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(P,C)-Cyclometalated complexes deriving from naphthyl phosphines: versatile and powerful tools in organometallic chemistry

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Abstract:

The chemistry of (P,C)-cyclometalated complexes deriving from naphthyl phosphines [^{Np}(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 the naphthyl framework inherently predisposes the phosphorus atom and transition metal to interact, the 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 group 7 to 11). Generally, the ^{Np}(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. [^{Np}(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.

Introduction

Since the pioneering contributions of Shaw in the early 1970's,^{1,2} cyclometalated complexes have attracted considerable interest and are now *classics* in organometallic chemistry. Their interest ranges from fundamental bonding/reactivity aspects to applications in catalysis, materials chemical science, medicinal, amongst 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.³⁻⁶ Here, PCP complexes **I** with a central benzene ring and two flanking phosphines have become the *reference* complexes (Chart 1).⁷ Their pincer structure results in a unique balance of stability/reactivity. The related (P,C)-cyclometalated complexes **II** featuring a single phosphine sidearm have also been widely investigated. In contrast, the corresponding naphthyl-based (P,C)-cyclometalated complexes **III**, denoted hereafter as $[\text{Np}(\text{P,C})\text{M}]$, 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) chemistry⁸ where the $[\text{Np}(\text{P,C})]$ framework opened new reactivity paths, enabled to authenticate unprecedented bonding situations and imparted unique catalytic activity.

Here, this topic is reviewed. P,C-Cyclometalated complexes deriving from naphthyl phosphines as well as related systems featuring fused/ π -extended systems, such as acenaphthalene, anthracene, phenanthrene and pyrene, are covered. The corresponding two arm stiff PCP complexes are not considered. $[\text{Np}(\text{P,C})]$ Complexes have been reported with metals from group 7 to 11, in line with the preference of the soft phosphine moiety for mid and late transition metals. Emphasis is given to 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**.

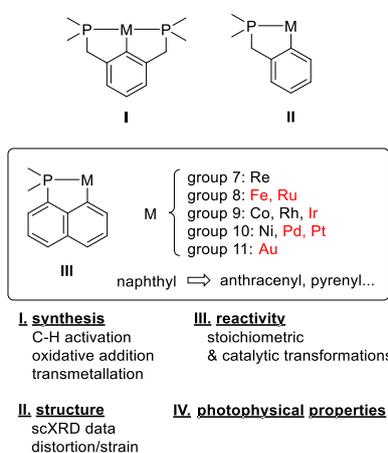


Chart 1. (P,C)-Cyclometalated complexes I-III, content and organization of this review (metals in red are the most represented ones among $[\text{Np}(\text{P,C})\text{M}]$ complexes III).

In the first part, the synthesis of $[\text{Np}(\text{P,C})\text{M}]$ 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 $[\text{Np}(\text{P,C})\text{M}]$ complexes are thoroughly analysed based on crystallographic and computational data. Special attention is given to the distortion/flexibility of the 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 $[\text{Np}(\text{P,C})\text{M}]$ complexes, in stoichiometric reactions and in catalytic transformations. The (P,C)-cyclometalated framework is retained in most cases, but not always. Finally, the few photophysical studies performed on $[\text{Np}(\text{P,C})\text{M}]$ complexes are described.

I. En route to $[\text{Np}(\text{P,C})\text{M}]$ complexes

Three main synthetic strategies can be distinguished to access (P,C)-cyclometalated naphthyl complexes, $[\text{Np}(\text{P,C})\text{M}]$ (Figure 1). They differ in the nature of the pro-ligands and in 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. C-H activation of 1-naphthyl phosphines occurs selectively on the *peri* position, due to *ideal* P-chelation (5-membered ring with rotation around the P-C_{naphthyl} bond as the only degree of freedom). It can be promoted by a basic ligand on the metal or the addition of an exogeneous base/halide scavenger. This route has been used to prepare a broad range of (P,C)-naphthyl complexes with transition metals from group 7 to 10. Recently, the renewed interest devoted to group 10 and 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 an halide or a metalloid in 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 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.

