Cyclometalation Using d-Block Transition Metals: Fundamental Aspects and Recent Trends

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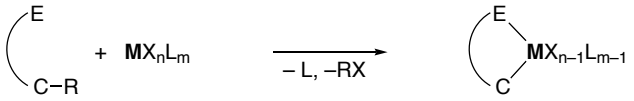
Table of Contents

1. Introduction

Cyclometalation refers to the transition metal-mediated activation of a C–R bond to form a metallacycle comprising a new metal-carbon σ bond (Scheme 1).[1,2] Typically, the reaction consists of two consecutive steps: initial coordination of the metal center via a donor group, and subsequent intramolecular activation of the C–R bond, which closes the metallacycle. The effective bond activation is thus most often a heteroatom-assisted process, involving classical donors such as N, O, P, S, Se, and As, though cases of carbon-assisted C–R bond activation are known as well. As a consequence, the cyclometalated product is not a metallacycle in the strict sense of the word[3] and often includes also heteroatoms other than the metal (Table 1). By far the largest portion of cyclometalation reactions occurs via C–H bond activation, but examples of carbon-carbon, carbon-oxygen, and carbon-silicon bond activation (*i.e.* R = C, O, Si in Scheme 1) are also known.

Scheme 1



C = C_{alkyl}, C_{aryl}, $C_{alkenyl}$
E = N, O, P, S, As, Se, C
R = H, C, N, O, Si, P

Table 1. Definitions applied in this review

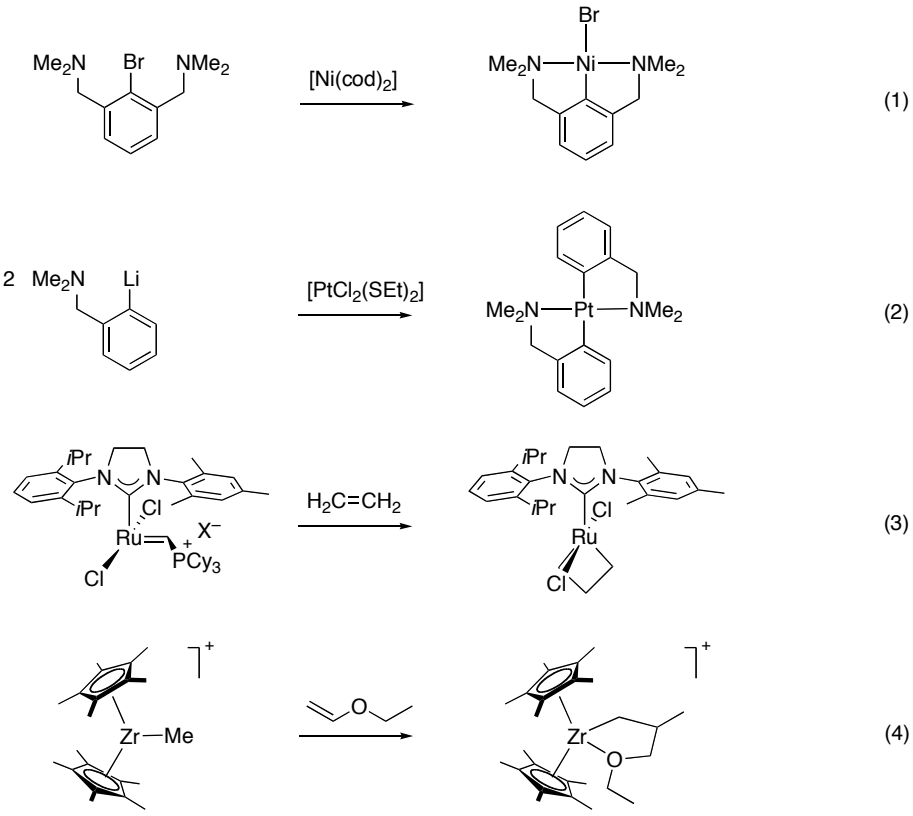
metallacycle	a cycle in which one member is a metal
C,E–metallacycle	a metallacycle in which the metal is σ-bonded to the atoms C and E
cyclometalation	metal-mediated C–R bond activation that transforms a molecule of type RC–E to a *C,E*-metallacycle (R = H, C, N, O, Si, P)

Cyclometalation, discovered in the early 1960s,[4,5] has become one of the most popular organometallic reactions, providing a straightforward entry to organometallic compounds that feature a metal-carbon σ bond. Simultaneously, cyclometalation allows for the investigation of the pertinent aspects governing the metal-mediated activation of unreactive bonds, especially the C–H bond. The reaction product is a metallacycle in which the metal is bound by a chelate

carboligand (*cf.* Scheme 1). Such chelation supports the generally highly susceptible M–C bond and results in organometallic compounds with increased stability. This enhanced stability may have been relevant in the early discovery of the reaction, and may have spurred further developments, making cyclometalation one of the most convenient methods for creating a metal-carbon bond. Soon after its discovery, the reaction has been routinely used in many laboratories and ever since, the field has grown enormously. Nearly all transition metals have been successfully employed for cyclometalation. The platinum group metals Ru, Os, Rh, Ir, Pd, and Pt have received most attention, with palladium being the transition metal that has been studied in greatest detail. Hence, mechanistic data are particularly vast for cyclopalladation reactions. Because of the tremendous progress achieved in cyclometalation chemistry, a comprehensive treatment of the topic would largely exceed the scope of a single review. Instead, this text aims at giving a systematic overview of the fundamental aspects of the cyclometalation reaction involving all d-block transition metals. It covers seminal fundamental literature as well as recent highlights and trends that emerged until early 2009, arranged according to the metal involved in the cyclometalation. A significant amount of reviews, books, and book chapters have appeared over the last decades,[6–22] some dwelling on specific metals,[23–28] on specific ligand scaffolds,[29–38] and on mechanistic aspects.[39–41] These compilations may provide useful complementary information on selected issues of cyclometalation.

Cyclometalation has received considerable attention as the reaction represents probably the mildest route for activating strong C–H and C–R bonds. Apart from the genuine interest in the mechanism and scope of this fundamental bond activation process, cyclometalation is a highly attractive and versatile synthetic method for creating organometallic entities, with wide application potential. Metallacycles have been successfully applied in traditional domains encompassing organic transformations and catalysis,[42–48] especially the catalytic activation of C–H bonds in unreactive alkanes,[49–51] and the stabilization of reactive intermediates.[52,53] In addition, they have been employed in various other domains of materials science, for example as active units in sensors,[54,55] in anticancer agents and for other bioorganometallic applications,[56–59] as photophysical devices in organometallic light-emitting diodes,[60–62] for light harvesting and energy transfer such as in photovoltaic cells,[63] as gelators[64] and birefringents in liquid crystalline materials,[65,66] and as molecular[67,68] or crystalline switches.[69]

Of note for the synthetic chemist, a variety of processes other than cyclometalation have been developed in order to prepare metallacycles, especially oxidative addition involving C–X bond activation (X = F, Cl, Br, I, OTf; see eq. 1 for an example[70]), and transmetalation, consisting of the activation of a C–M' bond (M' most often Li, Mg, Sn, B, Ag, Au, Zn, Hg; see eq. 2 for an example[71]). Similarly, metallacycles may be generated by elimination reactions,[72] by cycloaddition (see eq. 3 for an example),[73] and by hydrometalation, *i.e.* the insertion of unsaturated bonds such as C=C, C≡N, C≡C bonds into a metal–hydride, or more generally, into a M–R bond (see eq. 4 for an example[74]).



Although reactions as in eq. 1–4 all yield metallacyclic products, the metal-carbon bond forming processes are not donor-assisted and do not imply C–R bond activation. Therefore, these reactions do not belong to cyclometalations as defined here and are not further considered. Furthermore, this review is limited on d-block transition metals for cyclometalations only. Reactions involving main group metals are not discussed, despite the fact that, for example, the regioselectivity of many lithiation reactions is dictated by preliminary heteroatom coordination,[75,76] and a number of cyclolithiated complexes are known.[77] Metalations involving f-block transition metals will be described in a separate contribution of this special issue.[78] As a

final limitation, this review concentrates on the activation of C–R bonds exclusively, even though bond activation with elements other than carbon such as the (heteroatom-assisted) Si–H or N–H bond activation to build a *Si,E*- or a *N,E*-metallacycle are fundamentally akin to cyclometalation.[79–81]

Conceptually strongly related to the cyclometalation is the directed *ortho*-metalation (DoM). In this reaction, pioneered by Snieckus,[82] the heteroatom assists and directs C–H bond activation, though typically, the heteroatom-metal bond is not sufficiently stable to be conserved through the C–H bond activation process and scission of the metallacycle occurs. As a consequence, the formed product contains an unsupported metal-carbon bond, which is less stable than in a chelate complex. This reduced stability has been further exploited for devising catalytic reactions that involve metal-catalyzed C–R bond breaking and C–R' bond making *e.g.* catalytic arene functionalization.[83–87]. Where relevant, such reactions will be discussed briefly, as they typically rely on cyclometalation for inducing activity and selectivity. More comprehensive accounts on these developments can be found in the reviews by Sanford, by Colacot, and by Bergman and coworkers in this thematic issue of *Chemical Reviews*.[88–90]

2. General Principles

The cyclometalation reaction can be split into two main sequences, comprising the bonding of the metal center by the (hetero-)atom E, and the intramolecular C–R bond activation. Generally, heteroatom coordination precedes, and the bond activation may hence be considered as a templated process. Pre-coordination of the ligand alters the electron density at the metal center and furthermore, it provides steric constraints that assist in the bond activation step. Arranging the C–E bond and the metal center in close mutual proximity is assumed to be pivotal for reducing the entropic and enthalpic costs of the subsequent bond activation step and the metallacycle ring closure. These elements account for the ease of intramolecular bond activation as compared to intermolecular processes, rationalizing at least in part the enormous progress achieved in intramolecular C–H and C–R bond activation during the past decades. Successful cyclometalation depends on a number of steric and electronic factors that are now reasonably well understood. These factors concern all partners of the cyclometalation process, that is, the metal precursor, the donor site E and the C–R bond to be activated.

2.1. Influence of the metal precursor

An obvious prerequisite for a metal precursor that is appropriate for inducing cyclometalation consists of providing a coordination site for (hetero-)atom bonding, thus enabling the primary attachment of the ligand via M–E interactions.[40] Different classes of precursors are particularly well suited for bonding of the donor site E,[23-28] including *i)* dimeric or polymeric complexes that are readily cleaved into monomeric species in the presence of a donor, *e.g.* $[RuCl_2(cymene]_2$, $[RuCl_2(CO)_2]_\infty$, $[MCl(cod)]_2$ (M = Ir, Rh, cod = 1,5-cyclooctadiene); *ii)* precursors possessing loosely bound ligands such as $[PdCl_2(NCMe)_2]$, $[PtCl_2(SEt_2)_2]$, $[Os(PR_3)_2H_5]$ or $[Ir(PPh_3)_2H_5]$, considering that in the latter two complexes, two hydrogens are typically coordinating as dihydrogen molecule; *iii)*–ate complexes in which one of the anionic ligands is readily displaced by a neutral ligand, for example in K_2PdCl_4 or K_2PtCl_4.

The second step of cyclometalation, *i.e.*, the C–R bond activation process, is facilitated by strongly basic ligands at the metal precursor.[24] In particular C–H bond activation processes are greatly promoted by a metal-bound alkoxide, an alkyl ligand, or a hydride. Proton abstraction from the ligand then leads to the formation of an unreactive alcohol, an alkane, or H_2, respectively. Such product formation constitutes a thermodynamic driving force for the bond activation, which is advantageous for reversible cyclometalations. Acetate (AcO^-) has emerged as a privileged ligand for cyclometalation reactions, as AcO^- combines a number of beneficial properties, including a flexible metal coordination mode (κ^1, κ^2-chelating, κ^2-bridging), and it may thus assist in transiently generating a vacant coordination site at the metal center.[23] In addition, its conjugated acid HOAc, which results from C–H bond activation, is weak and does not interfere with the formed C–M bond (*cf.* also section 3.4). Moreover, the κ^2-bridging coordination mode may give a cyclic transition state involving metal coordination via one oxygen and interaction of the other oxygen with the C–H entity (*cf.* section 3). This configuration preorganizes the reactants and places the metal in close proximity to the carbon that participates in the C–H bond activation.[91] Apart from these steric considerations, favorable transfer of electron density ensues, since an increase of C–H···O interaction weakens the C–H bond and concomitantly enhances the partial negative charge at carbon. Simultaneously, the metal-oxygen bond strength decreases, that is, the C–O bond order increases, thus generating a more electropositive metal center. Final C–H bond breaking then completes the C–M bond forming process. Similar effects may be attributed to various ligands related to acetate, for example

carbonate (CO_3^{2-}), trifluoroacetate (tfa; CF_3COO^-), and triflate (OTf; $SO_3CF_3^-$), though the latter forms an acid that may be strong enough to cleave the M–C bond again.[92]

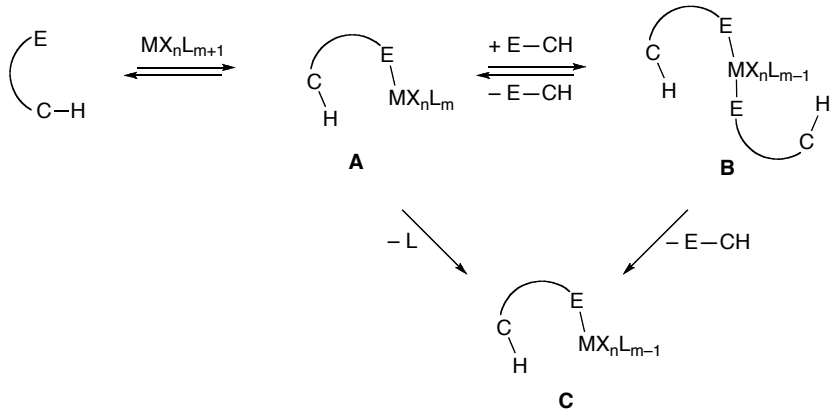
2.2. Influence of the donor group E

As a first step of cyclometalation, a weakly coordinating ligand in the metal precursor is typically exchanged for the donor site E of the potentially cyclometalated ligand. This ligand precoordination may be a trivial, thermodynamically controlled substitution or a dimer cleavage process, if the intramolecular coordination site is a strong neutral donor such as phosphine, imine, or amine. Yet it may be more complex or irreversible if E is for example, a carbanion, an anionic donor such as an amide (NR_2^-), or a neutral carbon ligand such as an *N*-heterocyclic carbene. The effect of the donor group E in cyclometalation reactions may broadly be classified according to its basicity and its steric impact, which may be mutually diverging. Appropriate donor groups generally match the hard-soft acid-base principles described by Pearson.[93] Thus, cyclometalation with high-valent early transition metals is most successful when the donor atoms are hard, as in alkoxides, aryloxides, or in amines. At the other end of the scale, soft transition metals, *e.g.* the platinum group metals, favor bonding to phosphines and sulfides as soft Lewis bases. Clearly, the hard-soft principle provides only guidelines, and numerous examples are known where relatively soft donor atoms have been used in cyclometalations with hard metals (e.g. pyridine in zirconium (IV) chemistry),[94] and likewise, hard amine donors have been used in combination with soft palladium(II).[95] Hard-soft mismatches may, however, lead to difficulties in regioselectivity of metalation.[96] Moreover, such mismatches have been exploited to develop the transcyclometalation reaction, a new type of cyclometalation where one cyclometalated ligand is exchanged for another one (*cf.* section 3.4.).

In the first step of the cyclometalation process, initial ligand coordination to the metal precursor affords complex **A** (Scheme 2). Often, another donor group E may substitute weakly bound ligands, leading to stable coordination complexes of the type $[M(E–CR)_2X_n]$ **B**. Such species have been detected and isolated.[97,98] Transient decoordination of either a ligand (L or X from **A**) or a donor site (from **B**) yields the coordinatively unsaturated complex **C** as the key intermediate for C–H bond activation. Obviously, formation of intermediate **C** is a delicate trade-off that is triggered by the M–E bond strength. Too strong and too stable bonding deteriorates ligand dissociation from the coordination complex **B**, while too weak bonding may shift the equilibrium

to the starting materials, thus likewise preventing formation of intermediate **C**. Both, steric and electronic factors govern the strength of the M–E bond and depending on the nature of the donor group E, one or the other factor may prevail.

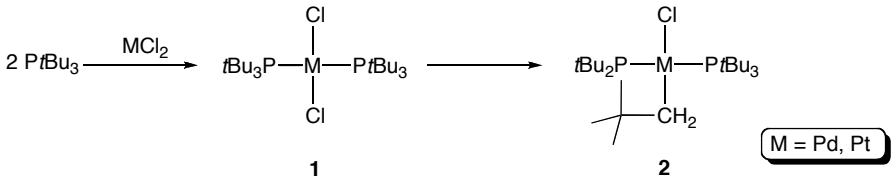
Scheme 2



For amines as donor sites (E = NR_2), generally, large N-substituents weaken metal coordination substantially.[99] Dimethylamino groups (E = NMe_2) have proven to be particularly suitable,[30] while NEt_2 groups coordinate much weaker and higher homologs (e.g. N*i*Pr_2) fail to coordinate to a metal center due to the excessive shielding of the nitrogen atom. Concurring with such a steric bias, N-substituted pyrrolidine (E = $N(CH_2)_4$) and piperidine (E = $N(CH_2)_5$) have donor properties that are similar to the NMe_2 moiety. Cyclometalation of primary amines is more demanding. For example, cyclopalladation is prevented from coordination compounds of type **B** and care has to be taken to keep a 1:1 ligand/palladium ratio to maximize the formation of compound **A**.[100]

For softer donors like phosphines and sulfides, metal coordination is well-known even when bulky substituents are present, as in P(*t*Bu)$_3$.[101] Steric effects ensure here that the M–P bond does not become too strong. For example in palladium complexes comprising phosphines with large cone angle, steric repulsion weakens the M–P bond. In addition, coordination of ligands in *cis* position is restricted. With bulky P(*t*Bu)$_3$, this effect allows for stabilizing coordinatively unsaturated metal complexes, and for generating the strained metallacycle **2** via formal HCl abstraction from the coordination complex **1** (Scheme 3).[102] Similar effects have been observed for P(*o*-tol)$_3$, which is similarly important for catalysis as P(*t*Bu)$_3$.[103]

Scheme 3



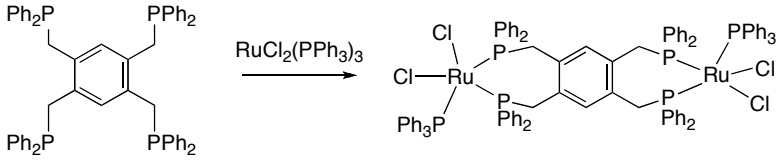
Shaw has first recognized and elegantly demonstrated the beneficial effect of steric bulk at phosphorus.[104] With sterically demanding phosphines, cyclometalation is favored due to entropic and enthalpic factors. Thus, rotational limitations of *t*Bu groups entropically favor the C–H bond activation, while the reduced number of *gauche* interactions in the metallacycle product provide the enthalpic driving force.[105] For example, cyclometalation of potentially *P,C,P*-tridentate coordinating pincer ligands requires considerably harsher conditions when the phosphine donors are PPh_2 groups rather than $P(tBu)_2$ units.[106,107] This concept is strongly related to the classical *gem*-dimethyl effect in organic cyclization reactions.[108]

The critical impact of the coordinating ability of the donor atom E is particularly relevant in ligand precursors featuring more than one donor site like in tridentate pincer-type ligands. In such systems, bridging[109] as well as intramolecular bidentate coordination[110,111] has been established with phosphine donors. The latter bonding mode directs the metal center towards the C–R bond *ortho* to both donor arms. As a result, cyclometalation using *P,C,P*-tridentate ligand precursors is well established for a variety of transition metals.[107] No such bidentate coordination has been observed thus far for analogous *N,C,N*-tridentate coordinating pincer ligands, which may be understood by considering the weaker M–N bond in late transition metal complexes. Taking into account this fact together with the higher electron density at the metal center upon coordination of phosphorus as opposed to nitrogen, it is not surprising that cyclometalation with NCN pincer ligands is much rarer than with PCP pincer ligands.[33]

Along these lines, cyclometalation of multitopic ligands sometimes becomes difficult. For example, the bis-pincer precursor **3** does not undergo cyclometalation (Scheme 4), although this reaction has been described for simple pincer analogs.[112,113] Instead, the bimetallic chelate **4** is formed in which two mutually *ortho* positioned phosphine sites bind one ruthenium(II) center each.[114] Such coordination appears to represent a thermodynamic sink and even upon prolonged heating, no cyclometalation is observed. In the corresponding coordination complex of simple PCP pincer ligands, the larger metallacycle destabilizes *P,P*-bidentate chelation and hence promotes cyclometalation. Notably, weaker coordination of pyrazole nitrogen donors in an

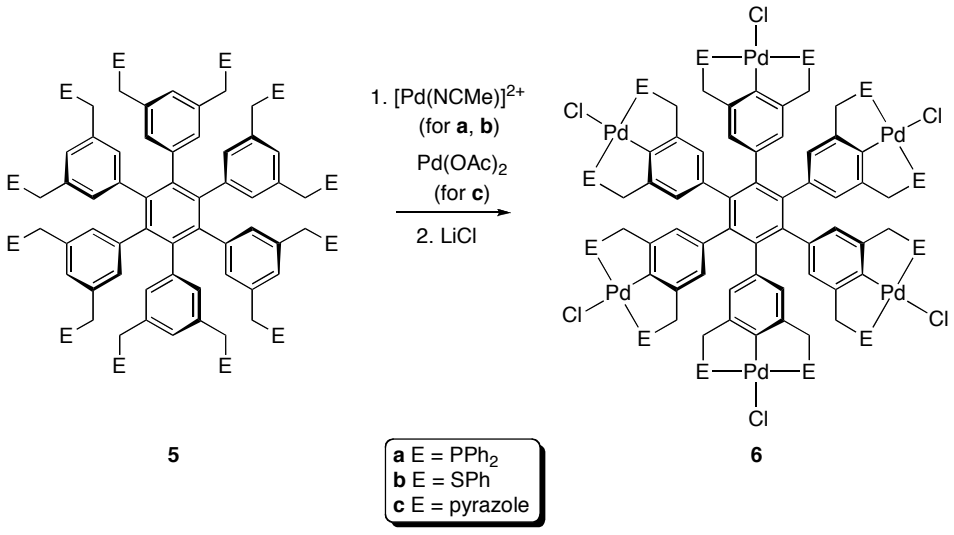
analog of **3** facilitates the double cyclometalation considerably.[115] The strong influence of the donor group may be further illustrated by the unsuccessful attempts to directly cycloruthenate the hexa-pincer 'cartwheel-type' ligand precursor **5**. Cyclopalladation proceeds very slowly with **5a** (110 h reaction time), yet significantly smoother (3-15 h) when weaker donors are incorporated like sulfides and pyrazoles in **5b** and **5c**, respectively (Scheme 5).[116,117] Again, polydentate donor bonding to the metal precursor may restrict the formation of the coordinatively unsaturated metal precursor and hence impede C–H bond activation.

Scheme 4



3 **4**

Scheme 5

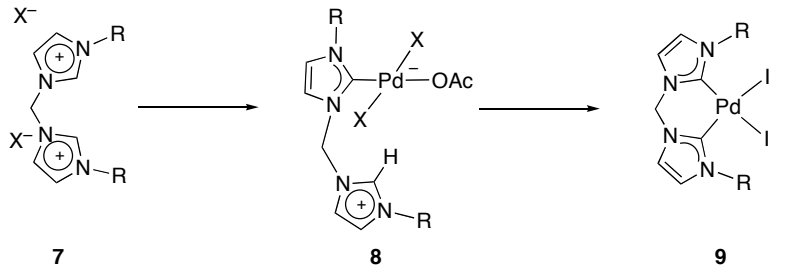


5 **6**

In some cyclometalation reactions, the anchoring of the metal and thus M–E bond formation is irreversible, for example in complexes containing derived from the diimidazolium salt **7** (Scheme 6). In these systems, M–C bond formation is typically controlled by kinetic factors such as the lability of the C–H bond. Metalation occurs in a stepwise process, producing first a monocarbene complex **8** which then cyclometalates via C–H bond activation to give the dicarbene complex **9**.[118] A special case arises when the kinetic differentiation between C–H bonds in the

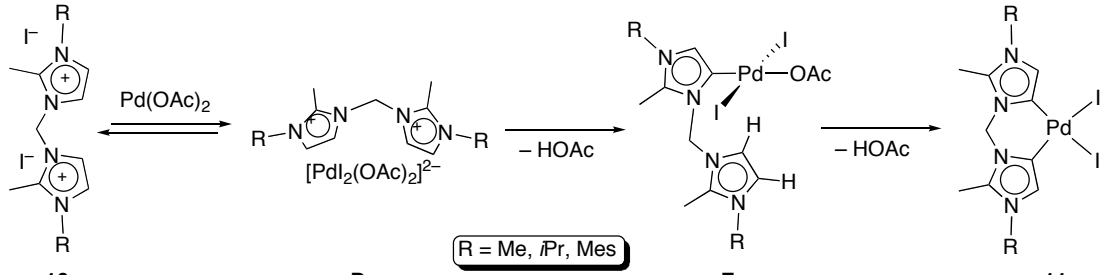
diimidazolium precursor is very low. For example, the diimidazolium salt **10** yields the cyclometalated complex **11** in high selectivity despite the fact that the ligand precursor possesses four equally active sites for the first metalation (Scheme 7).[119] It has been suggested that the efficient discrimination between the C4–H and C5–H for bond activation occurs through ion pairing of the diimidazolium dication with the –ate complex that forms upon coordination of the anions from the diimidazolium salt to the metal precursor (**D**, Scheme 7).[120] Alternatively, multiple anion–π interactions may be operational.[121] Such weak interactions provide a thermodynamic control that is principally related to that exerted by donor atom coordination to the metal precursor as discussed above (*cf.* Scheme 2). Moreover, metal-carbene bond formation can be reversed and hence subjected to thermodynamic control if (poly)hydride metal precursors are used, since metal-bound hydrides promote reductive carbene elimination.[122,123]

Scheme 6



7 **8** **9**

Scheme 7

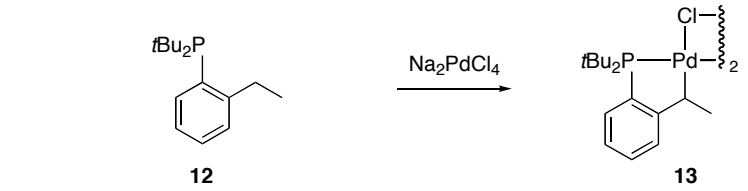


10 **D** **E** **11**

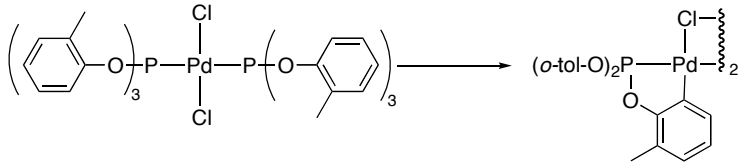
2.3. Influence of the C–R bond

The preference of transition metals to participate in five-membered metallacycles induces a certain degree of regioselectivity also in cyclometalation reactions. Originally formulated as a rule,[9] this preference allows for predicting the product outcome to a certain extent. Thus, cyclopalladation of the phosphine **12** occurs selectively via benzylic C–H bond activation and

affords the metallacycle **13**.[124] Similarly, the tris(*ortho*-tolyl)phosphite **14** undergoes exclusive C_{aryl}–H bond activation to generate the palladacycle **15** (eq. 5 and 6).[125]



12 **13** (5)

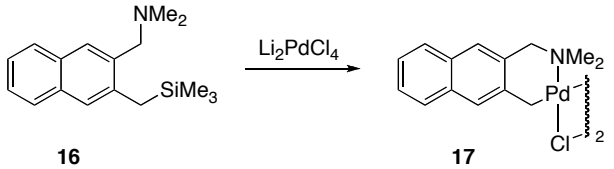


14 **15** (6)

In the absence of possibilities to form five-membered metallacycles, cyclometalation may occur also at different positions and both four- and six-membered metallacycles are common.[38] The smallest possible metallacycle constitutes of three atoms and examples have been isolated and characterized.[94] At the other end, up to eight-membered metallacycles have been generated via cyclometalation.[126]

Activation of a given position provides another methodology to direct the regioselectivity of cyclometalation. For example, it has been established that palladium(II) precursors prefer C–$SiMe_3$ bond activation over C–H bond cleavage.[127] Hence, incorporation of a $SiMe_3$ group in **16** directs the cyclopalladation to the naphthyl 3-position and leads to the six-membered metallacycle product **17** exclusively, despite the possibility of forming also a five-membered cycle upon C1–H bond activation (Scheme 8).

Scheme 8

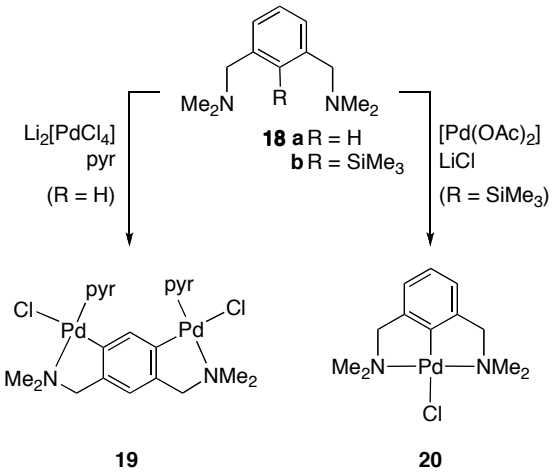


16 **17**

This preference has been exploited by van Koten and coworkers for the cyclopalladation of potentially *N,C,N*-tridentate pincer ligand precursors **18** (Scheme 9). In the absence of a directing group (**18a**, R = H), cyclopalladation occurs at the sterically least hindered position and yields the dimetallic complex **19**.[128,129] After incorporation of a directing silyl group (R = $SiMe_3$), **18b**

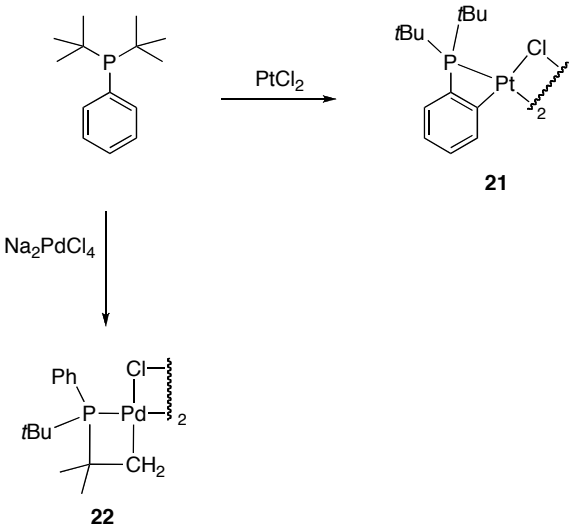
produces cleanly the monometallic, cyclometalated complex **20**.[129] Alternatively, tridentate coordination of such types of pincer ligands can be achieved by protection of the potential *meta* positions with alkyl groups.[115]

Scheme 9



Obviously, the electronic configuration of the C–R bond plays a pivotal role. Depending on the mechanism that is operative (see section 3), aromatic C(sp^2)–H bond activation is favored over C(sp^3)–H bond activation. The nature of the metal center and its ancillary ligands may, however, permute the selectivity. For example, cyclometalation of the phosphine PPh*t*Bu$_2$ occurs via C_{aryl}–H bond activation with platinum(II) and yields the four-membered *C,P*-metallacycle **21** (Scheme 10),[130] yet via C_{alkyl}–H bond activation with Na_2PdCl_4 to form the palladacycle **22**.[131] In general, C_{aryl}–H activation is more frequently observed, owing predominantly to the higher kinetic lability of aromatic protons as compared to protons in alkanes and alkenes.

Scheme 10



The lability of the C–R bond can be modulated by substituent effects. For example, the acidity of aliphatic C–H bonds has been enhanced by incorporating electron-withdrawing substituents in α-position. Similarly, the introduction of donor substituents at the arene has been successfully demonstrated to promote cyclometalations proceeding through an electrophilic C_{aryl}–H bond activation process.[39,40]

Steric congestion in the metal coordination sphere may constitute another driving force for inducing C–R bond activation. For example, numerous C–H bond activation processes have been observed in *t*Bu groups, and related C–H bonds that are confined in close proximity to the metal center. In such a highly preorganized configuration, bond activation is favored, since cyclization comes with only minimal entropic costs.

3. Mechanistic Concepts

A number of excellent reviews have summarized some of the mechanistic details of C–H bond activation in cyclometalation.[39–41,100] The three major pathways that have been distinguished thus far include electrophilic C–H bond activation, oxidative addition, and σ-bond metathesis. Each of these general concepts constitutes a theme with variations as detailed to some extent below. The electronic configuration at the metal center together with the nature of the C–H bond, in particular the hybridization at carbon, decisively determine which mechanism may be most probable. It should be noted, though, that for most cyclometalation processes, the exact mechanism is far from being understood and experimental data provide often a more diverging

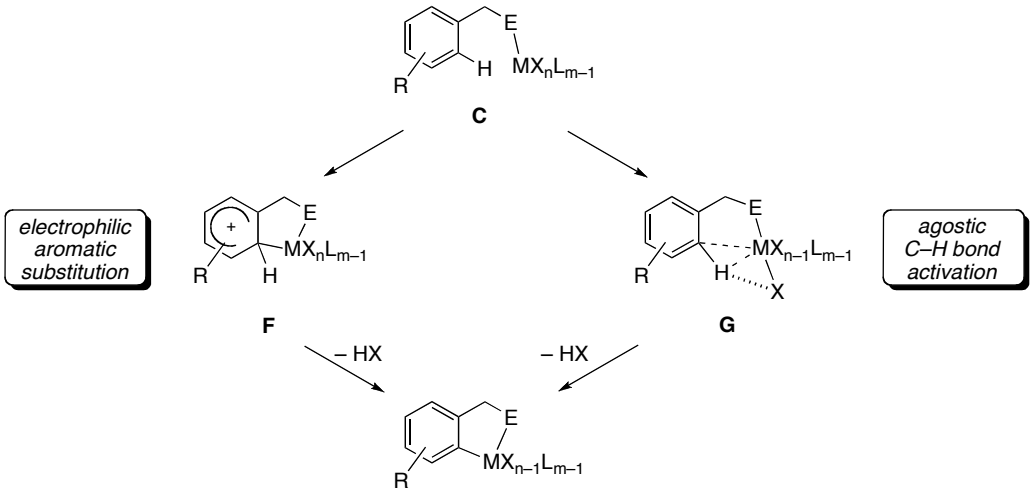
than converging picture. In addition, subtle changes in the ligand framework, for example in the donor site E, may influence the stability of certain conformations along the reaction coordinate and may transform a potential intermediate into a transition state and vice versa.

