*RhCl_2]_2$ as a catalyst and $Cu(OAc)_2$ as an oxidant.[143] However, under similar conditions, the



Scheme 65

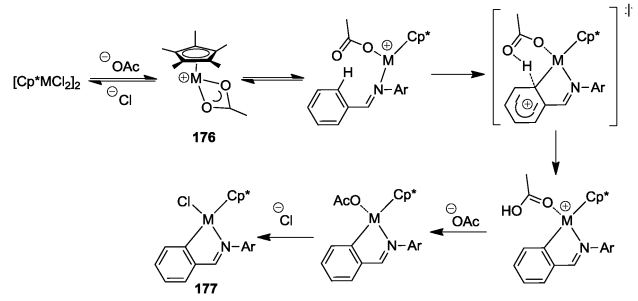


Scheme 66

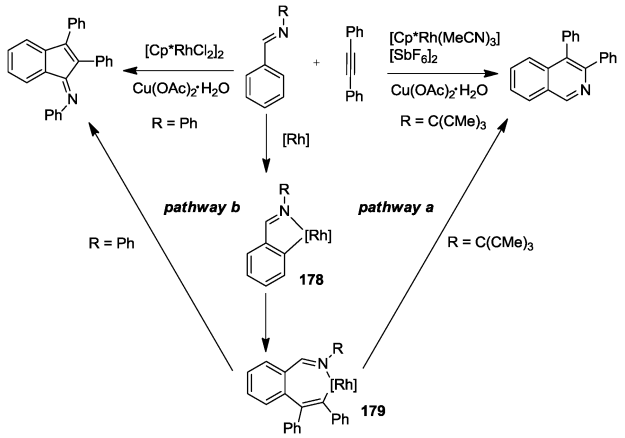
coupling between *N*-aryl-2-aminopyridines and acrylates gave *N*-(2-pyridyl)quinolones. The authors proposed a plausible pathway involving cyclometalation to afford the six-membered Rh(III) intermediate **173** followed by insertion of an incoming acylate (intermediates **174** and **175**) and subsequent β-hydride elimination (Scheme 66). The formed metal-bound *trans*-olefin intermediate can isomerise to the *cis* isomer, thus explaining the attack of the NH group on the carbonyl group of the *cis* intermediate generating the *N*-(2-pyridyl)quinolone.

As mentioned above, aromatic imines are good substrates in acetate-assisted iridium/rhodium-catalysed C–H activation reactions. The combined use of $[Cp^*MCl_2]_2$ (M = Ir, Rh) and NaOAc was reported by Davies *et al.*, generating the key intermediate cations **176** and resulting in fission of certain C–H bonds with the aid of an intramolecular imino group to afford the metalacycle complexes **177** (Scheme 67).[15] This chemistry has been deeply investigated by Jones and co-workers, and others.[19–24]

Q6 Based on the work of Davies and Jones,[19] Fagnou and Guimond developed an efficient method for the synthesis of isoquinoline through rhodium-catalysed C–H bond cleavage, C–C bond formation, and C–N bond reductive elimination using *N*-*t*-Bu aryl aldimines as the nitrogen source (path **a**).[144] Miura and co-workers found that the rhodium-catalysed oxidative coupling of benzophenone N–H imines with alkynes proceeds *via* regioselective C–H bond cleavage to produce indenone imine derivatives. In both of the two cases, five-membered (**178**) and seven-membered (**179**) rhodacycle intermediates may be formed through C–H activation and alkyne insertion (Scheme 68). In contrast to path **a**, intramolecular



Scheme 67



Scheme 68

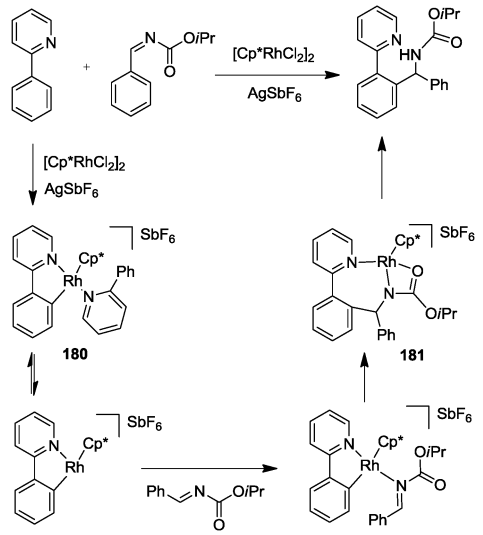
insertion of the imino moiety may occur in path **b**.[145] Chiba and co-workers reported the synthesis of azaheterocycles from aryl ketone O-acyloxime derivatives and internal alkynes using $[Cp^*RhCl_2]_2/Cu(OAc)_2$ as the potential catalyst system. A similar mechanism *via* path **a** was proposed.[146,147]

