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## (P,C)-cyclometalated complexes derived from naphthyl phosphines: versatile and powerful tools in organometallic chemistry†

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The chemistry of (P,C)-cyclometalated complexes derived from naphthyl phosphines [<sup>Np</sup>(P,C)M] is presented and analysed in this review. The three main synthetic approaches, namely P-chelation assisted C–H activation, oxidative addition and transmetalation, are described and compared. If a naphthyl framework inherently predisposes a phosphorus atom and transition metal to interact, a rigid metallacycle may induce some strain and distortion, as apparent from the survey of the single-crystal X-ray diffraction structures deposited in the Cambridge Structural Database (77 entries with metals from groups 7 to 11). Generally, the <sup>Np</sup>(P,C)-cyclometalation imparts high thermal and chemical robustness to the complexes, and a variety of stoichiometric reactions have been reported. In most cases, the metalacyclic structure is retained, but protodecyclometalation and ring-expansion have been sparingly observed. [<sup>Np</sup>(P,C)M] complexes have also proved to be competent and actually competitive catalysts in several transformations, and they act as key intermediates in some others. In addition, interesting phosphorescence properties have been occasionally pointed out.

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## Introduction

Since the pioneering contributions of Shaw in the early 1970s,<sup>1,2</sup> cyclometalated complexes have attracted considerable



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**Enrico Marelli**

Enrico Marelli received his MSc degree at the University of Milan in the group of Prof. C. Gennari, and his PhD degree at the University of St Andrews, working on Ni and Pd catalysis, under the supervision of Professors S. Nolan and R. Goss. He was then awarded a MSCA grant for a postdoc position in the group of Dr D Bourissou, in Toulouse, studying bifunctional complexes of Pd and Au. He currently works as a development chemist in Copenhagen, for H. Lundbeck.



interest and are now classics in organometallic chemistry. Their interest ranges from fundamental bonding/reactivity aspects to applications in catalysis, materials chemical science, medicine, and others. The easy access, broad structural modularity and versatile coordination properties of phosphines make them very powerful ligands for transition metals. It is thus not surprising that (P,C)-cyclometalated complexes occupy a forefront position.<sup>3–6</sup> Here, PCP complexes **I** with a central benzene ring and two flanking phosphines have become the reference complexes (Chart 1).<sup>7</sup> Their pincer structure results in a unique balance of stability/reactivity. The related (P,C)-cyclometalated complexes **II** featuring a single phosphine side-arm have also been widely investigated. In contrast, the corresponding naphthyl-based (P,C)-cyclometalated complexes **III**, hereafter denoted as  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$ , long remained underdeveloped although they are known for more than 50 years. Significant progress has been achieved over the past 5–10 years however, in particular, in gold(III) chemistry<sup>8</sup> where the  $[\text{N}^{\text{P}}(\text{P,C})]$  framework opened new reactivity paths, enabled unprecedented bonding situations to be authenticated and imparted unique catalytic activity.

Here, this topic is reviewed. P,C-cyclometalated complexes derived from naphthyl phosphines as well as related systems featuring fused/ $\pi$ -extended systems, such as acenaphthalene,

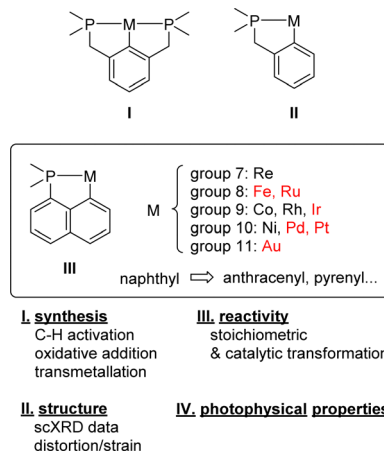


Chart 1 (P,C)-cyclometalated complexes **I–III**, content and organization of this review (metals in red are the most represented ones among  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes **III**).

anthracene, phenanthrene and pyrene, are reported. The corresponding two arm stiff PCP complexes are not considered.  $[\text{N}^{\text{P}}(\text{P,C})]$  Complexes have been reported with metals from groups 7 to 11, in line with the preference of a soft phosphine moiety for mid and late transition metals. Emphasis is given to



Blanca Martin-Vaca

Blanca Martin-Vaca studied chemistry at the University of Oviedo (Spain) where she obtained her PhD degree in 1995 under the supervision of Professor J. Gimeno in organometallic chemistry. She then joined Dr Rudler's group at the University Pierre et Marie Curie (Paris) as a postdoctoral fellow supported by the Spanish M.E.C. (1996–1998), and studied cyclopropanation and other cyclisation reactions with alkoxy-carbenes and ylide

complexes of tungsten. She was appointed as an Assistant Professor at the University Paul Sabatier (Toulouse) in 1998 and was promoted to a Full Professor in 2008. Her research interests deal with organometallic chemistry, organic catalysis of polymerization and biodegradable polymers. She is interested in non-innocent pincer complexes and their application in metal–ligand cooperative catalysis. She also works on the development of organic catalytic systems for the ring-opening polymerization reactions of lactones and cyclic carbonates (including functionalized ones) allowing the preparation of polyesters and polycarbonates of tuned structures.



Didier Bourissou

Didier Bourissou obtained his PhD degree from the Toulouse University with G. Bertrand. He then spent one year as a research associate at the Ecole Polytechnique with F. Mathey and P. Le Floch. Appointed as a Chargé de Recherche CNRS in 1998, he was promoted to a Directeur de Recherche in 2006. From 2006 to 2018, he was an Associate Professor at the Ecole Polytechnique. He has been a Director of the Laboratoire

Hétérochimie Fondamentale et Appliquée (LHFA) from 2011 to 2020. He was awarded the Bronze (2005) and Silver (2016) Medals of the CNRS, the Clavel Lespiau Distinction (2006) and Del Duca Grant (2020) from the French Academy of Sciences, the Acros (2009) and Organic Division (2018) Awards from the French Chemical Society in recognition of his work. His research interests concern new bonding situations and reactivity patterns arising from the main group elements, the transition metals and their interplay. He has pioneered ambiphilic ligands in the mid 2000's and developed the concept of  $\sigma$ -acceptor ligands. Part of his research deals with non-innocent pincer complexes and the unusual behavior of the coinage metals, in particular gold. He is also interested in biodegradable polymers (ring-opening polymerization, organic and dual catalysis, and drug delivery systems).



the influence of the rigid naphthyl-based metallacyclic framework on the structure, stability and reactivity of the complexes. Whenever possible, comparison is made with related phenyl-based (P,C)-cyclometalated complexes **II**.

In the first part, the synthesis of  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes is presented. The three main synthetic approaches, namely P-chelation assisted C–H activation, oxidative addition and transmetalation, are described and compared. Then, the structure and bonding of  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes are thoroughly analysed based on crystallographic and computational data. Special attention is given to the distortion/flexibility of a naphthyl spacer and its ability to accommodate a broad range of transition metals, despite its high rigidity. The following section deals with the reactivity of  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes in stoichiometric reactions and catalytic transformations. The (P,C)-cyclometalated framework is retained in most cases, but not always. Finally, a few photophysical studies performed on  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes are described.

## I. En route to $\text{N}^{\text{P}}(\text{P,C})$ -cyclometalated complexes

Three main synthetic strategies can be distinguished to access (P,C)-cyclometalated naphthyl complexes,  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  (Fig. 1). They differ in the nature of pro-ligands and the way the transition metal is introduced. C–H activation, starting from simple 1-naphthyl phosphines, is naturally the most direct and common approach. It is also the oldest one, pioneered by Shaw *et al.* as early as in 1972. The C–H activation of 1-naphthyl phosphines occurs selectively at the *peri* position, due to ideal P-chelation (a 5-membered ring with rotation around the P–C<sub>naphthyl</sub> bond as the only degree of freedom). It can be promoted using a basic ligand on the metal or the addition of an exogenous base/halide scavenger. This route has been used to prepare a broad range of (P,C)-naphthyl complexes with transition metals from groups 7 to 10. Recently, the renewed interest devoted to group 10 and group 11 metals has stimulated studies on alternative pathways to access (P,C)-naphthyl complexes based on the oxidative addition of C–X bonds or on

the transmetalation of mercury/tin derivatives. These routes employ prefunctionalized 1-naphthyl phosphines as starting materials, with a halide or a metalloid at the *peri* position. Naphthalene derivatives with a phosphorus atom bridging the *peri* positions are also predisposed to give (P,C)-cyclometalated complexes. A few such species have been shown to undergo ring-expansion by the oxidative addition of the strained P–C bond to group 10 metals and gold. These three routes will be successively presented in detail in this section.

### 1. Via C–H activation

With a unique and simple prefunctionalization on the naphthalene scaffold (to introduce the P atom), the activation of the *peri* C–H bond of 1-naphthyl phosphines is the most direct and common synthetic route to access  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$  complexes. This strategy was first described by Shaw in 1972 in a comprehensive study targeting  $[\text{N}^{\text{P}}(\text{P,C})\text{Ir}(\text{III})]$  complexes.<sup>1</sup> Different cyclometalation conditions taking the advantage of P-chelation were reported (Scheme 1).

Starting from Ir(III) complex **1** bearing three dimethyl 1-naphthyl phosphines coordinated in a meridional fashion, the first cyclometalation reaction was achieved in a good yield (75%) by thermal activation (124 °C) in methyl glycol. A second C–H activation could be efficiently performed by heating monocyclusmetallated iridium complex **2** with an external base, sodium acetate. Interestingly, the coordination mode of the three phosphorus atoms around the iridium center changed from meridional to facial after this second cyclometalation step. In these two steps, an Ir–H species, formed by  $\beta$ -hydride elimination from the alcoholic solvent, was postulated as a key intermediate. This hydride could then act as an internal base, generating H<sub>2</sub> as the by-product. No firm evidence for this mechanism was reported however. Concomitantly, the same strategy was tempted to prepare analogous rhodium complexes. The first electrophilic C–H activation worked well (84% yield). However, no further reactivity was observed in the case of  $[\text{N}^{\text{P}}(\text{P,C})\text{Rh}(\text{III})]$  complex **2**. An alternative pathway was also described to give bis-(P,C)-cyclometalated complex **3** starting from the iridium(I) precursor  $[\text{IrCl}(\text{cod})]_2$ . After a first C–H

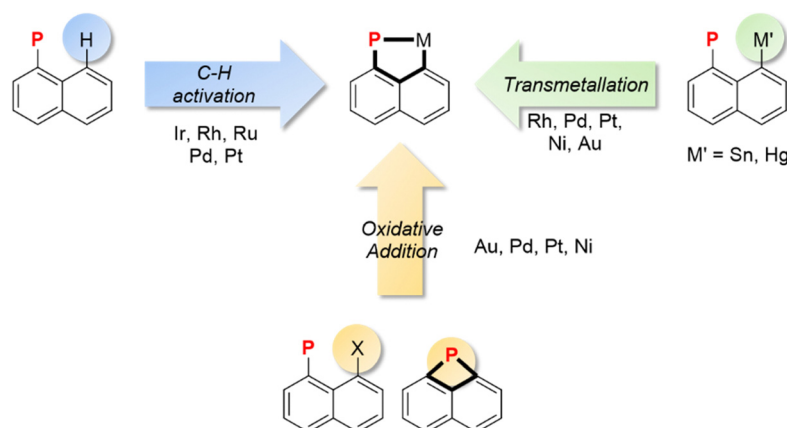
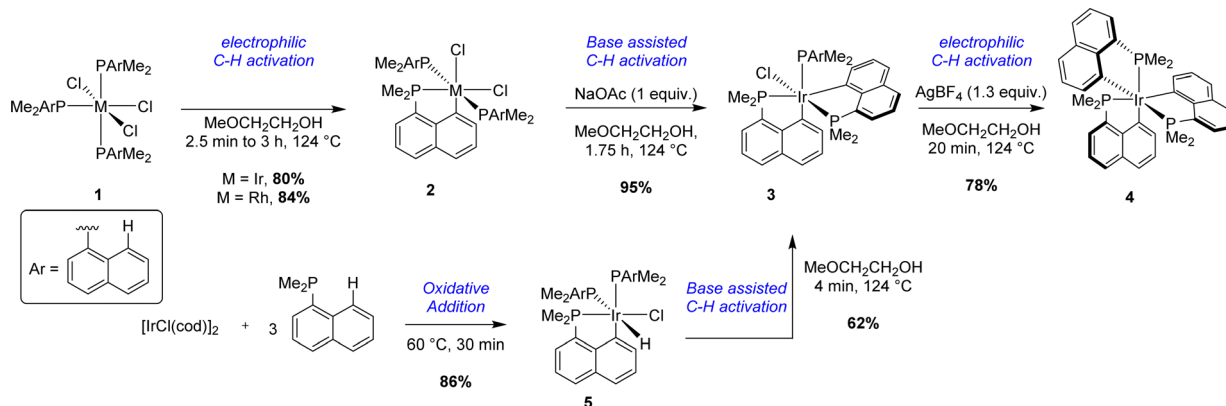


Fig. 1 Synthetic routes to access (P,C)-cyclometalated naphthyl complexes  $[\text{N}^{\text{P}}(\text{P,C})\text{M}]$ .





Scheme 1 Stepwise cyclometalation of naphthyl phosphines at Ir(III) via electrophilic/base-assisted C–H activations.

activation process by oxidative addition to iridium in boiling light petroleum, iridium(III) complex **5** was isolated in a very good yield (86%). **5** evolved quickly under reflux in methyl glycol to give complex **3** with gas evolution, presumably dihydrogen. Finally, the third metalation process was performed by abstraction of the last chloride at iridium with a scavenger (*i.e.* AgBF<sub>4</sub>) to give tris-(P,C)-cyclometalated complex **4**.

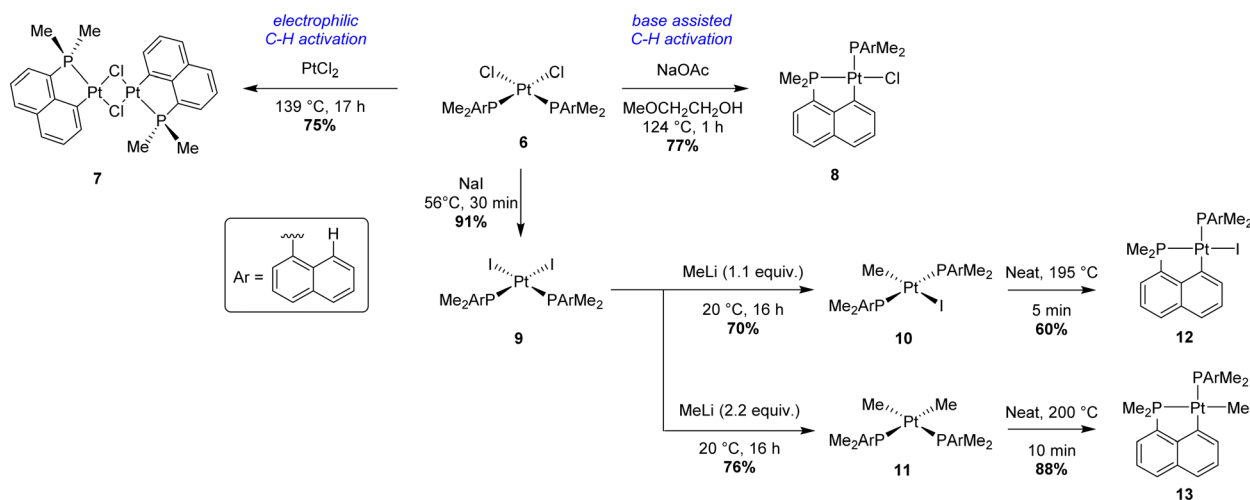
Two years later, Shaw prepared a family of [N<sup>P</sup>(P,C)Pt(II)] complexes starting from *cis*-dichloroplatinum(II) precursor **6** (Scheme 2).<sup>2</sup> Electrophilic C–H activation was performed by mixing PtCl<sub>2</sub> with **6** to yield bridged platinum(II) dimer **7** after prolonged heating in xylenes (139 °C). For monomeric (P,C)-cyclometalated chloroplatinum(II) complex **8**, the addition of sodium acetate was mandatory to obtain a good yield (77%). After halide exchange (chloride to iodide), alkyl and dialkylplatinum(II) complexes **10** and **11** were prepared using methyllithium. Pyrolysis at high temperatures (> 195 °C) then afforded the corresponding iodo **12** and methyl (P,C)-cyclometalated **13** complexes with methane evolution.