3.1. Electrophilic bond activation

Electrophilic bond activation pathways are generally observed with electron-poor late transition metals. A showcase is C_{aryl}–H bond activation mediated by palladium(II), renown for its electrophilic character, and to a lesser extent also by its 3rd row congener, platinum(II). Early mechanistic work has revealed an acceleration of aromatic C–H bond activation upon insertion of electron-donating substituents on the aromatic ring, which provides a close analogy to organic electrophilic aromatic substitutions. This analogy has been reinforced by the fact that many organic aromatic substitutions reactions are facilitated if a transition metal catalyst is employed. The organic model of electrophilic aromatic substitution[132] involves as crucial intermediates the formation of a π complex and subsequently a σ complex (arenium intermediate). Organometallic analogs of the σ complex have been observed in platinum-mediated C–C and C–H bond making and breaking processes in a NCN pincer scaffold.[133] No evidence for the existence of the π complex as preceding intermediate has been provided thus far.

Related π-bound intermediates may also become less important, if the metal precursor contains a directing and templating ligand. Acetate and likewise carbonate groups (CO_3^{2-} or M'CO_3^-) have found most widespread application. These anions provide multiple functionality in serving in the transition state simultaneously as ligand to the metal center and as hydrogen bond acceptor, and finally as proton scavenger for completing the bond activation process. With AcO^- and related ligands in the metal precursor, it is thus likely that the bond activation is initiated by direct formation of a σ complex, assisted by an exogenous bifunctional ligand, rather than through a putative π complex (**F** in Scheme 11, X = OAc).

Scheme 11



The model has recently been refined by theoretical considerations, which predict an agostic interactions at the initial stage of the bond activation process.[91] The corresponding intermediate **G** features a hydrogen–metal interaction and only weak carbon-metal stabilization. The rate-limiting step has been calculated to consist of displacing one oxygen donor of the κ^2-bound acetate ligand in the metal coordination sphere with the C–H bond. The computed activation barrier for this step corresponds to the experimentally determined range (13.0 *vs* 11–18 kcal mol^{-1}) for the cyclometalation of *N,N*-dimethylbenzylamine with $Pd(OAc)_2$. Stabilization of this intermediate has been postulated to occur predominantly via AcO···H–C_{aryl} hydrogen bonding. The remaining steps, *i.e.* C–H bond cleavage and metallacycle formation, have been calculated to proceed along a virtually barrierless reaction coordinate.

Notably, the role of the donor site and of the κ^2-bound ligand, in most cases acetate, is very similar for aromatic substitution and agostic activation. Geometrical parameters may be used to emphasize the distinct differences between the arenium intermediate **F** and the agostic intermediate **G**. In the agostic complex, the Pd···H contact is short and the C–H bond elongated due to the hydrogen bonding, while in the arenium system, the Pd···H distance is expected to be large and the Pd–C–H bond angle wide. In addition, the calculated atomic charges show in the agostic intermediate only alterations at the activated C–H bond, whereas in an arenium intermediate, the partial positive charge is spread over all conjugated carbons. Despite these pronounced differences, experimental distinction between the two intermediates is often difficult due to the lack of structural data on relevant intermediates. Perhaps the most straightforward differentiation between pathways involving either intermediate **F** or **G** is possible by correlating the rate-dependence of the cyclometalation with the donor ability of aromatic substituents:[91] a

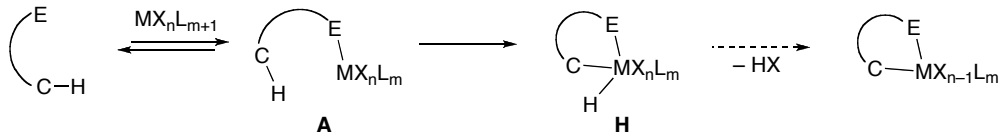
strong correlation, *i.e.* a large slope in the Hammett plot, suggests a process through an arenium intermediate, while a weak correlation puts forward an agostic activation step. Kinetic isotope effects are expected, however, to be small in either mechanism.

A snapshot of an agostic C–H bond activation process has been obtained in the reaction of a rhodium(I) precursor with a tridentate coordinating PCP pincer-type ligand system.[134] In this case, it has been demonstrated that the incorporation of multiple electron-donating alkoxy-groups at the aromatic ring has no accelerating effect, thus corroborating the low charge distribution in an agostic intermediate.

3.2. Oxidative addition

Bond activation via C–H (or C–R) oxidative addition obviously requires an electron-rich metal center. Oxidative addition is most common for cyclometalations using iridium(I) and rhodium(I),[135] as well as for some osmium(II) precursors, and it seems to prevail in most C_{alkyl}–H bond activations with late transition metals. In contrast to agostic interactions, an oxidative addition of a C–H bond occurs by direct population of the antibonding σ^* orbital of the C–H bond and induces a formal two-electron transfer from the metal to the ligands. The oxidative addition product **H** may undergo spontaneous or base-induced reductive elimination of HX or RX (**I**, Scheme 12), thus leading to a seemingly isohypsic process. The ease of reductive elimination depends on various factors, including the rigidity of the ligand scaffold, the stability of high metal oxidation states, and the reaction conditions (temperature, base).

Scheme 12



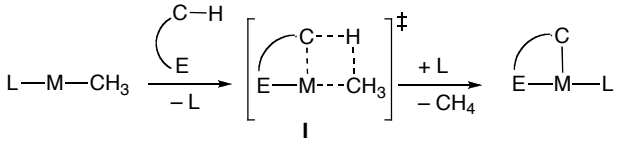
Oxidative addition can be distinguished from electrophilic cyclometalation by the different role of the C–H bond. Whereas in electrophilic processes, electron-donating interactions predominate, the ligand is in oxidative additions primarily an acceptor. Thus, C_{aryl}–H bond activation rates correlate with the electron-withdrawing ability of aromatic substituents, inverse to that expected for electrophilic aromatic substitution. Moreover, kinetic isotope effects are typically large.

These conceptual differences notwithstanding, it should be noted that the reaction coordinates are very similar. For example, intermediate **G** from agostic C–H bond activation featuring an elongated C–H bond and close contacts of the metal center to both the carbon and the hydrogen nuclei may be regarded as transition state of oxidative addition, *i.e.* of the transformation of **A** to **H**. Subtle effects then determine whether the hydrogen is subsequently transferred either directly to the base, providing a truly isohypsic process, or whether (transient) M–H bond formation occurs, thus implying an oxidative addition–reductive elimination sequence.

3.3. σ-Bond metathesis

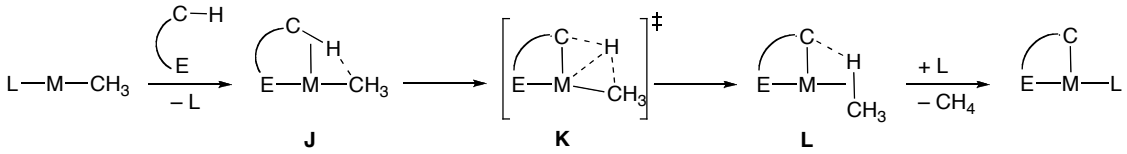
Cyclometalation reactions involving σ-bond metathesis has been considered as the predominant pathway when C–H bond activation is accomplished with electron-poor metal centers such as high-valent early transition metals, and perhaps also with carbonyl complexes. The generic process is depicted in Scheme 13 for a metal precursor comprising a CH_3 ligand and features a four-membered transition state **I**. Analogous reaction coordinates apply for other metal alkyl complexes and for hydrides.

Scheme 13



Such metathesis has been proposed also for late transition metals, albeit in a modified version.[136,137] Due to the significant electron density at late transition metal centers, the metal assists in stabilizing the σ complex **K** (Scheme 14). The process has therefore been termed σ-complex-assisted metathesis (σ-CAM). Such a mechanism needs to be considered in various cyclometalation reactions, especially those involving well-known rhenium, ruthenium, and osmium hydrides as precursors for cyclometalation.

Scheme 14

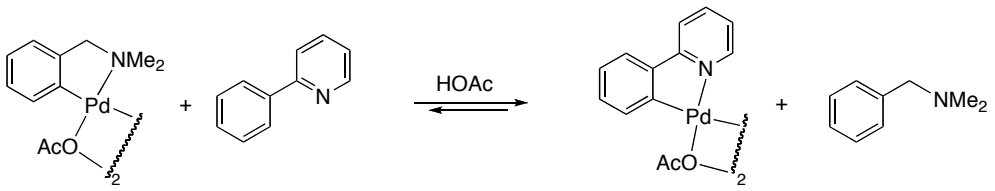


3.4. Special case: Transcyclometalation

The exchange of one cyclometalated ligand for another one, termed transcyclometalation,[138] represents a particular case of C–H bond activation. Transcyclometalation involves M–C bond making and breaking,[139–144] and depending on the sequence of these two events, may proceed either through an inorganic intermediate (M–C breaking before M–C' formation) or through a diorgano metal complex (M–C' making prior to M–C cleavage). Evidence for both mechanisms has been obtained.

The reaction has been investigated in elegant work by Ryabov, who observed initial ligand dissociation when reacting the palladacycle **23** in HOAc with phenylpyridine (Scheme 15).[145] The reaction finally yields the cyclometalated complex **24** and *N,N*-dimethylbenzylamine. Kinetic results are in agreement with a dissociative pathway involving full release of the amine ligand from the metal coordination sphere and formation of an inorganic palladium intermediate.[146] The first part of the reaction may be rationalized by metallacycle opening via de-coordination and protonation of the amine donor group in **23**, thus transforming the chelate into a monodentate *C*-bound ligand, which is highly susceptible to acidolysis. Subsequent cyclometalation may occur with either of the two ligand precursors available, *viz*. phenylpyridine or dimethylbenzylamine, according to the electrophilic pathways stipulated above. The product distribution qualitatively correlates with the ligand-metal affinity (*cf.* section 2.2). The reaction is under thermodynamic control and similar equilibria are reached in transcyclometalations using benzylamine ligands containing NMe_2 and NEt_2 donor groups, independently which of the two ligands is cyclometalated at the outset of the reaction.[147] Moreover, transcyclometalation experiments using polydeuterated AcOH-d_4 as solvent have indicated that deuterium is incorporated also into the non-metalated *ortho*-position of dmba.[148] This H/D exchange suggests that cyclopalladation is an equilibrium process in acetic acid and that Pd–C bond making and breaking is reversible.

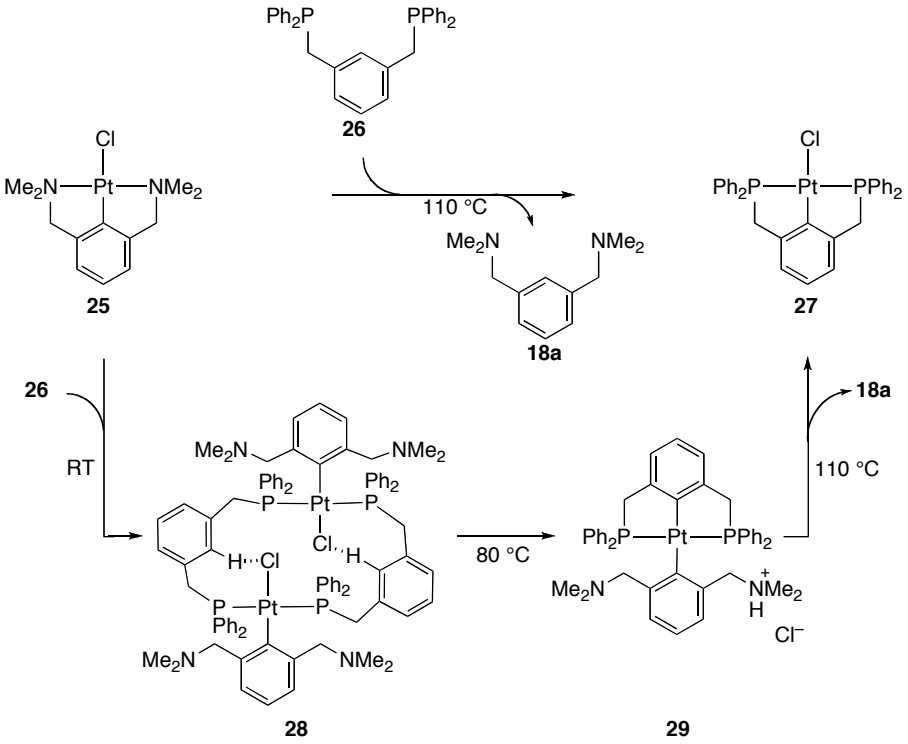
Scheme 15



23 **24**

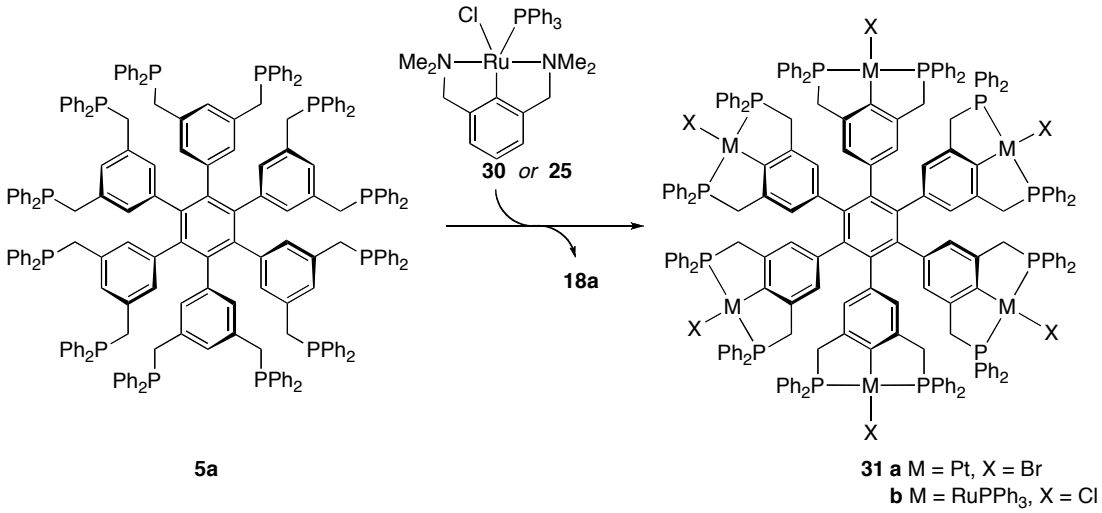
The acidic transcyclometalation has been demonstrated to be of significant scope, and has allowed for the exchange of a C(sp^2)-bound ligand with a C(sp^3)-containing chelate.[147] In addition, acid-catalyzed ligand exchange via dissociative Pd–C bond cleavage of **23** has been successfully used for synthesizing metallacycles bearing arsenic[149] or selenium as donor sites.[150] An associative reaction trajectory has been established for the formation of the PCP-platinum complex **27** from the analogous NCN-platinum complex **25** under acid-free conditions (Scheme 16).[138] Careful adjustment of the reaction conditions unraveled some mechanistic details of this transcyclometalation reaction. Similar to the dissociative pathway, the different coordination ability of the heteroatoms provides an important driving force for the reaction. The ligand exchange is thus initiated by the substitution of the NMe_2 donors in **25** by the stronger bonding phosphine donors from the pincer ligand precursor **26**, thus affording the macrocyclic bimetallic complex **28**. A distinct difference of this intermediate compared to direct cyclometalation consists of the *trans* coordination of the phosphines, while direct cyclometalations typically features an intermediate with pseudo *cis* coordinating phosphines.[110,111] Complex **28** is characterized by an intramolecular hydrogen bond between the metal-bound halide and the aromatic C–H group. Apart from activating the C_{aryl}–H bond, this Pt–Cl···H–C_{aryl} interaction preorganizes the reactive sites and locks the metal center and the aryl carbon in a confined arrangement. Dissociation of one phosphine donor from **28** has been suggested to create a coordinatively unsaturated metal center, which entails the cleavage of the activated C–H bond. The resulting platinum bis(aryl) complex **29** has been structurally analyzed and can thermally be transformed into the final product **27** and the neutral arene **18a**, probably mediated by acidolysis of the Pt–C bond of the monodentate ligand.

Scheme 16



Deuterium labeling studies on a related transcyclometalation using the NCN pincer ruthenium complex **30** indicate that reversible C–H bond making and breaking only occurs in the NCN pincer ligand but not in the PCP pincer unit.[151] Moreover, the reaction trajectory of this associative transcyclometalation process provides new synthetic opportunities,[142] allowing for cyclometalation of ligand precursors with strongly shielded C–H bonds. For example, the multisite ligand **5a** has a phosphine-dominated periphery and hence tends to stabilize coordination compounds when treated with inorganic metal precursors (*cf.* **4**, Scheme 4). However, using a transcyclometalation protocol and reacting **5a** with the cyclometalated metal precursor **25** or the ruthenium analog **30** cleanly produces the hexametallic complexes **31a** and **31b**, respectively (Scheme 17).[152] The process may be of general use when heteroatom coordination is impeding bond activation, *e.g.* at dendritic or polymeric peripheries where local concentrations of donor sites are typically rather high.

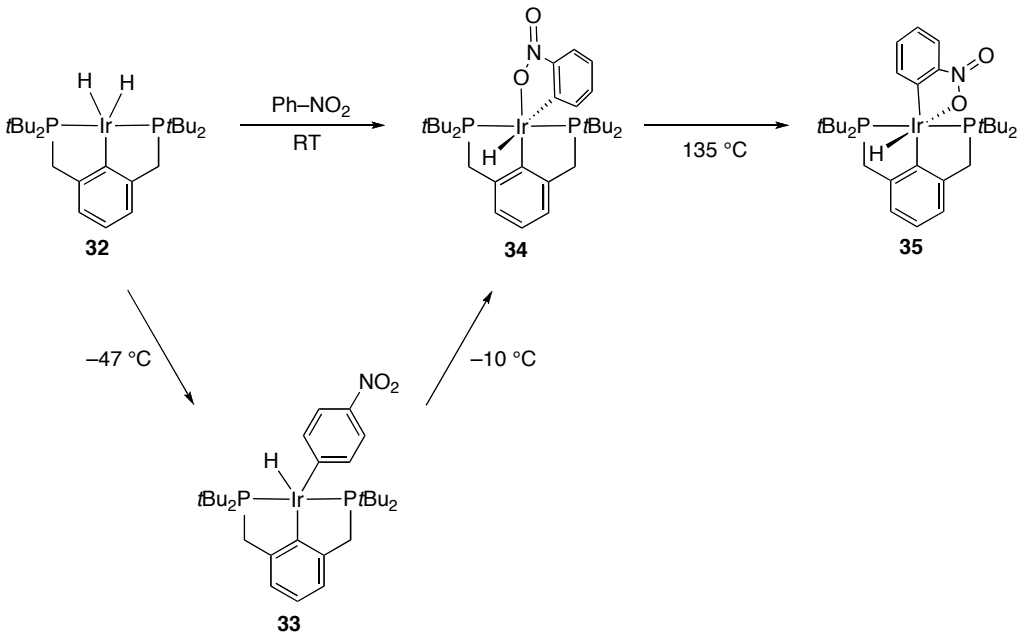
Scheme 17



3.5. Unsupported cyclometalations

While most cyclometalation reactions are identified quite readily, certain seemingly obvious cases may require caution. For example, the iridium complex **32** containing a *P,C,P*-tridentate coordinating pincer ligand reacts with nitrobenzene via C–H bond activation to give the *C,O*-iridacycle **34** (Scheme 18).[153] Product formation may point to a classical cycloiridation, albeit suffering from a relatively poor hard-soft match between the soft iridium center and the hard oxygen donor at the initial stage. This fact renders heteroatom coordination prior to the C–H bond activation step less likely, yet not impossible. Most strikingly, thermal treatment of complex **34** induces isomerization and affords complex **35,** which is thermodynamically favored because of the *trans* arrangement of the NO_2 group and the hydride, that is, the ligands with the weakest and the strongest *trans* influence, respectively. Notably, complex **35** also represents the expected product from a kinetically controlled heteroatom-assisted oxidative addition, since the aryl ligand and the hydride are in mutual *cis* configuration. These considerations paired with the propensity of the iridium complex **32** for activating C–H bonds in unfunctionalized arene substrates like benzene suggest a process for the formation of the metallacycle **34** different from classical, heteroatom-assisted cyclometalation. Low temperature experiments have indeed revealed initial C–H bond activation at the *para* position of nitrobenzene and the formation of complex **33** as a key intermediate. Hence, bond activation is sterically controlled rather than a heteroatom-assisted process. Subsequent migration of the metal center may be promoted by weak interactions between the nitro group and the metal-bound hydride and affords, eventually, the octahedral complex **34** rather than **35** directly.

Scheme 18



4. Cyclometalation using early transition metals (groups 3-5)

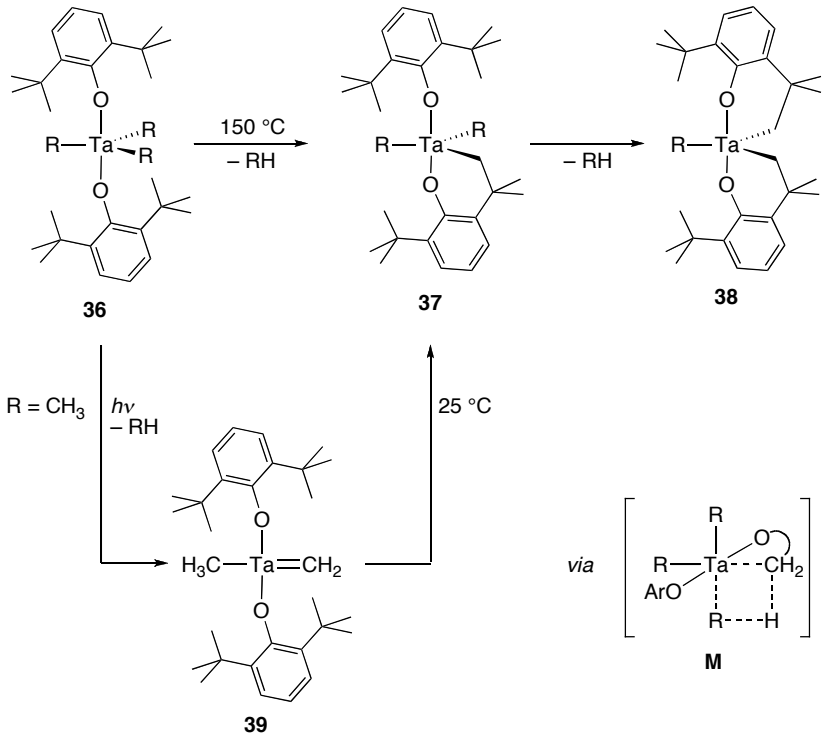
Of all d-block metals, early transition metals are generally the least prone to undergo C–H bond activation, and C–O or C–C bond cleavage has not been reported thus far as a methodology for metallacycle formation. Transmetalation reactions, in which the carbon has been previously functionalized with [MgX] or with Li constitutes the most common route for the formation of metallacycles with early d-block metals. Nevertheless, a number of cyclometalations have been disclosed, in particular using high-valent tantalum(V). Cyclometalations using other group 3–5 metals are much rarer and they usually follow the trends established for tantalum chemistry.

4.1. Tantalum

Aryloxide-assisted cyclometalation using high-valent tantalum has been studied in great detail by Rothwell and coworkers and an instructive account reviews some of the most important findings.[24] Salt metathesis between phenoxides and $TaCl_5$ as metal precursor followed by exchange of the remaining chloride ligands with a carbanion (R = methyl, benzyl) affords complex **36** which is preset for cyclometalation due to the strongly basic alkyl ligand and *t*Bu C–

H bonds in close proximity to the metal coordination sphere (Scheme 19). Upon heating complex **36**, twofold cyclometalation occurs under irreversibly elimination of two equivalents of alkane and affords the biscyclometalated complex **38** comprising two six-membered metallacycles. Mechanistic investigations — specifically the absence of any rate changes upon introducing *para*-substituents on the aryloxy-group and a significant kinetic isotope effect upon deuteration of the *t*Bu groups — support a σ-bond metathesis pathway for the C–H bond activation process. Such a mechanism involves a 4-center,4-electron transition state **M**. In agreement with the adoption of this proposed transition state, the $\Delta S^{\ddagger}$ values have been determined to be negative.[154] In addition, the orientation of the *t*Bu groups in an analog of **36** suggests that agostic interactions may be involved.[155]

Scheme 19



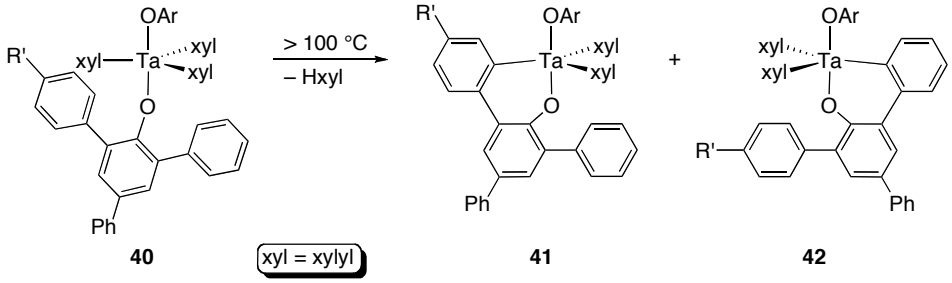
The cyclometalation reaction proceeds under significantly milder conditions, when complex **36** is photochemically activated to the corresponding alkylidene complex **39**.[156] From complex **39**, cyclometalation takes place already at room temperature (*cf.* 150 °C for the formation of **38**) and yields the monocyclometalated complex **37**. The higher propensity for cyclometalation from the alkylidene precursor has been rationalized by the fact that formation of the new Ta–C bond takes

place at the expense of a relatively weak π bond, while a stronger Ta–C_{alkyl} σ bond needs to be compensated when starting from the alkyl precursor **36**.

Upon substitution of the carbanion R in complex **37** from an alkyl to a phenyl group, cyclometalation is complicated by a secondary pathway involving first the formation of a metallacyclopropane ring resulting from *ortho* C–H bond activation of a phenyl ligand and concomitant release of benzene. Subsequent insertion of the *t*Bu group into the strained metallacycle, *i.e.* re-protonation of the *ortho*-phenylene ligand affords the final product. Deuterium labeling studies have convincingly established that this pathway co-exists with the σ-bond metathesis route.

Tantalum-mediated aryl C(sp^2)–H bond activation from the diphenyl aryloxide complex **40** proceeds similar to the C(sp^3)–H bond activation from **36** and gives the monocyclometalated complexes **41** and **42** (Scheme 20, xyl = *para*-xylyl).[157] Again, temperatures above 100 °C are required. The substituted aryl ring is preferably activated (3:1 ratio for R' = Cl, 3:2 ratio for R' = CH_3). The cyclometalation rates are slightly enhanced as compared to unsubstituted aryl rings, yet they are not significantly altered upon changing the substituents from electron-withdrawing to electron-donating groups. This latter result does not correlate with an electrophilic aromatic substitution pathway and has, instead, been rationalized in terms of ring torsion, which is smaller and hence better prearranged for cyclometalation when electroactive substituents are incorporated.

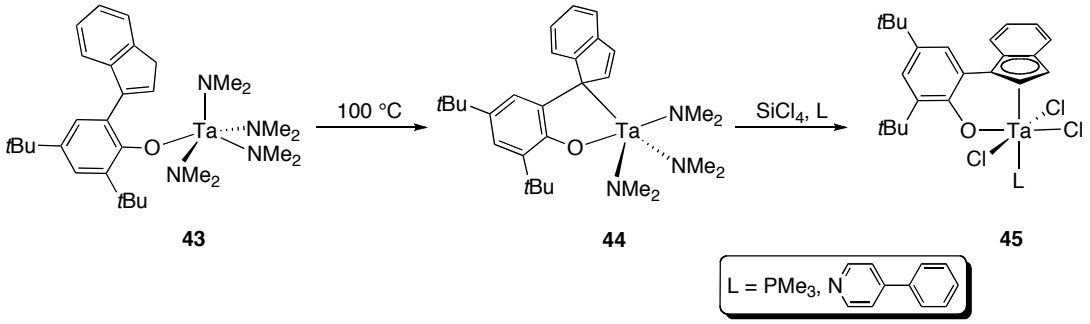
Scheme 20



40 41 42

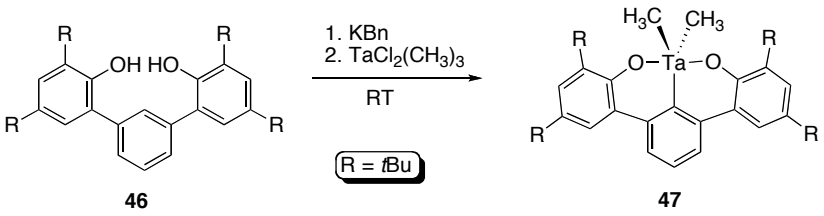
Related C–H bond activation and cyclometalation of the indenyl-functionalized aryloxide complex **43**, obtained from phenol deprotonation using $Ta(NMe_2)_5$ as precursor salt, affords the five-membered *C,O*-metallacycle **44** with an η^1-bound indenyl moiety (Scheme 21).[158] Upon reaction of this complex with $SiCl_4$ and subsequent addition of an exogenous ligand, the bonding mode of the indenyl ligand is changed from η^1 to η^5 and the octahedral complex **45** is formed.

Scheme 21



The mechanistic picture of cyclometalation using tantalum(V) precursors has recently been expanded by Bercaw and coworkers[159] using the potentially trianionic, *O,C,O*-tridentate coordinating ligand precursor **46** (Scheme 22). A salt metathesis route using KBn (Bn = benzyl) and $TaCl_2(CH_3)_3$ affords the cyclometalated complex **47** at room temperature, probably via an intermediate comprising *O,O*-bidentate ligand coordination similar to **36**. The considerably lower temperatures required to induce C–H bond activation and elimination of methane (*cf.* > 100 °C for **36** and **40**) have been ascribed to ligand chelation, which possibly locks the orientation of the central aryl ring favorably for σ-bond metathesis of [Ta–CH_3] with [C_{aryl}–H]. Crystallographic analysis of a related complex lends support to such an arrangement.

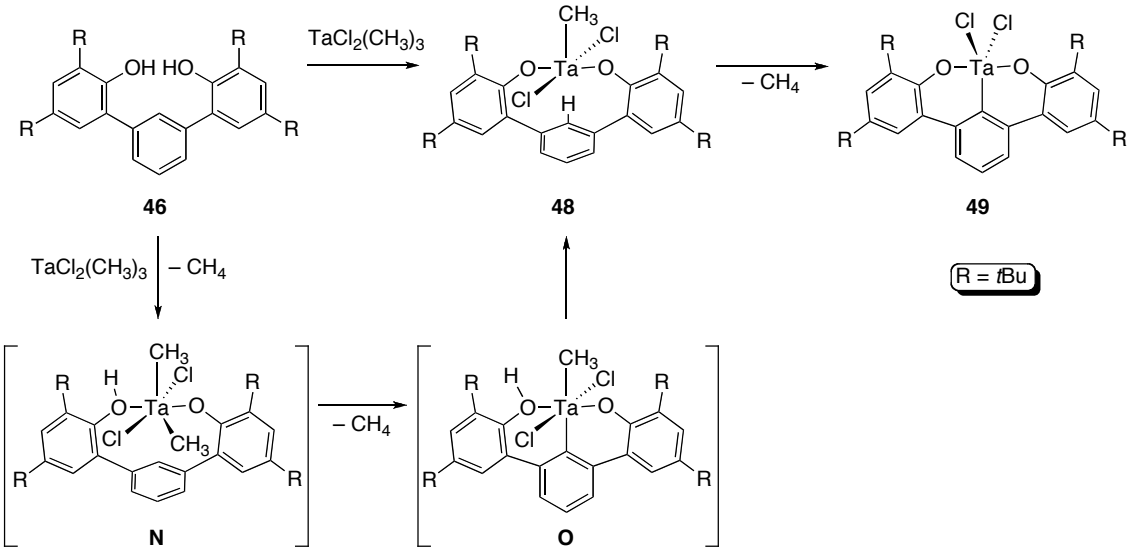
Scheme 22



Alternatively, cyclometalation has been induced by direct alkane elimination. Two molecules of methane are produced at room temperature, thus giving the coordination complex **48** (Scheme 23). This complex is pseudo-octahedral in the solid state, with the methyl group as the strongest *trans* influencing ligand *trans* to the weakly bound arene *ipso* carbon. Upon heating, cyclometalation to complex **49** proceeds in a first order reaction. Based on the small activation entropy and a moderate kinetic isotope effect (KIE = 1.6), generation of a fast pre-equilibrium has been concluded that arranges the CH_3 group *cis* to the arene *ipso* carbon, followed by rate-limiting σ-bond metathesis. Careful isotope labeling studies indicate, however, that reversible

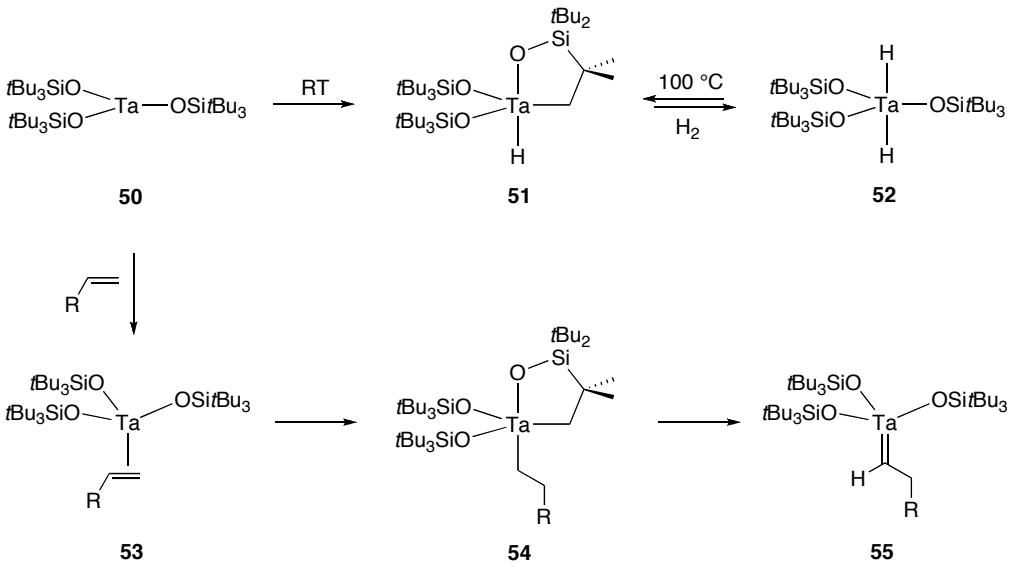
cyclometalation is already involved in the formation of **48**. The deuterium and protium contents in the products obtained from differently labeled ligand precursors consistently suggest that after deprotonation of one phenol residue, cyclometalation at the arene *ipso* carbon takes place (**O**). Selective activation of this sterically shielded C–H bond has been rationalized by a bidentate ligand bonding through an anionic aryloxide moiety and the oxygen of the neutral phenol (**N**). Subsequent protonation of the aryl ligand in intermediate **O** by the phenol then affords the coordination compound **48**. This mechanistic model suggests that cyclometalation and [C–H]/[M–CH_3] σ-bond metathesis may be faster than protonolysis, *i.e.* [O–H]/[M–CH_3] metathesis.