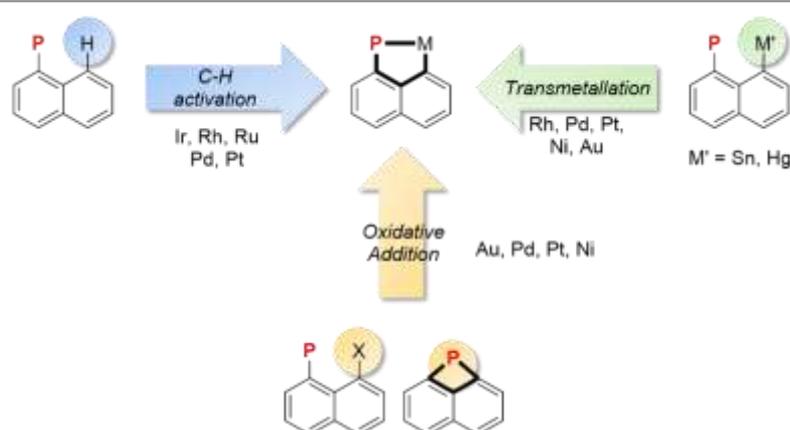
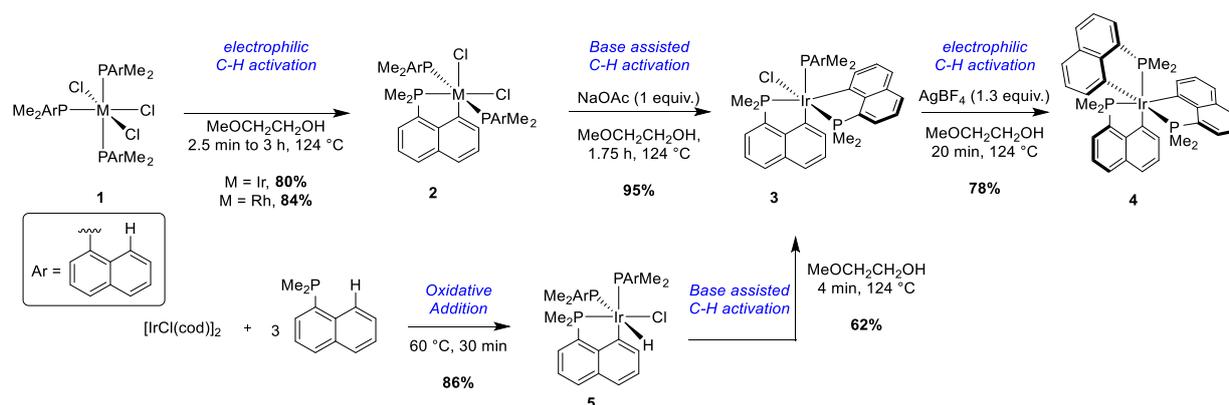


Figure 1. Synthetic routes to access (P,C)-cyclometalated naphthyl complexes $[N^p(P,C)M]$.

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 $[N^p(P,C)M]$ complexes. This strategy was first described by Shaw in 1972 in a comprehensive study targeting $[N^p(P,C)Ir(III)]$ complexes.¹ Different cyclometalation conditions taking advantage of P-chelation were reported (Scheme 1).

Starting from the Ir(III) complex **1** bearing three dimethyl 1-naphthyl phosphines coordinated in a meridional fashion, the first cyclometalation reaction was achieved in good yield (75%) by thermal activation (124°C) in methyl glycol. A second C–H activation could be efficiently performed by heating the mono-cyclometalated 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 β -hydride elimination from the alcoholic solvent, was postulated as key intermediate. This hydride could then act as an internal base, generating H₂ as 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 the $[N^p(P,C)Rh(III)]$ complex **2**. An alternative pathway was also described to give the bis-(P,C)-cyclometalated complex **3** starting from the iridium(I) precursor $[IrCl(cod)]_2$. After a first C–H activation process by oxidative addition to iridium in boiling light petroleum, the iridium(III) complex **5** was isolated in 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 was performed by abstraction of the last chloride at iridium with a scavenger (*i.e.* AgBF₄) to give the tris-(P,C)-cyclometalated complex **4**.