In these two seminal reports, Shaw thus depicted four different strategies to cyclometalate 1-naphthyl phosphines, including oxidative addition. The preparations of [N<sup>P</sup>(P,C)M]

complexes *via* C–H activation reported after 1974 are described in the following sections. Although no detailed mechanistic studies have been carried out on the C–H activation process, these contributions have been organized according to the conditions used to promote cyclometalation:

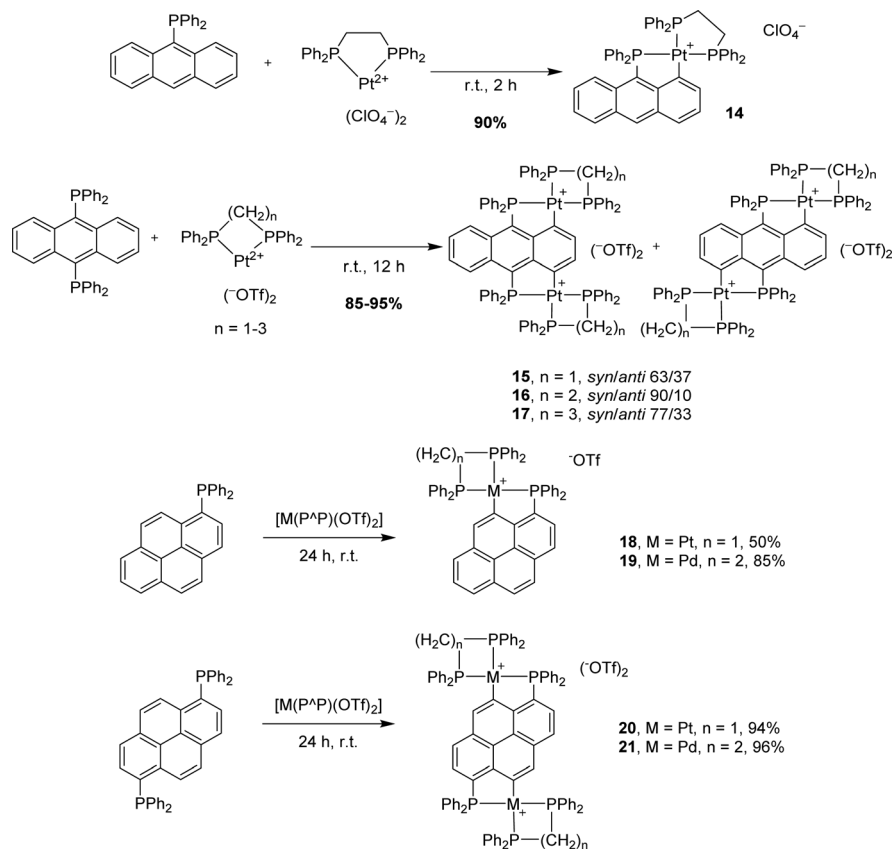
- Direct (electrophilic) C–H activation by a metal-halide (or metal-pseudohalide) precursor,
- C–H activation in the presence of a mild base (NaOAc, Et<sub>3</sub>N), bonded to the metal or external, acting in concert with the metal or not,
- C–H activation by a metal-alkyl precursor.

**a. Direct (electrophilic) C–H activation.** The first examples described by Shaw involved metal chloride precursors and required quite high temperatures. Using more electrophilic pseudo-halide complexes (perchlorate and trifluoromethane sulfonate) enables operating under milder conditions. Accordingly, Yip described, in the late 2000's, the synthesis of mono- and bis-(P,C)-cyclometalated complexes with  $\pi$ -extended naphthalene backbones (anthracene and pyrene) (Scheme 3).<sup>9,10</sup> Here, pseudo-cationic palladium(II) and platinum(II) complexes featuring diphosphine ligands were used as precursors. Cyclometalation proceeded within hours



Scheme 2 Synthesis of [N<sup>P</sup>(P,C)Pt(II)] complexes *via* C–H activation.



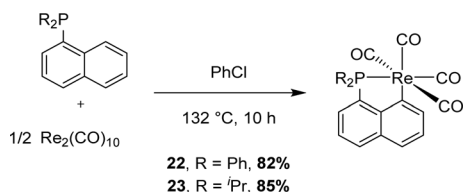


**Scheme 3** Synthesis of (P,C)-cyclometalated mono/dinuclear Pt(II) and Pd(II) complexes by electrophilic C–H activation of anthracenyl and pyrenyl mono/diphosphines.

at room temperature in this case. Of note, double cyclometalations of 9,10-bis-phosphino-anthracene systematically gave a mixture of *syn* and *anti*-bis-(P,C)-cyclometalated complexes (with a *syn/anti* ratio of > 60/40).

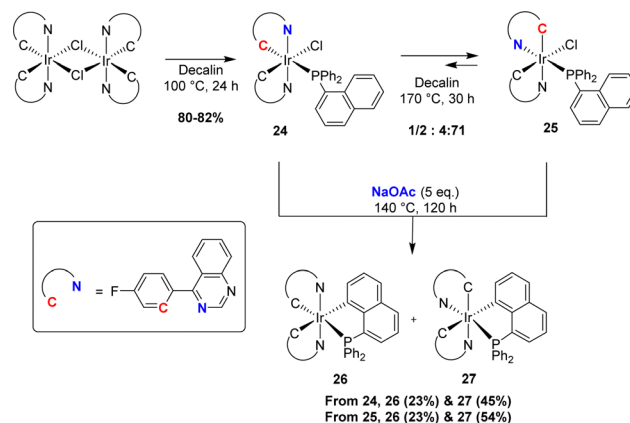
In 2017, Zhu reported the synthesis of two  $[\text{N}^{\text{P}}(\text{P,C})\text{Re}]$  complexes starting from  $\text{Re}_2(\text{CO})_{10}$  (Scheme 4).<sup>11</sup> The exact way the *peri* C–H bond is activated is unknown but the authors invoked P-chelation assistance prior to intramolecular activation.

**b. C–H activation in the presence of a mild base (NaOAc,  $\text{NEt}_3$ ).** The C–H metalation of 1-naphthyl phosphines assisted by a mild base, most often sodium acetate, is a simple, efficient and general strategy to prepare (P,C)-cyclometalated naphthyl complexes. Here, cyclometalation is based on the propensity of acetate to catch the *peri* H atom, thus facilitating the formation of the  $\text{M}-\text{C}_{\text{sp}^2}$  bond.<sup>12–14</sup>



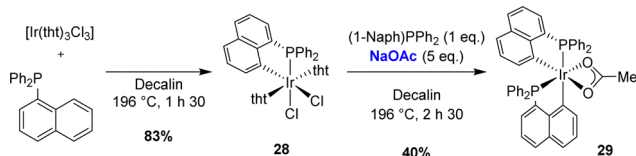
**Scheme 4** Synthesis of a  $[\text{N}^{\text{P}}(\text{P,C})\text{Re}(\text{II})]$  complex via C–H activation.

Following Shaw's pioneering contribution, the groups of Chi and Chou jointly reported in 2010 a stepwise preparation of phosphorescent  $[\text{N}^{\text{P}}(\text{Ph}_2\text{P,C})\text{Ir}(\text{III})]$  complexes (see Section IV).<sup>15</sup> First, the bis-N,C-cyclometalated iridium(III) chloride-bridged dimer was splitted by diphenyl 1-naphthyl phosphines upon heating at 100 °C for 24 h (Scheme 5). The initially formed complex **24** with two strong field ligands (carbon and phosphorus) at the *trans* position to each other could be isomerised



**Scheme 5** Synthesis of  $[\text{N}^{\text{P}}(\text{P,C})\text{Ir}(\text{III})]$  complexes via base-assisted C–H activation.



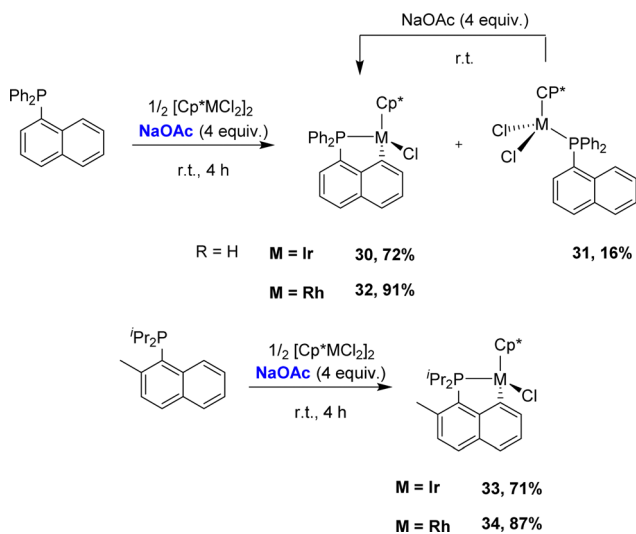


**Scheme 6** Synthesis of a bis-cyclometalated  $[\text{Np}(\text{P},\text{C})_2]\text{Ir}(\text{III})$  complex by subsequent thermal and base-assisted C–H activations.

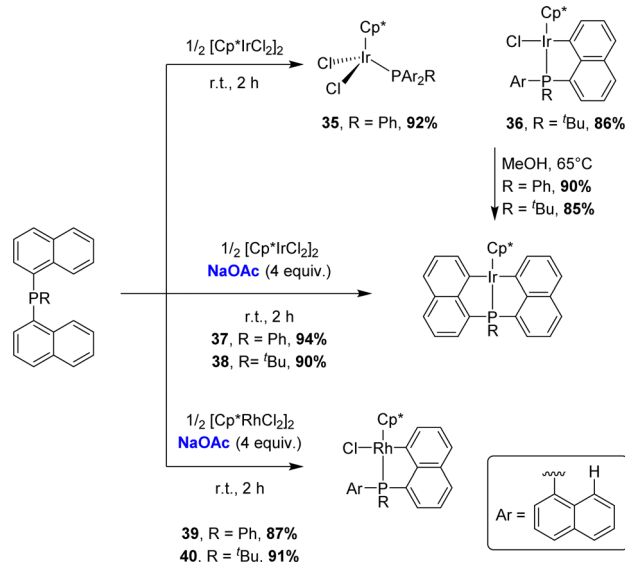
into more thermodynamically stable complex **25** (within 48 h at 170 °C). Cyclometalation was then achieved in the presence of sodium acetate (5 eq.) at a high temperature (190 °C). In both cases, a mixture of complexes **26** and **27** was obtained. Based on the absence of thermal interconversion between **26** and **27**, the authors proposed a stepwise process: the substitution of chloride by acetate at iridium, followed by C–H bond activation/metalation.

A year later, the same groups described the preparation of a bis-cyclometalated iridium(III) complex (Scheme 6).<sup>16</sup> The electrophilic C–H activation of diphenyl 1-naphthyl phosphines by  $[\text{IrCl}_3(\text{tht})_3]$  at 196 °C in decalin first afforded the mono-(P,C)-cyclometalated complex  $[\text{Np}(\text{Ph}_2\text{P},\text{C})\text{IrCl}_2(\text{tht})_2]$  (83% isolated yield). Following the addition of diphenyl 1-naphthyl phosphines, the second cyclometalation required the use of sodium acetate (5 equivalents) to give the  $[\text{Np}(\text{Ph}_2\text{P},\text{C})_2\text{Ir}(\kappa^2\text{-OAc})]$  complex.

In 2017, the group of Zhu studied in detail the cyclometalation of diphenyl 1-naphthyl phosphines by  $[\text{Cp}^*\text{MCl}_2]_2$  (M = Ir, Rh) in the presence of sodium acetate (Scheme 7).<sup>17</sup> The reactions were performed in methanol at room temperature for 4 h. The cyclometalated complex  $[\text{Np}(\text{Ph}_2\text{P},\text{C})\text{IrCl}(\text{Cp}^*)]$  **30** was thereby obtained in a good yield (72%) along with a small amount of the corresponding non-cyclometalated iridium dichloride complex **31**. The characterization of complex **31** supports a stepwise P-chelation assisted process for cyclometalation (an independent experiment actually confirmed the



**Scheme 7** Synthesis of  $[\text{Np}(\text{P},\text{C})\text{Ir}(\text{III})]$  and  $[\text{Np}(\text{P},\text{C})\text{Rh}(\text{III})]$  complexes via base-assisted C–H activation, selectivity for  $\text{C}_{\text{sp}^2}\text{-H}$  over  $\text{C}_{\text{sp}^3}\text{-H}$  bonds.



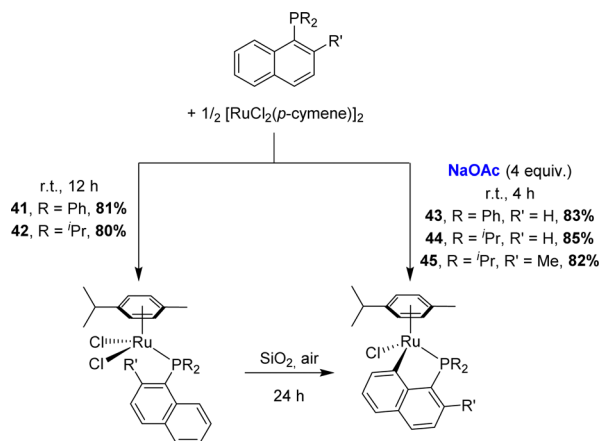
**Scheme 8** C–H activation of bis-naphthyl phosphines by  $[\text{Cp}^*\text{MCl}_2]_2$  (M = Ir, Rh) with/without base assistance.

conversion of **31** to **30** over time). By comparison, the C–H bond activation seemed to be faster with rhodium, since the rhodium analogue of **31** was not observed during the reaction. In addition, the authors compared the reactivity of  $\text{C}_{\text{sp}^2}\text{-H}$  and  $\text{C}_{\text{sp}^3}\text{-H}$  bonds towards cyclometalation using a 1-naphthyl phosphine featuring a methyl group adjacent to phosphorus. Only the  $\text{C}_{\text{sp}^2}\text{-H}$  bond activation was observed with both iridium and rhodium.

The cyclometalation of bis-1-naphthyl phosphines was then investigated (Scheme 8).<sup>18</sup> With  $[\text{Cp}^*\text{IrCl}_2]_2$ , very different outcomes were observed at room temperature depending on the substituent at phosphorus (R = Ph, *t*Bu). Indeed, only P-coordination without cyclometalation was observed for the phenyl phosphine, whereas the *tert*-butyl phosphine directly afforded the cyclometalated complex  $[\text{Np}(\text{tBu}_2\text{P},\text{C})\text{IrCl}(\text{Cp}^*)]$ . Here, C–H activation was probably favoured as it relieved the strain induced by the high steric demand at phosphorus. Upon heating at reflux in methanol, both complexes converted into the corresponding bis-cyclometalated iridium(III) complexes, which were also prepared in high yields without heating using sodium acetate. With  $[\text{Cp}^*\text{RhCl}_2]_2$ , no reaction occurred even upon heating, presumably due to lower electrophilicity of rhodium compared to that of iridium, but the addition of sodium acetate readily promoted cyclometalation, whatever the substituent at phosphorus. Yet, double cyclometalation could not be achieved in this case, even using a stronger base such as *t*BuOK.

Zhu also applied the C–H activation route to prepare  $[\text{Np}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes (Scheme 9).<sup>19</sup> Most convenient was to react 1-naphthyl phosphines with  $[\text{RuCl}_2(p\text{-cymene})]_2$  at room temperature in methanol in the presence of sodium acetate (4 eq.). Alternatively, non-cyclometalated phosphine complexes could be first prepared in dichloromethane without a base, and then stirred over silica gel under air to induce





Scheme 9 Preparation of  $[\text{Np}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes via a base or silica gel-assisted C–H activation.

cyclometalation. An analogous complex  $[\text{Np}(\text{Ph}_2\text{P},\text{C})\text{RuCl}(\text{C}_6\text{Me}_6)]$  was prepared soon after by Ishii starting from  $[(\eta^6\text{-C}_6\text{Me}_6)\text{-RuCl}_2]$ .<sup>20</sup> Given that *o*-tolyl phosphines were shown to undergo  $\text{C}_{\text{sp}^3}\text{-H}$  cyclometalation under the same conditions, the competition between  $\text{C}_{\text{sp}^2}\text{-H}$  and  $\text{C}_{\text{sp}^3}\text{-H}$  activations was assessed by Zhu.<sup>19</sup> Using iridium and rhodium, the 1-naphthyl phosphine featuring a methyl group adjacent to phosphorus was found to react with  $[\text{RuCl}_2(p\text{-cymene})]_2/\text{NaOAc}$  exclusively at the *peri*  $\text{C}_{\text{sp}^2}\text{-H}$  site.

Under the NaOAc-assisted conditions, Grabulosa prepared in 2019 a series of  $[\text{Np}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes from optically pure P-stereogenic phosphines featuring naphthalene (Chart 2), phenanthrene and pyrene scaffolds for applications in the asymmetric hydrogenation of ketones (see Section III).<sup>21</sup> The corresponding (P,C)-cyclometalated complexes were isolated in low yields (4–17%, except **49**, 71%) probably due to decomposition during purification by column chromatography. In most cases, they were obtained as diastereoisomeric mixtures (the ruthenium center becomes stereogenic upon cyclometalation). Only in the case of <sup>1</sup>Pr-substituted phosphine, good phosphorus to ruthenium chiral induction was apparently achieved, with the formation of a single diastereoisomer according to <sup>31</sup>P NMR spectroscopy.