Scheme 23



Cyclometalation from tantalum(V) precursors bearing bulky siloxide ligands has been performed by exchanging the chloride ligands at the metal center to hydrides.[160] Thermal C_{alkyl}–H bond activation in complex **52** induces cyclometalation and affords the metallacycle **51** (Scheme 24). The reaction can be reversed upon exposing complex **51** to a moderate overpressure of H_2 (3 bar). Alternatively, complex **51** forms irreversibly from the coordinatively unsaturated tantalum(III) precursor **50**.[161]

Scheme 24



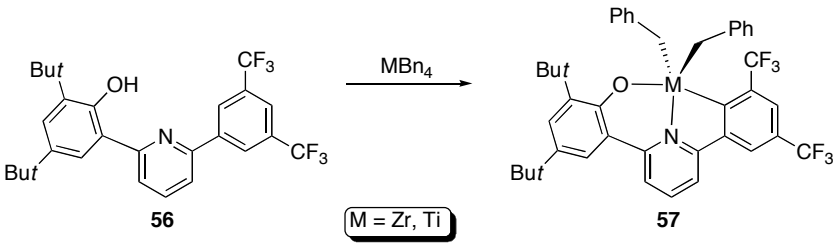
The cyclometalation can be reversed, albeit not microscopically, when an olefin ligand is available.[162] When heating complex **53**, C_{alkyl}–H bond activation takes place to give the metallacycle **54**, reminiscent to **51**, and eventually the alkylidene complex **55** (Scheme 24). Deuterium labeling experiments have revealed that the proton is selectively transferred from the *t*Bu group to the β-position of the alkyl ligand, thus supporting an olefin insertion mechanism for the transformation of the neutral alkene into an anionic alkyl ligand. Subsequent α-hydrogen elimination generates an alkylidene ligand and simultaneously cleaves the metallacycle. A direct atom transfer from one ligand to another has been convincingly ruled out as an alternative pathway. Metallacycle making and breaking is therefore related to a stepwise swap of a proton from a *t*Bu group to the alkene/alkylidene ligand.

4.2. Other early transition metals

Cyclometalations using other early transition metals have been investigated considerably less than tantalum(V). The metal precursor typically contains basic alkyl or amide ligands for scavenging the proton from C–H bond activation. In addition, the strong polarization of the M–N_{amid} and the M–C_{alkyl} bond in early transition metals presets this bond for σ-bond metathesis. For example, the polymerization catalyst precursor **57a** (M = Zr) and its titanium(IV) analog **57b** have been prepared by cyclometalation from the tetraalkyl metal precursor MBn_4 (M = Ti, Zr) comprising basic alkyl groups for σ-bond metathesis reactions (Scheme 25).[163] In these

complexes, weak interactions between the benzylic proton and a fluorine atom of the cyclometalated ligand have been established.

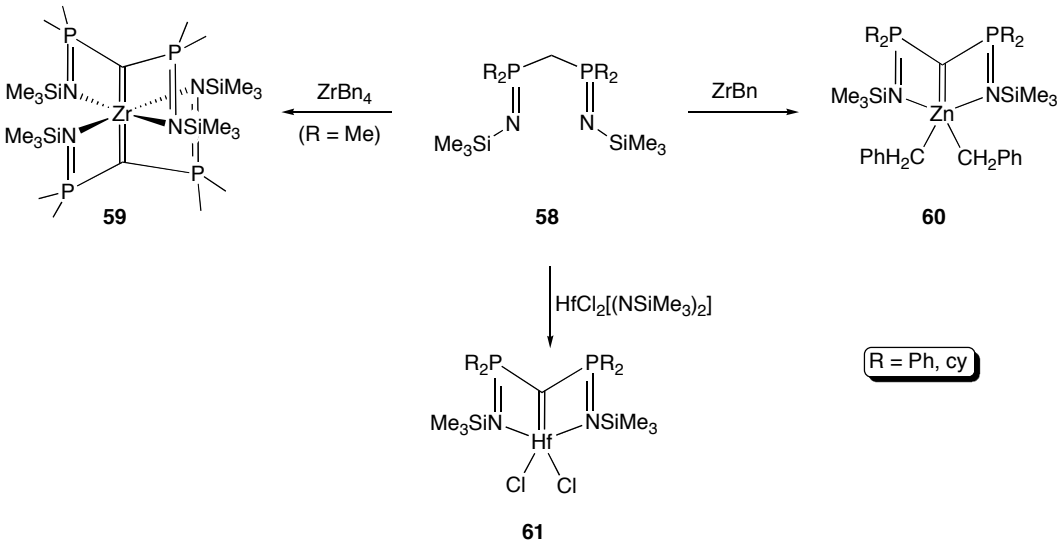
Scheme 25



56 **57**

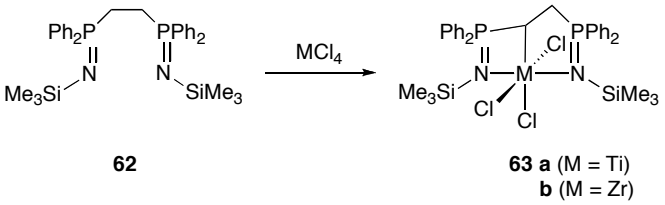
Cavell and coworkers[164] have explored the potential of the pincer ligand precursor **58** for cyclometalation reactions (Scheme 26). Upon reaction with $ZrBn_4$, cyclometalation is combined with α-hydrogen elimination, thus giving carbene complexes. Product formation is strongly depending on the substituents at phosphorus, leading either to the bis(carbene) complex **59** (R = Me),[165] or to monocarbene chelates **60** (R = Ph, cyclohexyl).[166] This selectivity indicates that steric factors may play a role, similar to the *gem*-dimethyl effect discussed in section 2. In either case, the ligand participates in two annelated four-membered metallacycles that are composed of four different elements. Related cyclometalation using the hafnium(IV) amide precursor $HfCl_2[(NSi(Me_3)_2]$ affords the corresponding monocarbene **61**.[167] The Hf=C bond in this complex, and likewise the Zr=C bond in the zirconium dichloride analog of **61** (obtained by transmetalation), participate in 1,2-additions as well as in [2+2]-cycloadditions.[168] For example, complex **61** adds CO_2, MeI, and bulky alcohols like adamantanol.

Scheme 26



The bis(iminophosphine) ligand precursor **62**, related to **59**, undergoes cyclometalation with high-valent $TiCl_4$ to form **63a**, affording simultaneously a four- and a five-membered metallacycle (Scheme 27).[169] Analogously, $ZrCl_4$ induces C–H bond activation and gives complex **63b** along with HCl rather than toluene as in the metalation of **59**.[170] Since the pincer-type ligand is meridionally coordinating in **63**, it is not surprising that the isolobal titanium(IV) precursor $TiCl_3(Cp^*)$ with a rigidly *fac*-coordinating Cp* ligand (Cp* = pentamethyl cyclopentadienyl) fails to activate the C–H bond in **62** and instead, induces dehalosilylation and N–Ti bond formation.

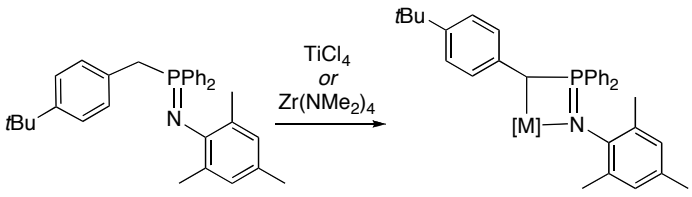
Scheme 27



Monocyclometalation involving the activation of a supposedly more activated benzylic C–H bond as in **64** proceeds only if the substituent at nitrogen is changed from $SiMe_3$ (*cf.* **62**) to mesityl (Scheme 28).[171] When using $TiCl_4$, the nitrogen-bound coordination compound preceding the C–H bond activation step has been characterized. At room temperature, this intermediate is unstable and cyclometalates under elimination of HCl, thus giving complex **65**. Similar cyclometalation with zirconium requires elevated temperatures (110 °C) and is only successful when $Zr(NMe_2)_4$ is used as metal precursor. Notably, a six-membered *C,N*-metallacycle

originating form aryl C–H bond activation has also been observed. Both the cyclometalated titanium(IV) and zirconium(IV) complexes display modest activity in ethane polymerization when activated with methylaluminoxane.

Scheme 28



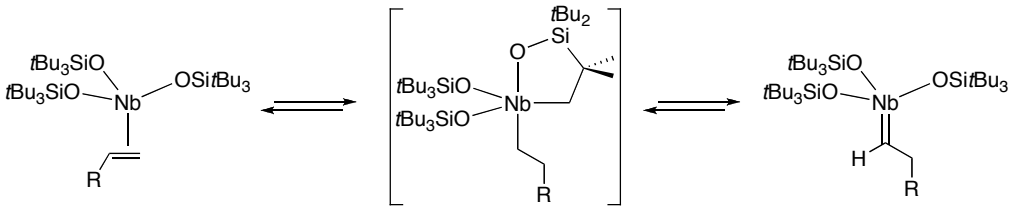
64 **65**

[M] = $TiCl_3$, $Zr(NMe_2)_3$

Cyclometalation using niobium is rare. In an attempt to expand the chemistry of tantalum to niobium(V), aryl C–H activation has been observed from a niobium alkoxide complex analogous to **40** (*cf.* Scheme 20).[157] Bond activation is faster than with tantalum(V), however product mixtures are obtained and pure complexes similar to **41** have not been isolated and characterized thus far.

In complex **66**, featuring a sterically crowded niobium coordination sphere and a *tert*-butyl ethylene (tbe) as potent H_2 acceptor, monocyclometalation involving C_{alkyl}–H bond activation in one *t*Bu substituent at silicon takes place, thus giving the five-membered metallacycle **67** (Scheme 29).[162] Complex **67** has been identified despite its instability to spontaneously rearrange to the alkylidene complex **68**. The reactivity, and presumably also the mechanism, is highly reminiscent to that observed for related tantalum complexes (*cf.* Scheme 24) and the hydrogen from C–H bond cleavage is formally not released, but transferred intramolecularly to the hydrogen acceptor olefin. In contrast to tantalum chemistry, the cyclometalated intermediate is typically not detectable in niobium-mediated olefin-to-alkylidene transformations. Complex **67** is an exception due in parts to the specific properties of tbe as olefin.

Scheme 29



66 **67** **68**

only observed for
R = *t*Bu

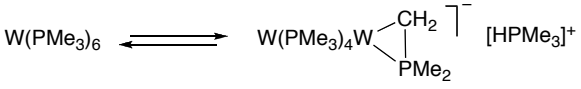
5. Cyclometalation using group 6 and group 7 metals

Little is known on cyclometalation using chromium and molybdenum.[172,173] Because of their versatile carbene and insertion chemistry evolving from the corresponding carbonyl and cyanide precursors, the most convenient access to metallacyclic complexes undoubtedly consists of insertion reactions rather than C–H bond activation. To the best of our knowledge, technetium has not been employed for cyclometalation reactions thus far.

5.1. Tungsten

Cyclometalation with group 6 metals has not been a particularly active field of research in the last years. In contrast to cyclometalations using early transition metals, the scattered reports on tungsten chemistry involve a low-valent configuration at the metal center. For example, the tungsten(0) complex $W(PMe_3)_6$ reversibly cyclometalates upon dissociation of one phosphine ligand and affords **69** (Scheme 30).[174]

Scheme 30

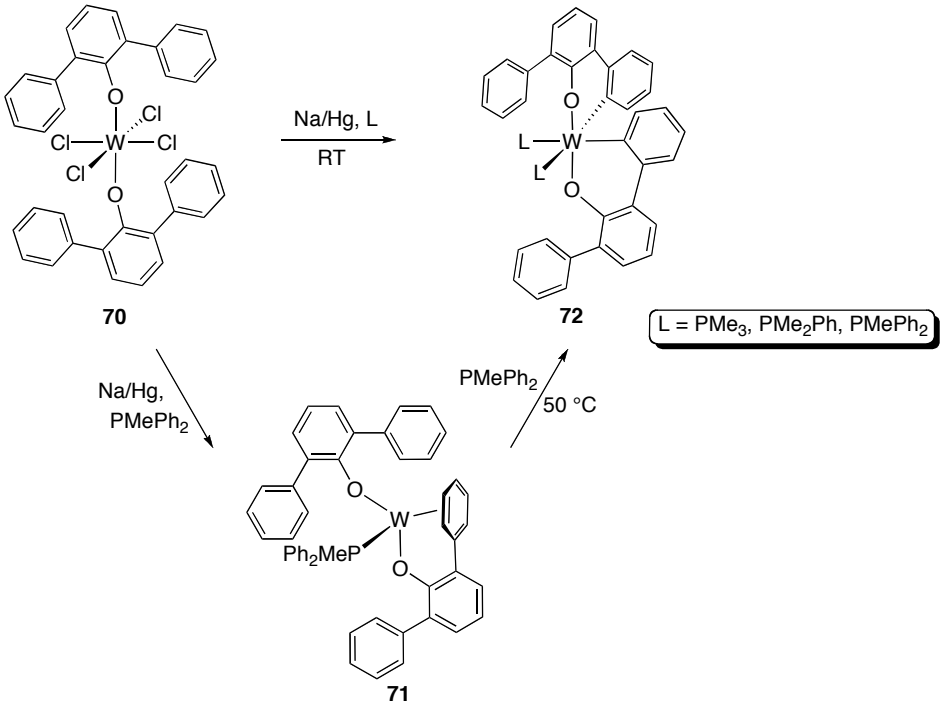


69

In line with these valence considerations, the tungsten(IV) center in complex **70** needs to be reduced first in order to activate a C_{aryl}–H bond (Scheme 31).[175] Formation of the doubly cyclometalated complex **72** has been suggested to be a stepwise process. The π complex **71** containing an η^6–bound phenyl residue has been isolated and characterized. This complex cyclometalates, presumably via a tungsten(IV) hydride, to finally give the biscyclometalated complex **72**. Dihydrogen has been identified as a secondary product of this reaction. The elevated

temperature required for the cyclometalation when starting from **71** indicates that this complex represents a side-product rather than a true intermediate in the cyclometalation of **70**.

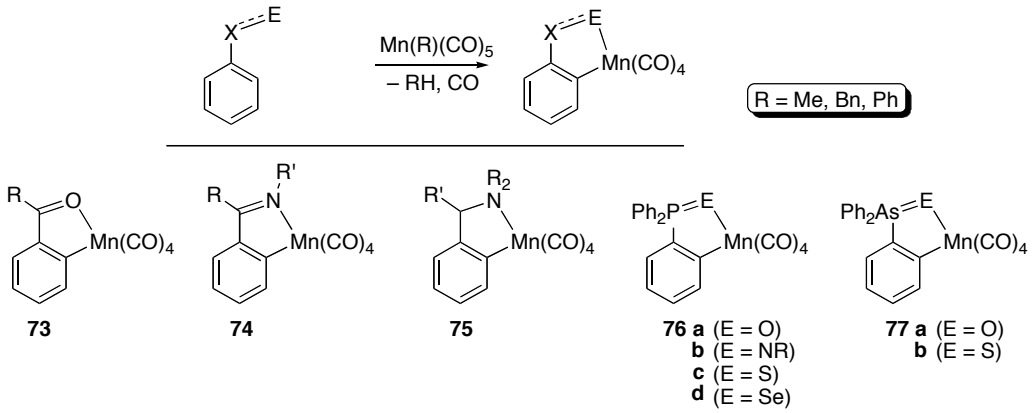
Scheme 31



5.2. Manganese

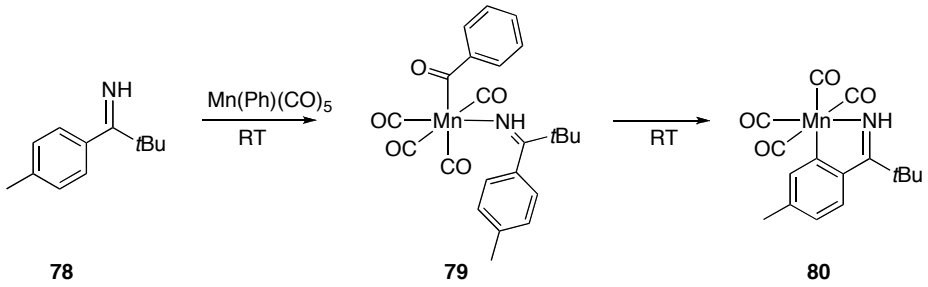
Cyclomanganation has been known for over 40 years.[176,177] The largest body of research encompasses the activation of C_{aryl}–H bonds of arenes and heteroarenes by using the manganese(I) precursor $Mn(R)(CO)_5$ (R = CH_3, Bn, Ph),[178] though C_{benzyl}–H bond activation is also known.[179] This precursor combines labile CO ligands for heteroatom coordination and a basic proton acceptor in order to assemble the metal and the C–H bond. A variety of donor groups have been employed, including carbonyl oxygens, imines, and P=E donors (E = NR, O, S, Se; **73–77** in Scheme 32).[180–183]

Scheme 32



Mechanistically, insertion of a carbonyl ligand into the Mn–R bond is likely to initiate the cyclometalation process in the presence of a donor ligand. The corresponding acyl product has been observed in the reaction of the imine **78** with $Mn(Ph)(CO)_5$ (Scheme 33).[184] Thermally induced C–H bond activation in **79** then produces the manganacycle **80**. Recent studies suggest that the C–H bond activation step involves a four-centered transition state derived from mutual interactions of the $Mn–C_{acyl}$ and the $C_{aryl}–H$ bonds,[185] though at present, no evidence is available as to whether the bond activation occurs via direct interligand hydrogen transfer, via an oxidative addition – reductive elimination cycle, via a substitution mechanism, or perhaps via σ-bond metathesis.

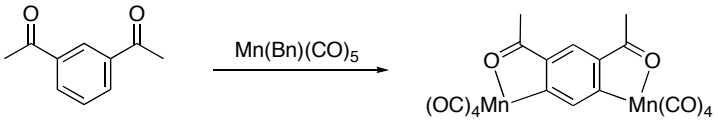
Scheme 33



The influence of aryl substituents on the ligand precursor has been discussed contradictorily. An early report indicates that electron-withdrawing substituents favor cyclometalation,[186] while more recent studies on a series of imine ligand precursor suggest rate-enhanced cyclomanganation with more electron-rich ligands.[187] Competitive cyclometalation experiments using differently substituted amine-containing ligand precursors with a $Cr(CO)_3$ unit bound to the arene have shown that the preference for manganation is not correlated with electronic effects of the substituents, which may indicate a multicenter metalation process.[188] If the ligand bears two

donor sites as in **81**, double cyclometalation takes place to give the bimetallic complex **82** (Scheme 34),[189] suggesting that cyclomanganation is electronically favored rather than hampered by the presence of a $Mn(CO)_4$ substituent at the arene. Such bimetallic synthons have been used to construct helical systems.[190,191]

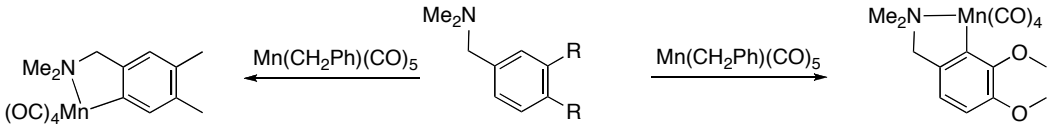
Scheme 34



81 **82**

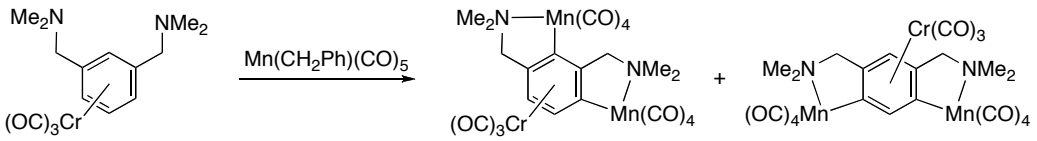
Steric influences have been investigated with benzylamine ligand precursors **83** (Scheme 35).[181] Substitution of the *meta* position with a CH_3 group directs the cyclomanganation to the sterically least shielded *ortho,para* position and affords the manganacycle **84**. In contrast, methoxy-substituents lead preferentially to the *ortho,ortho*-metalated complex **85**. In the solid state, favorable $O_{OMe}\cdots C_{CO}$ interactions have been identified. In addition, weak *N,O*-bidentate chelation of the manganese(I) precursor may direct the metalation to the *ortho,ortho* position. Such interactions may also account for the product distribution upon cyclomanganation of the *N,C,N* pincer precursor **86** (Scheme 36).[188] Double metalation has been observed independent of the ligand/metal stoichiometry, and complex **87** is in all cases the major product, while the sterically less hindered complex **88** forms only in minor quantities.

Scheme 35



84 **83 a** (R = CH_3) **b** (R = OCH_3) **85**

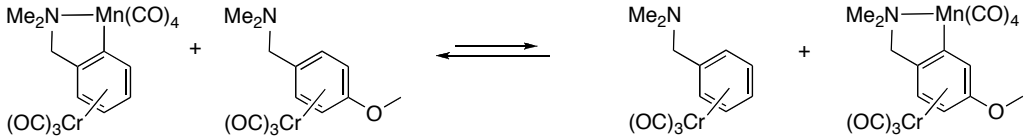
Scheme 36



86 **87** *major* **88** *minor*

In a series of reports, Pfeffer and coworkers investigated the synthesis and reactivity of cyclomanganated complexes bearing chromium(tricarbonyl) substituents at the arene fragment.[188,192,193] Despite the fact that the $Cr(CO)_3$ unit inverts the reactivity pattern of the arene and allows, for example, for nucleophilic rather than electrophilic substitutions, cyclometalation proceeds smoothly in refluxing heptane. A variety of bimetallic chromium-manganese complexes as well as trimetallic $CrMn_2$ systems (*cf.* **87**, Scheme 36) have thus been obtained.
Despite of the chelate effect, the Mn–C bond in these metallacycles is relatively labile. For example, insertion of acetylenes, carbenes, or SO_2 into the Mn–C bond have been observed.[194–197] Similarly, ICl successfully cleaves the Mn–C bond, providing a methodology for synthesizing aryl iodides.[198] Furthermore, evidence has been provided that the manganation is, to some extent, a reversible process.[181] Reversible C–H bond activation is further supported by the propensity of cyclomanganated complexes to engage in transcyclometalations (*cf.* section 3.4).[199] For example, exposure of complex **89** to the ligand precursor **90** affords after few hours a *ca.* 2:1 mixture of complexes **89** and **92** (Scheme 37). The ratio changes to 2:3 when complex **92** and the ligand precursor **91** were used as starting materials. The different ratios may reflect different reactivities of the complexes or just the fact that the equilibrium situation has not been reached yet. A likely mechanistic proposal is based on the reversible decoordination of one of the CO ligands from manganese and coordination of the amine of the ligand precursor. Subsequent hydrogen transfer from the non-cyclometalated to the cyclometalated ligand followed by decoordination of the originally bound ligand and CO re-coordination produces the new cyclometalated complex. The hydrogen transfer is expected to be fully reversible, and hence, product distributions should be thermodynamically controlled.

Scheme 37

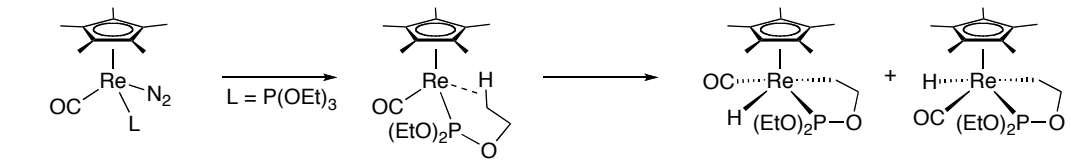


5.3. Rhenium

Cyclometalation using rhenium has grown concurrently with cyclomanganation.[179,200–204] To some degree, this parallel development may originate from the similarity of the most frequently

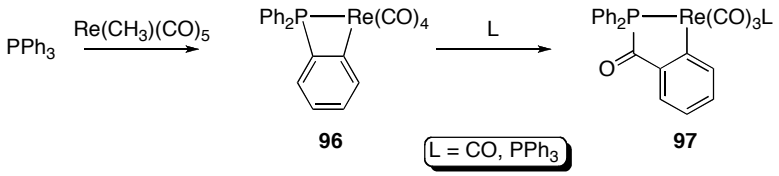
employed metal precursors. The rhenium(I) precursors of the general formulae $Re(X)(CO)_5$ (X = H, Me, also Cl, Br) are structurally and in terms of reactivity closely related to the manganese(I) precursors discussed in the previous section. The complex $Re(Cp)L_3$ (L = CO, PMe_3, or a mixture thereof) constitutes another useful precursor for cyclorhenation,[205] which can be activated photolytically. Irradiation induces the dissociation of one ligand L, thus creating a vacant coordination site for the coordination of an exogenous ligand. In the absence of exogenous ligands, either solvent C–H bond activation takes place,[205] or cyclometalation of a coordinating ligand in the transient, coordinatively unsaturated intermediate $Re(Cp^*)(PMe_3)_2$ to form a three membered *P,C*-metallacycle.[206] Strongly related to this outcome, photochemical elimination of the dinitrogen ligand from $Re(Cp^*)(CO)(N_2)L$ (**93**; L = PR_3, $P(OR)_3$) has been shown to induce cyclometalation of the phosphine or the phosphite ligand (Scheme 38).[207] According to detailed solution analyses, an agostic species **94** is initially formed in solution.[208] Subsequent C–H bond cleavage produces then the four-legged piano-stool complex **95** as a mixture of *cis* and *trans* isomers. Interestingly, the C–H bond activation pathway prevails even in the presence of chlorobenzene, when the starting complex **93** contains a $P(OPh)_3$ as ligand L, while rhenium complexes with different phosphites like $P(OEt)_3$ or $P(OMe)_3$ or with phosphine ligands promote oxidative C_{aryl}–Cl bond activation.[209]

Scheme 38



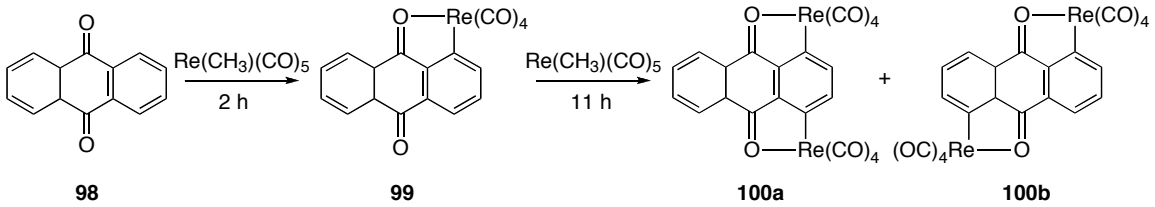
Generally, five-membered rhenacycles are the preferred products. For example, cyclometalation of PPh_3 with $Re(Me)(CO)_5$ initially gives the four-membered metallacycle **96**, which undergoes spontaneous CO insertion into the Re–C bond to give the five-membered metallacycle **97** (Scheme 39).[210] Similarly, $P(o\text{-tol})_3$ is cyclometalated via $C(sp^3)$–H bond activation in one methyl group,[211] rather than through C_{aryl}–H bond activation.

Scheme 39



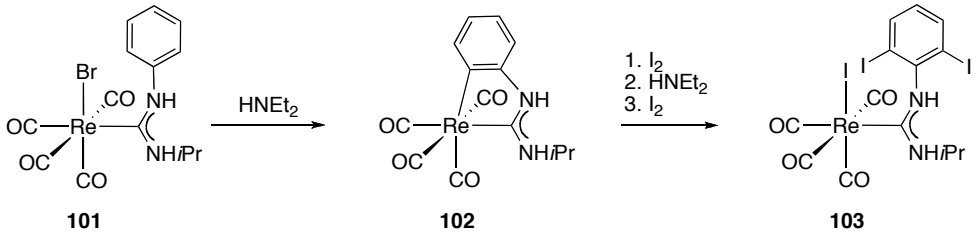
A variety of ligands have been employed for cyclorhenation, including N, O, P, and S donors. Ligands with two donor sites such as anthraquinone (**98**) have been metalated twice in a stepwise procedure, thus leading first to the mono-rhenium complex **99** (Scheme 40). Upon reaction of a second equivalent of the metal precursor at higher temperatures, the biscyclometalated complex **100** is obtained, whose isomeric structures are distinguished by different spectroscopic absorption properties.

Scheme 40



The diaminocarbene in complex **101** is a special donor type, since the donor group E is installed by a bond with considerably more covalent character than purely coordinating donor groups. In the presence of a secondary amine base, C–H bond activation in the phenyl substituent and formation of the cyclometalated complex **102** takes place (Scheme 41).[212] Notably, the chelate is readily cleaved by acids HX or by I_2, the latter providing a methodology for iodinating the phenyl substituents selectively in *ortho* position to give complex **103**.

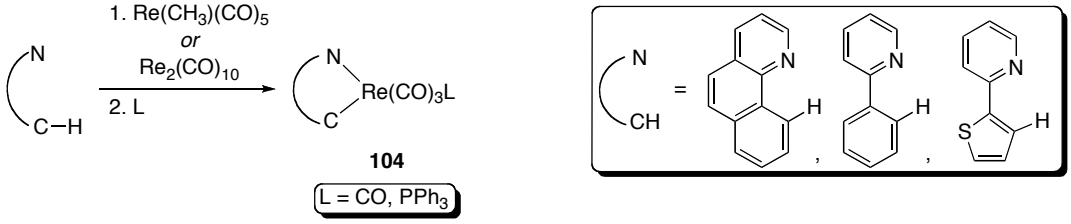
Scheme 41



The interest in cyclometalated rhenium(I) complexes has recently been revived through the discovery of luminescent properties in species like **104** (Scheme 42).[213] The excited state properties were investigated by high-resolution optical spectroscopy in a variety of *C,N*-

rhenacycles.[214,215] The first excited state has been identified as a ligand-centered $^3\pi$–π^* state with only little ^{1}MLCT character. A CH_3 group on the *ortho* position of the pyridine ring has only little impact on the excited state properties.[216] Lifetimes are generally short, about 100 ms at 10 K.

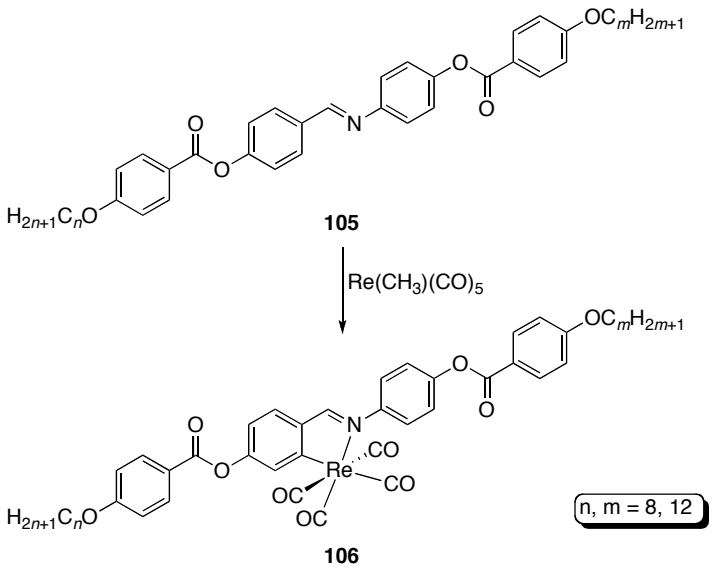
Scheme 42



Related complexes from cyclometalation of a monoanionic *N,C,N*-tridentate pincer-type ligand precursor with $Re(CH_3)(CO)_5$ feature green emission in THF solution at room temperature and orange emission in the solid state.[217] Calculations suggest that in this case, the emission is due to a d(Re)–π^*(ligand) MLCT excited state.