The synthesis of pyridines from readily available α,β-unsaturated oximes and alkynes under mild conditions and low temperatures using Rh(III) catalysis was developed by Rovis and co-workers.[148,149] Mechanistic studies suggested that the heterocycle formation proceeds *via* reversible C–H activation to provide a five-membered rhodacycle, followed by alkene insertion to generate a seven-membered metalacycle, and a C–N bond formation/N–O bond cleavage process.

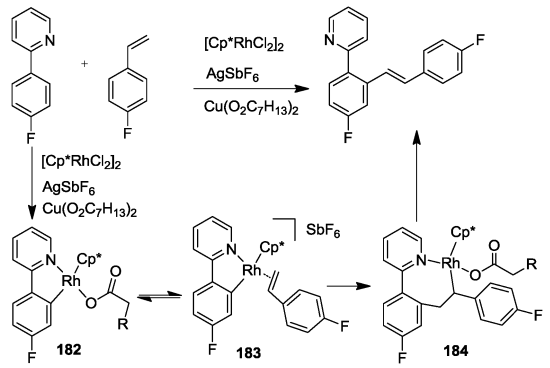
As described in Section 2, using 2-phenylpyridine as the substrate, the intermediate compounds **36** and **37** following C–H activation and alkyne insertion were fully characterised. Inspired by this work, Huang and co-workers developed an efficient Rh–O_2 catalytic system for oxidative C–H activation/annulation. A mechanism involving five- and seven-membered intermediates was proposed.[150]

In order to investigate the mechanistic steps of the Rh(III)-catalysed arylation of imines in the absence of acetate, Bergman, Ellman and co-workers provided a detailed study of the stoichiometric reactions of Rh-catalysed imine arylations with 2-phenylpyridine. The relevant cyclometalated intermediate complexes **180** and **181** were isolated and characterised (Scheme 69).[44] In a rhodium-catalysed C–C coupling between arenes and aziridines, a similar intermediate in which the rhodium center is stabilized by an *N*,*N*,*O* chelator was isolated by Li and co-workers.[151]

More recently, a mechanistic study of the coupling of styrene with fluorine-substituted 2-phenylpyridine catalysed by a $[Cp^*RhCl_2]_2/AgSbF_6$/copper carboxylate system was investigated.[45] Based on a kinetic study that identified the resting states and the turnover-limiting step for this transformation, and the isolation of the neutral carboxylate-ligated rhodacycle **182** and a series of cationic rhodacycles, a proposed catalytic cycle involving a sequence of C–H activation, alkene insertion, β-elimination, and oxidation steps is provided in Scheme 70.



Scheme 69



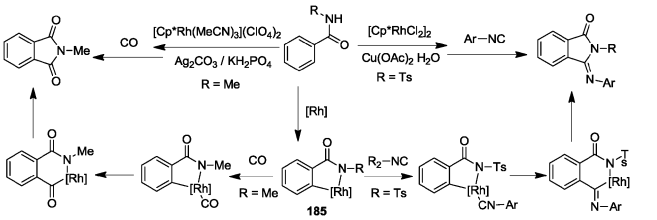
Scheme 70

Complex **182** is in equilibrium with **183** through the exchange of styrene with carboxylate. The new complex **184**, which comes from migratory insertion of the coordinated styrene, undergoes β-elimination to release the organic product.