Base-assisted C–H activation has also been applied to prepare (P,C)-cyclometalated naphthyl complexes with group 10 metals. The first examples were reported by Shaw in 1998.<sup>22</sup>

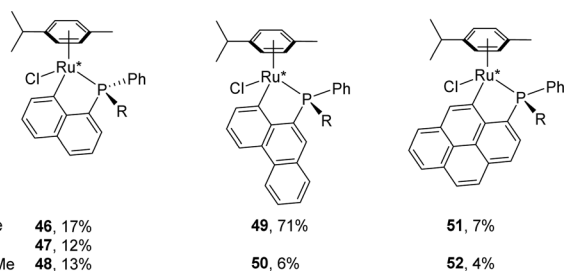
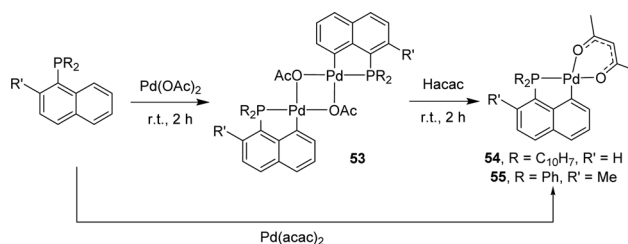


Chart 2 (P,C)-cyclometalated Ru(II) complexes derived from optically pure 1-naphthyl, 9-phenanthrenyl and 1-pyrenyl phosphines.

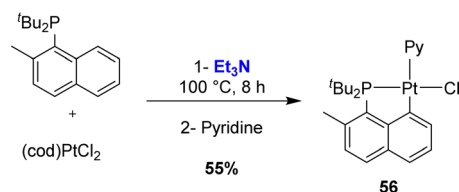


Scheme 10 Synthesis of dinuclear OAc-bridged and mononuclear acac  $[\text{Np}(\text{P},\text{C})\text{Pd}(\text{II})]$  complexes by base-assisted C–H activation.

Starting from the tri-1-naphthyl phosphine, a series of palladacycles were prepared as a result of monocyclometalation. With  $\text{Pd}(\text{OAc})_2$ , a dimeric acetate-bridged complex was obtained (Scheme 10). Subsequent treatment with acetyl-acetone gave the corresponding mononuclear acac complex  $[\text{Np}(\text{Np}_2\text{P},\text{C})\text{Pd}(\text{acac})]$  which can be alternatively prepared by reacting  $\text{PNP}_3$  with  $[\text{Pd}(\text{acac})_2]$ . The analogous complex  $[\text{Np}(\text{Np}_2\text{P},\text{C})\text{Pd}(\text{acac})]$  featuring a hexafluoro acetyl-acetonate co-ligand at palladium was prepared similarly. In 2005, the group of Herrmann applied the same strategy to synthesize palladacycles from the diphenyl 2-methylnaphthyl phosphine.<sup>23</sup> Upon treatment with  $\text{Pd}(\text{OAc})_2$ , cyclometalation proceeded readily and efficiently under mild conditions, with complete selectivity for the *peri*  $\text{C}_{\text{sp}^2}\text{-H}$  bond.

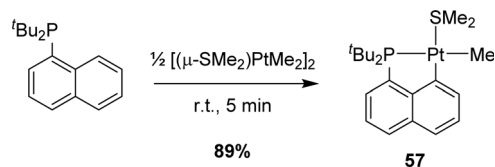
Finally, Vigalok and Vedernikov prepared in 2013 a Pt(II) complex using triethylamine as a base (Scheme 11).<sup>24</sup> The naphthyl phosphine featured a methyl group adjacent to phosphorus and again, complete chemoselectivity for  $\text{C}_{\text{sp}^2}\text{-H}$  over  $\text{C}_{\text{sp}^3}\text{-H}$  bond activation was observed.

**c. C–H activation by a metal-alkyl precursor.** As mentioned above, the group of Shaw pointed out in 1974 the ability of metal-alkyl complexes to cyclometalate 1-naphthyl phosphines, while the corresponding halide precursors remained unreactive.<sup>2</sup>  $[\text{Np}(\text{Me}_2\text{P},\text{C})\text{Pt}(\text{II})]$  complexes were prepared using this way, although the reaction required harsh conditions (195–200 °C, neat). In 2011, Goldberg reported a similar transformation from the di-*tert*-butyl 1-naphthyl phosphine and  $[(\mu\text{-SMe}_2)\text{PtMe}_2]_2$  (Scheme 12).<sup>25</sup> Here, gas evolution, most likely methane, was observed right after mixing at room temperature. The cyclometalated complex  $[\text{Np}(\text{tBu}_2\text{P},\text{C})\text{Pt}(\text{SMe}_2)\text{Me}]$  was quickly (5 minutes) and efficiently obtained (89% isolated yield). The presence of a single phosphine *per* metal and the steric demand of the <sup>t</sup>Bu groups at phosphorus are likely to trigger the C–H activation process *via* preorganization and/or strain release, which probably explains why the reaction proceeded under very mild conditions in this case.



Scheme 11  $\text{C}_{\text{sp}^2}$ -selective base-assisted C–H activation using a Pt(II) precursor.



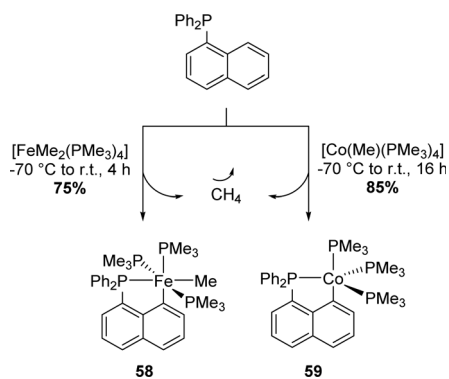


Scheme 12 Synthesis of a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  complex upon C–H activation by a Pt–Me precursor.

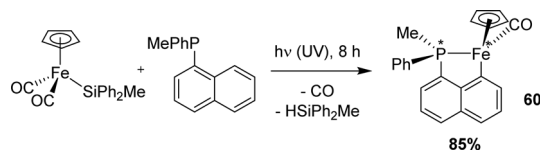
In 2000's, Klein and Beck extended the approach to first-row metals, namely cobalt and iron (Scheme 13).<sup>26</sup> The diphenyl 1-naphthyl phosphine was found to react smoothly with trimethylphosphine Fe(II)Me<sub>2</sub> and Co(I)Me precursors to give the corresponding (P,C)-cyclometalated complexes. The release of methane acts as a driving force and at the same time imparts irreversibility to cyclometalation.

Metal-silyl precursors may also be used to cyclometalate 1-naphthyl phosphines, as substantiated by Corriu in 1981 (Scheme 14).<sup>27</sup> Under UV irradiation, the di-carbonyl silyl iron complex [CpFe(CO)<sub>2</sub>SiPh<sub>2</sub>Me] was found to cleanly react with the P-stereogenic phosphine MePhP(Np). The cyclometalated complex  $[\text{N}^{\text{P}}(\text{PhMeP},\text{C})\text{FeCp}(\text{CO})]$  was obtained in 85% yield as a 1:1 mixture of diastereomers. The silane HSiPh<sub>2</sub>Me was concomitantly released (90% yield) and no deuterium incorporation was observed when the reaction was performed in deuterated benzene, suggesting that the silyl group indeed participated in the C–H activation process, catching the *peri* H atom. Of note, the authors attempted to prepare an optically active form of the cyclometalated complex starting from the phosphine in a non-racemic mixture, but sadly, phosphorus epimerization was faster than coordination/cyclometalation under UV irradiation.

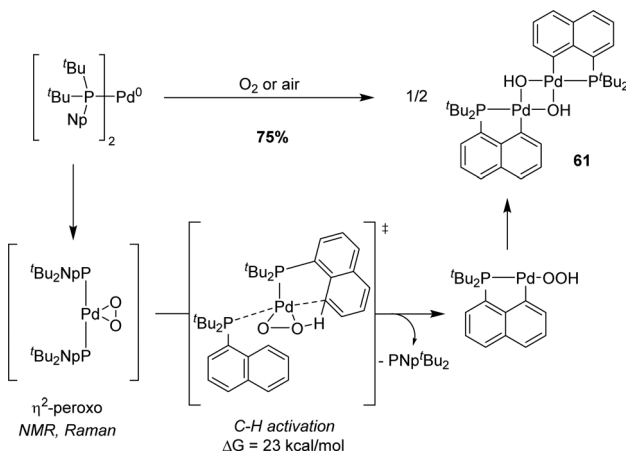
**d. O<sub>2</sub>-promoted C–H activation.** In 2014, the group of Goldberg reported a peculiar route to a dinuclear hydroxy-bridged  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}(\text{II})]$  complex (Scheme 15).<sup>28</sup> The di-phosphine Pd(0) complex  $[(^t\text{Bu}_2\text{Np})_2\text{Pd}]$  was found to readily react with dioxygen with the concomitant cyclometalation of the *peri* C–H bond and O–O cleavage. Reaction monitoring at low temperatures enabled an  $\eta^2$ -peroxo palladium complex to be authenticated as a key intermediate. Based on DFT



Scheme 13 Synthesis of the  $[\text{N}^{\text{P}}(\text{P},\text{C})]$ -cyclometalated complexes of first row metals by methane elimination.



Scheme 14 Synthesis of a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Fe}(\text{II})]$  complex by silane elimination under UV irradiation.



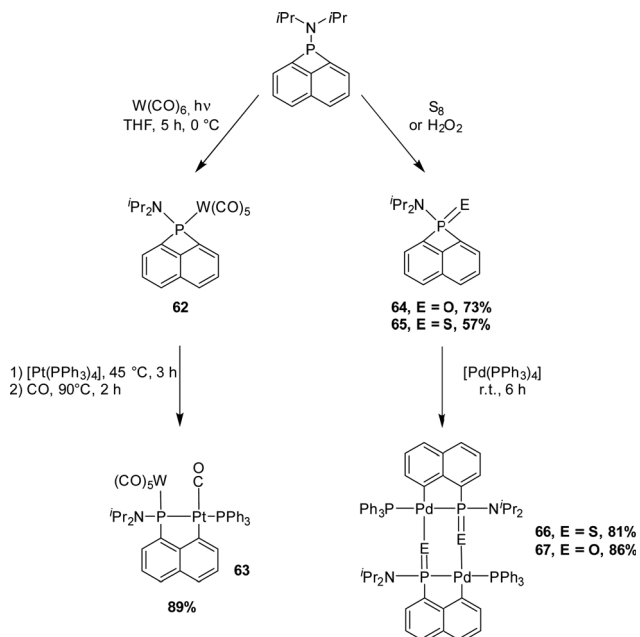
Scheme 15 Synthesis of a dinuclear hydroxy-bridged  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}(\text{II})]$  complex by O<sub>2</sub>-promoted C–H activation.

calculations, the authors proposed a plausible path for the C–H activation, by addition across one of the Pd–O bond with the concomitant release of a phosphine. The resulting Pd–OOH species would then lose an oxygen atom to give the dimeric hydroxy-bridged complex  $[\text{N}^{\text{P}}(^t\text{Bu}_2\text{P},\text{C})\text{Pd}(\mu\text{-OH})_2]$ .

## 2. Via oxidative addition

In 2002, the group of Mizuta reported an original P(III) *peri*-bridged naphthalene derivative (Scheme 16). This highly strained structure is prone to ring-expansion, as substantiated by the preparation of a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  complex.<sup>29,30</sup> The phosphorus lone pair was first masked with a W(CO)<sub>5</sub> fragment. Upon treatment with [Pt(PPh<sub>3</sub>)<sub>4</sub>], one of the P–C bonds oxidatively added to platinum and one of the PPh<sub>3</sub> co-ligands at platinum were then displaced by CO. Related  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}(\text{II})]$  complexes were then synthesized by the same group using a similar strategy, using [Pd(PPh<sub>3</sub>)<sub>4</sub>] as the palladium(0) precursor.<sup>31</sup> The phosphorus atom of the strained four-membered phosphacycle was preliminarily oxidized with hydrogen peroxide or elemental sulfur to give the corresponding P(V) pro-ligands. Oxidative addition of the strained P–C bond proceeded easily at room temperature to give the desired phosphapalladacycles in high yields (81–86%). Only one triphenylphosphine co-ligand remained coordinated to the palladium center. The complexes adopt dimeric structures with the P=E moiety (E = O, S) in a bridging mode. These results show the possibility to obtain (P,C)-cyclometalated complexes by the insertion of low valent metals into the strained four-



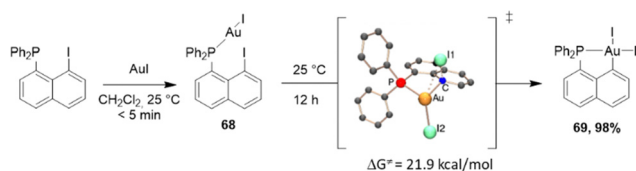


**Scheme 16** Phosphorus *peri*-bridged naphthalene derivatives and their ring expansion into (P,C)-cyclometalated naphthyl complexes by oxidative addition to Pt and Pd.

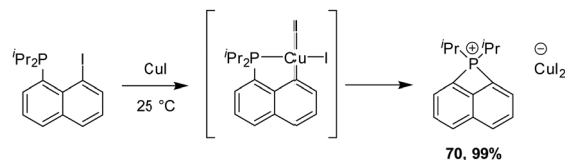
membered ring of phosphorus *peri*-bridged naphthalenes, but the generality and practical utility of this approach are limited by the access to the starting P compounds.

Naphthyl phosphines with halogen at the *peri* position are readily available from 1,8-dihalogenonaphthalenes.<sup>32</sup> They are predisposed to undergo P-chelation assisted oxidative addition, as first demonstrated by our group in 2014 with gold.<sup>33</sup> In the context of a lively debate about the feasibility of oxidative addition at gold, we described the straightforward synthesis of (P,C)-cyclometalated gold(III) complexes through the oxidative addition of a C<sub>sp2</sub>-I bond to a single gold(I) center under mild conditions (Scheme 17).<sup>33</sup>

P-chelation assistance was clearly substantiated by the spectroscopic characterization of the instantaneously formed gold(I) complex, followed by the progressive build-up of the [N<sup>P</sup>(P,C)Au(III)I<sub>2</sub>] complex. Kinetic and computational studies shed light on the intramolecular and unimolecular characters of the process involving a three-center transition state. With the corresponding *peri*-bromo phosphine, oxidative addition could also be successfully achieved upon increasing the reaction temperature to 130 °C (instead of 25 °C for the *peri*-iodo phosphine, in line with the relative strengths of C-Br and C-I



**Scheme 17** Synthesis of a [N<sup>P</sup>(P,C)Au(III)] complex by the P-chelation assisted oxidative addition of a *peri*-iodo naphthyl phosphine to Au.

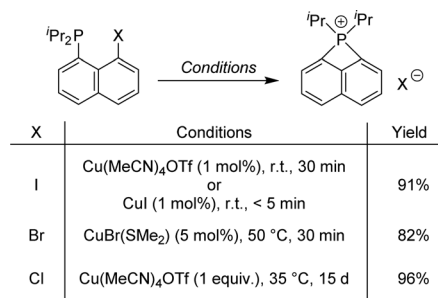


**Scheme 18** Formation of *peri*-bridged naphthyl phosphonium by P-chelation assisted C-I oxidative addition to Cu, followed by P-C reductive elimination.

bonds). However, no reaction was observed with the corresponding *peri*-chloro phosphine, even after several hours at 130 °C in xylene. Calculations confirmed the higher activation barrier for the oxidative addition of the C-Cl bond ( $\Delta G^\ddagger = 39.7$  kcal mol<sup>-1</sup>, compared to 32.1 kcal mol<sup>-1</sup> for C-Br and 21.9 kcal mol<sup>-1</sup> for C-I). Furthermore, in this case, the formation of the gold(III) complex is uphill in energy (+0.3 kcal mol<sup>-1</sup>) in contrast to the oxidative additions of the C-I and C-Br bonds (-9.1 and -7.2 kcal mol<sup>-1</sup>, respectively). Analogous [N<sup>P</sup>(P,C)AuI<sub>2</sub>] was subsequently prepared using the same approach using <sup>i</sup>Pr and Cy substituents at phosphorus.<sup>34,35</sup>

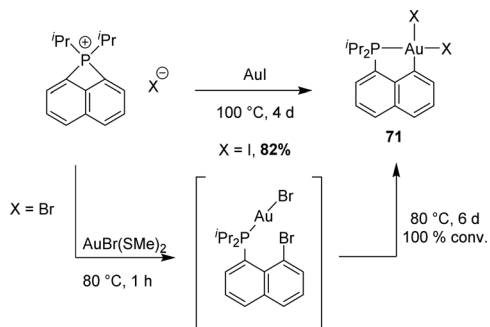
We also studied the behaviour of copper in such a process and reacted *peri*-halo naphthyl phosphines with various Cu(I) complexes (Scheme 18).<sup>36,37</sup> P-chelation was found to efficiently assist the oxidative addition of the C-I bond to copper, but the reaction did not stop there. The ensuing copper(III) species spontaneously underwent P-C reductive elimination to yield new *peri*-bridged phosphonio naphthalene. DFT calculations confirmed the feasibility and easiness of the C-I oxidative addition and P-C reductive elimination (activation barriers of 9.5 and 7.6 kcal mol<sup>-1</sup> in DCM, respectively). The formation of the *peri*-bridged phosphonio naphthalene compound is exergonic by 12.3 kcal mol<sup>-1</sup>.