Complexes **106**, obtained by cyclometalation of the corresponding ligand precursors **105** with $Re(CH_3)(CO)_5$ are birefringent and display nematic phases above 100 °C (Scheme 43).[218] Liquid crystalline properties are only present in a relatively narrow temperature window (5–35 °C), depending on the substitution pattern at the termini and at the aromatic sites of the ligand. Smectic phases as observed in the ligand precursor **105** are suppressed upon cyclometalation.

Scheme 43



6. Cyclometalations using late transition metals (groups 8-10)

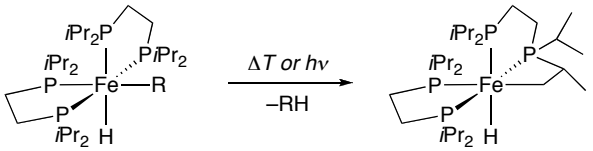
6.1. First row metals

6.1.1. Iron

Despite the fact that iron plays a prominent role in many biological C–H bond activation processes, studies on cyclometalation using iron have remained remarkably scarce. While the first reports on iron-mediated C–H bond activation were amongst the first reports on cyclometalation generally,[219,220] the reaction has never been widely applied. Various reasons may account for this lack, *inter alia* the low tendency of iron — especially in its most stable oxidation states +2 and +3 — to engage in σ-bond metathesis or two-electron oxidative addition reactions, the low stability of the Fe–C bond, even when stabilized through multidentate chelates, and the availability of efficient transmetalation protocols similar to the chemistry of early transition metals.

Early reports have demonstrated that iron(0) precursors can undergo oxidative addition reactions to give cyclometalated products. For example, *in situ* reduction of iron in the phosphine-containing complex **107** by photolytic elimination of H_2 (R = H), or by thermal elimination of methane (R = CH_3) induces cyclometalation and formation of **108** via activation of a C–H bond of the *i*Pr substituent at phosphorus (Scheme 44).[221] Similar cyclometalation has been observed with CH_3 substituents at phosphorus, leading to a strained three-membered metallacycle,[222] and by C_{aryl}–H bond activation in diphenylphosphine groups.[223]

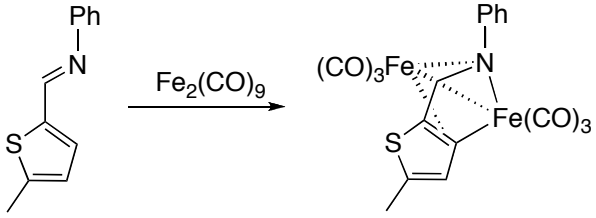
Scheme 44



107 **108**

Other zero-valent iron precursors for cyclometalation include the carbonyl compounds $Fe(CO)_5$ and $Fe_2(CO)_9$. The diiron precursor activates C–H bonds in a variety of Schiff'base heterocycles.[224–227] While typically, several products are formed, the Fe–Fe bond is preserved in the cyclometalated complex. For example, the thienyl Schiff base **109** undergoes C–H bond activation with formal transfer of the hydrogen from the heterocycle to the imine carbon, thus transforming the imine into a monoanionic amide ligand that adopts a μ^2 coordination mode and stabilizes both iron centers in **110** (Scheme 45). Similar reactivities have been established for pyrrole and pyridine ligand precursors functionalized with imine or diazo groups.

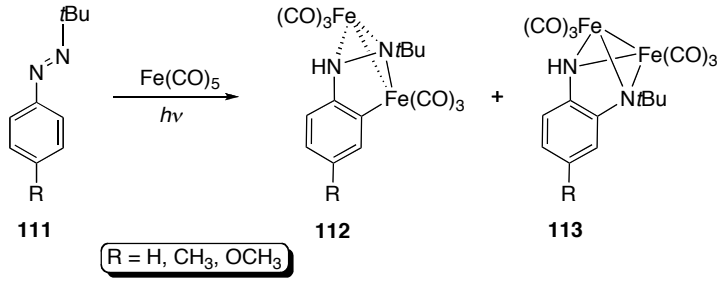
Scheme 45



109 **110**

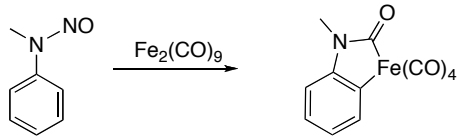
It has been noted that C_{aryl}–H bond activation in the diazo ligand **111** proceeds much cleaner when $Fe(CO)_5$ rather than $Fe_2(CO)_9$ is used for cyclometalation (Scheme 46).[228] The diiron complex **112** is obtained along with the coordination compound **113** resulting from N=N bond cleavage. The product distribution is strongly affected by the aryl substituent. A methoxy group favors the formation of **113** while a methyl substituent leads to the almost exclusive formation of the cyclometalated complex **112**.

Scheme 46



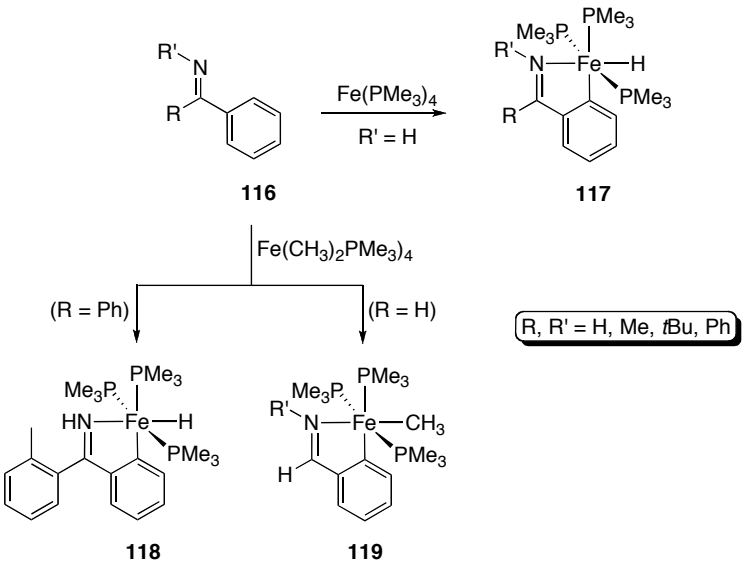
Cleavage of the Fe–Fe bond occurs in the cyclometalation of the *N*-methyl-*N*-nitrosoaniline **114** (Scheme 47).[229] The five-membered metallacycle in **115** originates from CO insertion into the originally formed Fe–N bond.

Scheme 47



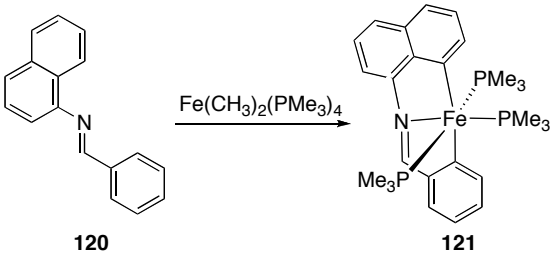
Recently, the basic complex $Fe(PMe_3)_4$ and its octahedral precursor $Fe(CH_3)_2(PMe_3)_4$ have been discovered as powerful reagents for cyclometalation reactions.[230–233] Oxidative addition of aryl imines such as **116** to $Fe(PMe_3)_4$ affords cyclometalated, thermally stable complexes **117** with an iron-bound hydride (Scheme 48).[230] When using $Fe(CH_3)_2(PMe_3)_4$ as metal precursor, cyclometalation produces a complex **118**, in which one phenyl ring is metal-bound and the other is substituted by a methyl group.[231] A likely pathway for this result involves initial cyclometalation of one phenyl ring, thus leading to an iron(II) intermediate comprising a CH_3 and a phenyl ligand. Reductive C–C bond formation then creates an iron(0) species that can activate the C_{aryl}–H bond of the second phenyl residue by oxidative addition. Remarkably, a similar reductive elimination of the carbon ligands is suppressed when simple benzylideneimines (**116**, R = H) or phosphines[232] are used, and the reaction stops after the first cyclometalation. Both, the iron-bound hydrogen in **117** and **118** as well as the CH_3 group in **119** can be substituted by iodide from CH_3I with concomitant elimination of methane and ethane, respectively.

Scheme 48



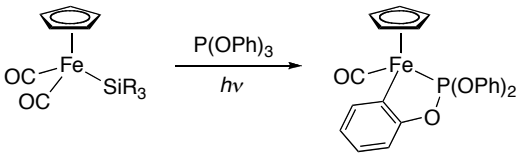
Double C–H bond activation rather than reductive elimination has been observed with ligand precursors that possess two C–H bonds close to the metal coordination sphere in the precoordination complex.[234] For example, imine **120** reacts with $Fe(CH_3)_2(PMe_3)_4$ to give the doubly cyclometalated complex **121** with a dianionic *C,N,C*-tridentate coordinating ligand (Scheme 49). Similar double cyclometalation has been noted also with vinyl C–H bonds.

Scheme 49



Photochemical activation of a labile ligand in half-sandwich Fe(Cp) complexes provides another access to create vacant coordination sites at iron and to induce cyclometalation. Irradiation of $Fe(Cp)(CO)_2(SiR_3)$, **122**, in the presence of $P(OPh)_3$ substitutes one CO ligand by a phosphite ligand (Scheme 50).[235] Due to the basicity of the silyl ligand, C–H bond activation is initiated, thus providing the cyclometalated complex **123** and silane. The reaction is of considerable scope and different phosphines and even $AsPh_3$ have been cyclometalated to obtain four-, five- and six-membered metallacycles.[173]

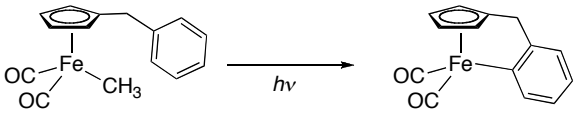
Scheme 50



122 **123**

An analogous C–H bond activation trajectory has been observed for diazo arenes when using the methyl homolog of **122**, *i.e.* $Fe(Cp)(CO)_2(CH_3)$ (**124**, Scheme 51). Functionalization of the Cp ligand with a benzyl group allows for intramolecular C–H bond activation, thus providing the chelate **125**.[236] In this case, the Cp ligand fulfills the role of the donor group in preorganizing the coordinatively unsaturated metal center and the C_{aryl}–H bond in close proximity after photolytic Fe–CO bond cleavage.

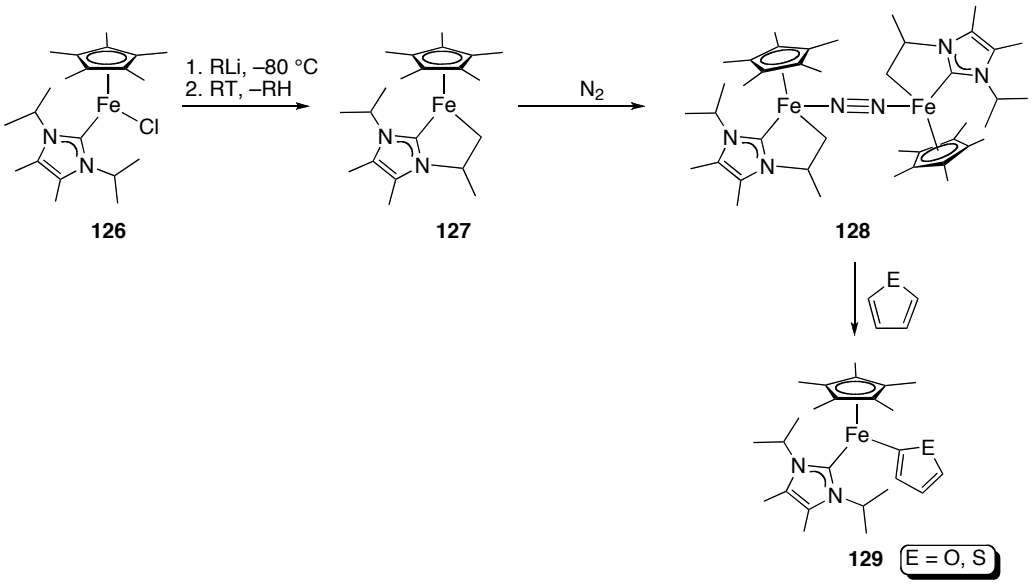
Scheme 51



124 **125**

Related to this cyclometalation process, C–H bond activation in the *i*Pr wingtip of the *N*-heterocyclic carbene ligand occurs in the coordinatively unsaturated complex **126** (Scheme 52).[237] Similar bond activation has been noted for mesityl wingtip groups. Exchange of the halide in **126** to a more basic methyl or phenyl ligand is essential to induce cyclometalation and formation of **127**. This complex spontaneously binds N_2 and forms a dinuclear adduct **128**. Addition of a heteroarene like pyridine, thiophene, or furane cleaves the dinuclear complex and induces C–H bond activation in the heterocycle. Formal hydrogen transfer to the carbene wingtip group opens the metallacycle and regenerates the monodentate bonding mode of the *N*-heterocyclic carbene ligand in complex **129**.

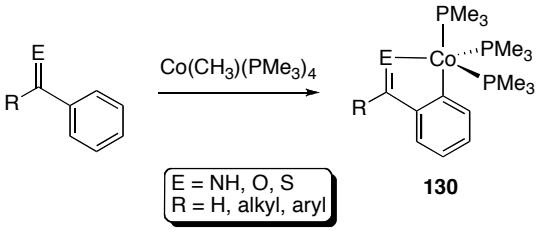
Scheme 52



6.1.2. Cobalt

Cobaltacycles are typically prepared by transmetalation reactions. The use of C–H bond activation methodologies is much less frequent. Klein and coworkers have exploited $Co(CH_3)(PMe_3)_4$ as metal precursor for the cyclometalation of a variety of ligands. Aryl ketones,[238] imines including azobenzene,[230,239] and thioketones[240] successfully undergo C–H activation, typically at temperatures around –70 °C, and give the corresponding five-membered cobaltacycles **130** (Scheme 53). When using benzylsulfides as donors, oxidative addition of the S–C_{benzyl} bond is observed, thus affording a cobalt(III)-containing *C,S*-metallacycle.[241]

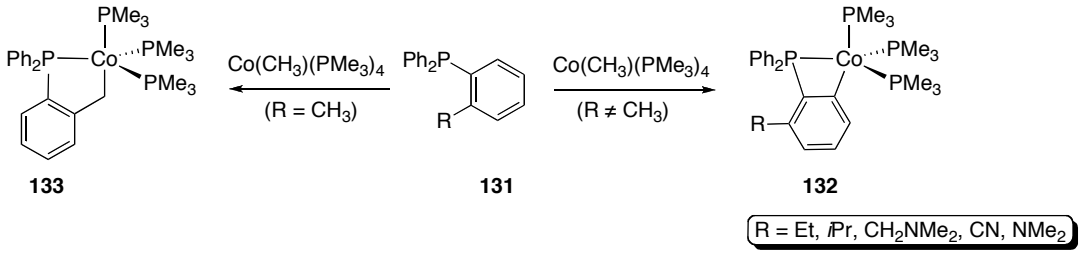
Scheme 53



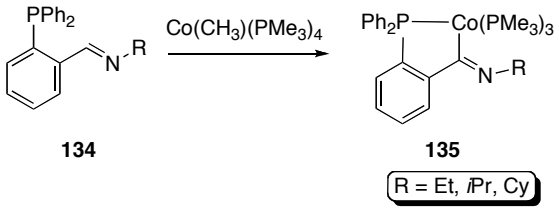
Phosphine ligands may form four-, five-, or six-membered metallacycles with $Co(CH_3)(PMe_3)_4$.[242–244] Variation of the substituent R in **131** indicates that electronic effects are small and do not modify the course of the reaction significantly (Scheme 54). Steric influences play a more dominant role. Thus, *ortho*-alkylation of one aryl ring in PPh_3 leads to four-membered metallacycle products **132**, if the substituent is different from a CH_3 group, and only

P(*o*-tol)(Ph)$_2$ produces a five-membered cobaltacycle **133** originating from C(sp^3)–H bond activation. Similarly, substitution of the imine nitrogen in **134** with a bulky *t*Bu group prevents activation of the C_{imine}–H bond and gives a four-membered metallacycle due to C_{aryl}–H bond cleavage in analogy to complex **132**. With less demanding substituents cyclometalation involves C–H bond activation at the benzylic position and affords the five-membered metallacycle **135** (Scheme 55).[245] The four-membered cycles readily insert CO into the Co–C bond. The five- and six-membered analogs lack such reactivity and instead, CO substitutes one of the PMe_3 ligands at cobalt. Furthermore, C(sp^3)–H bond activation in tetrahydronaphthyl phosphine requires considerably higher reaction temperatures than C(sp^2)–H bond activation in the corresponding naphthyl phosphine precursor.[246] All complexes produce pentacoordinate cobalt complexes which have, according to X-ray analyses and phosphorus coupling constants, persistent trigonal bipyramidal geometry with the carbanionic ligand and one PMe_3 ligand in the apical positions.

Scheme 54



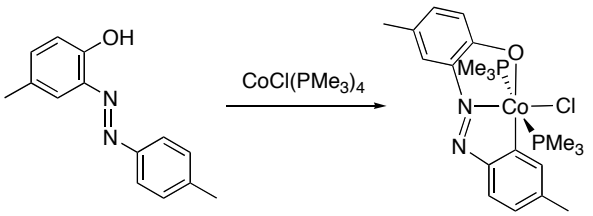
Scheme 55



Cyclometalation of the potentially *C,N,O*-tridentate ligand precursor **136** has been successfully performed using $CoCl(PMe_3)_4$ as precursor salt (Scheme 56).[247] The mechanism leading to the cobalt(III) complex **137** has been suggested to involve one sacrificial ligand equivalent that is cleaved into two aniline portions in order to scavenge the equivalent of H_2 that is formally produced upon O–H and C–H bond activation. Cyclometalated cobalt(III) complexes are also accessible by C–H bond activation with $Co(Cp)(PPh_3)I_2$.[248] When using this methodology,

addition of $AgBF_4$ is essential for creating an available site at the metal center for coordination of the donor group E.

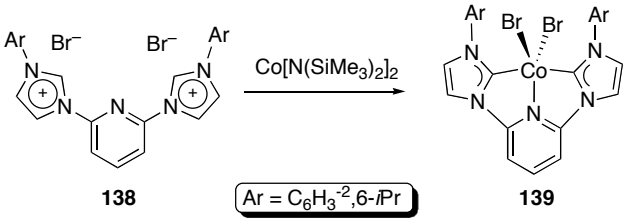
Scheme 56



136 **137**

The cobalt(II) complex $Co[N(SiMe_3)_2]_2$ has been employed for the cyclometalation of the *N*-heterocyclic carbene precursor **138** to yield the doubly cyclometalated dicarbene complex **139** (Scheme 57).[249] It is unclear whether the C–H bond activation is metal-mediated or a base-induced process, since the free $[N(SiMe_3)_2]_2^-$ anion is known to deprotonate imidazolium salts.

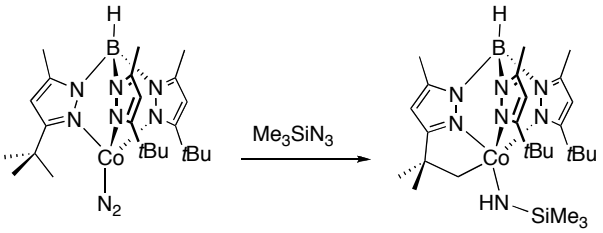
Scheme 57



138 **139**

Cobalt-mediated C–H bond activation has been observed occasionally in constrained ligands that are precoordinated to the metal center. For example, the tris(pyrazole)borate complex **140** bearing *t*Bu substituents reacts with Me_3SiN_3 to yield complex **141**, a rare five-coordinate cobalt(III) complex, in which one of the *t*Bu groups is cyclometalated (Scheme 58).[250] The reaction includes the liberation of N_2 and, formally, hydrogen atom transfer from a *t*Bu group to the nitrogen of an imido intermediate, thus stabilizing the resulting alkyl radical by formation of a Co–C bond. The relevance of radicals in this process is further underlined by the fact that *i*Pr substituents at the pyrazole do not give cyclometalated products but instead dimeric structures resulting from coupling of two methine carbons.

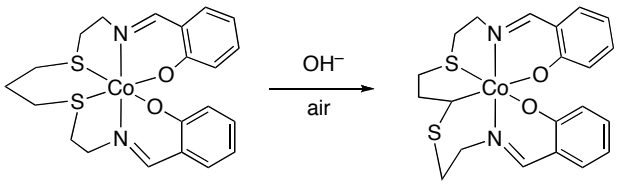
Scheme 58



140 **141**

Another constrained ligand environment has been generated in hexacoordinate ligands containing two salen units interlinked by a dithioether group, *e.g.* complex **142** (Scheme 59).[251] In the presence of a base, the dithioether moiety of this ligand rearranges within the cobalt coordination sphere and transforms from a *S,S*-bidentate coordination mode to a cyclometalated species **143** under concomitant oxidation of cobalt from formally +II to +III. A driving force for this process may be the formation of a five-membered rather than a six-membered metallacycle, which is supposed to release strain in the hexadentate ligand. In agreement with this proposal, ethylene-bridged dithioethers do not undergo any C–H bond activation. Complexes similar to **142** featuring different types of oxygen donors or having the oxygen donors replaced by pyrazines show a similar tendency for cyclometalation if the thioether groups are interconnected with a propylene linker.[252,253]

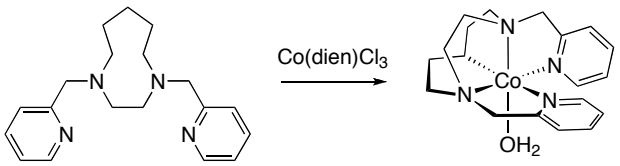
Scheme 59



142 **143**

The cobalt-mediated activation of unfunctionalized C_{alkyl}–H bonds has been successfully achieved in the constrained ligand **144** (Scheme 60).[254] Using either the cobalt(III) precursor Co(dien)Cl_3 (dien = diaminoethylene), or the hydrate of $CoCl_2$ in combination with O_2 affords the cobalt(III) complex **145** comprising a C_{alkyl}–Co bond and metallacycles that are exclusively five-membered.

Scheme 60



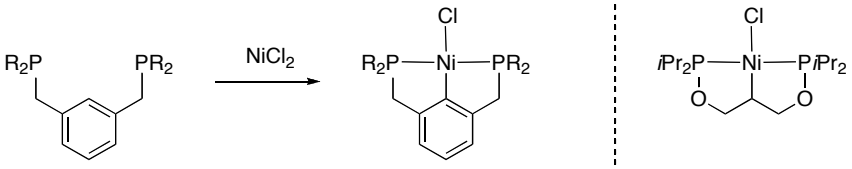
144 145

6.1.3. Nickel

Nickel occupies a special place in the historical development of the cyclometalation reaction since the first report on a cyclometalation reaction covers the cyclonickelation of azobenzene with $Ni(Cp)_2$.[4] Despite this hallmark, oxidative addition and transmetalation have become the preferred routes to nickelacycles, akin to most other d-block metals of the first row. Apart from slight variations in the Cp unit or the azobenzene skeleton,[255,256] nickelocenes have received only minor attention as precursors for cyclometalation.

Nickelacycles **146** have been prepared by C–H activation from pincer-type potentially *P,C,P*-tridentate coordinating ligand precursors **26** by using NiX_2 (Scheme 61),[107] either as hydrate or as an anhydrous $NiX_2(solv)_2$ complex (X = Cl, Br; solv = THF, MeCN). Various phosphine substituents are tolerated,[106,257,258] including phosphinites, and the central carbon may be sp^2-hybridized, *e.g.* phenyl, anthracyl,[259] or sp^3-hybridized as in **147**.[260] Activation of $C(sp^3)$–H bonds requires harsher conditions (5 h at 110 °C) as opposed to analogous $C(sp^2)$–H bond activation (1 h at RT). Apparently, strong *P,P*-bidentate coordination is essential for bond activation, since analogous complexes with *P,C*-bidentate ligands have not been prepared thus far. Similarly, no such cyclonickelation has been reported hitherto for donor groups other than phosphin(it)es.

Scheme 61



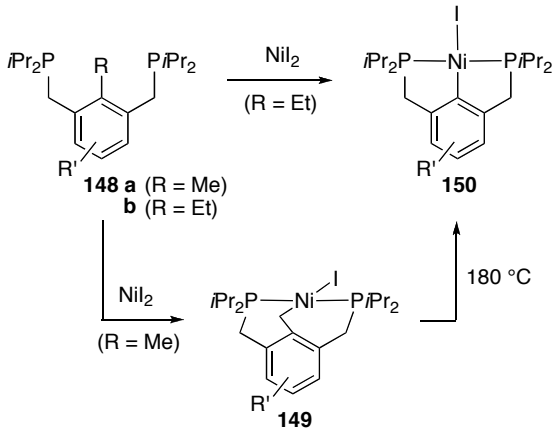
26 a R = Ph
b R = Me
c R = *i*Pr
d R = *t*Bu

146 **147**

Remarkably, the strong *P,P*-bidentate coordination mode of pincer ligands allows for the NiI_2-induced activation of C_{alkyl}–H, C_{alkyl}–O, and even of C_{aryl}–C_{alkyl} bonds.[261] For example, reaction of the methyl-substituted pincer ligand precursor **148a** with NiI_2 gives the cyclometalated

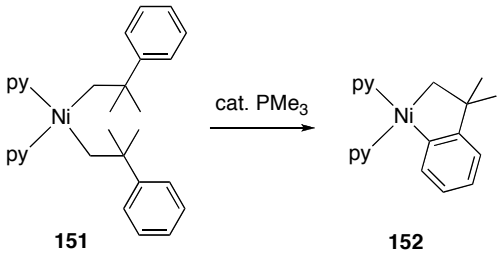
complex **149a** resulting from C_{alkyl}–H bond activation (Scheme 62). Thermolysis of this complex at 180 °C leads to C_{aryl}–C_{alkyl} bond activation and yields complex **150,** an analog of **146**. In contrast, cyclonickelation of the ethyl-substituted ligand precursor **148b** gives directly complex **150** without intermediacy of a complex originating from C–H bond activation. Substitution of the pincer ligand with a methoxy group (R = OMe in **148**) provides exclusively *P,O*-bidentate coordination products resulting from C_{alkyl}–O activation; no cyclometalation due to C_{aryl}–O activation has been observed.

Scheme 62



Nickel-mediated cyclometalation has been promoted in coordination compounds that impose steric constraints.[262,263] For example, complex **151** containing sterically demanding neophyl ligands readily cyclometalates to yield complex **152** under elimination of *tert*-butyl benzene (Scheme 63).[264,265] This reactivity may be related to the *gem*-dimethyl effect introduced by Thorpe and Ingold for organic cyclizations and adapted to cyclometalation by Shaw[105] (*cf.* section 2.2). The nature of the neutral spectator ligands is crucial for this reaction. With pyridine ligands, reductive C–C coupling is the predominant pathway whereas cyclometalation prevails in the presence of PMe_3 as ligand, even in catalytic amounts.

Scheme 63



151 152

In some cases, cyclometalation is induced by pre-activation of the C–H bond in the ligand precursor. Aldehyde C–H bonds have thus been activated in phenoxides or in triaryl phosphines using the dimeric alkyl nickel precursor $[NiMeCl(PMe_3)]_2$.[266,267] Introduction of a strongly electron-withdrawing substituent like an ester in α position to the C–H bond also facilitates the cyclonickelation.[268]

6.2 Platinum group metals

Cyclometalation using the platinum group metals, *viz.* Ru, Os, Rh, Ir, Pd, and Pt, is by far the most popular domain of cyclometalation and a vast number of metallacycles have been prepared by heteroatom-assisted C–H bond activation. A comprehensive treatment of these studies would be far too voluminous and is beyond the scope of this review. The section here aims, instead, at summarizing the most general aspects of cyclometalation using platinum group metals and at highlighting some of the most recent aspects of this chemistry.

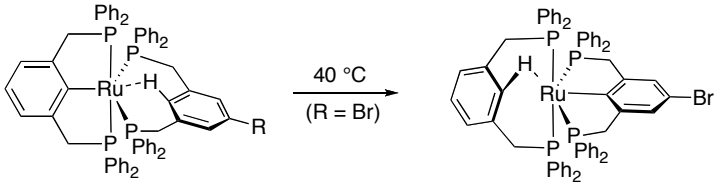
6.2.1 Ruthenium

Cyclometalated ruthenium complexes have found widespread application due to their photophysical and electrochemical properties, thus providing active sites, *e.g.* for solar cells[269] or intervalence electron transfer systems.[67,270,271] Moreover, ruthenacycles are amongst the most active catalysts known to date for transfer hydrogenation reactions.[272,273]

An excellent review has recently appeared,[28] which compiles a vast range of precursors and ligand settings used for cycloruthenation. Perhaps the two most important conclusions from this overview are that, first, cycloruthenation is extremely versatile and of very broad scope. Activation of C–H bonds in virtually any ligand environment has been accomplished, including for example $C(sp^2)$–H bonds in chromium arenes and ferrocenes.[274] The versatility of cycloruthenation originates last but not least from the great diversity of available ruthenium precursors. Second, a mechanistic picture of the cycloruthenation is far from being complete,

despite the numerous studies. Currently, no compelling evidence is available for a certain reaction pathway (*cf.* section 3). The agostic intermediate **153** has been isolated (Scheme 64),[110,275] and it has been demonstrated in the dissymmetric complex **153b** that the proton involved in the agostic bonding can migrate from the coordinated ligand to the cyclometalated ligand, thus formally completing a transcyclometalation step and formation of **154**.

Scheme 64

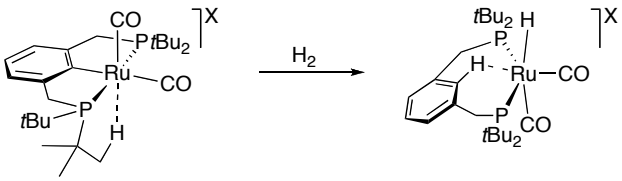


153 a (R = H)
b (R = Br)

154

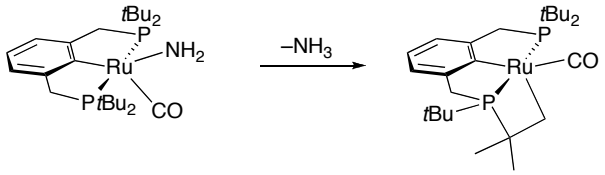
In this context, it is noteworthy that the PCP pincer ruthenium complex **155** features a stabilizing C–H···Ru interaction between one of the *t*Bu substituents and the metal center (Scheme 65).[276] Upon exposure to H_2, the cyclometalation is partially reverted and affords the agostic complex **156**, which may represent an intermediate in the actual cycloruthenation of the *P,C,P*-tridentate ligand precursor. The less electron-deficient ruthenium center in the amido analog **157** does not reveal any agostic interaction, yet it gradually loses NH_3 and forms the doubly cyclometalated complex **158** (Scheme 66).[277] This transformation may involve an agostic interaction akin to **155**. Furthermore, agostic interactions have been identified in a ruthenium complex with a (xylyl)(diphenyl)phosphine ligand.[278,279] Cycloruthenation by C(sp^3)–H bond activation of the xylyl fragment is promoted in this case by the addition of formaldehyde and NEt_3.

Scheme 65



155 **156**

Scheme 66



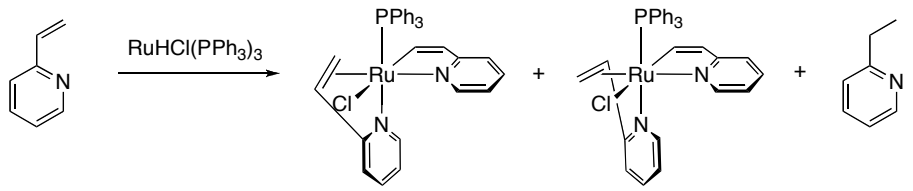
157 **158**

Related agostic interactions have been observed upon reacting arylated 1,8-naphthydrine with dimetallic $[Ru_2(CO)_4(NCMe)_2](BF_4)_2$,[280] and in a cyclometalated complex with a *C,P*-bidentate ligand exhibiting Si–H coordination to the ruthenium center.[281] Despite these results, it is difficult to generalize such agostic bond activation as a mechanism for cycloruthenation based on the data currently available.