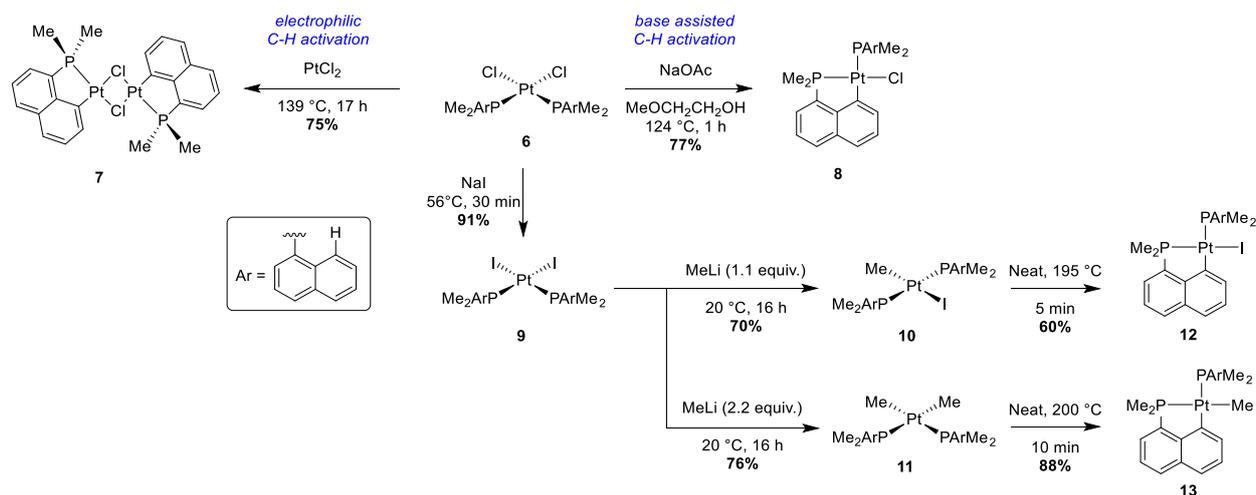
Scheme 1. Stepwise cyclometalation of naphthyl phosphines at Ir(III) via electrophilic/base-assisted C–H activations.

Two years later, Shaw prepared a family of $[N^p(P,C)Pt(II)]$ complexes starting from the *cis*-dichloroplatinum(II) precursor **6** (Scheme 2).² Electrophilic C–H activation was performed mixing PtCl₂ with **6** to yield a bridged platinum(II) dimer **7** after prolonged heating in xylenes (139°C). As for the 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** & **11** were prepared using methyllithium. Pyrolysis at high temperature (>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 $[^{Np}(P,C)M]$ complexes *via* C–H activation reported after 1974 are described in the next sections. Although no detailed mechanistic studies have been carried on the C–H activation process, these contributions have been organized according to the conditions used to promote cyclometalation:

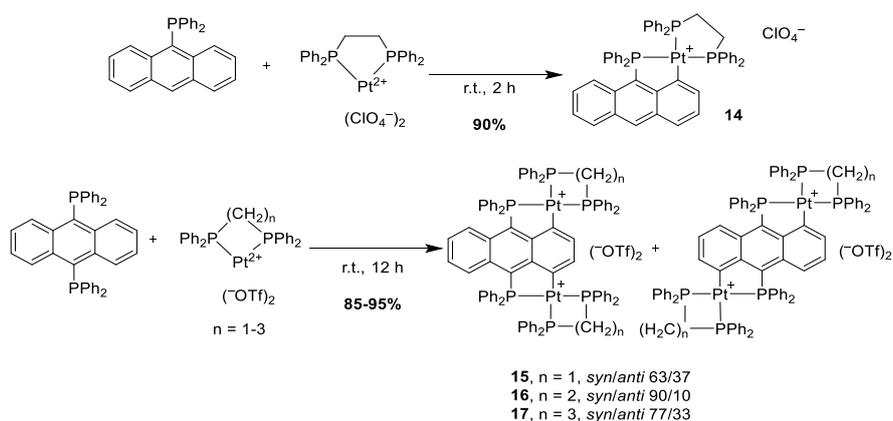
- Direct (electrophilic) C–H activation by a metal-halide (or metal-pseudohalide) precursor,
- C–H activation in the presence of a mild base (NaOAc, Et₃N), bonded to the metal or external, acting in concert with the metal or not,
- C–H activation by a metal-alkyl precursor.