The generality of the reaction was then examined. Replacing the <sup>i</sup>Pr substituents at phosphorus either by a diamino (<sup>i</sup>Pr)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>N(<sup>i</sup>Pr) moiety or Ph groups led to similar results. The halogen atom at the *peri* position was then varied, demonstrating that P-chelation enables copper to also activate C-Br and C-Cl bonds. Finally, efficient catalytic conditions were established to obtain *peri*-bridged naphthyl-phosphonium using only 1–5 mol% of copper(I) starting from *peri* iodo- or bromo-naphthyl phosphines (Scheme 19).<sup>38</sup>

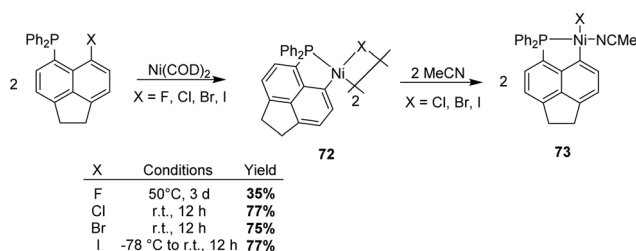


**Scheme 19** Copper-catalyzed/mediated formation of *peri*-bridged naphthyl phosphoniums.





Scheme 20 Reactions of the *peri*-bridged naphthyl phosphonium with the corresponding gold(I) precursor.



Scheme 21 Synthesis of  $[\text{AcNp}(\text{P,C})\text{Ni}(\text{II})]$  complexes by the P-chelation assisted oxidative addition of *peri*-halo naphthyl phosphines to Ni.

The ring strain of *peri*-bridged phosphonio naphthalenes is apparent from the acute  $C_{\text{peri}}\text{P}C_{\text{peri}}$  ( $77.34^\circ$ ) and  $\text{P}C_{\text{peri}}C_{\text{bridge}}$  ( $86.99^\circ$  and  $86.57^\circ$ ) bond angles. Given the rarity of intermolecular (not chelation-assisted) oxidative additions to gold, we wondered about the possibility to insert gold into the P-C bond and to access thereby  $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$  complexes. This proved indeed feasible, although it required relatively harsh conditions (Scheme 20).

In 2021, Beckmann extended the P-chelation strategy and prepared  $[\text{AcNp}(\text{P}_2\text{P,C})\text{Ni}(\text{II})]$  complexes (AcNp refers to acenaphthyl) *via* the oxidative addition of C-X bonds ( $X = \text{F}, \text{Cl}$ ,

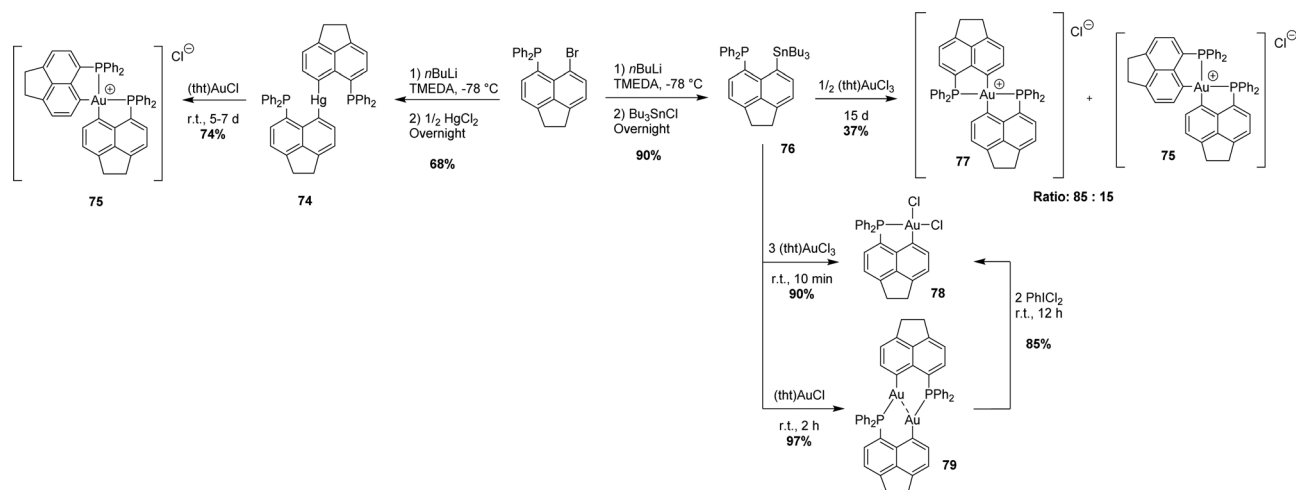
$\text{Br}$ , and  $\text{I}$ ) *peri* to phosphorus (Scheme 21).<sup>39</sup> Once again, halide was observed to have a major impact on the rate of the C-X bond activation. Indeed, the oxidative addition of the C-I bond proceeded at  $-78^\circ\text{C}$  and that of the C-Br/C-Cl bonds at room temperature, while heating at  $50^\circ\text{C}$  was required for the C-F bond. Highly air-sensitive dinuclear complexes were obtained. Addition of THF or MeCN subsequently gave rise to mononuclear complexes for  $X = \text{Cl}, \text{Br}$ , and  $\text{I}$  but not for  $X = \text{F}$ .

### 3. *Via* transmetalation

Recently, Beckmann has developed a complementary transmetalation route (Scheme 22). Accordingly, the  $[\text{AcNp}(\text{P}_2\text{P,C})]$  group was transferred from mercury or tin to groups 9–11 transition metals (Rh, Ir, Ni, Pd, and Au). Transmetalation from gallium to copper was also observed once, leading to a Cu cluster.<sup>40</sup> The mercury(II)/tin(IV) derivatives are readily prepared from the corresponding *peri*-bromo acenaphthyl phosphine. They are non-reductive and bench stable.

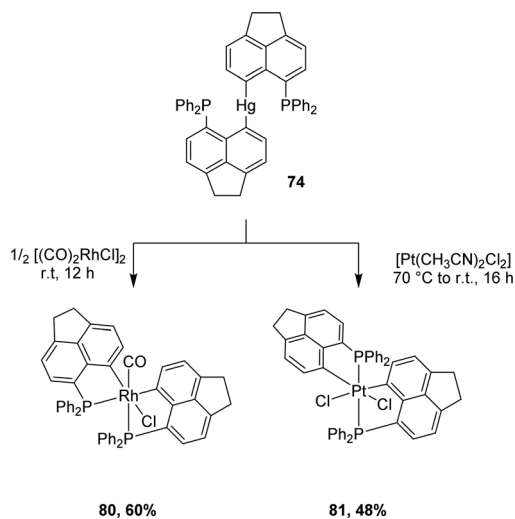
A transmetalation/redox process was first reported.<sup>41</sup> The  $[\text{AcNp}(\text{P}_2\text{P,C})]_2\text{Hg}(\text{II})$  derivative slowly reacted with (tth)AuCl (tth = tetrahydrothiophene) to give the cationic *cis*- $[\text{AcNp}(\text{P}_2\text{P,C})]_2\text{Au}^+$  complex along with mercury(0). Note that the same gold(III) complex was obtained later on in the mixture with its *trans* isomer (*cis/trans* ratio = 15 : 85) upon the reaction of the  $[\text{AcNp}(\text{P}_2\text{P,C})\text{Sn}^n\text{Bu}_3]$  derivative with half an equivalent of (tth)AuCl.<sup>42</sup> The factors controlling the *cis/trans* stereochemistry of gold(III) complexes remain unknown. When reacted with an excess of (tth)AuCl<sub>3</sub>, the tin derivative afforded the neutral  $[\text{AcNp}(\text{P}_2\text{P,C})\text{AuCl}_2]$  complex (90% yield). This mononuclear gold(III) species could also be prepared in two steps, reacting the tin derivative with one equivalent of the gold(I) precursor (tth)AuCl, and oxidizing the ensuing (P,C)-bridged gold(I) dinuclear complex with  $\text{PhICl}_2$ .

Besides gold(III) complexes, the transmetalation/redox strategy was applied to the preparation of bis-(P,C)-cyclo-metalated rhodium(III) and platinum(IV) complexes by reacting

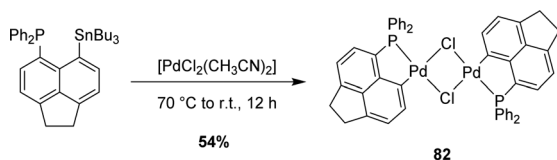


Scheme 22 Synthesis of  $[\text{AcNp}(\text{P,C})\text{Au}(\text{III})]$  complexes *via* mercury and tin to gold transmetalation.





**Scheme 23** Synthesis of  $[\text{AcNp}(\text{P,C})\text{Rh}(\text{III})]$  and  $[\text{AcNp}(\text{P,C})\text{Pt}(\text{IV})]$  complexes via mercury to rhodium/platinum transmetalation.



**Scheme 24** Synthesis of a  $[\text{AcNp}(\text{P,C})\text{Pd}(\text{II})]$  complex via tin to palladium transmetalation.

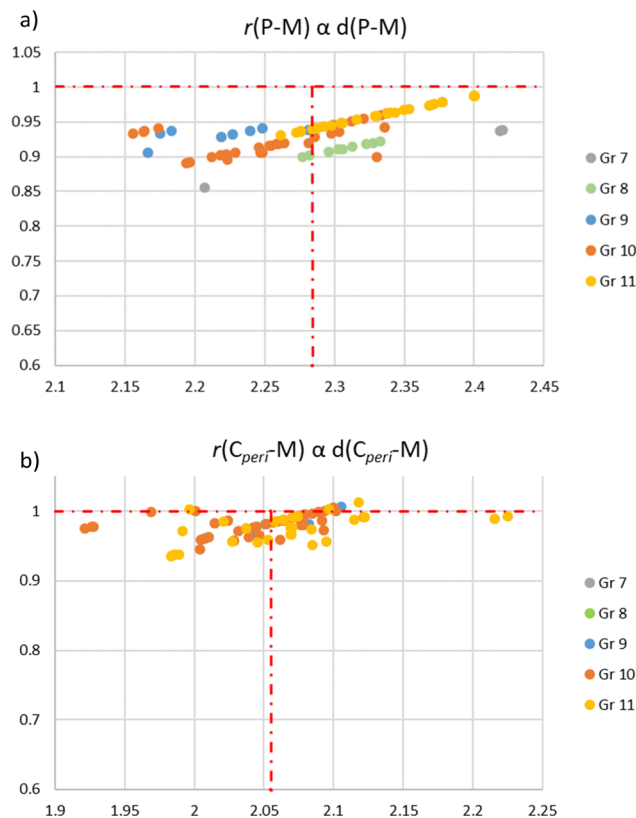
$[\text{AcNp}(\text{Ph}_2\text{P,C})_2\text{Hg}(\text{II})]$  with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  and  $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$ , respectively (Scheme 23).<sup>43</sup>

The transmetalation approach also works with palladium, as substantiated by the reaction of  $[\text{AcNp}(\text{Ph}_2\text{P,C})\text{Sn}^n\text{Bu}_3]$  with  $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$  (Scheme 24).<sup>43</sup> This led to a (P,C)-cyclometalated chloro-bridged dinuclear palladium(II) complex  $[\text{AcNp}(\text{Ph}_2\text{P,C})\text{PdCl}]_2$  analogous to the nickel complex obtained previously by the P-chelation assisted oxidative addition route.

## II. Structure and bonding analyses

A CCDC database search reveals 77 X-ray structures of (P,C)-naphthyl cyclometalated complexes. The key geometric features were collected (see the ESI,<sup>†</sup> Table S1) so as to analyse the geometric constraints and distortions. These data have been sorted according to the metal: from group 7 (2 Re complexes) to group 8 (6 Fe and 8 Ru complexes), group 9 (2 Co, 1 Rh and 6 Ir complexes), group 10 (4 Ni, 13 Pd and 13 Pt complexes), and group 11 (22 Au complexes).

First, looking at the bond distances, the P–M and M–C<sub>peri</sub> distances were compared with the sum of the corresponding covalent radii,<sup>44</sup> referring to the *r* parameters (Charts 3a and b). None of the structurally characterized complex shows a *r*(P–M) factor of above 1.00. About 20% of the structures, mainly Au complexes, possess a *r*(P–M) factor of 0.95–1.00. All the other complexes fall in the  $0.90 \pm 0.05$  range. The (P,C)-naphthyl backbone is thus very suited and very well accommodate all



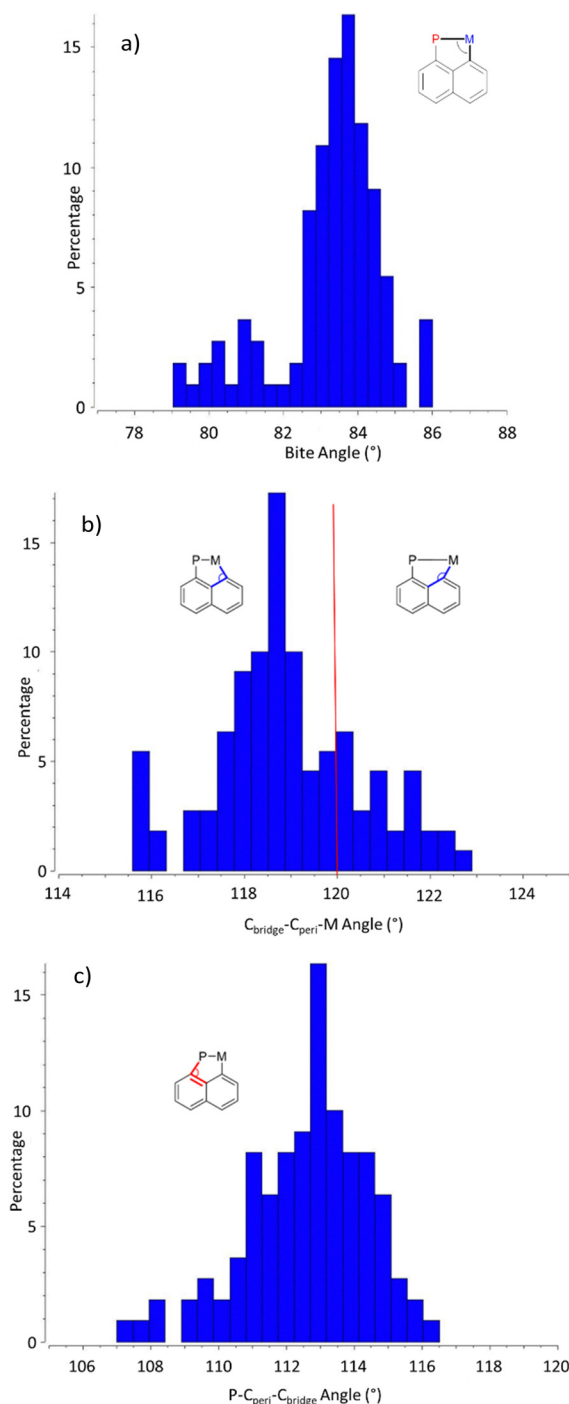
**Chart 3** (a) Plot of the  $r(\text{P-M})$  factor [ $r(\text{P-M}) = d(\text{P-M}) / (r_{\text{cov}}(\text{P}) + r_{\text{cov}}(\text{M}))$ ] against the P–M bond distance for Gr 7 to 11 transition metals, and the average P–M bond distance (2.284 Å) is indicated by a vertical red dotted line. (b) Plot of the  $r(\text{C}_{\text{peri}}\text{-M})$  factor [ $r(\text{C}_{\text{peri}}\text{-M}) = d(\text{C}_{\text{peri}}\text{-M}) / (r_{\text{cov}}(\text{C}) + r_{\text{cov}}(\text{M}))$ ] against the C<sub>peri</sub>–M bond distance for Gr 7 to 11 transition metals, and the average C<sub>peri</sub>–M bond distance (2.055 Å) is indicated by a vertical red dotted line.

metals. It does not induce significant constraint on the P–M and C–M bond lengths. This feature is even more apparent from the  $r(\text{M-C}_{\text{peri}})$  values that marginally deviate from 1.00 (87% fall in the  $1.00 \pm 0.05$  range).

For bond angles, the bite angle (P–M–C<sub>peri</sub>) varies very little, regardless of the transition metal and complex, with 88% of the registered structures displaying a value in between 82 and 85° (Chart 4a). Some in-plane distortions of the naphthalene scaffold are however observed, as apparent from the C<sub>bridge</sub>–C<sub>peri</sub>–M and P–C<sub>peri</sub>–C<sub>bridge</sub> bay angles (Charts 4b and c). While the C<sub>bridge</sub>–C<sub>peri</sub>–M bay angle does not deviate much from the ideal 120° value (by 2° at most), the P–C<sub>peri</sub>–C<sub>bridge</sub> bay angle is systematically found below 120°, with 85% of the structures falling in the range of 110–115°. The ability of the (P,C)-naphthyl framework to accommodate different metals thus seems to mainly arise from the P atom and the C<sub>peri</sub>–P bond.