Cycloruthenation of various phenyl-substituted amines and imines is promoted by acetate, thus occurring under mild conditions at room temperature.[282,283] Reactivity studies in the presence and absence of acetate lend support that during cycloruthenation, acetate coordinates to the metal center prior to ligand coordination and assists in the proton abstraction step. These results put forward an electrophilic mechanism reminiscent to cyclopalladation (*cf.* sections 3.1. and 6.2.5.). Accordingly, the C–H activation step is facilitated by synergistic bonding by the metal and intramolecular deprotonation by the acetate ion in a cyclic transition state. Of particular note in this context is that Pregosin and coworkers have observed the cleavage of a $P–C_{aryl}$ bond upon reaction of binap with the acetate-containing ruthenium precursor $Ru(cymene)(OAc)_2$ at elevated temperatures.[284]

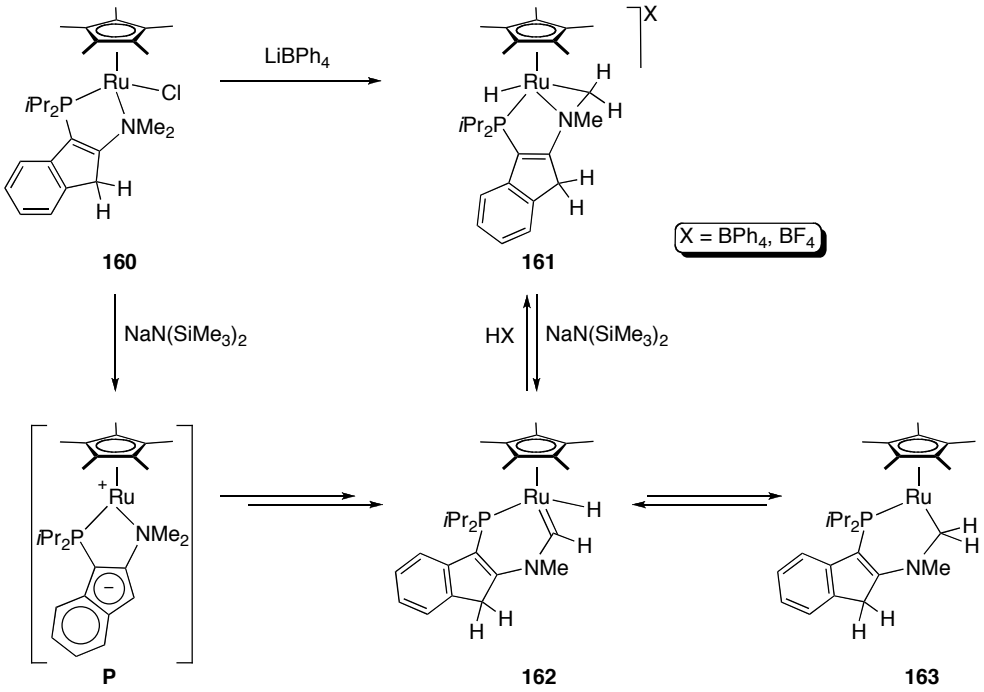
By far most cycloruthenation reactions involve the activation of (hetero-)aryl C–H bonds, though activation of C_{vinyl}–H bonds,[285,286] and in distinct ligand settings, also of C_{alkyl}–H bonds has also been accomplished. For these latter cycloruthenation reactions, typically, ruthenium hydride metal precursors like RuH_4(triphos) or $RuHCl(P\textit{i}Pr_3)_3$, or ruthenium aryl precursors, *e.g.* $Ru(Ph)Cl(CO)(P\textit{i}Pr_3)_2$, have been used since upon C–H bond activation they form supposedly stable and unreactive H_2 and benzene, respectively. Recent work using vinyl pyridine has shown,[287] however, that the formed H_2 is not innocent and reduces, presumably in a ruthenium-mediated process, the ligand precursor to ethylpyridine (Scheme 67). Accordingly, the use of one sacrificial ligand equivalent is necessary to achieve high yields of the cyclometalated complex **159**. Cycloruthenation without ligand reduction has been realized upon using $RuCl_2(PPh_3)_3$ as ruthenium source.

Scheme 67



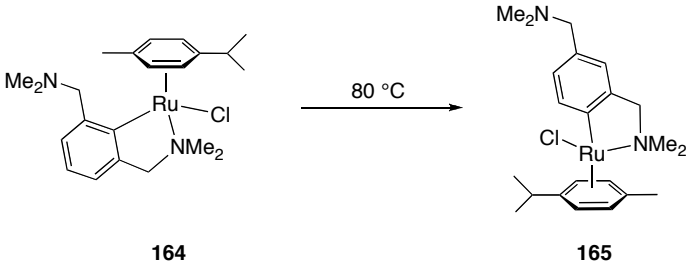
Cycloruthenation via activation of C(sp^3)–H bonds has generally[288] been performed from coordinatively unsaturated ruthenium centers. For example, the formally 14e-complex Ru(PNP)(OTf), where PNP is the monoanionic, *P,N,P*-tridentate ligand $N(SiMe_2CH_2P\textit{t}Bu_2)_2$, induces the net heterolytic cleavage of one CH_2–H bond in the *t*Bu substituent to afford a four-membered metallacycle.[289] In this process, the proton is transferred to the nitrogen, modifying the originally anionic amide coordination site into a neutral amine donor. Similarly, the replacement of the chloride in **160** by a non-coordinating $B(C_6F_5)_4$ anion induces the activation of a NCH_2–H bond and formation of complex **161** featuring a strained three-membered metallacycle (Scheme 68).[290] Reaction of complex **160** or **161** with a base affords the carbene metallacycle **162**.[291] Carbene formation from **160** is likely induced by deprotonation of the indene ligand and simultaneous chloride abstraction to give a zwitterionic intermediate **P** with a two-legged piano-stool geometry. Subsequent NCH_2–H activation and hydrogen transfer to the indenyl fragment followed by α-hydrogen elimination and a 1,3-hydrogen shift in the indenyl residue produces complex **162**. This carbene complex is in a dynamic equilibrium with the coordinatively unsaturated σ complex **163** (rate constant 59±1 s^{-1}),[292] indicating that α-H elimination is fully reversible and that the cyclometalated product is not rigid.

Scheme 68



Similar activation of a NCH_2–H bond has been identified previously during the thermally induced rearrangement of complex **164** comprised of a *C,N*-bidentate coordinating pincer ligand (Scheme 69). [293] Upon heating to 80 °C, this complex transforms into the sterically less congested isomer **165**. Deuterium labeling studies have indicated that isotope exchange occurs between the aryl proton involved in the C–H activation process and the NCH_3 groups, excluding a direct swap of ruthenium and protium/deuterium.

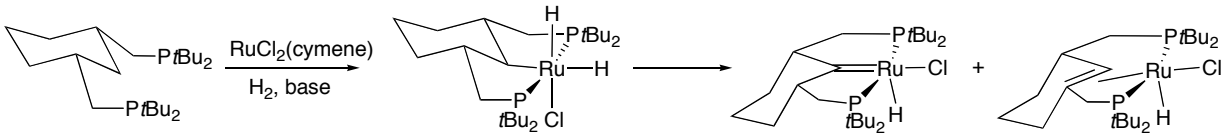
Scheme 69



Cycloruthenation via cleavage of an electronically unactivated C_{alkyl}–H bond, *i.e.* from an sp^3-hybridized carbon that is not substituted by electroactive heteroatoms, has been accomplished by using the potentially *P,C,P*-tridentate coordinating pincer ligand precursor **166** featuring a saturated cyclohexyl core (Scheme 70),[294] and its acyclic diphosphinopentane analog.[295] Thermally induced cyclometalation using $RuCl_2(cymene)_2$ as metal source, notably under an

atmosphere of H_2, yields the cyclometalated complex **167**. Heating of this complex in the absence of H_2 induces dehydrogenation. Formation of the carbene complex **168** resulting from α-hydrogen elimination is largely dominant over β-hydrogen elimination leading to the olefin complex **169** (both complexes as mixtures of *syn* and *anti* conformers). Probably, β-hydrogen elimination is restricted due to the constraints in the ligand backbone imposed by the two phosphine donors.

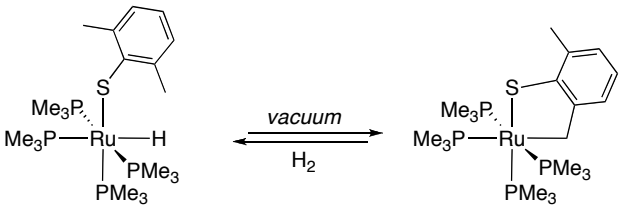
Scheme 70



166 **167** **168** *major* **169** *traces*

Reversible cycloruthenation has been evidenced recently for complex **170** (Scheme 71), obtained by metalation of the corresponding 2,6-dimethyl thiophenol with *cis*-$RuH_2(PMe_3)_4$.[296] Under vacuum, this complex looses H_2 and forms the ruthenacycle **171**, while ambient H_2 pressure reverts the cyclometalation. Based on this reversibility, a procedure has been developed for the selective deuteration of the methyl protons in the xylyl fragment of **170** by using D_2. Notably, the presence of excess PMe_3 stabilizes the coordination compound **170**, yet it decelerates the deuterium exchange. Reversible ruthenacycle ring opening and closing has also been demonstrated in a bipyridine-appended thiophene complex.[297] Addition of acid and base allows for toggling between thiophene coordination via sulfur and cyclometalation via C3–H bond activation, respectively.

Scheme 71

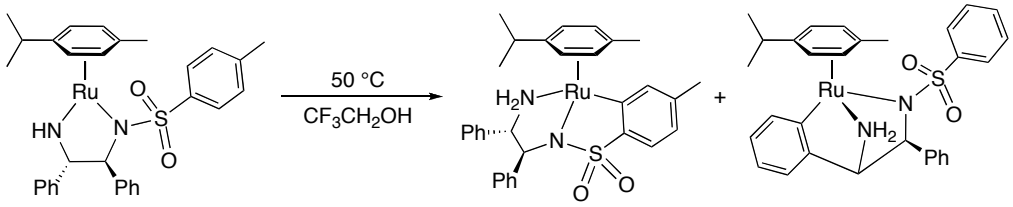


170 **171**

Reversible cyclometalation is crucial for the ruthenium-catalyzed functionalization of C–H bonds in (hetero-)arenes.[298–301] In certain cases, however, such cycloruthenation constitutes an unwanted

catalyst deactivation pathway. For example, Noyori's transfer hydrogenation catalyst **172** undergoes cyclometalation when warmed in CF_3CH_2OH (Scheme 72).[302] Two types of metallacycles have been identified, originating either from C–H bond activation of the tosyl group (**173**) or from C_{phenyl}–H bond activation (**174**). Along similar lines, Grubbs has demonstrated[303] that under an atmosphere of argon rather than nitrogen, second generation metathesis catalysts undergo wingtip C–H bond activation and transform into inactive ruthenacycles.

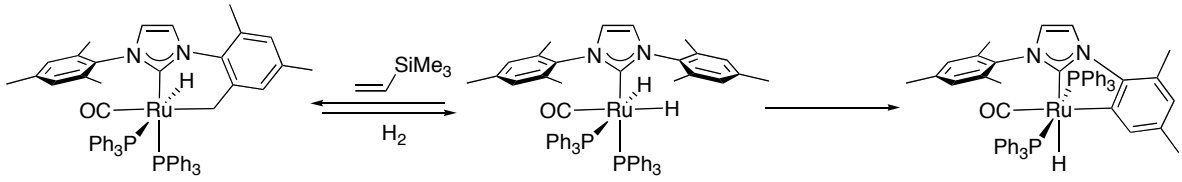
Scheme 72



172 **173** **174**

By using a combination of experimental and theoretical techniques, Whittlesey and Macgregor have studied in great detail the ruthenium-meditated wingtip activation in carbene complexes. Thermolysis of complex **175** (Scheme 73), obtained in a slow ligand substitution reaction from bis(1,3-mesityl)imidazol-2-ylidene (IMes) and $Ru(H)_2(CO)(PPh_3)_3$, at 110 °C yields the C–C insertion product **176** resulting from C_{aryl}–CH_3 bond cleavage.[304,305] Experiments using selectively labeled reagents and solvents indicate that the bond cleavage process is not straightforward. Isotope exchange involves the solvent, the ruthenium-bound hydride and the PPh_3 ligand. In the presence of a hydrogen acceptor, C_{alkyl}–H bond cleavage is favored over C–C bond scission, thus yielding complex **177**. This complex does not seem to be en route to the C–C activated product, yet it transforms to the starting material in the presence of H_2.

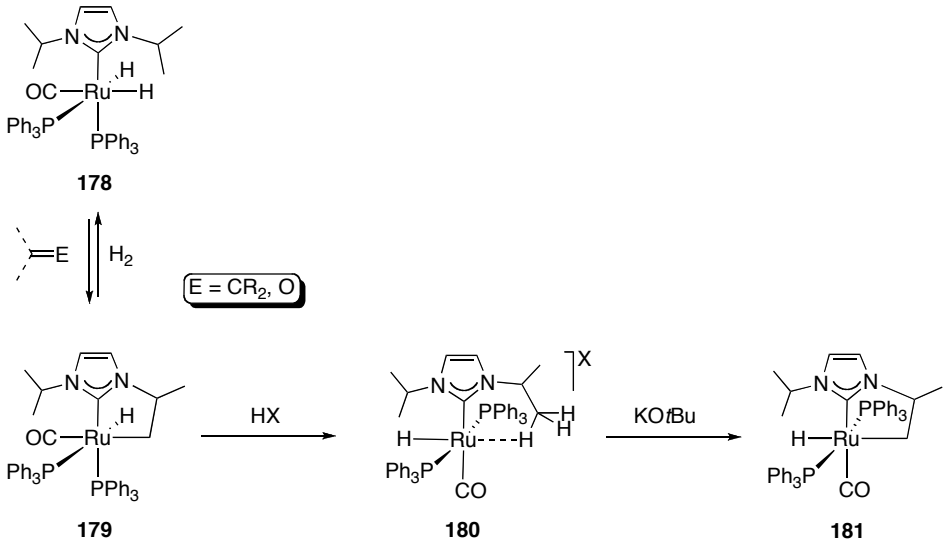
Scheme 73



176 **175** **177**

Exclusive CH_2–H bond activation takes place in the carbene ruthenium complex **178** bearing *i*Pr wingtip groups and yields complex **179** (Scheme 74).[306] Hydrogenation again reverts the process, while protonation opens the ruthenacycle to give complex **180**, in which the metal center is stabilized by an agostic bond. Deprotonation affords complex **181**, an isomer of **179** with the phosphines in mutual *trans* conformation. Isotope labeling and DFT calculations consistently suggest that bulky bases abstract one of the two methyl protons that are not involved in the agostic interaction. This mechanism hence distinctly deviates from acetate-assisted C–H bond activation.

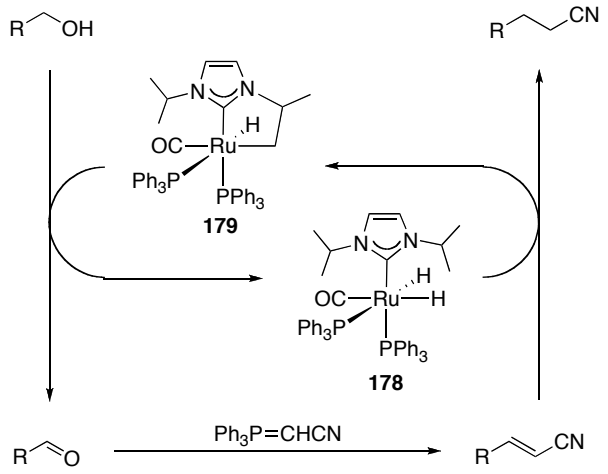
Scheme 74



Computational analyses suggest that the C–H bond breaking process leading to complex **181** is thermodynamically favorable due to the strong Ru–H bond in the product.[307] Calculations further point to a marked influence of the arrangement of co-ligands around the ruthenium center. Specifically, a *trans* CO ligand promotes the cleavage of π donating aryl ligands. Accordingly, it should be possible to tune the stability of carbene wingtip groups both for cases where cyclometalation is undesired as well as for processes where cyclometalation is crucial.
Based on the reversibility of the cycloruthenation involving carbene wingtip activation, a cascade catalytic process has been devised that allows for expanding a carbon skeleton by a C_2 unit in a one-pot procedure.[308] In this process, complex **179** serves as a transient H_2 reservoir and catalyzes the dehydrogenation of the alcohol (Scheme 75). The resulting ketone is subsequently transformed in a Wittig reaction into an α,β-unsaturated nitrile and subsequently hydrogenated

by complex **178**. Release of formally H_2 reverts the ruthenium complex to the cyclometalated species **179** and reduces the C=C bond to give the corresponding alkyl nitrile.

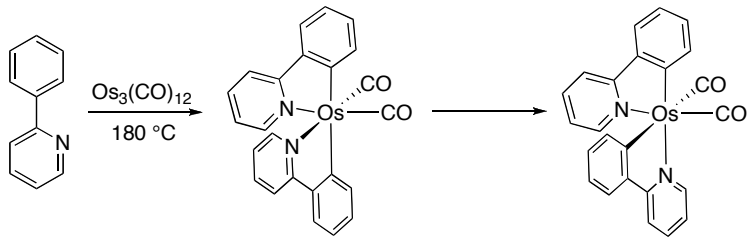
Scheme 75



6.2.2. Osmium

Cyclometalation using osmium has received far less attention when compared to its second row analog ruthenium. Most cyclometalation reactions involving osmium-mediated C–H bond activation are thought to involve oxidative addition of the C–H bond of a pre-coordinated ligand. Accordingly, low-valent osmium centers are particularly attractive for cyclometalations. The most common osmium(0) precursor, $Os_3(CO)_{12}$, has been used indeed frequently for activating donor-substituted arenes.[309–311] However, the ligand typically[312] adopts a bridging μ^2,κ^2 coordination mode to the Os_3 core, thus forming a metallacycle including two metal centers. Only in a rare case,[313] thermal cleavage of the osmium cluster with phenylpyridine has been observed at high temperature (180 °C) to give the monometallic complex **182** (Scheme 76). The isomer possessing *trans* arranged phenyl ligands is kinetically favored. Upon prolonged reaction, the *cis* isomer forms. The latter is luminescent due to a readily accessible, $^3\pi$–π^* dominated excited state. An increased MLCT contribution to the first excited state and higher quantum yields have been noted upon exchanging one of the π-acidic CO ligands by a phosphine.

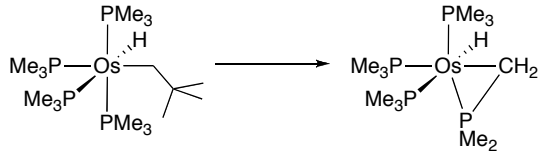
Scheme 76



trans–**182** *cis*–**182**

Various osmium(II) precursors provide access to transient osmium(0) species. For example, $OsMe_2(Cp^*)(DMSO)$ has been successfully employed for the cyclometalation of benzoic acid to yield a *C,O*-bidentate chelate, presumably via the elimination of two mol equivalents of CH_4, and as a result of oxidative addition of a C_{aryl}–H bond.[314] Along similar lines, the reaction of $OsHCl(Cp)(P\textit{i}Pr_3)(SiPh_3)$ with the lithium enolate of acetone has been postulated to transiently yield the low-valent, coordinatively unsaturated 16e species $Os(Cp)(P\textit{i}Pr_3)(SiPh_3)$, which subsequently induces the activation of a C_{aryl}–H bond.[315] Facile reductive elimination is also likely to occur in the cyclometalation of vinyl pyridine with $OsH_2Cl_2(P\textit{i}Pr_3)_2$.[316] A detailed mechanistic study[317] on the formation of the 3-membered osmacycle **184** from the precursor **183** strongly supports osmium(0) intermediates and a subsequent oxidative addition process for the C–H bond activation (Scheme 77). Kinetic studies and isotope labeling experiments indicate a solvent-dependent process. Key intermediates have been identified to be either $Os(PMe_3)_4$, resulting from initial neopentane elimination in mesitylene as solvent, or $Os(PMe_3)_3$, originating from initial PMe_3 dissociation and subsequent reductive neopentane elimination ($SiMe_4$ as solvent).

Scheme 77



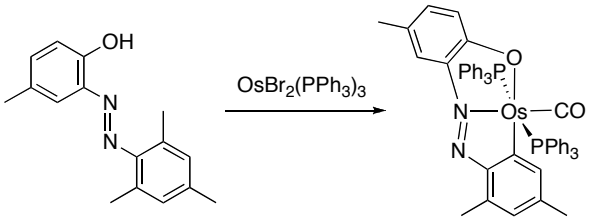
183 **184**

Cyclometalation has been studied in a series of complexes $OsX(Cp)(PR_3)_2$. Upon abstraction of the metal-bound anion (*e.g.* chloride abstraction with $NaPF_6$) or upon using an anion that is only weakly coordinating like X = OTf,[318] C–H bond activation and cyclometalation of one of the phosphine substituents ensues. $C(sp^2)$–H[319] as well as $C(sp^3)$–H[320] bond activation has been observed in PPh_3 and $P\textit{i}Pr_3$ ligands, respectively. A heteroleptic precursor containing both, PPh_3

and P*i*Pr$_3$ ligands shows a clear preference for C_{aryl}–H bond activation, in line with general trends in cyclometalation. Similarly, *N,C*-bidentate chelates are accessible by replacing one phosphine ligand in the osmium precursor by the imine $Ph_2C{=}NH$.[321]

The dichloride $OsCl_2(PPh_3)_3$ and its dibromide analog are suitable precursors for the activation of C_{vinyl}–H bonds in vinyl pyridine,[287] and of C_{aryl} –H bonds in the cyclometalation of *C,O*-bidentate ligands[322] and of the potentially *C,N,O*-tridentate coordinating precursor **136** (*cf.* Scheme 56).[323] Notably, this precursor also activates a C_{aryl}–C_{alkyl} bond when starting from the methylated analog of **136**, *viz.* **185** (Scheme 78). The carbonyl ligand in **186** has been identified to origin from the cleaved methyl group, which is oxidized in the presence of H_2O.[305] Related C_{aryl}–CHO bond activation has been observed in the osmium-mediated decarbonylative cyclometalation of substituted benzaldehydes using $OsCl_2(PPh_3)_3$.[324]

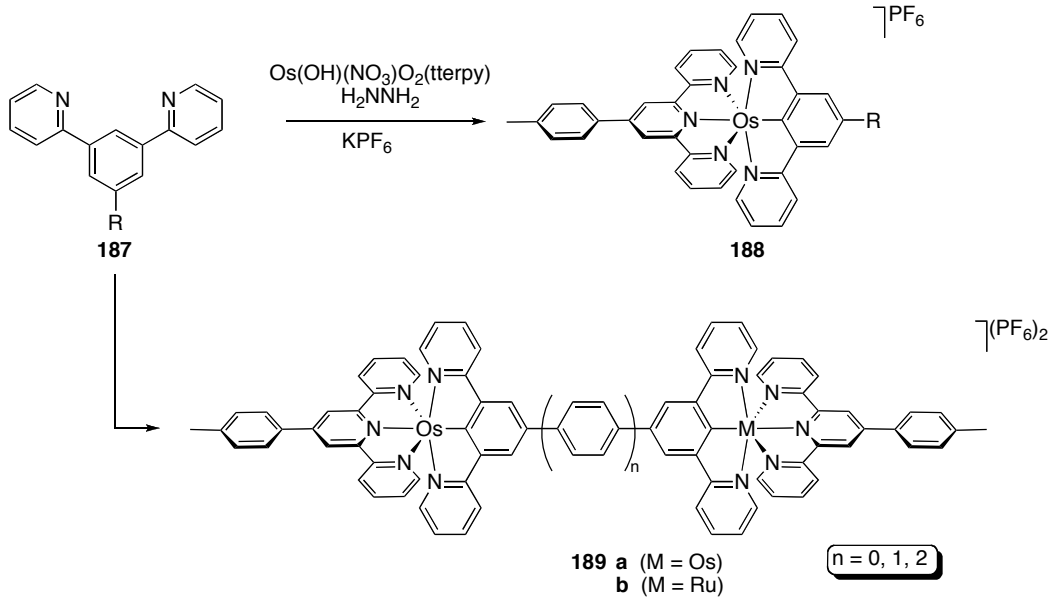
Scheme 78



185 **186**

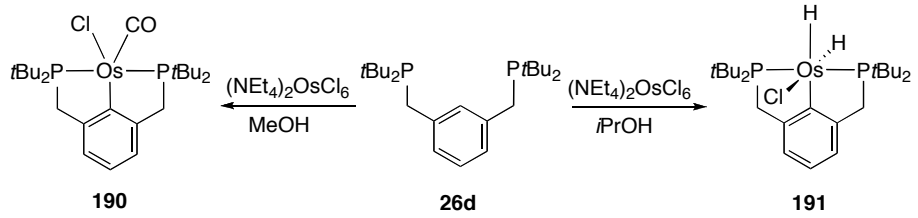
A variety of metal precursors of the general formula OsX_2L_n (n = 3, 4) has been successfully employed for cyclometalation, including $OsBr_2(bpy)_2$,[325] $Os(tfa)_2(CO)(PPh_3)_2$, $OsH(tfa)(CO)(PPh_3)_2$,[326] and $Os(R)Cl(CO)(P{i}Pr_3)_2$.[327] Of particular note are the osmium(II) salts $OsCl_3$(tterpy) (tterpy = 4'-*p*-tolyl-2,2':6',2''-terpyridine) and $Os(OH)(NO_3)$(tterpy)(O_2), the latter in combination with hydrazine. They are the precursors of choice for the metalation of the potentially *N,C,N*-tridentate coordinating ligand **187**, thus yielding the cationic complex **188** (Scheme 79).[328] Starting from ditopic ligand precursors, Sauvage and coworkers have prepared homobimetallic complexes **189a** that show highly coupled mixed-valence states. Heteronuclear analogs **189b**, prepared by sequential cyclometalation with ruthenium and then with osmium,[329] are luminescent and allow for investigating energy transfer processes.[330]

Scheme 79

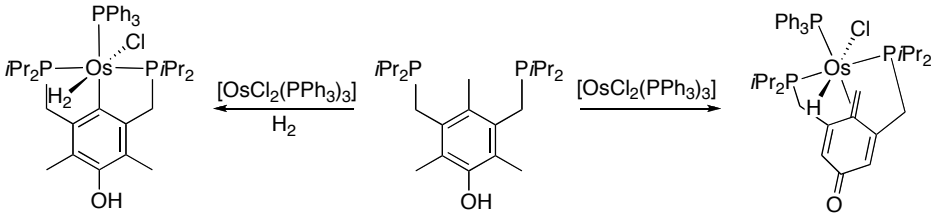


The PCP pincer complex **190** has been synthesized by cyclometalation using the osmate $[Et_4N]_2OsCl_6$ in MeOH/isoamyl alcohol solvent mixtures (Scheme 80).[331] Alcohol dehydrogenation appears to take place spontaneously, thus affording the carbonyl complex. When the reaction is performed in *i*PrOH, solvent dehydrogenation affords the dihydride **191**. The dihydride complex effectively mediates the redistribution of phenylsilane and provides access to silylene complexes.[332] A related PCP pincer complex **193** has been prepared by C_{aryl}–C_{alkyl} bond activation starting from the ligand precursor **192** and $OsCl_2(PPh_3)_3$ in the presence of H_2 (Scheme 81).[333] In the absence of H_2, ligand dehydrogenation is taking place, affording the non-cyclometalated complex **194** comprised of a quinone methide ligand.

Scheme 80



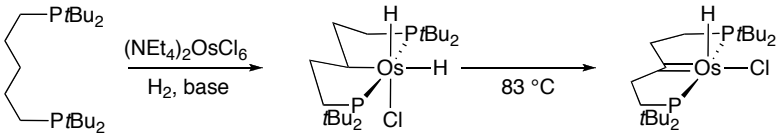
Scheme 81



193 **192** **194**

Activation of a C_{alkyl}–H bond in the diphosphine ligand precursor **195** proceeds in analogy to its ruthenium homolog (*cf.* Scheme 70) and is only successful if the reaction is performed under H_2 atmosphere (Scheme 82),[334] emphasizing again the relevance of (transiently formed) osmium hydride species for the C–H bond activation process. The formed osmacycle **196** thermally dehydrogenates to yield the carbene complex **197**. Incorporation of a NMe_2 substituent at one of the β carbons provides a method for creating chiral osmacycles.[335] In addition, one N–CH_3 group is involved in the cyclometalation process, thus yielding osmium complexes with a tetradentate coordinating ligand. The hexachloro osmate precursor has also been efficient in cyclometalating *C,P*-bidentate ligands.[336]

Scheme 82



195 **196** **197**

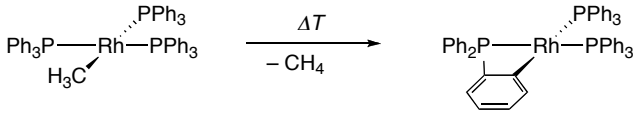
Esteruelas and coworkers have developed an elegant procedure relying on the osmium polyhydride $OsH_6(PiPr_3)_2$ for the cyclometalation of a variety of ligand precursors, including imine- and oxygen-assisted C_{aryl}–H[337,338] and C_{alkyl}–H bond activation.[339,340] Experimental and DFT studies consistently suggest that cyclometalation is initiated by the loss of two molecules of H_2, induced by heteroatom coordination. The formed coordinatively unsaturated osmium(II) center then entails oxidative C–H bond addition. Such polyhydride precursors are undoubtedly highly versatile for a wide range of bond activation processes.

Because of the pronounced base sensitivity, an electrophilic pathway has been suggested for the cyclometalation of benzylamines and phenylpyridines using $[OsCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$.[341] Accordingly, this precursor differs distinctly from the previously discussed osmium salts in its mode of action and may be a complementary metalating agent for electron-rich substrates where oxidative additions tend to fail.

6.2.3. Rhodium

Heteroatom-assisted C–H bond activation by rhodium centers has been known since the late 1960s, for example in the thermally induced formation of the rhodacycle **199** and methane from $Rh(CH_3)(PPh_3)_3$ (**198**, Scheme 83),[342] an analog of Wilkinson's catalyst. Cyclorhodation has been studied ever since in various facets. It has received particular attention probably because rhodium(I) complexes, and even more so their iridium(I) congeners,[343] have constituted model systems *par excellence* for investigating oxidative addition reactions. In line, cyclometalation using a rhodium(I) precursor is generally accepted to follow an oxidative addition pathway.[344], Apart from the methyl containing precursors derived from **198** and its hydride congeners, typical precursors for cyclometalation encompass dimers of the type $[RhX(olefin)_2]_2$ and $[RhX(CO)_2]_2$ and their monomeric analogs $RhXL(olefin)_2$ and $RhXL(CO)_2$ (where X = coordinating anion like Cl, Br, alkoxide, and L a neutral donor such as a phosphine, pyridine). Care has to be taken when metallacycle formation involves the activation of acidic C–H protons, *e.g.* in imidazolium salts.[345] Especially when using *in situ* generated precursors that possess a weakly coordinating *t*BuO$^-$ anion, surmised as $[Rh(OtBu)(diolefin]_2$, a deprotonation-metalation sequence may be competitive with a cyclometalation, though only the latter involves rhodium-mediated C–H bond activation.

Scheme 83



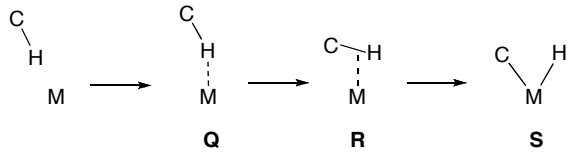
198 **199**

Metal chelation as imposed in cyclometalation reactions offers interesting opportunities, either to enhance the oxidative addition propensity, thus increasing the reactivity at the metal center for activating even highly unreactive bonds, or to decelerate reactions in order to identify intermediates and to establish pertinent reaction pathways. Both lines of research have been successfully pursued.

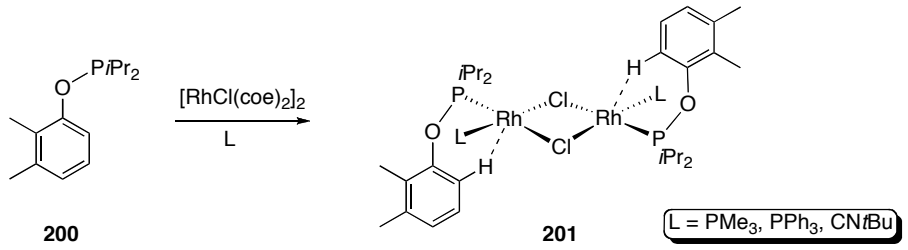
Careful choice of the donor atom, the rhodium precursor, and the reaction conditions has allowed for the structural and spectroscopic characterization of key intermediates of the generic oxidative C–H bond activation (Scheme 84). Thus, reaction of the phosphinite **200** with $[RhCl(coe)_2]_2$ (coe

= cyclooctene) in the presence of an exogenous ligand like PPh_3 produces a dimeric complex **201** featuring a preagostic Rh···H_{aryl} interactions (Scheme 85)[346] as a representative of intermediate **Q** in Scheme 84. Crystallographic and NMR spectroscopic analyses consistently reveal close contacts between the *ortho* proton of the phenol residue and the rhodium center. Indeed, functionalization of the *ortho* position in the presence of an alkene proceeds smoothly with complex **201** and affords the olefin insertion product.