Similarly, in order to investigate the rhodium-catalysed direct amidation of arenes using azides as the amine source, a rhodium amido species, which was formed *via* amido insertion into a benzo[*h*]quinoline-based cyclometalated Rh(III) complex, was isolated and characterised by Chang and co-workers.[152,153] Similar samples have also been reported by Shi and co-workers.[154,155]

As analogs of 2-phenylpyridine, 1-phenylpyrazoles have proven to be efficient and versatile substrates for rhodium-catalysed oxidative coupling reactions with alkynes and alkenes. The reaction seems to proceed *via* steps similar to those proposed for the oxidative coupling of 2-phenylpyridine with alkynes and alkenes using a rhodium catalyst and a copper oxidant.[156,157]

In 2011, an efficient strategy for the oxidative carbonylation of aromatic amides *via* C–H/N–H activation was developed by

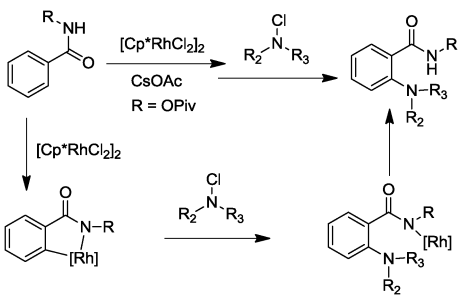


Scheme 71

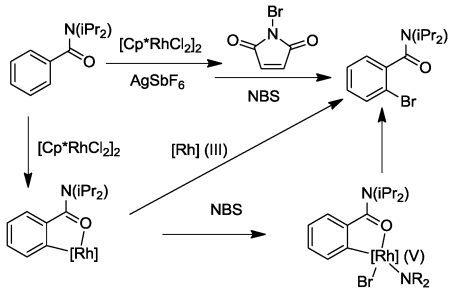
Rovis and co-workers to form phthalimides using a Rh(III) catalyst in the presence of Ag_2CO_3.[158] In the same year, the rhodium-catalysed annulation of *N*-benzoylsulfonamide with isocyanide *via* C–H activation was reported by Zhu *et al.*[159] The similar postulated mechanism is depicted in Scheme 71. The cycle begins with the generation of a five-membered rhodacycle *via* C–H activation. The five-membered rhodacycle, in the presence of a molecule of CO or isocyanide, could be coordinated to the rhodium center, which then undergoes migratory insertion of CO or isocyanide into the Rh–C bond to form six-membered rhodacycles. The corresponding product was released through reductive elimination.

Glorius,[160] Yu[161,162] and their co-workers independently reported the rhodium-catalysed direct C–H amination of *N*-chloro-amines. Mechanistic studies revealed that the C–H activation is the slow but irreversible step of the catalytic cycle in the presence of *N*-chloroamines (Scheme 72). *N*-Chloroamines might undergo an electrophilic amination of the rhodacycle to give the metalated species, which upon protodemetalation afford the amination product.

Glorius and co-workers discovered that the *ortho* bromination and iodination of benzamide substrates with NXS (X = Br, I) in the presence of a cationic Rh(III) catalyst, resulted in C–Br and C–I bond formation (Scheme 73).[163] It is notable that different classes of aromatic compounds, not only tertiary benzamide substrates, secondary benzamides, acetamides, and phenylpyridines, but also simple ketones and benzoic esters, can be applied as substrates. For this carbon–halogen bond formation, two different mechanistic pathways from the same five-membered rhodacycle were proposed by the authors. A probable Rh(V) intermediate was hypothesised in one of the pathways.



Scheme 72



Scheme 73

7. Conclusions

Numerous diverse examples of the cyclometalative C–H activation of various ligands coordinated to half-sandwich iridium and rhodium complexes have been summarised. Many cyclometalation reactions on half-sandwich iridium and rhodium complexes have been described where a 5-, 6-, or 7-membered chelate ring is formed, in which an aromatic ring bearing a functional group such as those based on nitrogen, carbon, phosphorus, or oxygen bound to the metal center, is attacked by the metal *ortho* to the functional group. The mechanistic concepts that have been elaborated for cyclometalation are generally accepted involving five- and seven-membered intermediates. The synthesis and isolation of the intermediates is very useful to understand the catalytic cycle and design new reactions. The application of generating metallacyclic materials using cyclometalation has also been established. Moreover, cyclometalated complexes have been employed in various other domains of material science, for example, as catalysts in water oxidation,[79,164,165] and as anticancer agents.[166,167] Considering the huge potential application of cyclometalated half-sandwich iridium–rhodium complexes, as well as the persisting ambiguities related to the mechanistic details, we may expect that studies of cyclometalated intermediates will provide unprecedented success in the future.

Acknowledgements

Financial support from NSFC (21371036, 91122017), the Program for Changjiang Scholars and Innovative Research Team in University (IRT1117), the Fundamental Research Funds for the Central Universities (20520133030), and Shanghai Rising-Star Program (11QA1400300) are gratefully acknowledged.

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