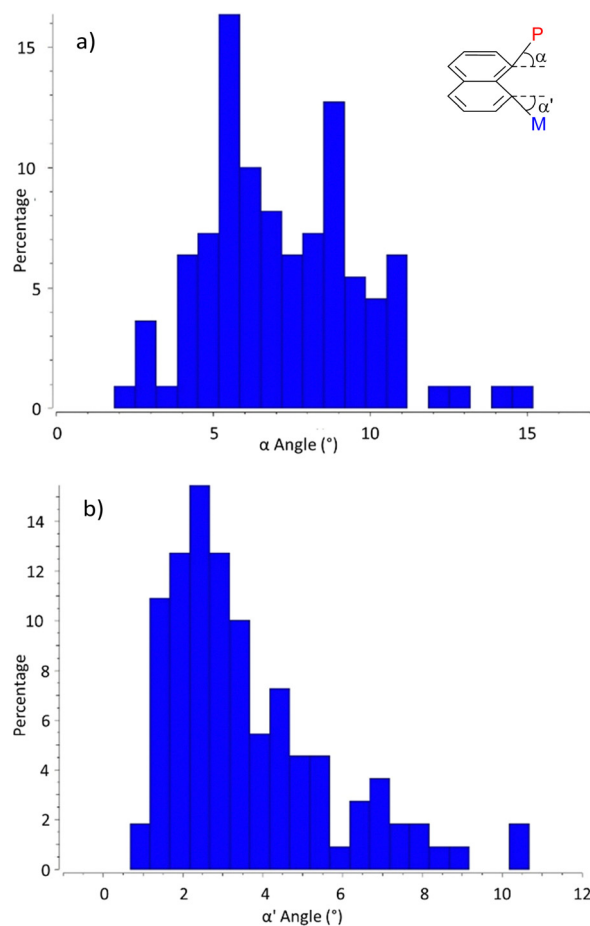
Out-of-plane distortions were also examined through the deviations of the P and M atoms at *peri* positions from the naphthalene plane (tilt angles  $\alpha/\alpha'$ , Charts 5a and b). In general, only minor deviations are observed. No correlation was found between the variations of  $\alpha, \alpha'$  and  $r(\text{P-M})$  (Charts S1 and S2, ESI<sup>†</sup>). The largest deviations concern the P atom (with out-of-





**Chart 4** Histograms showing the distribution (in percentage) of the bite angle (a), the  $C_{\text{bridge}}-C_{\text{peri}}-M$  bond (b) and the  $P-C_{\text{peri}}-C_{\text{bridge}}$  bond angle (c) among crystallographically characterized  $[N^P(P,C)M]$  complexes.

plane distortions  $\alpha$  up to  $10^\circ$  and 94% of the structures in the  $4-10^\circ$  range) while the metal usually remains close to the naphthalene plane (71% of the structures display  $\alpha'$  values between 1 and  $5^\circ$ ). It is to note that even if the deviations are small, the P and M atoms are systematically tilted in opposite directions (up and down the naphthalene plane), probably to minimize steric repulsions between the substituents at phosphorus and the co-ligands at M.



**Chart 5** Out-of-plane deviations of the P and M atoms at *peri* positions from the naphthalene plane illustrated by the distribution of the tilt angles  $\alpha$  (a) and  $\alpha'$  (b).

The bonding situation within  $[N^P(P,C)M]$  complexes has been occasionally assessed by computational means. Mebs, Hupf and Beckmann performed atom-in-molecules, electron localizability indicators and non-covalent interaction analyses on rhodium, nickel, palladium, platinum and gold complexes.<sup>39,42,43</sup> In all cases, the P–M and C–M bonds were found to be of polar covalent nature. The covalent and ionic contributions are slightly lower in the P–M bonds than in the C–M bonds.

### III. Applications of $[N^P(P,C)M]$ cyclometalated complexes: stoichiometric reactivity and catalytic transformations

In this section, the stoichiometric reactivity and catalytic application of cyclometalated naphthyl (P,C) complexes will be presented. It is organized *per* metal, starting from gold(III), then palladium(II), platinum(II/IV), iron(II) and ruthenium(II). In most cases, the metalacyclic structure is retained and these reactions



are reported first. Finally, miscellaneous examples involving the cleavage of the M–C bond are discussed.

### 1. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$ complexes

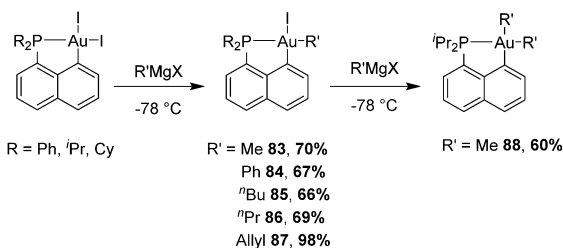
In the previous section, we presented the easy access to cyclometalated (P,C)-Au(III) complexes *via* chelate-assisted oxidative addition of the C–X bond to gold(I). The rigid nature of the (P,C) naphthyl ligand and its strong coordination to gold gives highly stable derivatives and allows us to explore the reactivity of gold(III) complexes.

Most of the elementary steps (migratory insertion,  $\beta$ -H elimination, *etc.*) known with isoelectronic metals (nickel(II), palladium(II) and platinum(II)) were not described with gold(III) complexes a decade ago. In this section, we present our work consisting of meticulous experimental and theoretical studies aiming to demonstrate the ability of gold(III) to efficiently undergo these elementary transformations.

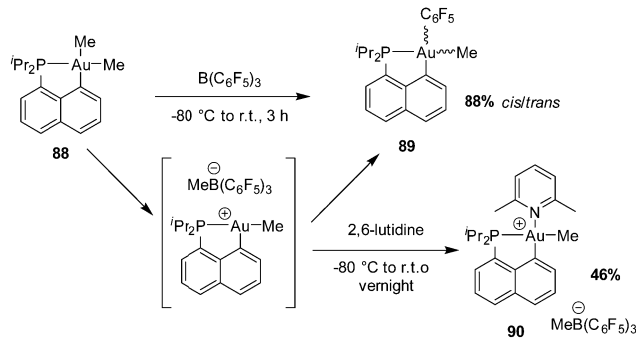
For this purpose, we took advantage of the selective modulation of cyclometalated (P,C)-AuI<sub>2</sub> giving easy access to (P,C)-AuR<sub>2</sub> complexes by the reaction with the corresponding Grignard reagent (Scheme 25).<sup>34,45,46</sup> In the presence of one equivalent of an organometallic reactant, the organic fragment sits *trans* to the phosphorus as apparent from NMR ( $J_{\text{C-P}} \geq 100$  Hz for *trans* isomer compared to 5.7 Hz for methyl at the *cis* position in  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{AuMe}_2]$ ) and in line with *trans* effects.

**a. Migratory insertion of alkenes in Au(III)–C bonds.** In 2015, we took advantage of the robustness of the  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{AuMe}_2]$  complex to demonstrate the feasibility of the migratory insertion of alkenes into Au(III)–C bonds (Scheme 26).<sup>34</sup> The 3-coordinated cationic gold(III) complex was generated by methyl abstraction with tris(pentafluorophenyl) borane. Due to its high electrophilicity, it proved highly unstable and spontaneously grasped a pentafluorophenyl group from the borate counter-anion to give the neutral  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{AuMe}(\text{C}_6\text{F}_5)]$  complex (obtained as a mixture of *cis/trans* isomers). The 3-coordinated cationic gold(III) complex could nevertheless be trapped before to rearrange, as substantiated with 2,6-lutidine.

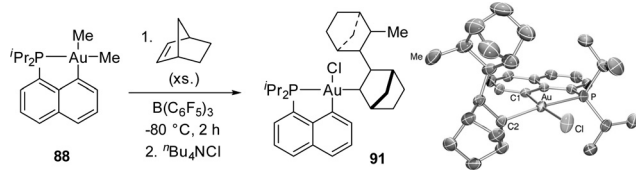
The reaction of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{AuMe}_2]$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  was then carried out in the presence of alkenes with the aim to achieve migratory insertion. Using ethylene or styrene, no sign of alkene incorporation was observed, but with norbornene (nbe), a strained and more reactive alkene, double insertion into the Au(III)–Me bond occurred (Scheme 27). The ensuing



Scheme 25 Synthesis of mono- and dialkyl  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  complexes using Grignard reagents.



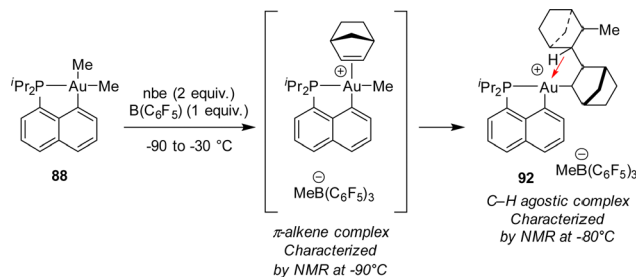
Scheme 26 Generation and rearrangement/trapping of the 3-coordinate cationic Au(III) complex  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{AuMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ .



Scheme 27 Double insertion of norbornene into an Au(III)–Me bond.

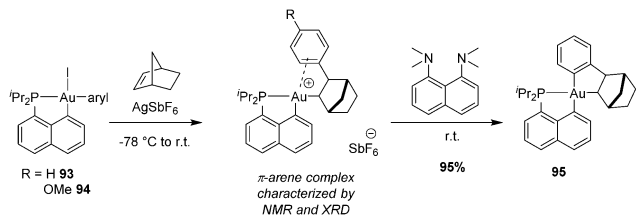
gold(III) complex was isolated and fully characterized (HRMS, NMR spectroscopy, and XRD) after trapping with tetrabutylammonium chloride (or pyridine). *Syn* additions across the C=C double bond of nbe attested unequivocally to the inner-sphere migratory addition process (as opposed to the usual outer-sphere addition *anti* to gold).

The mechanism of this reaction was thoroughly investigated by computational and experimental means (Scheme 28).<sup>34,47</sup> Accordingly, it classically involves coordination–insertion of alkene and because of the electronic dissymmetry of the cyclometalated (P,C) ligand, the first insertion was found slightly more demanding energetically than the second one (activation barriers of 18.7 and 15.7 kcal mol<sup>−1</sup>, respectively), in line with the observation of double insertion. Low-temperature monitoring by NMR spectroscopy enabled detecting two key intermediates: the first  $\pi$ -alkene complex and the double insertion product before trapping with chloride. The latter species represents the first example of an agostic complex with gold. Coordination of the  $\gamma$  C–H bond of the bis-norbornyl moiety to



Scheme 28  $\pi$ -Alkene and C–H agostic complexes authenticated upon low-temperature NMR monitoring of the double nbe insertion at Au(III).



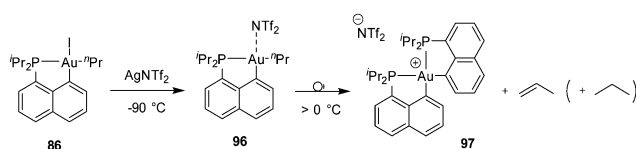


**Scheme 29** Insertion of norbornene into Au(III)–aryl bonds and the base-assisted cyclometalation of the ensuing  $\pi$ -arene Au(III) complex.

gold was apparent from the reduced  $^1J_{\text{CH}}$  coupling (97 Hz) as well as NBO and AIM analyses.<sup>48</sup>

We then envisioned to extend the migratory insertion of alkenes to gold(III) aryl complexes, with the idea to access and characterize  $\pi$ -arene gold(III) complexes (Scheme 29).<sup>49,50</sup> Such species were proposed as the initial stage of the C–H activation of arenes at gold(III). The  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{Ph})\text{I}]$  complex was reacted with  $\text{AgSbF}_6$  in the presence of norbornene. Here, mono-insertion took place rapidly and cleanly to give a  $\pi$ -arene gold(III) complex. According to NMR spectroscopy, XRD analysis (of the *p*-methoxy derivative) and DFT calculations, the arene moiety is  $\eta^2$ -coordinated to gold. The reaction profile of nbe insertion into the Au(III)–Ph bond was analysed by DFT calculations. Coordination–insertion was found to be facile (with an even lower activation barrier than that for the Au(III)–Me complex, 10.7 vs. 18.7 kcal mol<sup>-1</sup>). Then, *cis/trans* isomerization proceeds readily to give the  $\pi$ -arene gold(III) complex obtained. Of note, the auration of  $\pi$ -coordinated arene could be triggered easily by adding a base such as the proton sponge. This demonstrates the relevance of such  $\pi$ -arene complexes to the electrophilic metalation of arenes at gold(III).

**b.  $\beta$ -Hydride elimination.** As pointed out by Köppel and Hashmi in 2013,  $\beta$ -hydride elimination is intrinsically highly disfavoured in gold(I) alkyl complexes. With a  $d^8$  configuration, gold(III) alkyl complexes are *a priori* more prone to  $\beta$ -H elimination, although direct experimental evidence was long lacking. Taking advantage of the stability of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  complexes, we carried out in 2016 a comprehensive study on 3-coordinated cationic gold(III) *n*-alkyl complexes (Scheme 30).<sup>45</sup> The target compounds ( $^n\text{Pr}$  and  $^n\text{Bu}$ ) were easily generated by reacting the corresponding neutral iodide complexes with  $\text{AgNTf}_2$  at  $-90$  °C, and their reactivity was monitored by variable-temperature NMR spectroscopy. Accordingly, above  $0$  °C, the *n*-propyl complex was found to transform into the known cationic bis-cyclometalated species with the concomitant release of propylene as a result of  $\beta$ -hydride elimination (propane is also formed by a bimolecular pathway).



**Scheme 30**  $\beta$ -Hydride elimination from the cationic  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  *n*-propyl complex.

A similar process was observed from the corresponding *n*-butyl gold(III) complex, with the release of *cis* and *trans* 2-butenes, as well as butane (Scheme 31). The formation of internal alkenes indicates that the initially generated 1-butene rapidly re-inserts into the Au(III)–H bond resulting in a chain walking process. Computational studies have estimated the activation barriers for such  $\beta$ -H eliminations to 8–14 kcal mol<sup>-1</sup> (compared to  $<2$  kcal mol<sup>-1</sup> for the olefin re-insertion into the Au(III)–H bond). In addition, reacting the corresponding  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  methyl complex with ethylene (7 bars) at  $50$  °C afforded a mixture of propene and butenes. Here, the slow insertion of ethylene into the Au(III)–Me bond is followed by rapid  $\beta$ -H elimination.

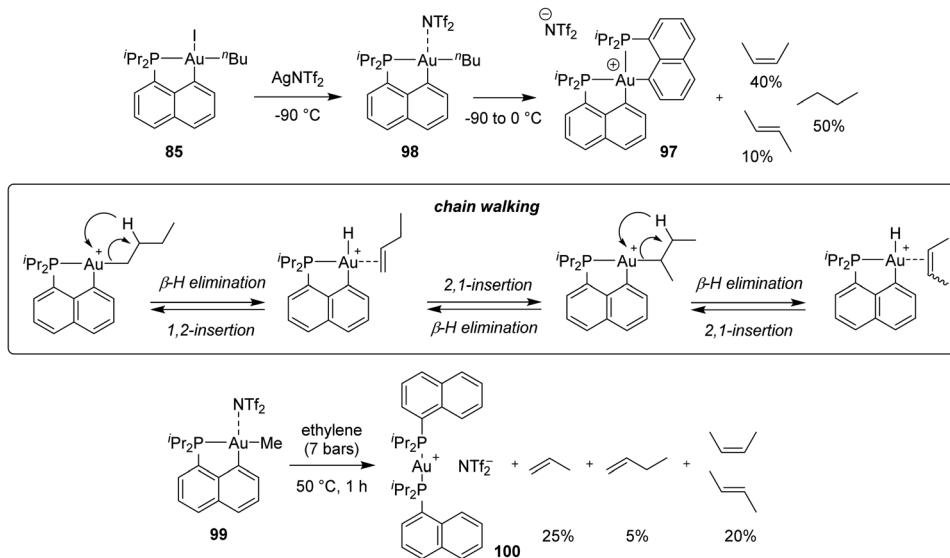
A reaction sequence involving coordination–insertion and  $\beta$ -hydride elimination was also observed by reacting the  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})\text{Ph}]$  complex with ethylene (Scheme 32).<sup>49</sup> In this case, styrene re-insertion is very facile, much more than its dissociation. As a result, the reaction gives a gold(III) styryl complex stabilized by  $\pi$ -arene coordination.