Scheme 84

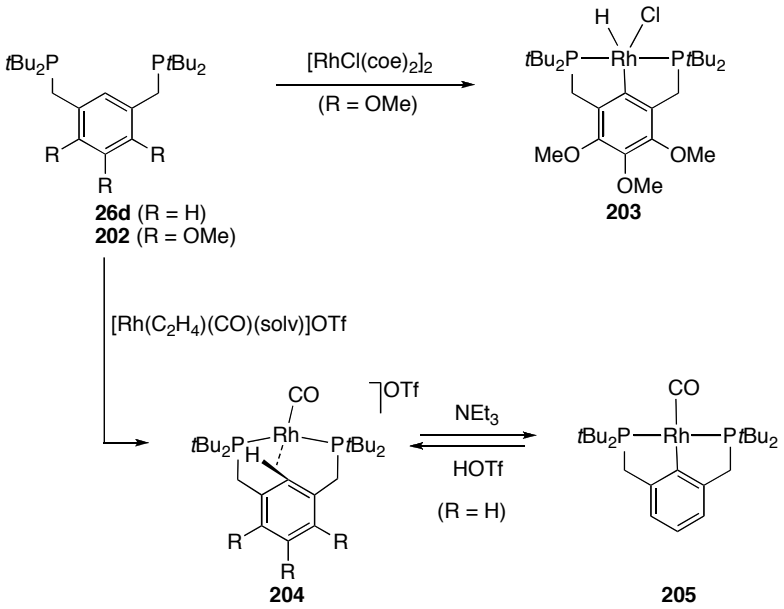


Scheme 85



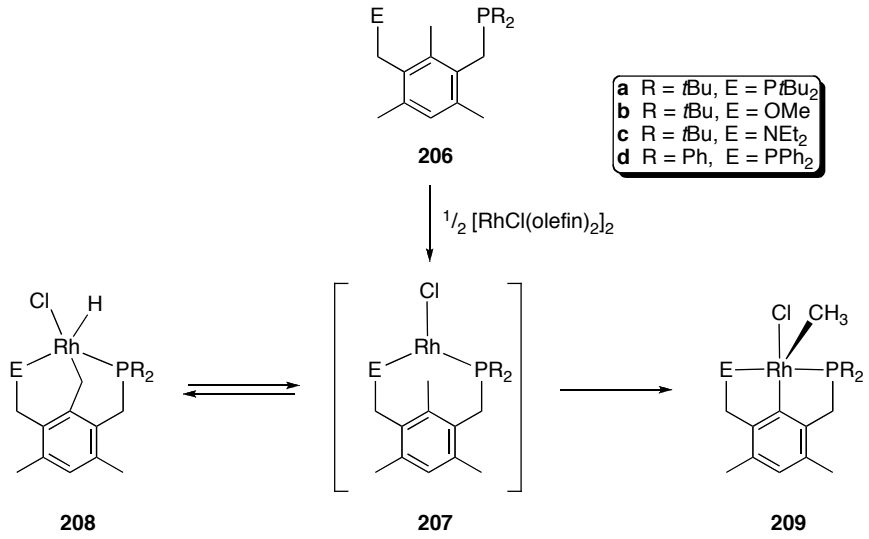
While cyclorhodation of **200** stops at the preagostic stage, cyclometalation of the PCP pincer ligand precursor **26d** or **202** with [Rh(coe)(CO)$(solv)_2$]OTf arrests one stage further (Scheme 86).[347] Complex **204** displays an agostic Rh···H interaction and hence constitutes an example of the generic intermediate **R** (*cf.* Scheme 84). Agostic interactions have been evidenced crystallographically and in particular by the unusual high-field shift of the aryl-bound hydrogen, which has lost a considerable portion of its aromatic character and appears as a doublet due to coupling to ^{103}Rh (δ_H 4.1). Unlike in the ruthenium complex **153** (*cf.* Scheme 64), proton abstraction and completion of the cyclometalation reaction is feasible and produces the cyclometalated complex **205**. Notably, addition of a strong acid reverts the cyclometalation and regenerates the agostic species **204**. Small changes in the rhodium precursor significantly modify the product outcome and lead at fast rates to the cyclometalated complex **203**, that is, the final oxidative addition product **S**. Similarly, alkene C–H bond activation has been observed to occur readily in a PCP ligand setting.[348]

Scheme 86



Milstein and coworkers developed a procedure for preparing the cyclometalated PCP, PCN, or PCO pincer complexes **209** by rhodium-mediated cleavage of a strong C_{aryl}–C_{alkyl} bond (Scheme 87).[32,349,350] Kinetically, C_{alkyl}–H bond activation is competitive and complex **208** is formed as a second product at essentially similar rates. However, C–C bond cleavage appears to be the thermodynamically more favored process. Obviously, the higher energy required for C_{aryl}–C_{alkyl} bond activation (bond dissociation energy 427 kJ mol^{-1}) compared to C–H bond breaking (368 kJ mol^{-1}) is compensated by the stronger Rh–C_{aryl} bond and the formation of two five- rather than six-membered metallacycles.

Scheme 87

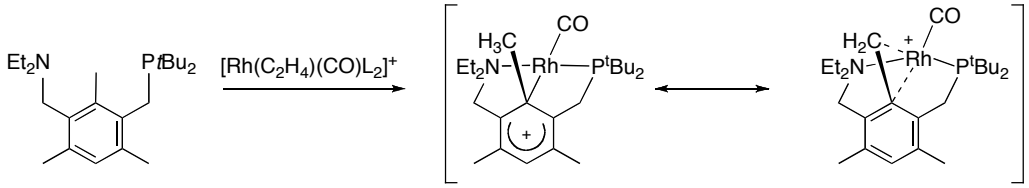


Because rhodium-mediated C_{aryl}–C_{alkyl} and C_{alkyl}–H bond activation in **206** are thermodynamically and kinetically very similar processes,[351] subtle changes in the ligand parameters strongly affect the reaction outcome. For example, PPh_2 donors induce C–H bond cleavage to afford **208d** exclusively at ambient temperatures. C–C activation and formation of **209d** is only induced upon heating under H_2 atmosphere,[352] presumably because these conditions allow the product selectivity to be controlled thermodynamically. In contrast bulky P*t*Bu$_2$ donors as in **206a** promote C–C bond activation already at room temperature and the aryl complex **209a** is the only product observed. Similarly, replacing one phosphine donor by a harder NEt_2 group or the use of less basic phosphinite donors results in selective C–C bond cleavage at room temperature. These preferences suggest steric factors to play a more dominant role than electronic differences in determining the C–C *vs.* C–H selectivity. Steric congestion induced by the donor substituents has been proposed to arrange the orbitals of the metal center to be directed towards the C–C bond rather than towards the C–H bond.[353]

Kinetic investigations have identified the coordination compound **207** as a common intermediate of C_{alkyl}–H and the C_{aryl}–C_{alkyl} bond activation. Based on the similar rates for both cleavage processes and because of the absence of any detectable intermediate, formation of **207** and not C–H or C–C bond activation appears to be rate-limiting. While displacement of a weakly bound olefin ligand in the metal precursor may be fast, formation of the 8-membered metallacycle in **207** may be less favored, especially due to the potential for forming di- and polymeric coordination compounds. It is worth noting that upon substituting the PCP pincer ligand to a PCN

donor array, the coordination complex **207c** becomes stable at low temperature and has been spectroscopically characterized.[354] As a consequence, the rate-determining step is shifted to a later stage on the reaction coordinate. Notably, slight modifications in the metal precursor, that is, utilization of $[Rh(C_2H_4)(CO)(solv)_2]BF_4$ instead of $[RhCl(C_2H_4)_2]_2$, alters the stability of the intermediates and produces complex **210** (Scheme 88).[355] This complex may be represented by an agostic interaction of the C–C bond with the rhodium center, or alternatively by an arenium structure including an sp^3-hybridized *ipso* carbon. Due to only weak C_{ipso}–Rh interactions in solution (*e.g.* the absence of any ^{103}Rh coupling), the agostic description is favored. The different product outcome has been presumed to originate from the reduced electron density at the cationic rhodium(I) center due to the strongly withdrawing CO ligand and the relatively weak Rh–N bond. This configuration impedes the complete C–C bond cleavage and the reaction is interrupted at the agostic stage. Higher electron density at the metal center, *e.g.* imposed by the chloride ligand in neutral $[RhCl(C_2H_4)_2]_2$, allows for sufficiently populating the antibonding C–C σ^* orbital to induce bond scission.

Scheme 88

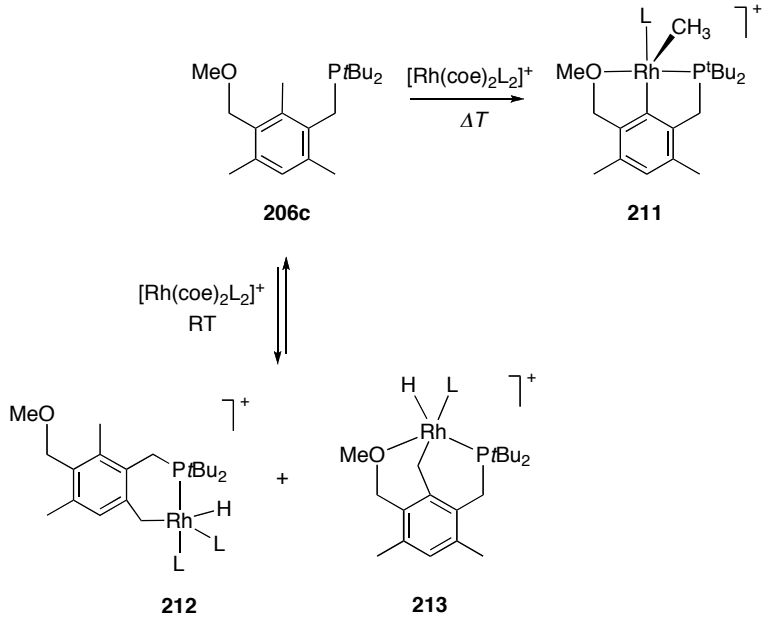


206b **210**

The transoid bidentate chelation of the donor groups in **207** is essential for C–C bond activation at room temperature. When using monophosphine ligand precursors, C–H bond activation takes place exclusively and no C–C bond cleavage is observed.[356] With the PCO pincer ligand precursor **206c**, cyclometalation via C–H activation is kinetically preferred at room temperature (Scheme 89).[357] However, this reaction is not selective and produces a mixture of **212** and **213**. Formation of mixtures indicates that both C–H bonds in *ortho* position to the phosphine are activated, thus reflecting the reduced preference of rhodium(I) to coordinate to hard oxygen donors. Upon heating, C–C bond activation takes place selectively at the position *ortho* to the O and P donor groups to afford **211**. This outcome illustrates that the C_{alkyl}–H bond activation is reversible, and more importantly, that bidentate ligand bonding is required for C_{aryl}–C_{alkyl} bond activation but not for C_{alkyl}–H bond activation. While these results provide further evidence for

the unique potential of pincer-type chelation in tailoring metal centers for uncommon processes, they may also rationalize the inherent difficulty of using these systems as catalysts for intermolecular activation of C–C bonds.[358]

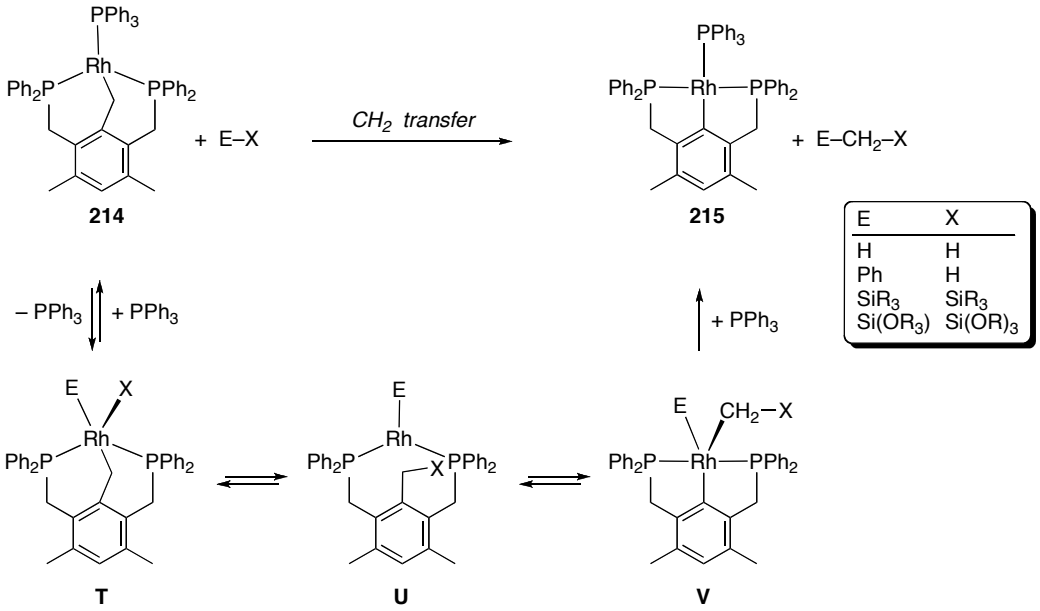
Scheme 89



Further support for the tricoordinate, 14e complex **207** as key intermediate in C_{aryl}–C_{alkyl} bond cleavage has been obtained from the strong solvent dependence of the bond activation process.[359] In MeCN, C–H bond activation becomes the predominant reaction pathway, since solvent coordination stabilizes the rhodium center. Conversely, weakly coordinating solvents such as THF favor C–C bond cleavage.

When using $RhH(PPh_3)_3$, the interplay between C_{alkyl}–H and C_{aryl}–C_{alkyl} bond activation in **206d** is strongly influenced by the absence or presence of H_2. Under H_2 atmosphere, reductive C–H elimination is favored, thus populating the three-coordinate intermediate (*cf.* **207**, Scheme 87) and eventually shifting the reaction selectivity towards C–C bond activation. From an organic point of view, the net transformation of **214** to **215** may be considered as a formal transfer of the methylene fragment from **214** to dihydrogen as acceptor molecule, thus yielding CH_4 (Scheme 90). This approach has been expanded successfully towards various other substrates as suitable methylene acceptors E–X, like benzene, disilanes R_3Si–SiR_3, and disiloxanes $(RO)_3Si$–$Si(OR)_3$.[360]

Scheme 90

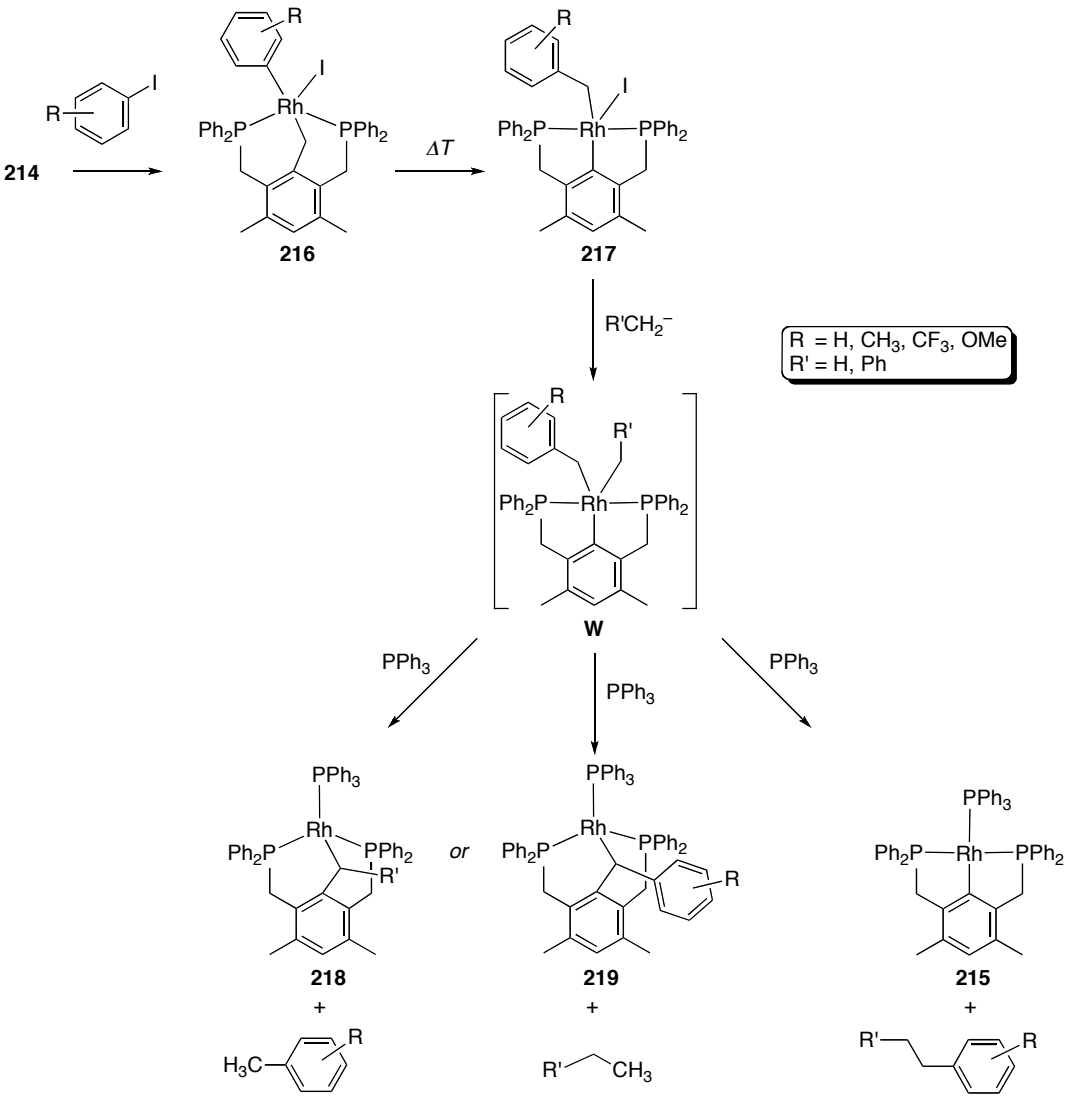


Mechanistic and theoretical investigations support the pathway detailed in Scheme 90.[361] Accordingly, methylene transfer is initiated by reversible dissociation of the PPh_3 ligand from **214** and oxidative addition of the acceptor molecule (**T**). Reversible C–X reductive elimination (X = H, SiR_3) subsequently produces a three-coordinate intermediate **U** related to **207**, which can either revert by C–X oxidative addition or — more likely — may induce C–C bond activation, thus forming complex **V**. Finally, irreversible reductive elimination yields the methylene insertion product and the PCP rhodium complex **215**. Rhodium phosphinite complexes similar to **214** have been demonstrated to undergo apparent α–hydrogen elimination, thus providing an alternative mechanism for the release of the CH_2 fragment.[362] Moreover, no products originating from double CH_2 insertion such as ethylbenzene from reactions using Ph–H as acceptor have been detected. This result indicates that the activation of C_{alkyl}–H and C_{aryl}–C_{alkyl} bonds, present both in toluene and in the PCP ligand in **214**, is restricted exclusively to the confined bonds of the ligand, which are located in close proximity and in a fixed orientation with respect to the rhodium center.

Further mechanistic work has identified the oxidative addition of the acceptor molecule, *i.e.* formation of **T**, as rate-limiting step when using arene acceptors.[363] Consistent with these findings, substituting the arene by an aryl halide promotes fast oxidative addition already at room temperature. The corresponding rhodium(III) complex **216** undergoes a methylene transfer at slightly higher temperatures and yields the (benzyl)(aryl) complex **217** (Scheme 91). Reductive

elimination requires the substitution of the rhodium-bound iodide by a nucleophile like a hydride or a carbanion, and addition of a coordinating ligand such as PPh_3. Different products have been observed upon reductive elimination. Thus, cross-coupling of the benzylic ligand and the nucleophile generates complex **215**. This reaction pathway along with formation of toluene is predominant when hydride is the nucleophile. With primary carbanionic nucleophiles $R'CH_2^-$, reductive migration of one of the alkyl groups to the *ipso* carbon has been observed additionally, corresponding to a back-transfer of the methylene group to the PCP ligand (Scheme 91). Competitive migration of the carbanion and the benzyl ligand affords either complex **218** or **219**, and the corresponding organic product from reductive elimination. Variation of the substituent R in the benzylic fragment strongly influences the reaction outcome. Electron-donating groups (R = OMe) increase the migration tendency and yield predominantly complex **219**. In contrast, electron-withdrawing groups ($R = CF_3$) decelerate benzyl migration and give complex **218** as well as significant amounts of the cross-coupling product and **215**. These results suggest the triorgano rhodium(III) complex **W** as common intermediate for all three pathways.

Scheme 91

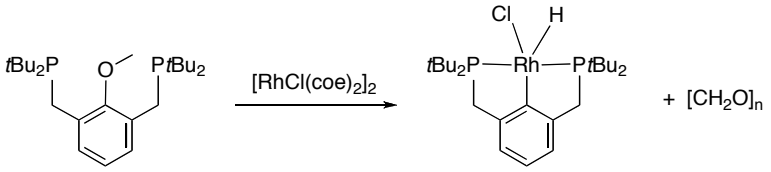


A catalytic methylene transfer process has been devised based on the observation that complex **214** can be regenerated from complex **215** by addition of CH_3I followed by base-promoted abstraction of HI.[360] Hence, CH_3I may be used as methylene source. Catalytic CH_2 transfer has been illustrated by the hydrosilylation of a C_{aryl}–C_{alkyl} single bond, though the low turnover frequencies (10 turnovers in 48 h) may need to be improved to make the process synthetically attractive.

In analogy to the C–C bond activation process discussed above, cyclometalation has also been achieved through unusual rhodium-mediated C_{aryl}–O bond cleavage in the PCP pincer precursor **220** (Scheme 92).[364] The cyclometalated complex **221** and formaldehyde are formed in this reaction, while insertion into the less strong C_{alkyl}–O bond and formation of two six-membered

metallacycles is apparently unfavored. The reaction mechanism is assumed to be related to that described previously for C_{aryl}–C_{alkyl} bond activation (*cf.* Scheme 87). Accordingly, initial formation of an (aryl)(alkoxy) rhodium(III) complex is followed by rapid *β*–hydrogen elimination to yield **221** and formaldehyde. Notably, *β*-hydrogen elimination can be suppressed in the presence of an acceptor for the $–OCH_2–$ fragment. For example, running the reaction in the presence of a silane $HSiR_3$, produces CH_3OSiR_3 as organic product rather than formaldehyde.

Scheme 92

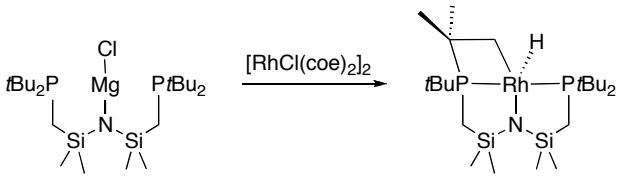


220 **221**

Several parameters are crucial for achieving high selectivity. The bidentate, mutually transoid coordination of the phosphines of the pincer ligand appears to imposes steric rigidity that directs the metal center towards the C_{aryl}–O bond rather than to the C_{alkyl}–O bond. With monophosphine ligand precursors, the weaker C_{alkyl}–O bond is preferably activated while the C_{aryl}–O bond remains unaffected.[365]

Cyclometalation involving the rhodium-mediated activation of benzylic C–H bonds occurs in *N*-heterocyclic carbene complexes that contain bulky mesityl wingtip groups,[366] and in *ortho* substituted aryl phosphines.[367] An example of strikingly facile C_{alkyl}–H bond activation has been observed upon transmetalation of the amido ligand **222** with $[RhCl(coe)_2]_2$ (Scheme 93).[368] In an alkane solvent, this reaction produces the rhodium(III) complex **223** comprised of a *P,N,P,C*-tetradentate ligand and a metal-bound hydride originating from oxidative C–H bond addition of one of the P*t*Bu methyl groups. Variable-temperature NMR experiments indicate fluxional behavior of complex **223** due to rapid metallacycle opening and closing (ca. 10^3 s^{-1}), which involves all 12 methyl groups of the four *t*Bu substituents.

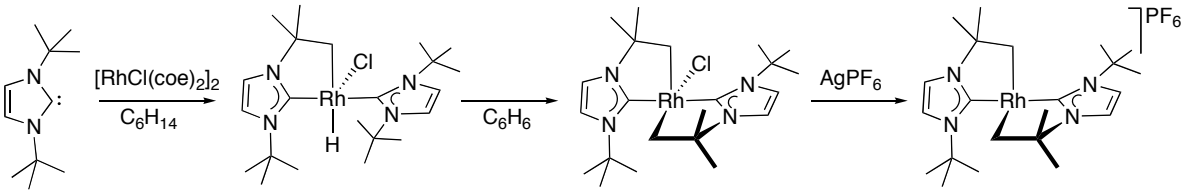
Scheme 93



222 **223**

Cyclometalation via C(sp^3)–H bond activation also takes place in the sterically encumbered imidazolium salt **224** (Scheme 94).[369] Reaction with $[RhCl(coe)_2]_2$ affords the monocyclometalated carbene complex **225**, which may be considered as an analog of the coordination compound **A** (*cf.* Scheme 2), albeit with a covalent and kinetically inert M–C bond rather than a labile M–E bond. A second cyclometalation is initiated by changing the solvent from hexane to benzene, thus giving complex **226**. The $AgPF_6$-promoted abstraction of the rhodium-bound chloride provides access to the rhodium(III) complex **227**, a rare cyclometalated 14e species. Characterization of **227** by X-ray diffraction does, surprisingly, not show any agostic interactions or hydrogen bonding that may stabilize the unusual configuration at the metal center.

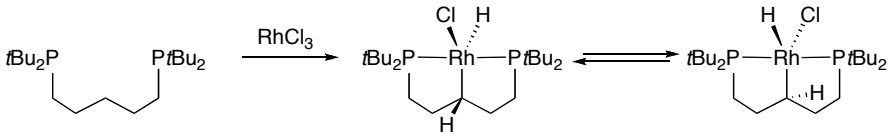
Scheme 94



224 **225** **226** **227**

Although the rhodium-mediated cyclometalation reactions discussed thus far have all involved rhodium(I) precursors, higher-valent rhodium(III) salts have also proven to be useful starting materials for cyclometalation. From early work, it is known that $RhCl_3$ allows for cyclometalating P(*o*-tol)$_3$ ligands involving the activation of a benzylic C–H bond.[370] More recently, analogous C–H bond activation has been successfully applied for the cyclometalation of diimidazolium salts to afford rhodium(III) dicarbene complexes.[371] The activation of generally less reactive alkane C–H bonds has also been accomplished in the α,ω-diphosphinopentane **195** (Scheme 95).[372] Reaction with $RhCl_3$ gives the five-coordinate rhodium hydride **228**, which is fluxional on the NMR time scale owing to rapid and reversible fission of a C–H bond, thus interconverting **228** to **229**. The putative carbene intermediate of this process has been isolated and characterized in the analogous iridium complex.[373]

Scheme 95

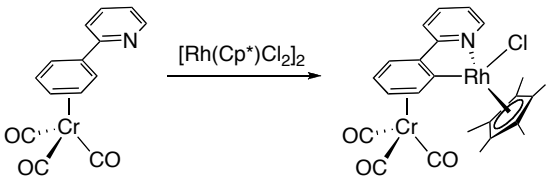


195 **228** **229**

Since accessing rhodium(V) oxidation states is energetically costly, an oxidative addition – reductive elimination sequence seems less favored. Based on the electrophilic nature of the metal salts, *e.g.* in the dimer $[Rh(Cp^*)Cl_2]_2$, cyclometalation is surmised to involve an electrophilic C–H bond activation step. In contrast to the activation of C_{aryl}–H bonds in potentially *P,C*-bidentate ligand precursors,[374] cyclometalation of *N,C*-bidentate ligand precursors is rare. Progress during the last few years includes the cyclorhodation of benzylamines, benzylimines and phenyl oxazolines with $[Rh(Cp^*)Cl_2]_2$ in the presence of NaOAc under mild conditions.[282] If imines are used as donor groups, cyclometalation and subsequent alkyne insertion constitutes an efficient process to generate isoquinoline salts with regeneration of the rhodium precursor.[375]

This cyclorhodation procedure has recently been expanded to the cyclometalation of tricarbonylchromium-ligated arenes.[376] Despite the strongly electron-withdrawing nature of the $Cr(CO)_3$ fragment, the C_{aryl}–H activation of complex **230** is still swift and proceeds at room temperature (Scheme 96). Remarkably, cyclometalation and formation of complex **231** is diastereoselective and affords only products in which the chloride and the $Cr(CO)_3$ fragment are in a mutually *anti* configuration. DFT calculations predict that the *syn* isomer is destabilized by some 7–8 kcal mol^{-1} due to electrostatic repulsion between the rhodium-bound chloride and the $Cr(CO)_3$ group. These results are consistent with thermodynamically controlled and hence reversible rhodacycle formation.

Scheme 96



230 **231**

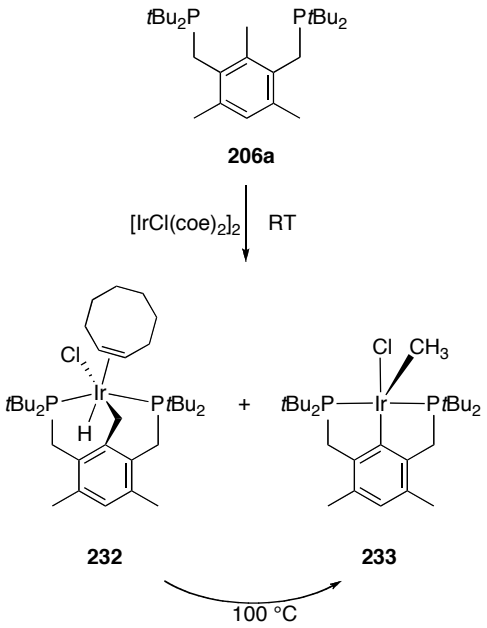
An elegant assembly of a cyclometalated ligand within the rhodium coordination sphere has been accomplished by using the new rhodium precursor $[Rh(Cp^*)(NH_2Me)_3](OTf)_2$, which is accessible from the dimeric $[Rh(Cp^*)Cl_2]_2$.[377] Upon addition of acetophenone, a Schiff'base reaction and C_{aryl}–H bond activation ensue, thus forming a *C,N*-rhodacycle.

6.2.4. Iridium

Interest in cycloiridated complexes has been greatly stimulated by the discovery of exceptional activities of iridacycles in catalysis and for photophysical applications. Specifically, iridium complexes containing *P,C,P*-tridentate coordinating pincer ligands are outstanding catalysts for alkane dehydrogenation as well as for the dehydrogenation of aminoborane and for the dehalogenation of alkyl halides.[49,378] In addition, triscyclometalated iridium(III) complexes have been recognized as powerful organic light emitting diodes (OLEDs).[379] Their application potential as phosphorescent dopants is further increased by the possibility to tune the excitation energy and hence the emission wavelength through modifications in the cyclometalated ligand. Cycloiridation provides a direct synthetic access to such compounds typically without entailing any laborious pre-functionalization of ligand precursors, nor involving the manipulation of air- or moisture-sensitive intermediates.

The most common low-valent precursors for cycloiridation encompass $[IrX(olefin)_2]_2$, $[IrX(CO)_2]_2$, and their monomeric and cationic analogs (*cf.* section 6.2.3.). Cycloiridation reactions resemble in many aspects cyclorhodations. For example, the formation and stability of the 14e rhodium complex **227** (*cf.* Scheme 94) is paralleled by its iridium analog.[380] In many cases, however, slight differences are apparent due to the intrinsic reactivity differences of rhodium and iridium, partially imposed by the different atomic radius and consequentially the different charge density. Thus, cycloiridation of the potentially *P,C,P*-tridentate pincer ligand precursor **206a** at room temperature affords the biscyclometalated complex **232** originating from C–H bond activation as the major product, while the C–C bond activation product **233** is obtained only in minor quantities (Scheme 97).[351] Complex **232** is, unlike its rhodium analog, stable at ambient temperatures. Only when heated to 100 °C, it transforms to the thermodynamically favored complex **233** with two five-membered metallacycles. The lower reactivity of complex **232** is compatible with the higher stability of iridium hydride species as compared to rhodium analogs.

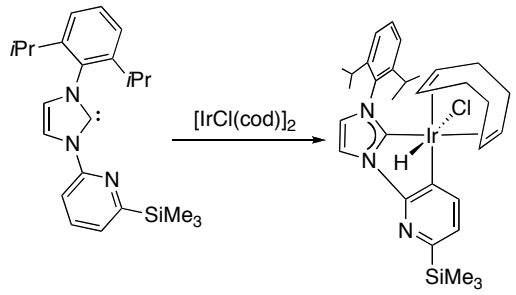
Scheme 97



Cycloiridation via breaking of a strong O–C_{alkyl} bond has recently been disclosed upon reacting anisole or phenyl ethyl ether with a coordinatively unsaturated iridium tris(pyrazole)borate precursor. The alkyl group is transferred to the aryl ring, and affords a mixture of alkylidene and alkene iridium hydride complexes.[381,382]

Iridium hydrides have also been generated via cyclometalation of pyridyl-functionalized carbenes. Upon reaction of the free carbene **234** with $[IrCl(cod)_2]_2$, $C_{pyridyl}$–H bond oxidative addition occurs to yield the *C,C*-iridacycle **235** rather than pyridine *N*-coordination (Scheme 98).[383] When using the analogous rhodium precursor, oxidative addition is arrested and a potential intermediate comprising a $C_{pyridyl}$–H···Rh hydrogen bond is isolated. Despite the fact that *N*-coordination of the pyridyl group is principally possible,[384] apparently, the bulky *ortho* substituent renders the C–H bond activation pathway more favorable.

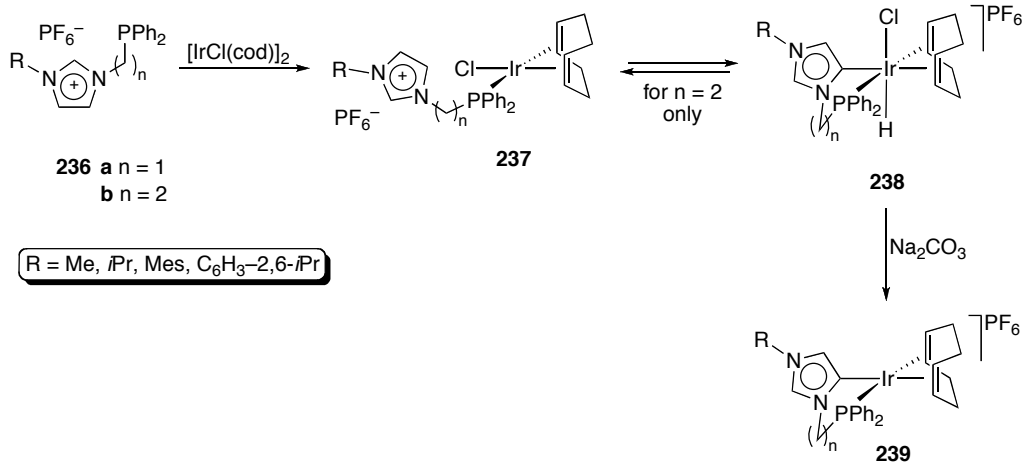
Scheme 98



234 **235**

Further evidence for an oxidative addition process in cycloiridation using iridium(I) precursors[385] has recently been provided by a detailed study on the cyclometalation of phosphine-substituted imidazolium salts **236** (Scheme 99).[386,387] Iridium coordination to the phosphine gives the fully characterized coordination complex **237**. Subsequent C–H bond activation occurs selectively at the imidazolium C4 position, thus affording the oxidative addition product **238**. Bond activation is reversible for the ethylene-linked imidazolium phosphine **237b**, yet irreversible for the methylene-linked congener **237a**. Base-promoted reductive elimination releases formally HCl and affords the cyclometalated abnormal carbene iridium(I) complex **239**.