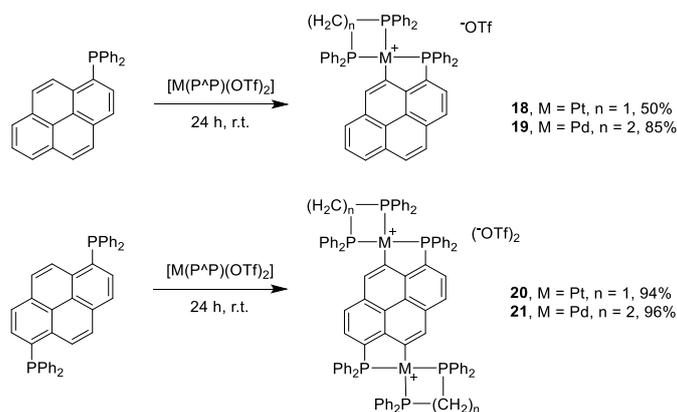


Scheme 2. Synthesis of $[^{Np}(P,C)Pt(II)]$ complexes *via* C–H activation.

a. Direct (electrophilic) C–H activation

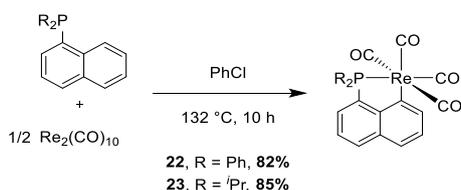
The first examples described by Shaw involved metal chloride precursors and required quite high temperatures. Using more electrophilic pseudo-halide complexes (perchlorate, trifluoromethane sulfonate) enables to operate under milder conditions. Accordingly, Yip described in the late 2000's the synthesis of mono and bis-(P,C)-cyclometalated complexes with π -extended naphthalene backbones (anthracene and pyrene) (Scheme 3).^{9,10} Here, pseudo-cationic palladium(II) and platinum(II) complexes featuring diphosphine ligands were used as precursors. Cyclometalation proceeded within hours at room temperature in this case. Of note, double cyclometalations of the 9,10-bis-phosphino-anthracene systematically gave a mixture of *syn* and *anti*-bis-(P,C)-cyclometalated complexes (with a *syn/anti* ratio > 60/40).





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.

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).¹¹ The exact way the *peri* C–H bond is activated is unknown but the authors invoked P-chelation assistance prior to intramolecular activation.

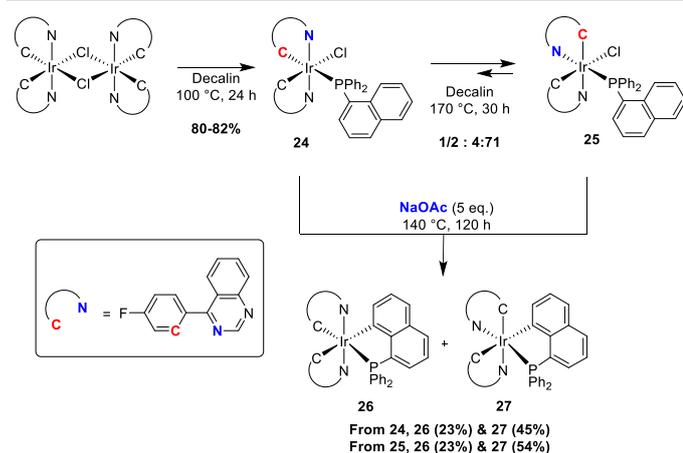


Scheme 4. Synthesis of a $[\text{N}^{\text{p}}(\text{P,C})\text{Re}(\text{I})]$ complex via C–H activation.