**c.  $\pi$ -Allyl gold(III) complexes.** While palladium(II)  $\pi$ -allyl complexes are iconic in organometallic chemistry, analogous gold(III) species remained elusive until recently. In 2020, we took advantage of the rigid and robust  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  platform to prepare and study  $\pi$ -allyl gold(III) complexes (Scheme 33).<sup>46</sup> They were readily prepared from the corresponding neutral  $\sigma$ -allyl precursors, by iodide abstraction with  $\text{AgSbF}_6$ . The thorough analysis of the bonding situation by NMR spectroscopy, XRD and DFT calculations revealed the static and highly symmetric  $\eta^3$ -coordination of the  $\pi$ -allyl moiety to gold. Of note, the related (N,C)-cyclometalated gold(III)  $\pi$ -allyl complexes prepared simultaneously and independently by Tilset proved to adopt highly fluxional and unsymmetric  $\sigma + \pi$  structures instead.<sup>51</sup> To draw parallel with palladium(II) complexes, we reacted the  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$   $\pi$ -allyl complexes with  $\beta$ -dicarbonyl carbanions. The corresponding C–C coupling products were obtained in good to excellent yields, as the result of nucleophilic addition to the  $\pi$ -coordinated allyl moieties.

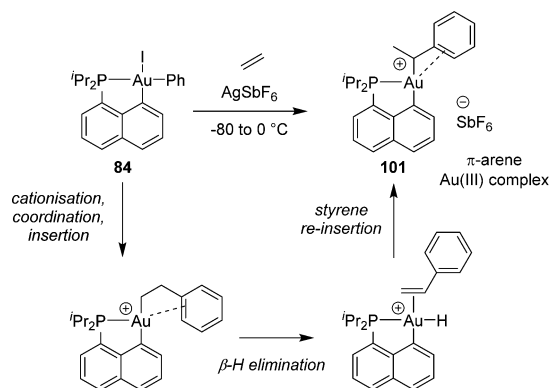
A meticulous mechanistic study combining *in situ* NMR monitoring at low temperatures and DFT calculations revealed a complex and rich picture for this apparently simple transformation (Scheme 34).<sup>35</sup> If the C-allylation product is readily obtained whatever the  $\pi$ -allyl substitution ( $\text{R} = \text{H}, \text{Me}$ ) and  $\beta$ -dicarbonyl nucleophile ( $\text{R}' = \text{OEt}, \text{Ph}$ ), nucleophilic attack can occur initially at either the terminal or the central positions of  $\pi$ -allyl, as well as at the metal itself. Reactive intermediates resulting from these 3 competitive paths were actually all authenticated spectroscopically and/or crystallographically. For palladium(II)  $\pi$ -allyl complexes, the regioselectivity of the nucleophilic addition is under orbital rather than charge control. The close inspection of the molecular orbital diagram for  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$   $\pi$ -allyl complexes showed the presence of three vacant orbitals with major contributions of gold and the terminal/central positions of  $\pi$ -allyl within a small energy gap. This explains why nucleophilic attacks to the 3 sites are intrinsically in competition.

Of note,  $\pi$ -allyl gold(III) complexes were amenable to catalytic allylation. Using a  $\text{P}^*\text{N}$  hemilabile ligand, we could cross-

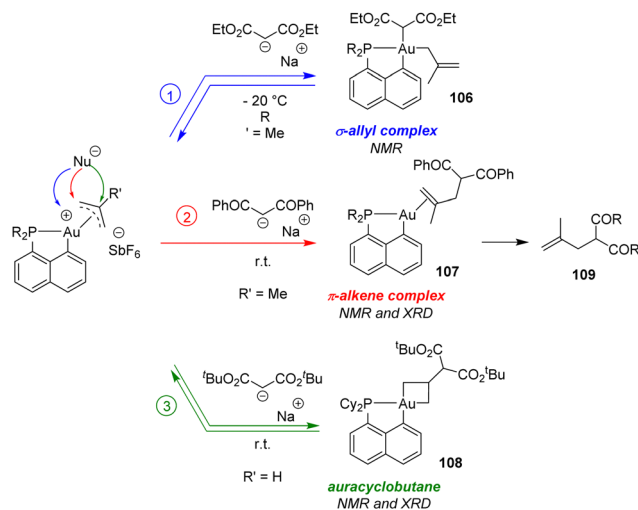




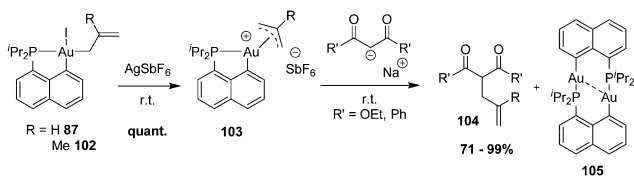
Scheme 31 Reactions of the cationic  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  *n*-butyl and methyl complexes involving  $\beta$ -H elimination.



Scheme 32 Formation of a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$   $\pi$ -arene complex by a coordination–insertion/ $\beta$ -hydride elimination/isomerisation sequence.



Scheme 34 Three reactive sites for the addition of  $\beta$ -dicarbonyl nucleophiles to  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$   $\pi$ -allyl complexes and the ensuing products authenticated experimentally.



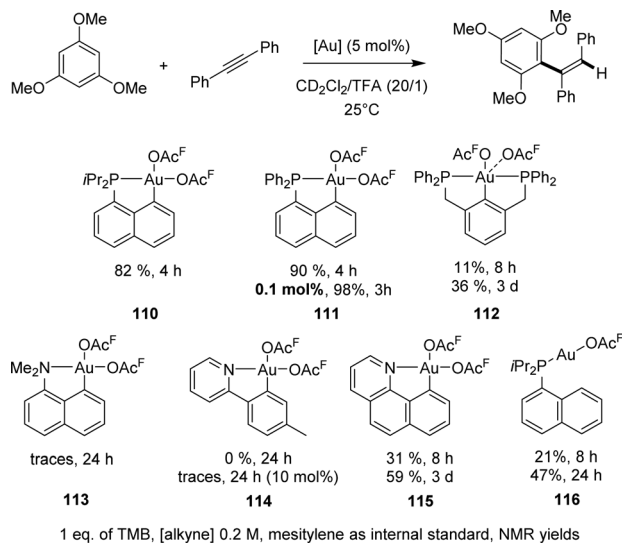
Scheme 33 Synthesis of cationic  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$   $\pi$ -allyl complexes and their C–C coupling with  $\beta$ -dicarbonyl carbanions.

couple allyl acetates and alcohols with indoles with complete selectivity for the branched C3-allylated products.<sup>52</sup>

**d. Hydroarylation of alkynes catalysed by  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  complexes.** The ability of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  complexes to engage in migratory-insertion, C–H activation and  $\beta$ -H elimination prompted us to consider their possible use as catalysts in the intermolecular hydroarylation of alkynes.<sup>53</sup> This transformation, pioneered by Fujiwara with platinum and palladium

complexes,<sup>54,55</sup> gives straightforward access to styrene derivatives and represents an attractive alternative to the Heck coupling, using aryl-H instead of aryl-X substrates. This formal addition of aryl-H bonds to alkynes prevents the pre-functionalization of the arene substrate. (P,C)-cyclometalated gold(III) complexes **110** and **111** with labile trifluoroacetate  $\text{OAc}^{\text{F}}$  co-ligands were readily prepared. Using trifluoroacetic acid (TFA) as a co-solvent facilitates  $\text{OAc}^{\text{F}}$  dissociation and enables operating under silver-free conditions. Using the addition of 1,3,6-trimethoxybenzene (TMB) to diphenylacetylene (DPA) as the test reaction, the (P,C)-cyclometalated gold(III) complexes proved extremely active, while the related (N,C)-cyclometalated complexes showed no or low activity (Scheme 35). Poor results



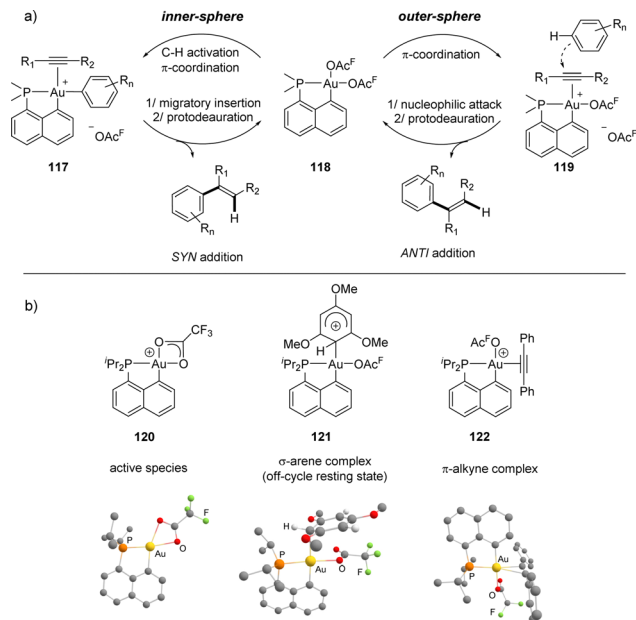


**Scheme 35** Comparison of the catalytic activities of a range of gold complexes in the hydroarylation of diphenylacetylene with 1,3,6-trimethoxybenzene.

were also observed with a (P,C,P) gold(III) complex as well as a non-cyclometalated gold(I) complex. The  $[\text{N}^{\text{P}}(\text{P,C})\text{Au}(\text{III})]$  complexes are thus unique to show high robustness and activity in this transformation. Substituting the phosphorus atom by a Ph instead of an  $^i\text{Pr}$  group reduces the steric hindrance and increases the electrophilicity of the gold(III) center, resulting in enhanced activity. Ultimately, the coupling of TMB and DPA could be achieved in a 98% yield at 0.1 mol% loading within 3 h.

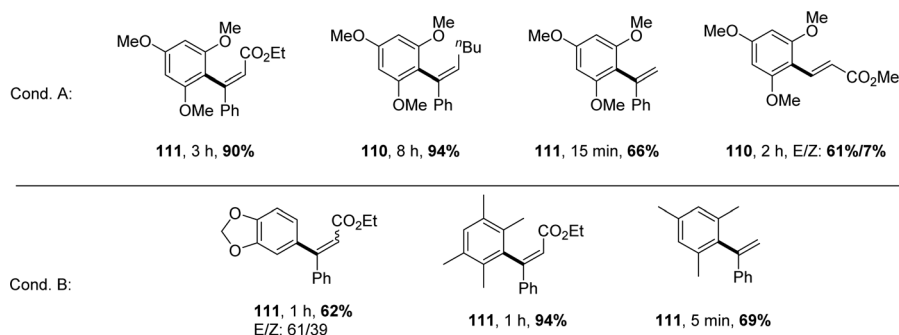
$[\text{N}^{\text{P}}(\text{P,C})\text{Au}(\text{III})]$  complexes showed high activity with a rather broad scope of substrates (Chart 6). The reaction works efficiently with internal alkynes featuring aryl, alkyl, ester and keto substituents, as well as terminal alkynes. Other electron-rich arenes than TMB can also be used, including dialkoxybenzenes, durene and mesitylene. In all cases, hydroarylation is fully regioselective, and it is generally fully stereoselective, affording the *anti*-addition product.

*A priori*, two paths are conceivable to account for such Au(III)-catalyzed arene/alkyne coupling (Scheme 36). One involves the



**Scheme 36** (a) Schematic representation of the inner- and outer-sphere mechanisms conceivable for the hydroarylation of alkynes catalyzed by  $[\text{N}^{\text{P}}(\text{P,C})\text{Au}(\text{III})]$  complexes. (b) Related intermediates authenticated experimentally and optimized geometry computed at the SMD(CH<sub>2</sub>Cl<sub>2</sub>)-B97D/SDD+f(Au)/6-31G\*\* (other atoms) level of theory.

$\pi$ -coordination of the alkyne to gold yielding **119**, the outer-sphere nucleophilic addition of the arene and finally protodeauration. The other one starts by the C-H activation of the arene affording **117**, followed by the migratory insertion of the alkyne and finally protodeauration. The outer-sphere path was initially inferred indirectly, based on the observed formation of the *anti*-addition products. A thorough mechanistic study was then performed,<sup>56</sup> to track reactive intermediates and better understand the factors at play. Accordingly, using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as the co-catalyst instead of TFA as the co-solvent enabled us to characterize by low temperature NMR spectroscopy the cationic complex  $[\text{N}^{\text{P}}(\text{P,C})\text{Au}(\text{OAc}^{\text{F}})]^+$ , the active species easily shifting from  $\kappa^2$  to  $\kappa^1\text{-OAc}^{\text{F}}$  coordination, and its TMB adduct



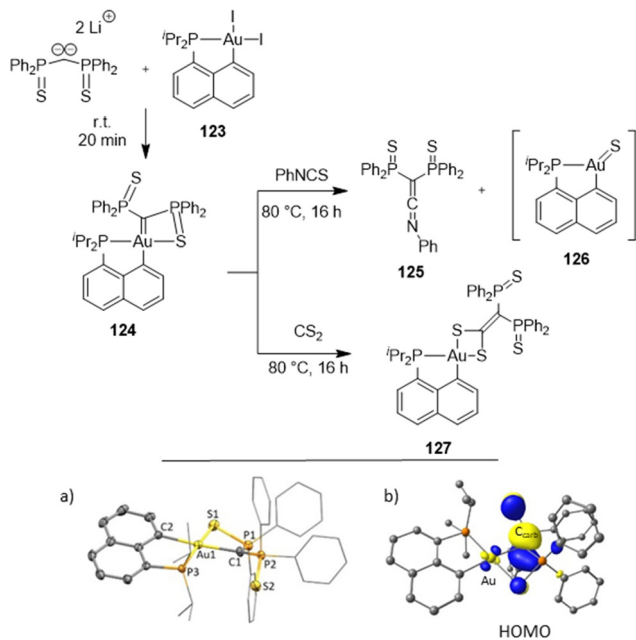
Conditions A: DCM/TFA (20/1), 1 equiv. arene, [alkyne] = 0.2M.  
Conditions B: DCM/TFA (1/4), 2 equiv. arene, [alkyne] = 1M.

**Chart 6** Selected examples of intermolecular hydroarylation of alkynes catalysed by  $[\text{N}^{\text{P}}(\text{P,C})\text{Au}(\text{III})]$  complexes.



$[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{OAc})^{\text{F}}(\text{TMB})]^+$ , an off-cycle resting state and actually the first Wheland-type  $\sigma$ -arene complex of Au(III) to be authenticated. The key  $\pi$ -alkyne complex was also generated and characterized in the gas phase by mass spectrometry using ion-molecule collision techniques. The energy profiles for the coupling of TMB/DPA were also analysed computationally and the outer-sphere path was found to be much less demanding energetically than the inner-sphere mechanism.

**e. A Schrock-type nucleophilic Au(III) carbene complex.** In contrast with electrophilic Fischer-type gold(I) carbene complexes, which are now relatively well-established and understood species, gold(III) complexes with a reactive carbene moiety were elusive until recently. In 2017, the groups of Mézailles and Bourissou combined a geminal dianion stabilized by electron-withdrawing  $\text{P}^{\text{V}}$  substituents with a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]_2$  complex to prepare an original gold(III) carbene complex (Scheme 37).<sup>57</sup> The gold center is in square-planar environment, as expected for gold(III), and the carbene center is its trigonal planar geometry. One of the  $\text{P}(=\text{S})\text{Ph}_2$  side-arm is coordinated to gold, and the other remains pendant. Variable-temperature  $^{31}\text{P}$  NMR indicated a dynamic situation, with the rapid exchange of the two  $\text{P}(=\text{S})\text{Ph}_2$  moieties at room temperature. The  $^{13}\text{C}$  NMR signal for the carbene center was found at  $\delta$  18.2 ppm, very much shielded compared to those of electrophilic cationic Au(I) carbene complexes ( $\delta$  from 200 to 321 ppm), indicating a completely different bonding situation and an electron-rich carbene center. Consistently, DFT calculations revealed a high energy HOMO centered at the carbene center. The nucleophilic, Schrock-type character of the carbene center was actually substantiated experimentally by Wittig-type reactions with phenylisothiocyanate and  $\text{CS}_2$ .



**Scheme 37** Synthesis and reactivity of a nucleophilic  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$  carbene complex. X-ray structure (a) and its HOMO (b).

## 2. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}(\text{II})]$ complexes

In 1998, Shaw demonstrated the high catalytic activity and robustness of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}]$  acetate and acetylacetonate complexes **128** and **129** in the Heck reaction (Scheme 38).<sup>22</sup> The coupling of iodobenzene and styrene could be achieved at extremely low catalytic loadings (down to 0.0001 mol%) under forcing conditions (up to 13 days at 95 °C) to reach TON as high as 1 120 000. Of note, related cyclometalated complexes derived from benzyl phosphines led to significant lower TON (900 at best). A few years later, Herrmann extended this study to bromo- and chloro-arenes, working at 130 °C and 0.1 mol% catalyst loading.<sup>23</sup> Under these conditions, the Heck coupling products could be obtained in high yields from bromo-arenes (with TON up to 1,000) but not from chloro-arenes (29% at best).

With these more challenging substrates, the  $[\text{B}^{\text{n}}(\text{P},\text{C})\text{Pd}]$  complexes perform best, with TON values up to 329 000 achieved from bromo-arenes.