Scheme 99



236 **a** n = 1
b n = 2

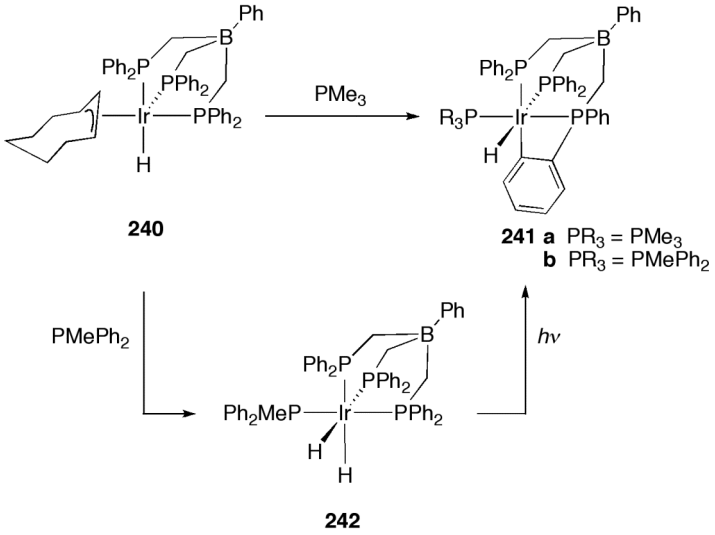
R = Me, *i*Pr, Mes, C_6H_3–2,6-*i*Pr

237 **238** **239**

The trisphosphine borate iridium(III) complex **240** constitutes a masked iridium(I) precursor for cyclometalation (Scheme 100). In the presence of PMe_3, intramolecular activation of a C_{aryl}–H bond takes place to give complex **241a** with a tetradentate cyclometalated ligand.[388] Reductive elimination of coe, promoted by external PMe_3, is supposed to produce a coordinatively unsaturated, electron-rich iridium center, which readily undergoes oxidative addition reactions. In the presence of $PMePh_2$, β-hydrogen elimination rather than reductive elimination takes place,

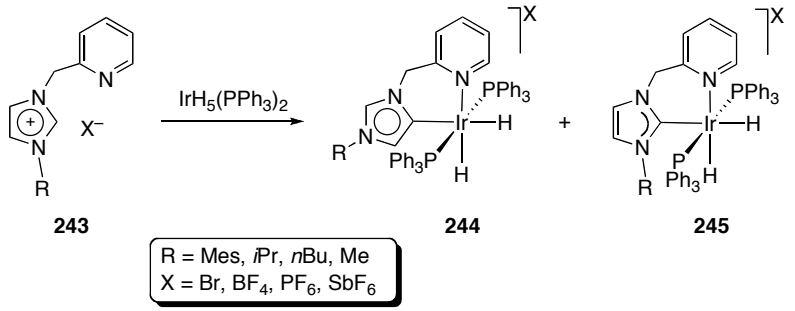
thus yielding the dihydride **242** and 1,3-cyclooctadiene. Photochemically induced dissociation of H_2 from this complex generates the corresponding coordinatively unsaturated iridium(I) intermediate and cyclometalation ensues. C–H bond activation from **242** is a competitive process due to the presence of phenyl groups in the trisphosphine ligand as well as in $PMePh_2$. Related $C(sp^3)$–H bond activation has been reported also for a close analog of **240** featuring *i*Pr instead of phenyl substituents at phosphorus,[389] and for a rare iridium(II) complex containing *t*Bu substituted phosphine alkoxide donors.[390]

Scheme 100



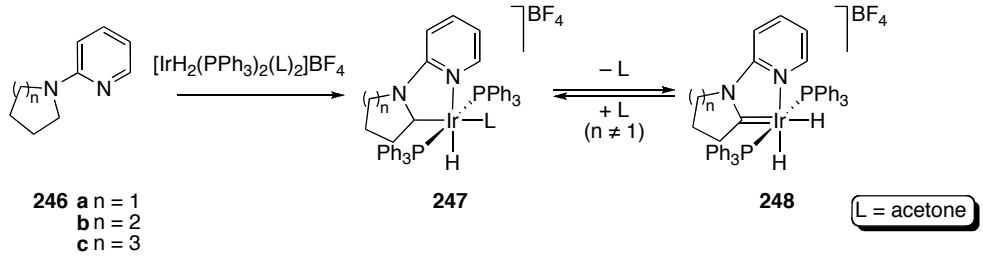
The family of high-valent iridium precursors for cyclometalation is considerably larger than for rhodium, because of the high affinity of iridium for stabilizing hydrides. Thus, cycloiridation has been pursued with a number of iridium (poly)hydride precursors like $[IrH_2(PPh_3)_2(acetone)_2]^+$ or $[IrH_5(PPh_3)_2]$, which release H_2 after C–H bond activation, thus providing a thermodynamic driving force for cyclometalation. The pentahydride precursor efficiently produces the abnormal carbene complex **244** and the normal analog **245** from the corresponding picolyl-substituted imidazolium salts **243** via C–H bond activation (Scheme 101).[123,391] Studies using non-heteroatom substituted imidazolium salts have revealed,[392] however, that the C–H bond activation process proceeds also in the absence of a wingtip donor group. Hence, this bond activation is not necessarily heteroatom-assisted and.

Scheme 101



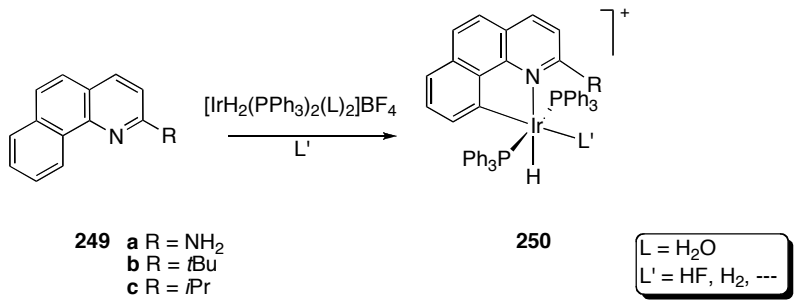
Reaction of the iridium dihydride with *N,N*-dimethylaminopyridine[393] or the cyclic aminopyridines **246** induces C(sp^3)–H bond activation at room temperature and yields the metallacycle **247** (Scheme 102).[394] In coordinating solvents, this complex is stable. In non-coordinating solvents, however, decoordination of acetone induces an α-hydrogen elimination and affords the carbene complex **248**. The hydrogen migration is reversible and upon addition of acetone, complex **247** is regenerated. A similar solvent dependent equilibrium between a cyclometalated (benzyl)iridium complex and a (benzylidene)iridium hydride has been observed upon activation of a benzylic C–H bond in 2-ethyl phenol mediated by a tris(pyrazole)borate iridium(III) precursor.[395]

Scheme 102



By using an analogous cyclometalation procedure, Crabtree and coworkers have investigated the effect of pyridine *ortho* substitution on the *cis*-positioned ligand in complex **250** (L' = HF, H_2; Scheme 103). Hydrogen bonding (for L' = HF)[396] and reversible proton transfer (for L' = H_2)[397] to the amino group in **250a** has been detected. If the *ortho* substituent is a bulky and shielding *t*Bu group (**250b**), agostic interactions rather than coordination of an external ligand has been noted.[398] Interestingly, no such agostic interaction has been identified in the related complex **250c** bearing an *i*Pr group in *ortho* position, despite the fact that the coordination site *trans* to the aryl ligand is vacant.

Scheme 103



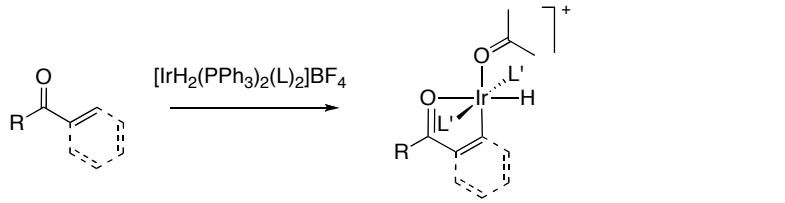
249 **a** R = NH_2
b R = *t*Bu
c R = *i*Pr

250

L = H_2O
L' = HF, H_2, ---

Apart from imines and phosphines, also keto groups (**251**) have been shown to be suitable donor groups to direct the C–H bond activation using the dihydride iridium(III) precursor $[IrH_2(PPh_3)_2(acetone)_2]^+$ (Scheme 104).[399] Cyclometalation is induced despite the poor match of the hard oxygen donor with the soft iridium center. Acetophenones give *ortho*-metalated complexes, and α,β-unsaturated ketones and esters yield the corresponding metallacycles **252** via β-hydrogen abstraction.

Scheme 104



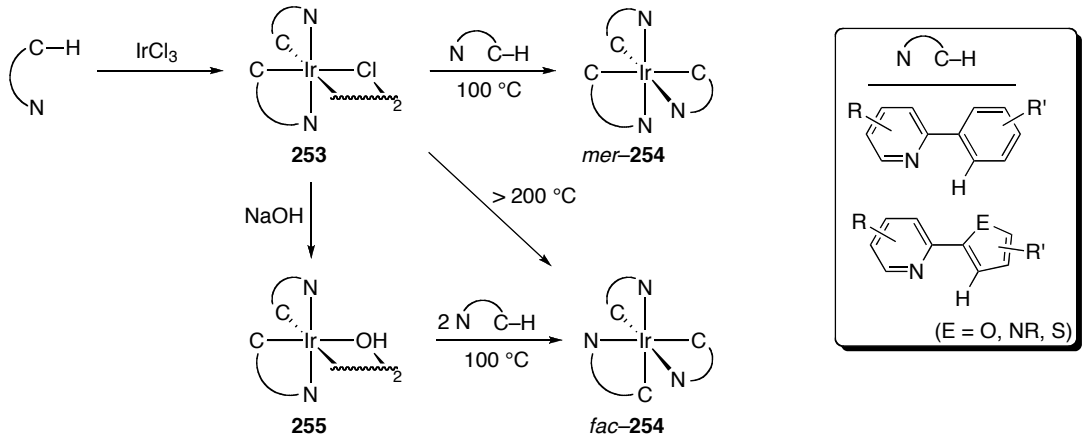
251 **a** R = Me
b R = OMe

252

L = acetone, L' = PPh_3

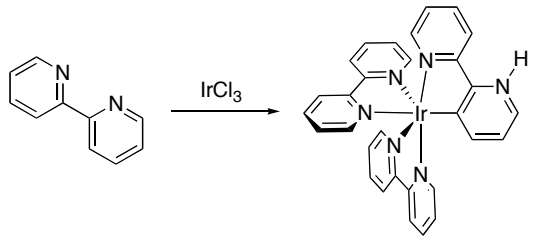
Iridium trichloride is the precursor of choice for preparing light-emitting triscyclometalated *C,N*-iridacycles.[400] Thermally induced C–H bond activation affords the μ-chloro-bridged dimer **253** (Scheme 105). The third cyclometalation step is generally performed at high temperatures (> 200 °C) in order to avoid formation of the *mer*–isomer **254** and to obtain the photophysically much more efficient though kinetically unfavored *fac*-isomer.[401] Recently, a milder procedure has been reported starting from the μ-hydroxy-bridged dimer **255**.[402] When using an excess ligand, temperatures as low as 100 °C are sufficient for producing selectively the desired *fac*-isomer.

Scheme 105



Cycloiridation of bipyridine with $IrCl_3$ at high temperatures yields complex **256**, originating from C3–H bond activation in one of the bipyridine ligands (Scheme 106). Since bipyridine is well-known for its *N,N*-bidentate coordination to metal centers, cyclometalation has been disregarded initially.[403] The speculative assignment has evoked a controversial discussion that only settled with multiple crystal structure determinations and sophisticated NMR analyses several years later, unambiguously evidencing the unusual *N,C*-bidentate coordination mode of the bipyridine ligand.[404–407] The reaction mechanism has been suggested to involve a roll-over of the metal and has been exploited in particular in platinum chemistry (*cf.* section 6.2.6).

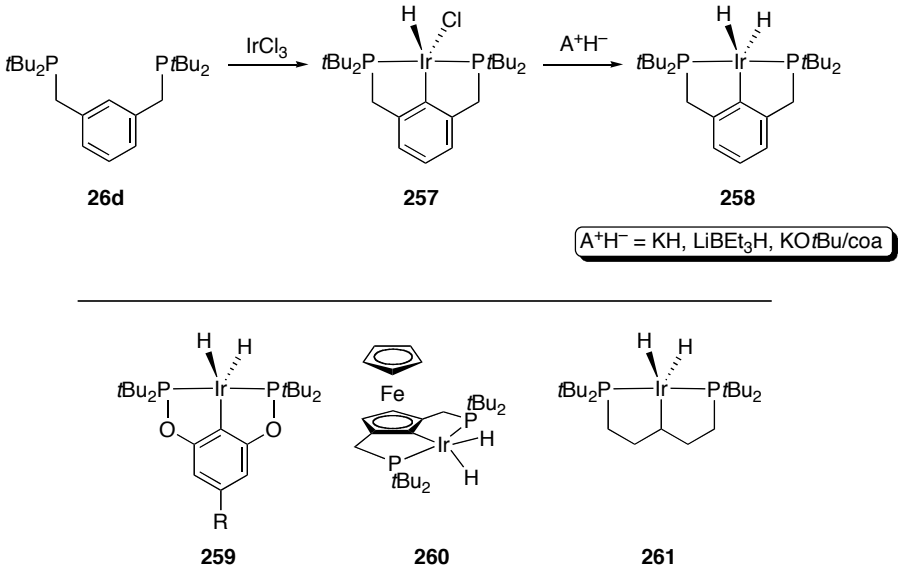
Scheme 106



Hydrated $IrCl_3$ also cyclometalates the potentially *P,C,P*-tridentate coordinating ligand precursor **26d** to yield the iridium(III) complex **257** (Scheme 107).[107,373] Substitution of the chloride in **257** by hydride and formation of **258** has been accomplished originally by using KH,[408] later also with $LiBEt_3H$,[409] or simply with a non-nucleophilic base in the presence of an alkane like cyclooctane (coa).[410] The latter procedure affords an equilibrium between **258** and an iridium(I) complex comprising the PCP pincer ligand and coe. Complex **258** and variations thereof (*e.g.* **259–261**) are highly active for a number of reactions, including CO_2 reduction,[411] ammonia activation,[412] and the dehydrogenation of aminoborane.[413,414] For synthetic purposes most appealing,

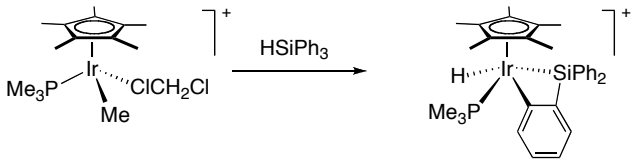
complexes **258–260** and derivatives are highly efficient catalysts for the homogeneous dehydrogenation of unfunctionalized alkanes.[415] The initial selectivity for terminal olefins is high,[416] and turnover numbers as high as 3300 mol alkane per mol catalyst have been achieved.[417]

Scheme 107



Iridium(III) complexes containing a Cp* ligand constitute another powerful class of precursors for cycloiridation. Different reaction trajectories have been put forward, depending largely on the nature of ligands in the precursor complex. For example, the iridium dihydride $[Ir(Cp^*)H_2(PMe_3)]$ eliminates photochemically or thermally H_2, thus forming a coordinatively unsaturated iridium(I) complex that is able to activate unfunctionalized alkanes.[418] Similarly, the dimethyl analog $[Ir(Cp^*)Me_2(PPh_3)]$ activates benzene.[419] As a competitive reaction, C–H bond activation in one of the phosphine-bound phenyl groups takes place, thus forming a four-membered iridacycle. Although details of the reaction mechanism have not yet been disclosed, it is interesting to note that the related cationic complex **262** reacts with $HSiPh_3$ to afford the *C,Si*-metallacycle **263**, which is formally an iridium(V) species (Scheme 108).[420] Likely, the iridium oxidation occurs upon cyclometalation, *i.e.* the activation of the C_{aryl}–H bond. Similar activation of a C_{alkyl}–H bond is observed when mesityl- rather than phenyl-substituted silanes are used, though the product is unstable and isomerizes to a silylene complex. Nevertheless, these investigations clearly underline that oxidative addition pathways should not be disregarded *a priori* when using iridium(III) precursors.

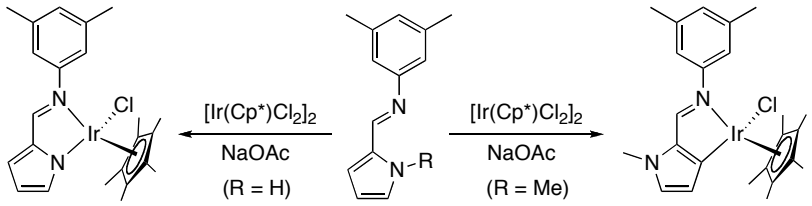
Scheme 108



262 **263**

Cycloiridation with dimeric $[Ir(Cp^*)Cl_2]_2$ has been widely used for the phosphine-directed intramolecular activation of C–H bonds,[374] yet less frequently for the imine-assisted activation of C_{aryl}–H[421] and C_{alkyl}–H bonds.[422] Recent expansion of this protocol to amines has been demonstrated,[282] again revealing the beneficial role of the AcO^- ion in mediating proton abstraction and metal coordination (*cf.* section 6.2.3). Under typical conditions, reductive chlorine elimination seems less likely. Calculations have shown that the barriers for cyclometalation of *N,N*-dimethylbenzylamine are smallest for an electrophilic C–H bond activation ($\Delta G^{\ddagger}$ = +16.0 kcal mol^{-1}). The computed energies of the transition states for oxidative addition ($\Delta G^{\ddagger}$ = +30.7 kcal mol^{-1}), or a complex-assisted metathesis pathway ($\Delta G^{\ddagger}$ = +22.8 kcal mol^{-1}) are substantially higher.[423] Apart from C_{aryl}–H bond activation, the $[Ir(Cp^*)Cl_2]_2$ / AcO^- system also allows for the cyclometalation of heterocycles like the pyrrole imines **264b** (Scheme 109).[424] In order to direct product selectivity towards the C–H bond-activated complex **265**, the pyrrole needs to be *N*-substituted. In *N*-unsubstituted pyrrole **264a**, N–H bond activation dominates and yields the *N,N*-chelate **266**. Such intramolecularly assisted N–H bond activation is conceptually related to cyclometalations involving C-H bond activation (*cf.* section 1). The computed reaction profiles for both bond activation processes suggest a similar transition state involving a six-membered metallacycle with some degree of agostic interaction. The calculations further support the reaction outcome as N–H bond activation is preferred over C–H bond cleavage both thermodynamically ($\Delta\Delta G°$ = +4.1 kcal mol^{-1}) and kinetically ($\Delta\Delta G^{\ddagger}$ = +6.4 kcal mol^{-1}).

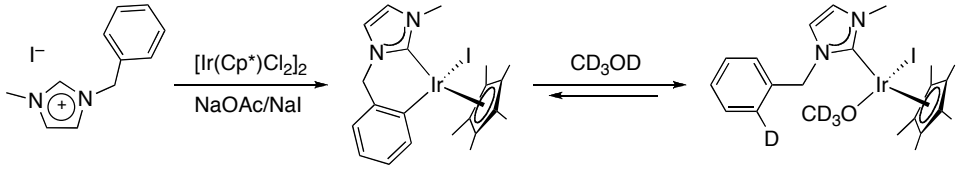
Scheme 109



266 **264** **a** R = H **b** R = Me **265**

The synthetic methodology is also applicable for the double C(sp^2)–H bond activation using an *N*-heterocyclic carbene as an anchoring group. Thus, iridation of the benzyl-functionalized imidazolium salt **267** with $[Ir(Cp^*)Cl_2]_2$ in the presence of NaOAc yields the cyclometalated complex **268** (Scheme 110).[425] In CD_3OD, reversible cleavage of the Ir–C_{aryl} bond has been noted, establishing an equilibrium between the iridacycle **268** and complex **269** with a monodentate carbene ligand. This reactivity has been exploited for devising a catalytic process for the H/D exchange in a variety of solvent molecules.

Scheme 110



267 **268** **269**

6.2.5. Palladium

Cyclopalladation has undoubtedly been studied most extensively in cyclometalation chemistry. Various reviews focusing specifically on cyclopalladation and on the wide application potential of palladacycles have appeared.[23,40,43] Cyclopalladation is enormously versatile and has been accomplished with a great variety of ligand systems, including donor groups based on nitrogen (primary, secondary, and tertiary amines, imines), phosphorus (phosphines, phosphinites, phosphites), and sulfur (specifically sulfides).[23] Cyclometalations that are assisted by oxygen, arsenic, and selenium donors are also known, though they are much rarer.[149,150]
Chirality has been incorporated, for example through asymmetric ligand synthesis,[426–430] or by applying a chiral Re(Cp) complex containing a phosphinoalkyl ligand as donor for palladium coordination.[431] Double and even triple C–H bond activation of benzene, substituted with

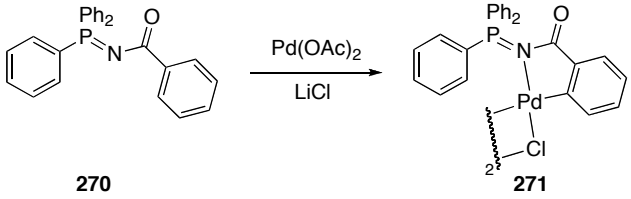
pyridine donor sites has been achieved.[432,433] Product formation may be controlled by an appropriate choice of solvent. For example, azobenzene is cyclopalladated only once when methanolic $PdCl_2$ is used,[5,434] while double C–H bond activation takes place in DMF solutions.[435] The most widely used precursor for cyclopalladation is $Pd(OAc)_2$, which does not require the addition of extra NaOAc as discussed in related iridium and rhodium chemistry. Much rarer are cyclometalations using $Pd(tfa)_2$ comprising a less basic ligand than AcO^-, and $[Pd(NCMe)_4]^{2+}$ as a highly electrophilic reagent. Another class of precursor palladium salts suitable for cyclometalation encompasses $[PdCl_4]^{2-}$, $PdCl_2$ and its soluble versions, *e.g.* $PdCl_2(NCMe)_2$. Less frequently used precursors include the rigidly *cis*-configured $PdCl_2(cod)$, and $PdCl_2(PR_3)_2$, since the PPh_3 ligands are difficult to be displaced by a donor group other than a phosphine. $Pd(OAc)_2$ is actually a $[Pd(OAc)_2]_3$ trimer that splits easily into monomeric $[Pd(OAc)_2L_2]$ in the presence of coordinating groups.[436] Monomers are also present in solvents like benzene at high temperatures. Acetic acid is often the solvent of choice for $Pd(OAc)_2$-mediated cyclopalladation.[437] Different advantages have been put forward, such as the enhanced basicity of acetate in this solvent. As a consequence of the stronger bonding of acetate to the palladium(II) center, dissociation and reductive elimination to undesired palladium(0) is precluded. In addition, acetic acid favors monomeric rather than trimeric $Pd(OAc)_2$,[438] and it has been noted that with amine donors, the coordination equilibrium prior to C–H bond activation is shifted in acetic acid from the PdX_2L_2 species (*cf.* **B**, Scheme 2; L = amine donor) towards the coordinatively unsaturated and active species PdX_2L (*cf.* **C**, Scheme 2). In apolar solvents, ligand dissociation from PdX_2L_2 is hampered, though it can be accelerated by the addition of catalytic amounts of a strong acid like triflic acid.[439] The equilibrium between species of type **B** and type **C** is particularly unfavorable when using primary amines.[440,441] For some cyclopalladations, hence a 1:1 $Pd(Ac)_2$/amine stoichiometry is preferred over the 1:2 ratio typically employed for tertiary amines.[442] Alternatively, cyclometalation of primary amines has been accomplished with $PdCl_2$ and by subsequent $AgClO_4$-mediated abstraction of a chloride from the coordination complex to generate coordinative unsaturation, thus inducing C–H bond activation.[443]

The mechanism of the cyclopalladation reaction involving arene C–H bond activation has been studied in great detail and compelling evidence for an electrophilic pathway has been provided.[40] Reaction rates and regioselectivities of C–H bond activation correlate well with the electron-donating ability of the substituents on the arene. This close analogy to aromatic electrophilic

substitution prompted the formulation of a related mechanism for cyclopalladation.[39] Indeed, in many cases a reaction trajectory reminiscent to aromatic electrophilic substitution seems to offer a satisfying mechanistic rational. Recent theoretical calculations on the cyclopalladation of *N,N*-dimethylbenzylamine with $Pd(OAc)_2$ yet point to a reaction profile including an agostic interaction as a key structural feature that initiates the C–H bond activation,[91] as opposed to the π complex for aromatic substitutions (*cf.* section 3.1).

The *endo*/*exo* preference of cyclopalladation has been investigated. For example, the iminophosphorane **270** possesses two different types of C–H bonds that may be activated by a nitrogen-assisted mechanism (Scheme 111).[444,445] Upon reaction with $Pd(OAc)_2$, exclusive *exo* cyclopalladation has been noted. The corresponding *endo* product was only observed when the benzoyl moiety was replaced by a pyrrolidine or morpholine group that has low tendency to undergo C–H bond activation. Theoretical calculations suggest a substantially higher transition state for *endo* metalation, even though the product was computed to be more stable than the *exo* complex **271**.

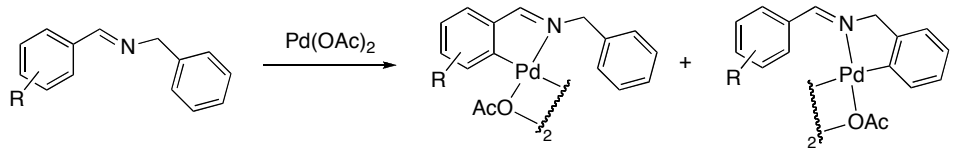
Scheme 111



270 **271**

In contrast, cyclopalladation of benzylidene benzylimines **272** with $Pd(OAc)_2$ yields preferentially the *endo* metallacycles **273** (Scheme 112).[446] Products **274** from *exo* metalation are only formed if *endo* metalation requires the activation of an $C(sp^3)$–H bond (*e.g.* R = 2,6-CH_3) to form a less favored, six-membered metallacycle, or when steric constraints disfavor the *endo* cyclopalladation (*e.g.* R = 2-NO_2). Aliphatic *endo* cyclopalladation in turn is only feasible if the complex from metalation at the *exo* position would yield a four-membered metallacycle, *i.e.* when *N*-phenyl benzylimines are used.

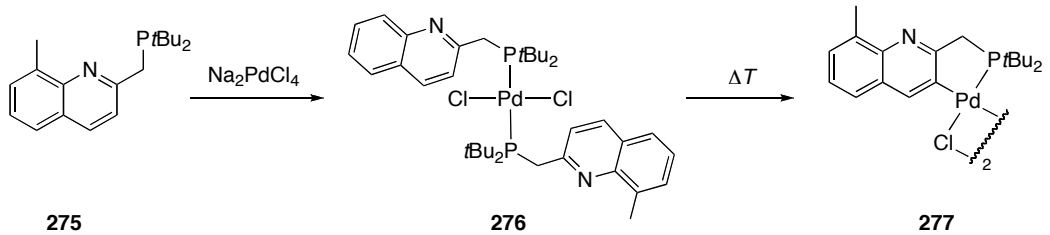
Scheme 112



272 **273** **274**

A mechanism different from the electrophilic reaction profile applies for the activation of C(sp^2)–H bonds in electron-deficient aromatic systems such as in pyridines and related heterocycles. Typically, these ligands are cyclopalladated with relatively electron-rich palladium(II) precursors like the palladate $[PdCl_4]^{2-}$. The metalation of phosphine-substituted methylquinoline **275** may be illustrative (Scheme 113).[447] In the presence of Na_2PdCl_4, the coordination complex **276** is obtained at room temperature. Thermally induced cyclometalation affords the C3-metalated dimer **277**. Upon exchanging the donor group from a phosphine to an imine, the C–H bond activation is less selective and produces a cyclopalladated complex analogous to **277** along with a palladacycle originating from competitive activation of the methyl C(sp^3)–H bond in nearly equal ratios (*vide infra*).

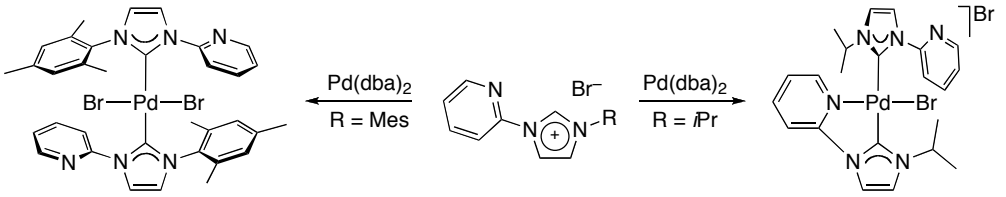
Scheme 113



275 **276** **277**

Activation of a heterocyclic C–H bond has also been achieved by cyclopalladation of the imidazolium salt **278a**, which affords the palladium complex **279** containing a chelating and a monodentate *N*-heterocyclic carbene ligand (Scheme 114).[448] Cyclometalation has been accomplished with $Pd(dba)_2$ and oxidative C–H bond addition, which is presumably directed by the pyridine donor. The intermediate from this reaction has been surmised to be an electron-rich palladium(II)–hydride, which engages in a second C–H bond activation to give complex **279**. The stability of the formed metallacycle depends on the steric requirements of the wingtip group. With bulky mesityl rather than *i*Pr substituents on the imidazolium salt, the palladation of ligand **278b** gives complex **280** featuring only monodentate coordinating carbenes.

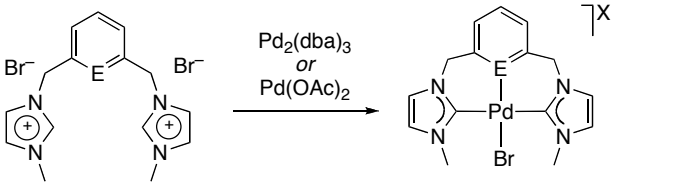
Scheme 114



280 **278 a** R = *i*Pr **b** R = Mes **279**

Similar oxidative addition of palladium(0) as been applied to initiate cyclometalation of ligand **281a** (Scheme 115). Double C–H bond activation yields the *C,C,C*-tridentate pincer-type complex **282a**,[449] In this case, oxidative addition fulfills a similar role as heteroatom coordination. It provides the initial interaction that directs the metal center to the C–H bond to be activated, hence constituting an example of carbon-assisted C–H bond activation.[450] Imidazolium C–H bond activation takes place in the pyridine analog **281b**, yielding the *C,N,C*-tridentate pincer complex **282b**. However, C–H bond activation is precluded if the palladium center is not anchored at the central ring, and no reaction takes place when starting from ligand precursor **281c**.

Scheme 115

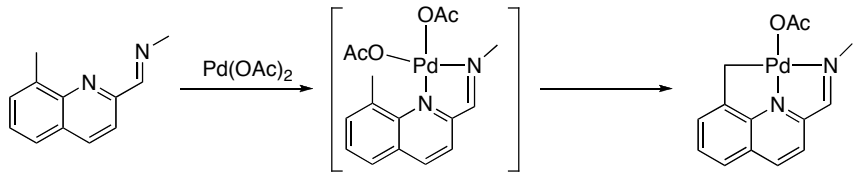


281 **a** E = C–Br **b** E = N **c** E = C–H **282** **a** E = C, X = -- **b** E = N, X = Br

Cyclopalladation involving the activation of C(sp^3)–H bonds adjacent to a (hetero-)aryl moiety has been extensively studied, perhaps promoted by the enhanced acidity of the benzylic proton as compared to other C(sp^3)-bound hydrogens. The cyclopalladation of substituted 8-methylquinolines uncovered some key details on the specific reaction trajectory (Scheme 116).[451] Reaction of the imine-functionalized ligand precursor **283** with $Pd(OAc)_2$ affords the palladacycle **284**, resulting from the activation of a benzylic C–H bond. Concurrent N_{imine} and $N_{quinoline}$ coordination to the palladium center may favor the formation of an intermediate **X**, in which the palladium coordination plane and the quinoline plane coincide. Such an arrangement brings the acetate ligand and the C8-bound methyl group in close proximity, thus stimulating the C–H bond activation. Both agostic and electrophilic mechanisms have been suggested for the

bond activation, involving anion-assisted abstraction of the benzylic proton and simultaneous coordination of the carbon to the palladium center.[20] If the quinoline substituent is a phosphine rather than an imine, activation of the quinoline C3–H bond takes place exclusively (*cf*. **277**, Scheme 113). Activation of the benzylic C–H bond may be impeded by the strong Pd–P bond, which makes $N_{quinoline}$ coordination less relevant, and by the flexibility of the donor substituent, which allows for a significant torsion of the metal coordination plane out of the quinoline plane. Removing the donor site as in 2,8-dimethylquinoline prevents cyclopalladation completely.

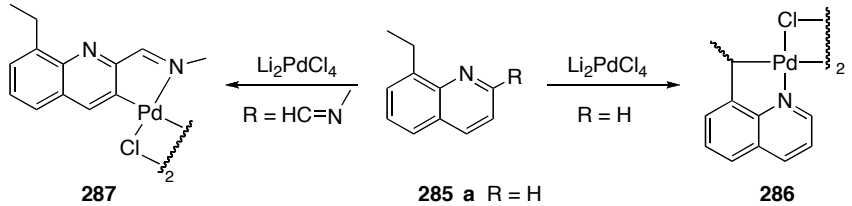
Scheme 116



283 **X** **284**

Cyclopalladation of 8-ethylquinoline **285** proceeds analogously. The resulting palladacycle **286** contains a center of chirality at the metal-bound carbon (Scheme 117).[452] Notably, incorporation of an imine donor group at C2 affords the cyclometalated complex **287** originating from $C_{pyridyl}$–H bond activation, while activation of the C(sp^3)–H bond is hindered, presumably due to the instability of an intermediate like **X**. These experiments reflect the delicate balance between steric congestion and steric promotion of C–H bond activation. Moreover, they illustrate similar activation energies for benzylic C–H and pyridyl C–H bond activation.

Scheme 117



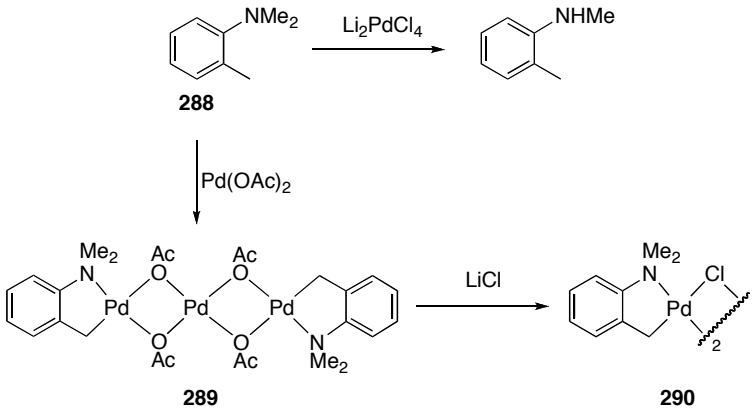
287 **285** **a** R = H **b** R = CH=NMe **286**

Benzylic C–H bond activation in phosphines that bear *ortho*-substituted aryl groups is well established. Examples that are most relevant to catalysis include the cyclopalladation of P(*o*-tol)$_3$ and P(Mes)$_3$ with $Pd(OAc)_2$ or Na_2PdCl_4 to give the corresponding five-membered palladacycles.[103,453] The basicity of the phosphines paired with their large cone angle (θ = 194° and 212°, respectively) labilize *cis*-coordinated ligands. Cyclopalladation thus provides a means

for the palladium center to attain a square-planar geometry and to avoid coordinative unsaturation due to ligand dissociation.

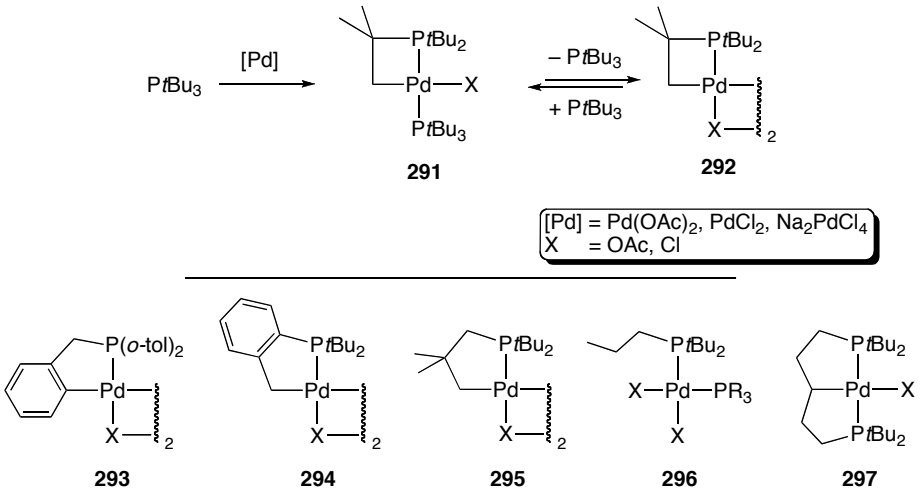
Contrary to phosphines, *ortho*-substituted anilines are significantly more difficult to cyclopalladate. In the presence of Li_2PdCl_4, the dimethylaniline ligand precursor **288** undergoes an unprecedented C–N bond cleavage and yields mono *N*-methylated aniline (Scheme 118).[454] With $Pd(OAc)_2$ cyclopalladation takes place and affords complex **289** as an unusual trimer, which transforms to the expected dimeric species **290** upon treatment with a chloride salt.[455]

Scheme 118



Cyclopalladations involving the activation of a C_{alkyl}–H bond typically require strongly basic and bulky ligands and have been observed with phosphine donors, yet only rarely[456] with other donor groups. For example, P*t*Bu_3 is cyclopalladated with a variety of palladium sources including $Pd(OAc)_2$ and $PdCl_2$ and affords the four-membered palladacycle **291** (Scheme 119).[102,457] Such cyclopalladation may occur in many palladium-catalyzed reactions that are promoted by P*t*Bu_3.[458] Dissociation of the coordinated P*t*Bu_3 ligand produces the catalytically inactive dimer **292**. This catalyst deactivation pathway can be suppressed by employing an excess of P*t*Bu_3, which minimizes ligand dissociation and hence shifts the equilibrium towards **291**.

Scheme 119



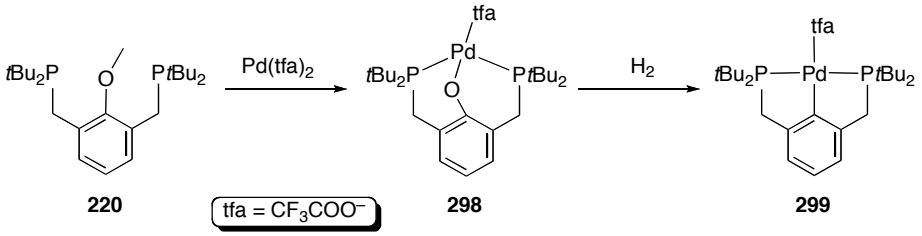
291 **292** **293** **294** **295** **296** **297**

Shaw and coworkers have evaluated the propensity of a variety of phosphines to engage in cyclopalladation (**293–297**, Scheme 119).[459,460] The results allow some of the key trends of phosphorus-assisted C–H bond activation to be illustrated. Most of these trends may be extrapolated to cyclometalation in general:

- $C(sp^2)$–H bond activation is favored over $C(sp^3)$–H bond activation (**293**)
- formation of five-membered palladacycles is preferred over four-membered metallacycles (**294**, **295**)
- the *gem*-dimethyl effect facilitates cyclopalladation (**295** *vs* **296**)
- bidentate heteroatom coordination pre-arranges otherwise unreactive C–H bonds for cyclopalladation (**297** *vs* **296**)

Cyclopalladation has also been effected by C–O bond cleavage starting from the pincer-type ligand precursor **220** (Scheme 120).[364] Unlike in related rhodium chemistry, $Pd(tfa)_2$ preferably cleaves the C_{alkyl}–O bond and affords complex **298** comprising a phenoxide ligand moiety. A similar outcome has been observed previously with analogous monophosphine ligands.[461] However, the presence of two six-membered metallacycles in **298** imposes substantial ring strain, which has been exploited to induce cyclometalation. In the presence of H_2 and at high temperatures, complex **298** undergoes a formal oxygen transfer reaction, affording the biscyclometalated PCP pincer palladium complex **299** and H_2O. When the pincer ligand precursor bears a sterically more demanding ethoxy group instead of a methoxy substituent, C_{aryl}–O bond activation and direct cyclometalation becomes more favorable, even though the main product remains the phenoxide complex (product ratio **298**/**299** ca. 9:1).

Scheme 120

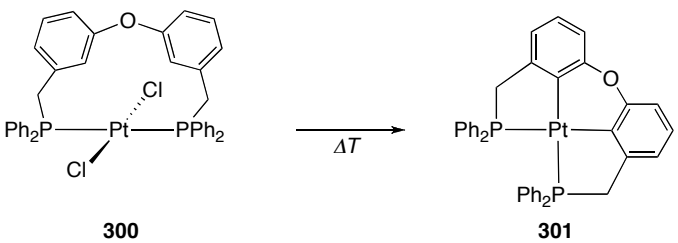


6.2.6. Platinum

Cycloplatination is in many aspects strongly related to cyclopalladation. Perhaps the largest discrepancy arises from the lower electrophilicity of platinum(II), thus reducing the scope of electrophilic pathways for C–H bond activation.[462] On the other hand, this enhanced electron density induces a better stability of higher oxidation states, which facilitates oxidative addition as an alternative mechanism to the electrophilic pathway. Indeed, platinum(IV) products have been isolated from cycloplatination.[463]

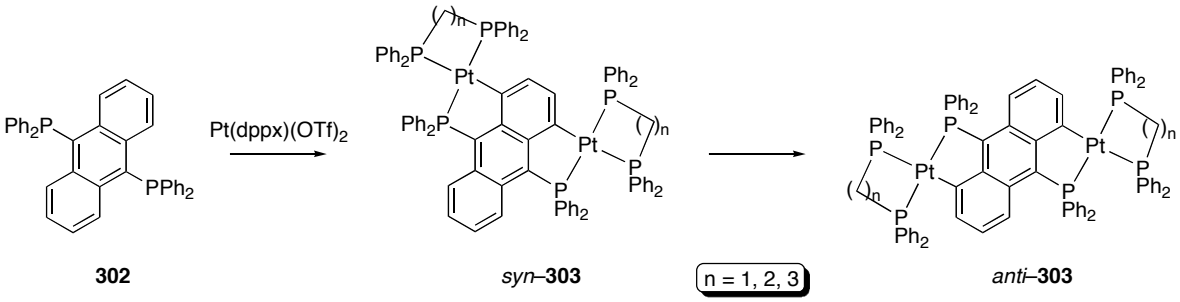
The lower activity of platinum(II) in cyclometalation is reflected, for example, by the facile formation of PCP pincer complexes,[107, 464] while only specific NCN pincer ligand precursors undergo platinum-mediated C–H bond activation.[465] In some cases, it is possible to exchange the donor site after cycloplatination, which illustrates the remarkable stability of the Pt–C bond.[466] Early mechanistic investigations on the intramolecular activation of C(sp^2)–H bonds using a *trans*-coordinating diphosphine ligand **300** indicate that cycloplatination is reversible (Scheme 121).[467] Formation of the doubly cycloplatinated complex **301**, and specifically the selective hydrogen migration from one of the central aryl rings to a phosphine-bound phenyl ring, have been explained by a multistep process involving reversible Pt–C bond making and breaking.

Scheme 121



Further evidence for reversible cyclometalation originates from experiments using bis(diphenylphosphino)anthracene **302** (Scheme 122).[468] Upon cycloplatination with Pt(dppx)$(OTf)_2$, the *syn*-isomer of the diplatinum complex **303** is formed as the kinetic product. Prolonged reaction times induce a rearrangement to the *anti*-isomer, supposedly via an electrophilic attack of the platinum ions.

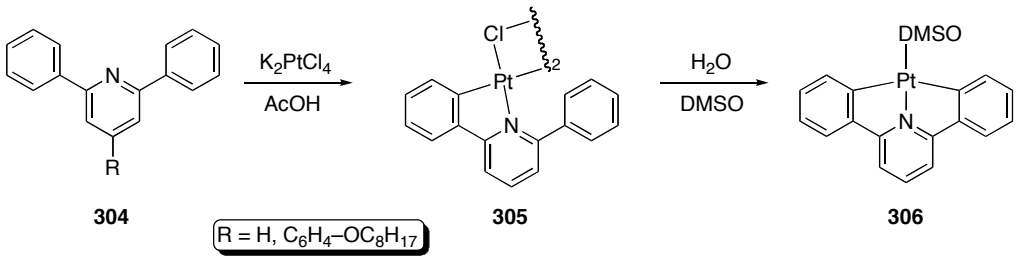
Scheme 122



302 *syn*–**303** *anti*–**303**

Kinetic and mechanistic studies have pointed out the relevance of the ancillary ligands for providing cationic species[469] or for generating a vacant coordination site[470,471] in order to initiate the C–H bond activation process. Peters and coworkers[472] have elegantly combined these factors in a constrained diphosphine complex containing a remote intramolecular phenylborate anion. When coordinated to platinum, oxidative addition of the C_{phenyl}–H bond has been observed. The cycloplatination of the diphenyl pyridine **304** represents another intriguing example that illustrates these aspects (Scheme 123).[473] Heating **304** with K_2PtCl_4 in acetic acid induces bond activation and affords the monocycloplatinated complex **305** as a thermally stable dimer. The second bond activation only occurs in the presence of water and gives complex **306**. Several factors have been suggested to influence the formation of **306**, including the solvation of the formed HCl, and the operation of two different mechanisms for the first and the second C–H bond activation, the second likely being and electrophilic process.

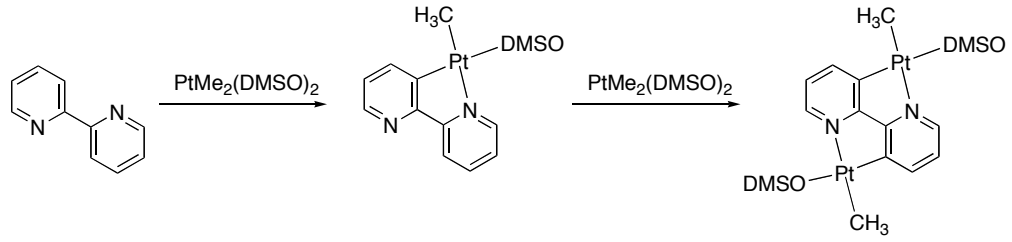
Scheme 123



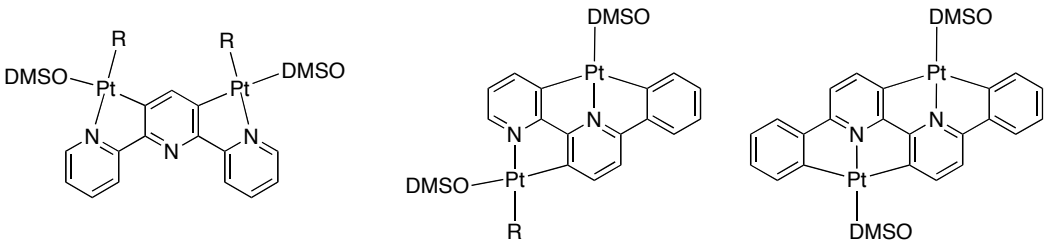
Most of the early work on cycloplatination has relied on $[PtCl_4]^{2-}$ as metal precursor. Further common starting materials for cycloplatination include $PtCl_2(solv)_2$, $PtMe_2(solv)_2$, (solv = SMe_2, DMSO), $Pt(acac)_2$ (acac = acetylacetonate), and the dimeric species $[PtMe_2(SMe_2)]_2$. Recently, the platinum amide $Pt(cod)Cl(N(SiMe_3)_2)$ and platinum acetate have been suggested as a new powerful precursors for cyclometalation.[474,475] Furthermore, a mixture obtained from K_2PtCl_4 and aqueous HI has been reported to be an efficient precursor for the cycloplatination of primary amines.[476] The mixture has been surmised to contain some K_2PtI_5, which may overcome the notorious inertness of K_2PtI_4 in cycloplatination reactions.

Zucca and coworkers have explored the cycloplatination of bipyridine and its derivatives. They have deduced a so-called 'rollover' mechanism for the $C(sp^2)$–H bond activation, which leads to the less common *C,N*-cyclometalation of bipyridine rather than *N,N*-coordination (*cf.* **255**, Scheme 106). When using the electron-rich platinum(II) salt $PtMe_2(DMSO)_2$, bipyridine is cyclometalated to afford complex **307** (Scheme 124).[477] Notably, complex **307** can be cyclometalated a second time, producing the bimetallic complex **308** with a dianionic bipyridyl ligand.[478] Variations in the bipyridine skeleton gives access to a range of bimetallic complexes via sequential rollover cyclometalation, *e.g.* complexes **309** featuring an unusual dianionic coordination mode of terpyridine,[479] as well as complexes **310** and **311**.[480,481] Exchange of the platinum-bound methyl group for a hydride has been accomplished by first adding HCl to generate the platinum chloride species, followed by $NaBH_4$-mediated reduction.[482]

Scheme 124



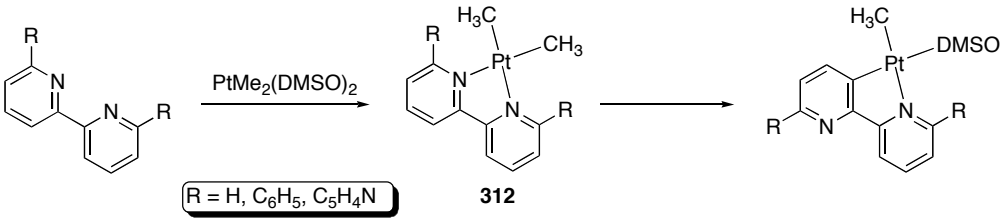
307 **308**



309 **310** **311**

Mechanistic investigations have unambiguously revealed a consecutive reaction profile for the rollover cycloplatination,[483] consisting of initial *N,N*-coordination of bipyridine to form **312** (Scheme 125). The subsequent rollover is promoted by the strong *trans* effect of the CH_3 ligand and, to a lesser extent by the steric bulk at the pyridine C6-position, both factors that weaken the Pt–N bond in **312**.

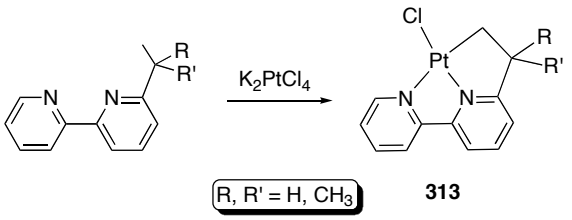
Scheme 125



312

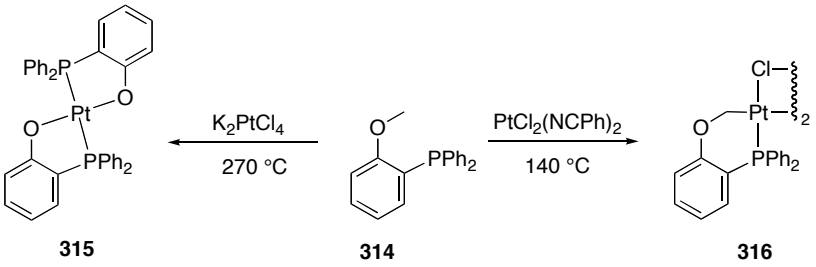
When 6-substituted 2,2'-bipyridines are reacted with K_2PtCl_4 rather than $PtR_2(DMSO)_2$, a rollover cyclometalation is suppressed. Instead, cycloplatination involving C–H bond activation of the *ortho* substituent is observed, thus affording complex **313** (Scheme 126).[484] The C–H bond activation process is significantly slower for ethyl bipyridine (R = R' = H) than for bipyridines bearing *i*Pr or *t*Bu substituents. This reactivity pattern may underline the *gem*-dimethyl effect discussed earlier by Shaw.[105]

Scheme 126



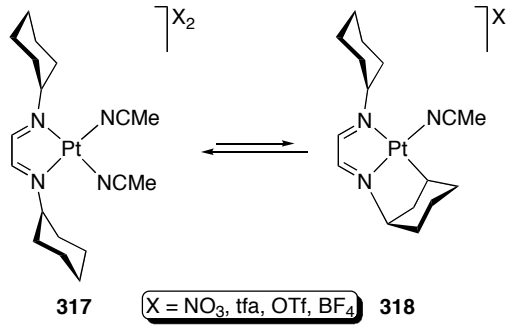
Cyclometalation of the methoxy-substituted phosphine **314** also shows a strong dependence on the platinum precursor and on the reaction conditions used (Scheme 127).[462] With K_2PtCl_4 in polar solvents C_{alkyl}–O bond activation occurs, leading to the coordination complex **315**, whereas $PtCl_2(NCPh)_2$ induces C_{alkyl}–H bond activation and produces the six-membered *C,P*-platinacycle **316**.

Scheme 127



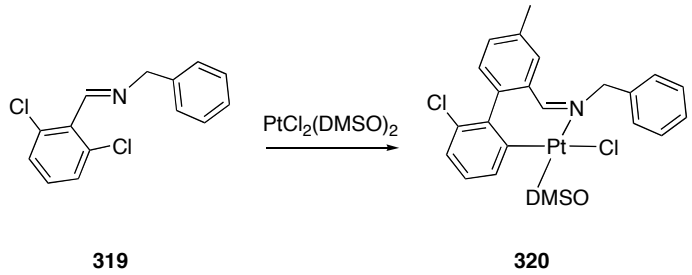
Furthermore, anions may affect the C–H bond activation process considerably. For example, the cyclohexyl-substituted diimine ligand in **317** undergoes cycloplatination of one of the cyclohexyl groups (Scheme 128).[485] The reaction is incomplete and reaches an equilibrium situation, which favors in trifluoroethanol the cyclometalated product **318** if X = BF_4, yet the starting dicationic complex **317** for X = OTf. A different influence of the anion has been noted in the cycloplatination of tetramethylthiourea with *cis*-$PtX_2(PPh_3)_2$.[486] Cyclometalation in CH_2Cl_2 proceeds smoothly with X = NO_3, tfa, OTf, yet slower with X = BF_4, and is suppressed for X = OAc, acac. The different effects may be strongly associated with the solvents that have been used in these two studies, as ionized intermediates are significantly better stabilized in polar trifluoroethanol than in CH_2Cl_2.

Scheme 128



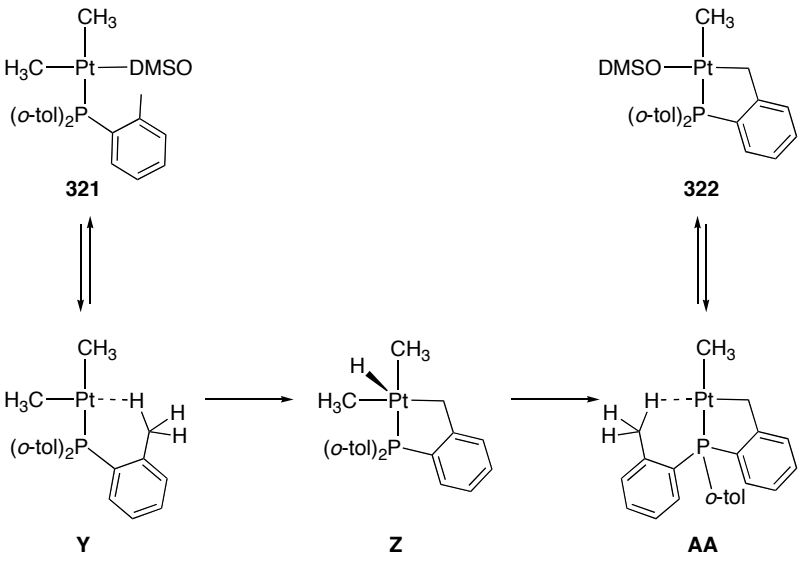
The role of the solvent is further emphasized by results from cycloplatination of the dichlorinated benzylidene benzylimine **319** (Scheme 129).[487] In MeOH, cyclometalation occurs as expected at the unsubstituted arene similar to cyclopalladation (*cf.* Scheme 112), while in toluene, C–Cl bond activation and solvent insertion takes place to yield the seven-membered metallacycle **320**. A similar C–C bonding process has been observed from platinum(IV) complexes comprising two metal-bound phenyl ligands.[488]

Scheme 129



Computational studies on the mechanism of cycloplatination involving C(sp^3)–H bond activation in P(*o*-tol)$_3$ in **321** suggest a multistep mechanism (Scheme 130).[489] Reversible dissociation of the DMSO ligand gives the 14e complex **Y**, which undergoes intramolecular oxidative addition of the C–H bond to produce intermediate **Z**. Subsequent reductive H–CH_3 elimination produces another 14e complex **AA**, which cyclometalates upon re-coordination of DMSO to give the final *C,P*-platinacycle **322**. Obviously, this process, especially its initiation, is strongly solvent dependent, thus providing a rational for the influence of the platinum precursor on the C–H bond activation process as discussed above.

Scheme 130



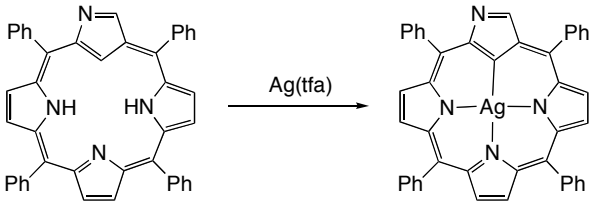
It is worth noting that a formal 14e intermediate comprising a C–H···Pt interaction reminiscent to **Y** has been isolated and crystallographically characterized.[490,491] This interaction is labile and in the presence of weak donors like THF, a 16e complex is formed due to donor coordination. While this latter complex indeed undergoes cycloplatination, it is unclear whether or not the crystallized 14e complex represents an intermediate en route to the platinacycle.

7. Cyclometalation using group 11 and group 12 metals

Cyclometalations using the heavier group 11 and group 12 metals are often difficult to be identified. First of all, uncertainties arises from the low coordination number typically encountered for these metals in their most common oxidation states, *viz.* mercury(II), silver(I), and gold(I). Coordination numbers below 4 require specific ligand geometries for chelation, for example bite angles around 120° or wider. Often such wide bite angles are accessible only by introducing flexibility in the ligand framework, thus reducing the directional influence of the heteroatom in cyclometalation. Even though the C–H bond activation process may be directed by initial heteroatom coordination, generally, the products are not metallacyclic due to the mismatch of ligand geometry and metal coordination number. As a consequence, C–H bond activations mediated by silver(I), *e.g.* as Ag(tfa) or Ag_2O, or using $Hg(OAc)_2$ as mercury(II) source generally afford products that do not contain a metallacycle, irrespective of whether an additional donor atom is present or not.[492] Inversely, products with close donor–metal contacts may be misleading, as the C–H bond activation process mediated by group 11 and 12 metals may *not* be heteroatom-assisted and the donor stabilization may ensue only after M–C bond formation.

A successful strategy for silver-mediated cyclometalation has been developed based on *N*-confused porphyrins. Metalation of the macrocycle **323** with Ag(tfa) affords the cyclometalated diamagnetic silver(III) complex **324** (Scheme 131).[493] Extension of this work to doubly *N*-confused porphyrins and to variable substitution patterns has been achieved and allows different silver salts such as $AgBF_4$ and AgOAc to be used as precursors for cyclometalation.[494–496]

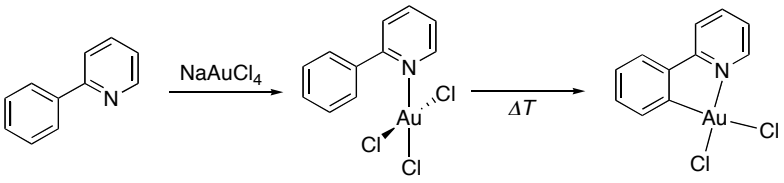
Scheme 131



323 **324**

Most progress in cyclometalation using group 11 or 12 metals has been accomplished undoubtedly by using gold-mediated C–H bond activation, particularly because high-valent gold(III) is isoelectronic to palladium(II) and platinum(II) and readily accessible. In addition, the square-planar coordination geometry of gold(III) supports *cis*-bidentate ligand chelation. A recent review reflects the activity in this area during the last 20 years,[497] which has been stimulated last but not least by the potential antitumor activity of chelate-stabilized gold(III) ions. Cycloauration most frequently features the nitrogen-assisted activation of a C_{aryl}–H bond using aurates like $NaAuCl_4$, $HAuCl_4$, or neutral $AuBr_3$ as gold(III) sources. Only few examples involving $C(sp^3)$–H bond activation are known.[498] With nitrogen-containing ligand precursors, the ligand displacement reaction is often detectable, thus leading to the formation of a coordination product of the type $AuCl_3(L)$ (*cf.* **A**, Scheme 2). If C–H bond activation is not spontaneous, it may be induced thermally. Thus, heating the coordination complex **325** in a polar solvent at moderate temperatures (80–100 °C) promotes the cycloauration of phenylpyridine and affords complex **326** (Scheme 132).[499] A range of nitrogen donor groups has been employed to direct the C–H activation process, and these donor groups have a pronounced influence on the stability and reactivity of the resulting auracycle. For example, hard NMe_2 groups coordinate strongly and hence hamper ligand substitution reactions with phosphines, whereas azo groups tend to be more labile.

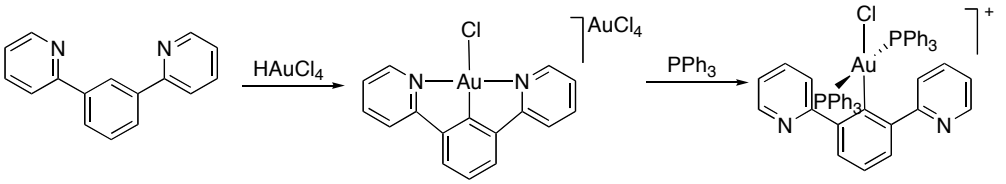
Scheme 132



325 **326**

Recent advances include the cycloauration of the potentially *N,C,N*-tridentate pincer ligand precursor **327** (Scheme 133).[500] Direct C–H bond activation has been achieved by reacting the ligand precursor with $HAuCl_4$ in acetic acid at high temperatures and in the presence of a base. Although yields of complex **328** are moderate, this procedure is an attractive alternative to the more frequently used transmetalation from the mercurated ligand. Despite the tridentate coordination mode, phosphines readily displace the pyridine donors and yield complex **329** comprised of a monodentate aryl ligand.

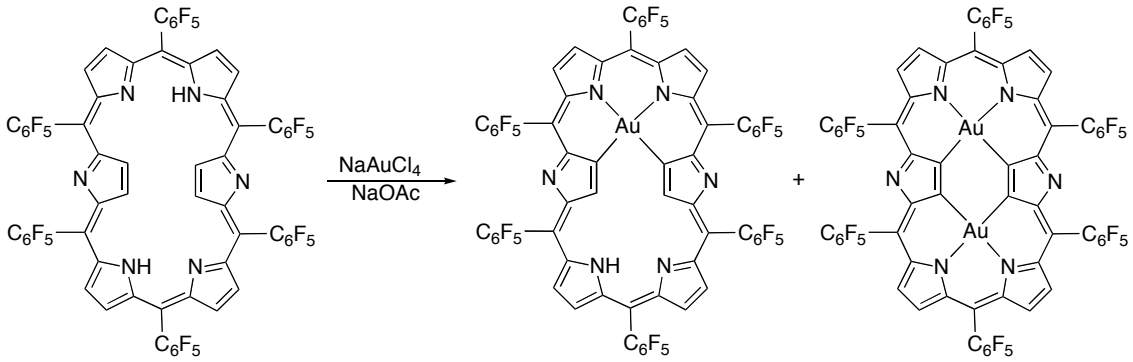
Scheme 133



327 **328** **329**

In analogy to the cyclometalation of *N*-confused porphyrins and related ligand precursors with silver(I) (*cf.* Scheme 131), hexaphyrin **330** has been cyclometalated with excess $NaAuCl_4$ in the presence of NaOAc (Scheme 134).[501] Metalation is slow and affords a mixture of mono- and bimetallic complexes, **331** and **332**, respectively, which can be separated by column chromatography. Crystallographic analyses indicate a planar, slightly twisted structure for **331**, whereas the bimetallic complex **332** displays a concave shape.

Scheme 134



330 **331** **332**

8. Conclusions and Perspectives

Nearly half a century after its discovery, cyclometalation has become a mature reaction with most of the key principles being established. The mechanistic concepts that have been elaborated for cyclometalation are generally accepted and they also seem to be directly relevant to C–H bond activation reactions that are not supported by heteroatom precoordination. In its own right, cyclometalation constitutes a highly versatile reaction with wide synthetic utility for generating metallacyclic materials that are very efficient, *e.g.* for catalysis, energy conversion, or for biomedical applications. Moreover, cyclometalation is most useful for understanding existing catalytic reactions and for designing new processes such as the *ortho*-functionalization of substituted benzenes and heterocycles. Future developments along these lines may encompass, for example, catalytic carbon-carbon bond cleavage reactions that are based on heteroatom-assisted C–C bond activation. Considering the huge application potential of metallacycles as well as the current limitations, including the persisting ambiguities on mechanistic details, it is safe to predict that further progress in cyclometalation will pave the way for new reaction mechanisms and for the development of unprecedented synthetic transformations.

9. Acknowledgments

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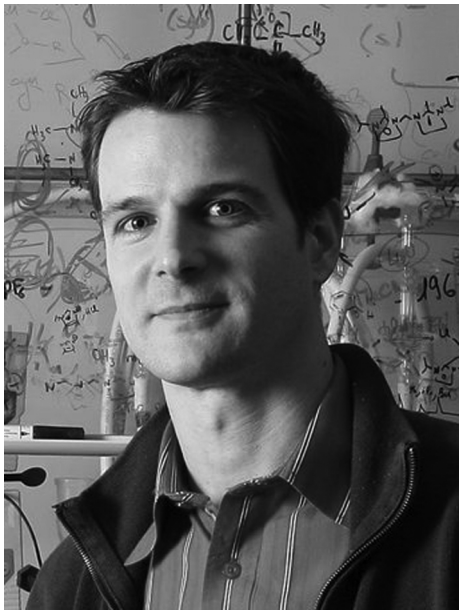

Martin Albrecht is currently leading an enthusiastic research group at the University College Dublin, Ireland. He received his undergraduate education from the University of Bern (Switzerland) and obtained his Ph.D under the supervison of Gerard van Koten from Utrecht University (The Netherlands) in 2000. After postdoctoral work with Robert H. Crabtree (Yale) and with Ciba SC (Basel, Switzerland), he received an Alfred Werner Assistant Professorship and started his independent research at the University of Fribourg (Switzerland) before joining the faculty at UCD as full professor. His research interests focus on the tailoring of metal centers in a well-defined environment for synthetic, catalytic, biomimetic, and spintronic applications. In this context, cyclometalation and chelate stabilization have been efficient and versatile tools, sometimes with a surprising impact.

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