Conversely, Hou obtained good results with the rigid (P,C)-naphthyl ligand in the intermolecular [4+2] cycloaddition of bicyclic alkenes with terminal ynones affording polysubstituted furans.<sup>58</sup> An exhaustive catalyst screening was conducted, from simple commercially available Pd compounds to (P,C)-cyclometalated complexes derived from binaphthyl, biphenyl, benzyl and naphthyl phosphines. Good yields (>60%) were only obtained when using  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}]$  complexes.

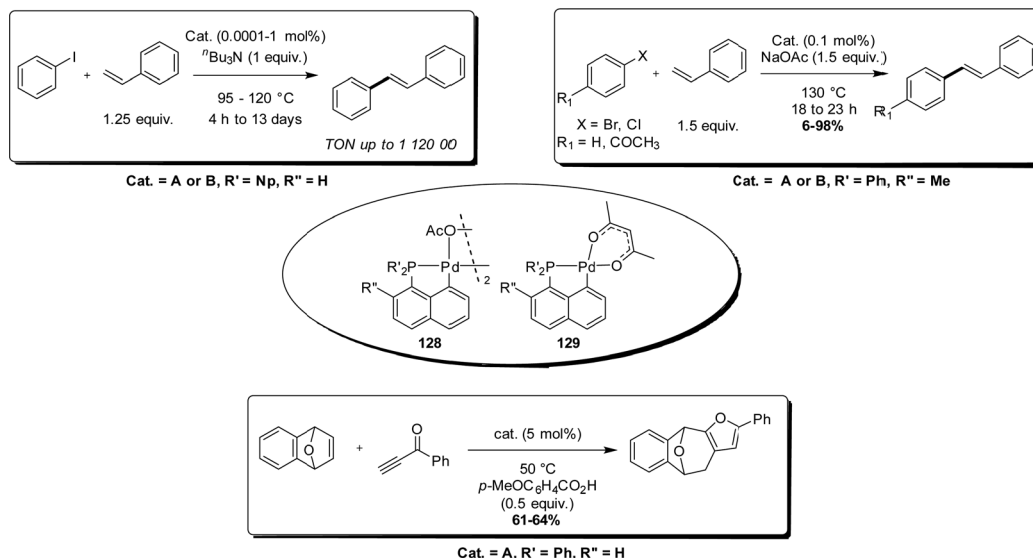
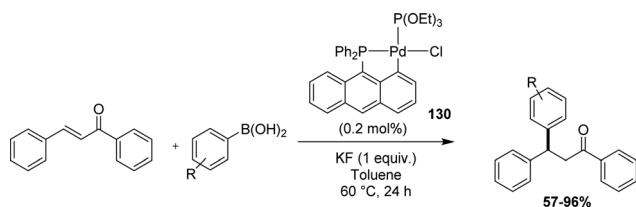
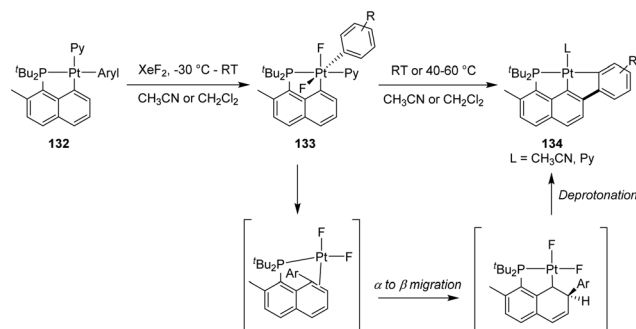
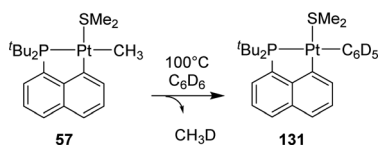
Recently, Yamamoto applied 9-(diphenylphosphino)anthracene-based phosphapalladacycles as catalysts for the conjugate addition of arylboronic acids to electron-deficient alkenes (Scheme 39).<sup>59</sup> *In situ* tests using  $\text{Pd}(\text{OAc})_2$  and phosphines showed the higher performance of the anthracenyl phosphine (95% yield in coupling product from phenylboronic acid and  $\text{PhCH}=\text{CHC}(=\text{O})\text{Ph}$ ) over the corresponding naphthyl phosphine ( $\text{Ph}_2\text{PNp}$ , 53%) and triphenylphosphine (<5%). Using the preformed  $[\text{A}^{\text{n}}(\text{P},\text{C})\text{Pd}]$  complex with  $\text{P}(\text{OEt})_3$  as the co-ligand, the catalytic loading could be decreased to 0.2–0.5 mol% keeping high reactivity over a large substrate scope.

## 3. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II/IV})]$ complexes

In 2011, Goldberg reported the C–H activation of benzene upon thermolysis (100 °C) of a cyclometalated  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  methyl complex in  $\text{C}_6\text{D}_6$  (Scheme 40).<sup>25</sup> Methane was identified as the co-product (with  $\text{CH}_3\text{D}$  as the major isotopomer) and the addition of an excess of  $\text{SME}_2$  was found to inhibit the C–H activation. The authors thus proposed a mechanism involving the displacement of  $\text{SME}_2$  by benzene- $\text{D}_6$  at platinum, followed by the oxidative addition of a C–D bond/reductive elimination of  $\text{CH}_3\text{D}$  or a  $\sigma$ -bond metathesis process.

In the context of the electrophilic fluorination of arenes with high valent transition metals, Vigalok and Verdernikov investigated the oxidation of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  aryl complexes with  $\text{XeF}_2$  (Scheme 41).<sup>24</sup> The ensuing platinum(IV) complexes showed moderate stability and evolved at 20–60 °C *via* an 1,3-aryl migration from the platinum center to the  $\beta$ -carbon of the naphthyl fragment to yield (P,C,C)Pt(II) pincer complexes.

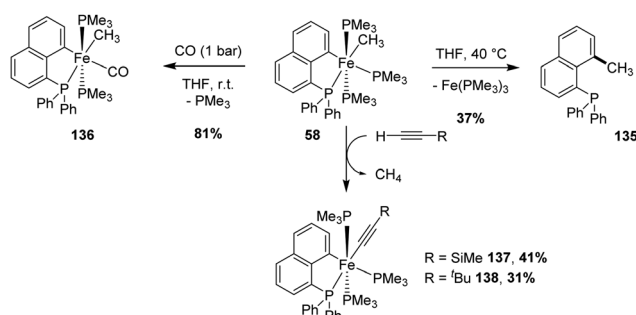


Scheme 38 Catalytic applications of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pd}]$  complexes **128** and **129**.Scheme 39 Catalytic application of an  $[\text{A}^{\text{n}}(\text{P},\text{C})\text{Pd}]$  complex in the conjugate addition of arylboronic acids to electron-deficient alkenes.Scheme 41 Electrophilic fluorination of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  aryl complexes leading to  $(\text{P},\text{C},\text{C})\text{Pt}(\text{II})$  pincer complexes.Scheme 40 C-H bond activation of benzene by a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$  methyl complex.

Based on DFT calculations, the authors proposed a stepwise mechanism for this unprecedented  $\text{C}_{\text{sp}^2}\text{-C}_{\text{sp}^2}$  coupling. Following pyridine dissociation and C-C coupling, the aryl group would migrate from the  $\alpha$ -position to the  $\beta$ -position of the naphthyl ring to generate a naphthylidene complex. Finally, deprotonation of the naphthyl ring would restore the aromatic naphthalene system.

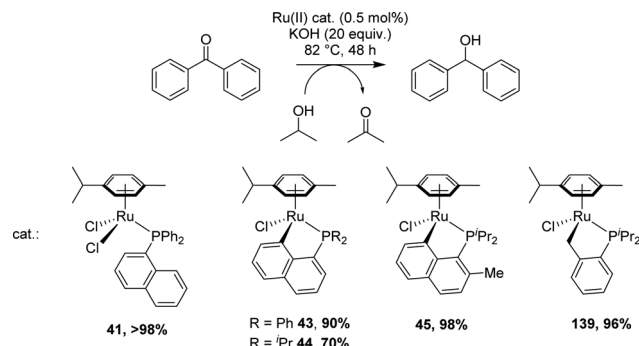
#### 4. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Fe}(\text{II})]$ complexes

The  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Fe}(\text{II})]$  methyl complex was found by Beck and Sun to be unstable thermally (Scheme 42).<sup>60</sup> The iron center is in octahedral geometry with the Me group at the *cis* position to the carbon atom of the  $(\text{P},\text{C})$ -cyclometalated ligand. Upon gentle heating (40 °C, 4 h), reductive elimination took place to give the corresponding C-methylated naphthyl diphenylphosphine.

Scheme 42 Stoichiometric reactions of a  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Fe}(\text{II})]$  methyl complex.

Nonetheless, some stoichiometric reactions with the retention of the cyclometalated  $\text{N}^{\text{P}}(\text{P},\text{C})$  framework were also reported. With carbon monoxide, the ligand exchange of one trimethylphosphine co-ligand proceeded smoothly at room temperature, while C-H activation occurred with terminal alkynes to give the corresponding acetylide complexes with release of methane.



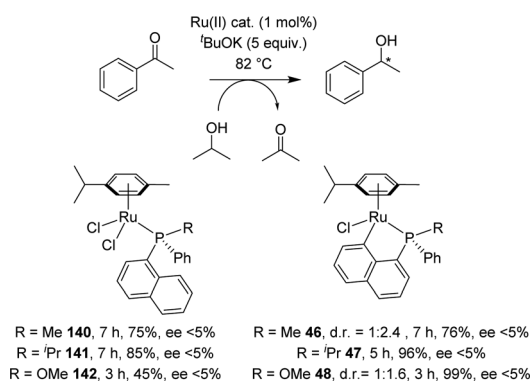


Scheme 43 Reduction of ketones catalyzed by *p*-cymene phosphine Ru(II) complexes.

## 5. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}(\text{II})]$ complexes

$[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes were applied to the catalytic reduction of ketones by transfer hydrogenation with isopropanol. In 2007, Zhu compared the catalytic activities of various *p*-cymene phosphine complexes under similar conditions: 0.5 mol% catalyst loading, 82 °C (boiling  $^i\text{PrOH}$ ), 48 h, KOH (20 eq.) (Scheme 43).<sup>19</sup> Whatever the substituent at phosphorus (Ph or  $^i\text{Pr}$ ), the  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}(\text{II})]$  complex showed lower activity (70–90% yields for the reduction of benzophenone) compared to the non-cyclometalated complex (>98% yield) and the benzyl cyclometalated complex (96% yield). However, a significant increase in yields was observed upon introducing a methyl group at the *o*-position of phosphorus of the  $[\text{N}^{\text{P}}(^i\text{Pr}_2\text{P},\text{C})\text{Ru}]$  complex (from 70 to 98%).

Two years later, Grabulosa envisioned to develop an asymmetric version by chirality transfer from a P-stereogenic center to the ruthenium center (Scheme 44).<sup>21</sup> Starting from homochiral naphthyl phosphines, the cyclometalation step proceeded with disappointingly low diastereoselectivity (d.r. = 1:2.4 for R = Me and d.r. = 1:1.6 for R = MeO). Only the  $^i\text{Pr}$ -substituted phosphine induced full control of the ruthenium chiral center, but unfortunately, the cyclometalated complex was formed in a very low yield (15%). Evaluation of these  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes in asymmetric transfer hydrogenation of acetophenone reveals very low, if any, enantioselectivity



Scheme 44 Attempts for Ru-catalyzed asymmetric hydrogenation of acetophenone with P-chiral naphthyl phosphine complexes.

(ee < 5%). Nevertheless, it is interesting to note that cyclometalation of the naphthyl phosphinite ligand (R = OMe) resulted in a noticeable increase of the catalytic activity (from 45% yield in reduction product after 3 h with the non-cyclometalated complex, to 99% yield with the cyclometalated complex).

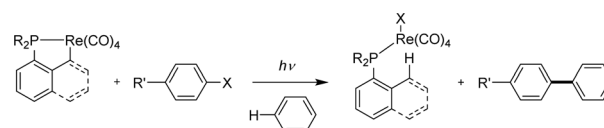
## 6. Miscellaneous examples involving M–C cleavage

$[\text{N}^{\text{P}}(\text{P},\text{C})\text{M}]$  metalacycles are very robust and in all the previously described reactions and catalyses, they remain intact throughout the transformations. However, M–C bond cleavage was found to occur in a few cases, presented hereafter.

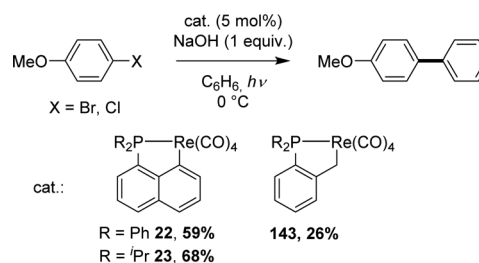
**a.  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Re}]$  complexes.** In 2017, the group of Zhu investigated the decyclometalation of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Re}]$  complexes<sup>11</sup> inspired by the work of Lu on homologous N,C-cyclometalated complexes.<sup>61</sup> The cleavage of the Re–C bond was achieved under UV irradiation at room temperature in chloroform or bromoform to yield the corresponding rhenium halide complexes. Protodecyclometalation was also reported with trifluoroacetic acid under photolytic conditions at room temperature. The photolysis of various (P,C)Re cyclometalated complexes in the presence of aryl halides in benzene was then investigated (Scheme 45). The corresponding biphenyl products were thereby obtained in high yields (80–98%) and short reaction times (few hours) along with the decyclometalated Re complexes (as a result of formal HX trapping).

Taking advantage of the facile cyclometalation of naphthyl phosphines at rhenium in the presence of a base, the cross-coupling of 4-bromoanisole and benzene (used as the solvent) was then possible under catalytic conditions, in the presence of 1 equivalent of sodium hydroxide (Scheme 46). Of note, the ancillary  $\text{N}^{\text{P}}(\text{P},\text{C})$  ligand was found to outperform its more flexible  $\text{C}_{\text{sp}^3}$  variant (59 vs. 26% yield) and replacing the Ph groups at phosphorus for  $^i\text{Pr}$  led to an increase in stability of the rhenium catalyst (no free ligand observed with  $^i\text{Pr}$ ) and thus a better yield in the coupling product (68%).

**b.  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}]$  and  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Rh}]$  complexes.** In the course of their work on the insertion/remote rearrangement of internal



Scheme 45 Aryl halides/benzene coupling upon the photochemical reaction of cyclometalated rhenium complexes.



Scheme 46 Re-catalyzed arylation of benzene with aryl halides.

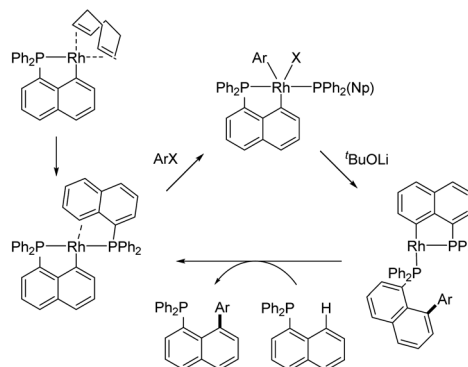
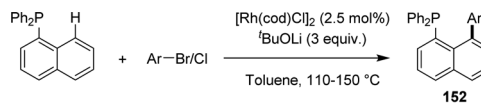


alkynes in ruthenium complexes, the group of Ishii reported a rare example of P–C reductive elimination at ruthenium (Scheme 50).<sup>20</sup> When exposed to an halide abstractor and an internal alkyne, the  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}]$  complex undergoes the 1,2-insertion of the alkyne ( $\text{R} = \text{alkyl or aryl}$ ) in the Ru–C bond followed by P–C reductive elimination to yield sandwich complex **146**. This mechanism was supported by the isolation of intermediate **147** resulting from the 1,2-insertion of diphenylacetylene in the presence of  $\text{NaBAR}^{\text{F}}_4$  at room temperature. Heating at 70 °C for 24 hours allows the P–C reductive elimination to take place. Phosphalenium salts can then be released using oxidants ( $\text{I}_2$  and  $\text{CuCl}_2$ ) or  $\text{CO}$ .<sup>62</sup>

Recently, Ishii synthesized the analogous alkenyl rhodium(III) complex coordinated with pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) by the 1,2-insertion of diphenylacetylene in the presence of  $\text{NaBAR}^{\text{F}}_4$  (Scheme 51).<sup>63</sup> An addition of 1.0 equivalent of di-*p*-tolylacetylene to this complex results in an equilibrium between the two corresponding alkenylrhodium complexes with a 43:57 ratio. The authors proposed that an alkyne exchange occurs *via*  $\beta$ -carbon elimination, for which the activation barrier was estimated computationally to be accessible (15.6 kcal mol<sup>-1</sup>). This represents one of the rare examples of  $\beta$ -carbon elimination from an alkenyl complex (*i.e.* the reverse process of alkyne insertion).

Recently, Zeng reported an original Ru-catalyzed alkylation of naphthyl phosphines occurring selectively on the remote C5 position (Scheme 47).<sup>64</sup> The transformation proceeds under relative mild conditions (50–80 °C) with bromo-alkanes as alkylating reagents. It takes advantage of the facile and reversible formation of  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}]$  complexes by phosphine-directed cyclometalation/protodemetalation. Bromo alkanes are proposed to oxidize the ruthenium center *via* a single-electron transfer (SET), the alkylation would then occur by radical electrophilic substitution on the naphthyl ring. The high C5-regioselectivity (C5/others >20/1) is tentatively assigned to the inductive effect of the  $\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}$  metallacycle.

In 2018, Yu and Che described jointly the Rh-catalyzed *peri* arylation of naphthyl phosphines (Scheme 48).<sup>65</sup> Using 2.5 mol% of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  and 3 equivalents of  ${}^t\text{BuOLi}$  as a base, naphthyl phosphines could be efficiently coupled with bromoarenes (within 24 h at 110 °C) as well as chloroarenes (within 24 h at 150 °C) in good to high yields. The reaction is fully selective for *peri* arylation and works with bromo/chloro hetero-



Scheme 48 Rh-catalyzed C–H arylation of 1-naphthyl diphenylphosphines involving  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Rh}]$  complexes.

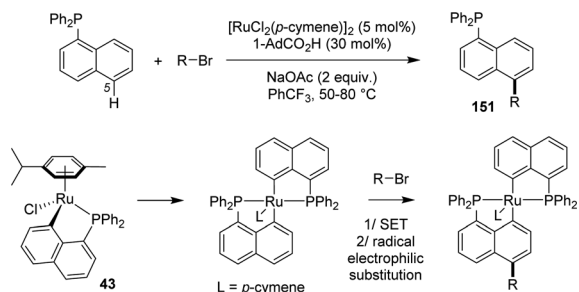
arenes as well. Mechanistic studies by mass spectrometry suggest a Rh(I)/Rh(III) catalytic cycle. The bis-phosphine complex  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Rh}(\text{PPh}_2)\text{Np}]$  was proposed to be the active species.

Very recently, Hierso and Roger extended this methodology to polycyclic aromatic hydrocarbons, in particular 1-pyrenyl diphenylphosphine (Scheme 49).<sup>66</sup> The reaction works well with a large scope of bromo-arenes substituted by electron-donating and electron-withdrawing groups, as well as bromo-heteroarenes. It is fully selective for the arylation of the position *peri* to phosphorus, and is also applied to phenanthryl and fluoranthenyl phosphines. The  $[\text{Rh}(\text{I})(\text{cod})_2]\text{BF}_4$  and  $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$  complexes can be used and gave similar results. (P,C)-cyclometalated Rh(III) complexes were prepared and their activities were evaluated. The neutral species gave poor results and was assumed to be a deactivated out-of-cycle resting state, while the di-phosphine cationic complex showed high catalytic activity.

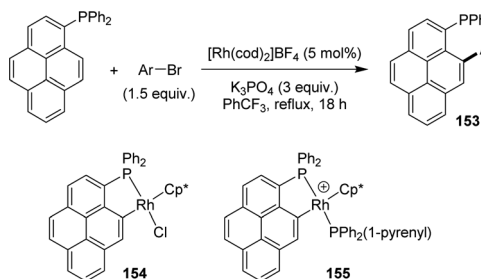
## IV. Luminescence properties and optoelectronic applications of $[\text{N}^{\text{P}}(\text{P},\text{C})\text{M}]$ complexes

### 1. $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Pt}(\text{II})]$ complexes

In 2009, Yip reported an interesting study on (P,C)-cyclometalated platinum complexes derived from pyrenes.<sup>10</sup>

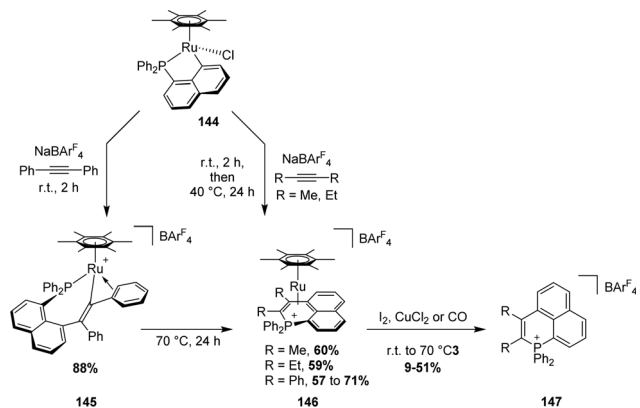


Scheme 47 Ru-catalyzed C5-selective alkylation of naphthyl phosphines involving  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Ru}(\text{II})]$  complexes.

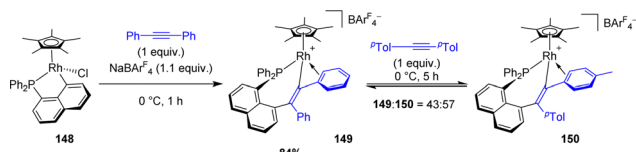


Scheme 49 Rh-catalyzed C–H arylation of 1-pyrenyl diphenylphosphines involving  $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Rh}]$  complexes.





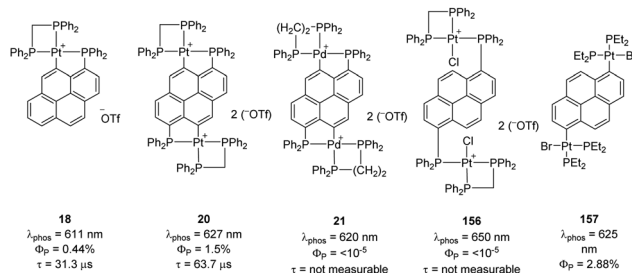
**Scheme 50** Reaction of a  $[\text{Np}(\text{P,C})\text{Ru}(\text{II})]$  complex with internal alkynes leading to phosphanelium salts.



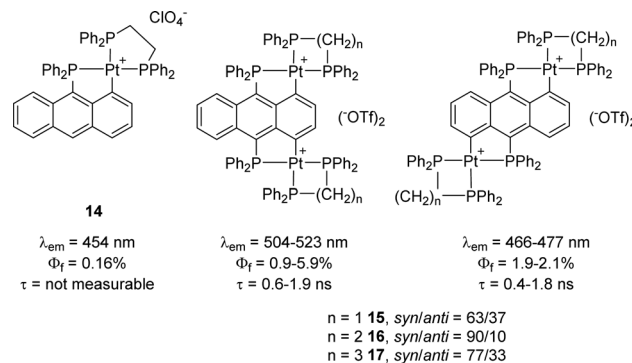
**Scheme 51** Synthesis of complex **149** by alkyne insertion in the  $\text{C}_{\text{peri}}\text{-Ru}$  bond and the exchange reaction of the alkenyl moiety using di-*p*-tolylacetylene.

The fluorescence properties of pyrene derivatives are well-known and widely used, while phosphorescence is usually very weak. Phosphorus substitution and subsequent cyclometalation of the *peri* C–H bond were envisioned as a mean to introduce Pt on the pyrene ring and benefit from the internal heavy-atom effect to enhance phosphorescence. Accordingly, the mono and dimetallic platinum complexes **18** and **20** showed phosphorescence at  $\lambda_{\text{em}}$  611–627 nm in oxygen-free acetonitrile solution at room temperature, with quantum yields of 0.44–1.5% and lifetimes of 31.3–63.7  $\mu\text{s}$  (Fig. 2). The heavy-atom effect of Pt was supported by the very weak phosphorescence of the related Pd dinuclear complex under the same conditions ( $\lambda_{\text{em}}$  650 nm, quantum yields < 0.001%). Cyclometalation is beneficial, as apparent from comparison with the corresponding metalated platinum(II) complex lacking (P,C)-cyclometalation.<sup>67</sup> The related complexes with dangling (non-cyclometalated) Pt centers showed very weak phosphorescence if any.

Note that the same authors performed a similar photophysical study on analogous anthracene-derived complexes two years before.<sup>9</sup> The bis-cyclometalated complexes were found to emit at  $\lambda_{\text{em}} \sim 460\text{--}510$  nm in the dichloromethane solution at room temperature, with quantum yields of 1–6% and short half-lifetimes < 2 ns (Fig. 3). Only weak fluorescence was observed in this case, with no apparent enhancement of phosphorescence due to the heavy-atom effect. Comparison of the *syn* and *anti*-isomers revealed little changes, while the corresponding mono-cyclometalated complex showed weaker



**Fig. 2** Phosphorescence properties of (P,C)-cyclometalated and non-cyclometalated pyrene derivatives.

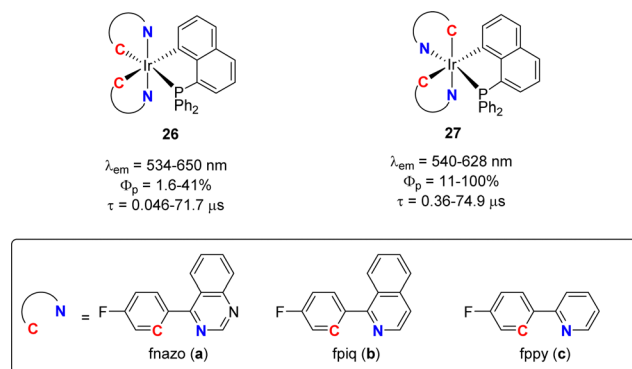


**Fig. 3** Fluorescence properties of (P,C)-cyclometalated Pt complexes derived from anthracene (similar data were observed with dpmm and dppp instead of dppe as ancillary diphosphines).

fluorescence (0.16% quantum yield) with a too-short lifetime to be measured.

## 2. $[\text{Np}(\text{P,C})\text{Ir}(\text{III})]$ complexes

Cyclometalated iridium(III) complexes such as [(phenylpyridyl)<sub>3</sub>Ir] are strong phosphorescent emitters of interest for optical devices such as organic light-emitting diodes (OLEDs). Varying the ligands at iridium offers a simple means to modulate and eventually improve the stability and photophysical properties of the complexes. In this regard, Chi and Chou jointly studied in 2010 heteroleptic complexes combining two C<sup>N</sup> and one P<sup>C</sup> cyclometalated ligands (Fig. 4).<sup>15</sup> Attempts to



**Fig. 4** Phosphorescence properties of heteroleptic tris-cyclometalated Ir(III) complexes.



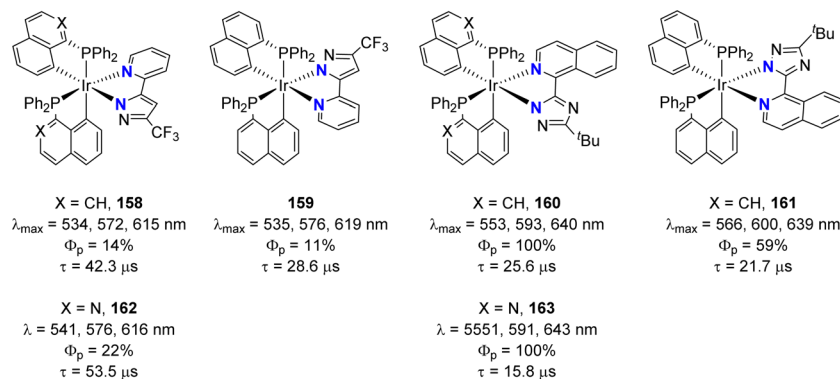


Fig. 5 Structural modulation of the phosphorescent heteroleptic cyclometalated Ir(III) complexes: naphthalene and isoquinoline-derived phosphines and N^N azolate ligands.

prepare analogous complexes from benzyldiphenylphosphine failed, preventing the authors to assess the influence of the naphthyl ring on the luminescence properties. Whatsoever, complexes **26** and **27** proved robust (as long as the N^C ligand is equipped with a fluorine atom) and phosphorescent in oxygen-free dichloromethane solution at room temperature with  $\lambda_{\text{em}}$  of 530–650 nm and quantum yields from 1.6 to 100%. Significantly higher quantum yields were systematically observed for the complexes in which the two nitrogen atoms occupy *cis* positions. The impact of the N^C cyclometalated ligand at iridium was thoroughly examined. Thanks to time-dependent DFT calculations, the emission transitions were shown to involve MLCT (metal-to-ligand charge transfer) and LLCT (ligand-to-ligand charge transfer) or MLCT and ILCT (intra-ligand charge transfer), depending on the N^C ligand. In particular, the (P,C)-naphthyl ligand was proposed to act as the CT acceptor when iridium is ligated by the phenyl-pyridine ligand. Of note, the proof of the feasibility of incorporating such complexes in devices was substantiated. Orange-red emitting OLEDs with decent quantum efficiencies (up to 12.5% at 500 cd m<sup>-2</sup> brightness) were prepared.

In a following study, the same authors further extended the structural diversity of iridium(III) emitters.<sup>16</sup> Complexes with one N^N azolate ligand and two P^C-cyclometalated ligands derived from diphenyl 1-naphthyl phosphine (or its isoquinoline analog) were shown to also display phosphorescence (with  $\lambda_{\text{em}}$  of 530–640 nm and quantum yields from 11 to 100%) (Fig. 5).

## Conclusions

As shown in this review, (P,C)-cyclometalated complexes derived from naphthyl phosphines have been discovered early on but long remained neglected. They have however attracted growing interest recently and been shown to display rich chemistry and open interesting perspectives. The chemistry of the [N<sup>P</sup>(P,C)] complexes is now much more developed than that of the related [N<sup>P</sup>(N,C)] complexes derived from the well-known 1,8-dimethylaminonaphthyl ligand DAN.<sup>68–71</sup>

The historical P-chelation assisted C–H activation route pioneered by Shaw 50 years ago remains the most straightforward and general route to prepare [N<sup>P</sup>(P,C)M] complexes. This shows complete selectivity for the C<sub>sp<sup>2</sup></sub>-H bond at the *peri* position to phosphorus, even when a methyl group is present next to phosphorus. *peri*-Halo naphthyl phosphines are readily available. Their P-chelation assisted oxidative addition has become a valuable alternative route to C–H activation. First introduced to demonstrate the feasibility of C<sub>sp<sup>2</sup></sub>-X oxidative addition to a single gold(I) center, it has then been extended to nickel. A third complementary route applied to groups 7–11 metals relies on transmetalation from stable mercury or tin *peri*-metalated naphthyl phosphines.

From a structural viewpoint, the [N<sup>P</sup>(P,C)] framework is well suited and nicely accommodates metals from groups 7 to 11, as apparent from the P–M and C<sub>peri</sub>–M bond lengths, which only slightly deviate from the respective sums of the covalent radii. The naphthyl moiety imparts rigidity, but retains some flexibility, by bending the C<sub>peri</sub>–P bond toward the metal and out of the naphthalene plane.

Reactivity studies on [N<sup>P</sup>(P,C)M] complexes long remained sparse and isolated, but the robustness and synthetic potential of palladium, platinum and ruthenium complexes were recognized early on in several transformations (the Heck reaction, the conjugate addition of aryl boronic acids to electron-deficient alkenes, the transfer hydrogenation of ketones, *etc.*). N<sup>P</sup>(P,C)-cyclometalation turned to be particularly fruitful in gold(III) chemistry, where it has opened new reactivity paths (migratory insertion,  $\beta$ -H elimination, and nucleophilic addition to  $\pi$ -allyl) and has enabled many new bonding situations to be authenticated (C–H agostic,  $\pi$  and  $\sigma$ -arene,  $\pi$ -allyl, and Schrock-type nucleophilic carbene complexes), resulting ultimately in unique catalytic activity in the intermolecular hydroarylation of alkynes. [N<sup>P</sup>(P,C)M] complexes have also been shown recently to be key intermediates in the Ru-catalyzed alkylation of the remote C5 position of naphthyl phosphines and Rh-catalyzed arylation of the *peri* position of naphthyl/pyrenyl phosphines.

Very little is known yet about the photophysical properties of [N<sup>P</sup>(P,C)M] complexes. Interesting phosphorescence properties



have been occasionally pointed out but further studies are certainly needed to better understand the very influence of  $^{NP}(P,C)$ -cyclometalation and develop its use in opto-electronic systems.

It is likely that the chemistry of  $[^{NP}(P,C)M]$  complexes will keep developing and new facets will be discovered in near future. Although not all transition metals may form stable  $[^{NP}(P,C)M]$  complexes, there is certainly room to expand the actual diversity. First-row metals are certainly worth to consider and explore thoroughly. There is no manganese complex known to date, only one tetranuclear copper(I) cluster and very few complexes with iron, cobalt and nickel. So far, only alkyl and aryl groups have been introduced at phosphorus. The substitution pattern may be varied further using heteroaryl, alkoxy, and amino groups to significantly decrease/increase the electron-density at phosphorus. Other P-containing groups than phosphines may also be incorporated. The rich chemistry displayed by  $[^{NP}(P,C)Au(III)]$  complexes will certainly stimulate research towards highly reactive complexes, basic transformations and catalytic applications with other metals. Being readily accessible, broadly modulable and very robust, the  $[^{NP}(P,C)M]$  platform is very attractive and holds much potential. To date, applications have focused essentially on catalysis, but materials science and medicinal chemistry are certainly worth to be considered too. Indeed,  $[^{NP}(P,C)M]$  complexes may well complement and eventually outperform the commonly used rigid (N,C)-cyclometalated complexes.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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