b. C–H activation in the presence of a mild base (NaOAc, 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 the acetate to catch the *peri* H atom, thus facilitating the formation of the M–C_{sp²} bond.^{12–14}

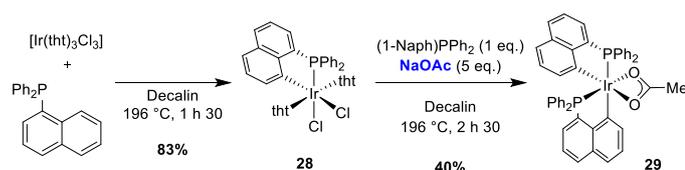
Following Shaw's pioneering contribution, the groups of Chi and Chou jointly reported in 2010 a stepwise preparation of phosphorescent $[\text{N}^{\text{p}}(\text{Ph}_2\text{P,C})\text{Ir}(\text{III})]$ complexes (see section IV).¹⁵ First, the bis-N,C-cyclometalated iridium(III) chloride-bridged dimer was splitted by diphenyl 1-naphthyl phosphine upon heating at 100 °C for 24 h (Scheme 5). The initially formed complex **24** with two strong field ligands (carbon and phosphorus) in *trans* position to each other could be isomerised into the more thermodynamically stable complex **25** (within 48 h at 170 °C). Cyclometalation was then achieved in the presence of sodium acetate (5 eq.) at 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: substitution of the chloride by acetate at iridium, followed by C–H bond activation/metalation.



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

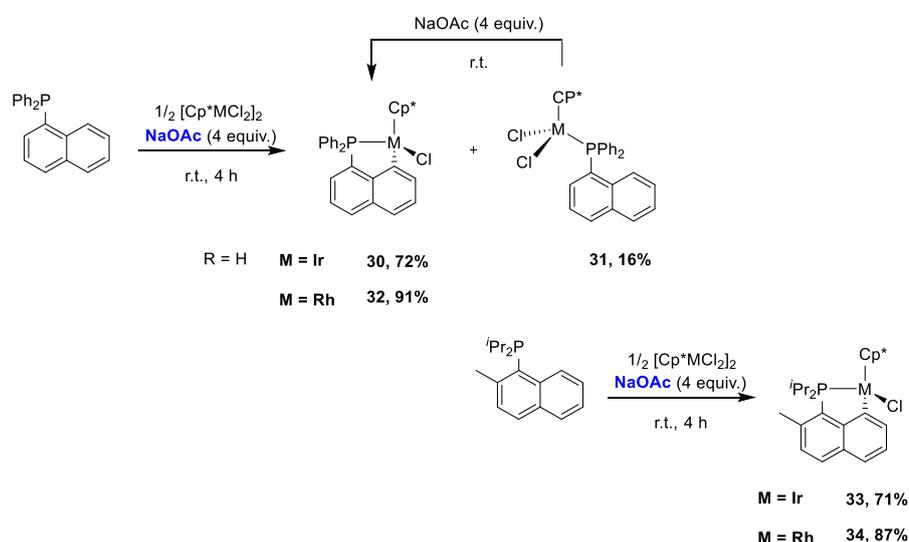
A year later, the same groups described the preparation of a bis-cyclometalated iridium(III) complex (Scheme 6).¹⁶ Electrophilic C–H activation of diphenyl 1-naphthyl phosphine by $[\text{IrCl}_3(\text{tht})_3]$ at 196 °C in decalin first afforded the mono-(P,C)-cyclometalated

complex $[\text{Np}(\text{Ph}_2\text{P,C})\text{IrCl}_2(\text{tht})_2]$ (83% isolated yield). Following addition of diphenyl 1-naphthyl phosphine, the second cyclometalation required the use of sodium acetate (5 equivalents) to give the $[\text{Np}(\text{Ph}_2\text{P,C})_2\text{Ir}(\kappa^2\text{-OAc})]$ complex.



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

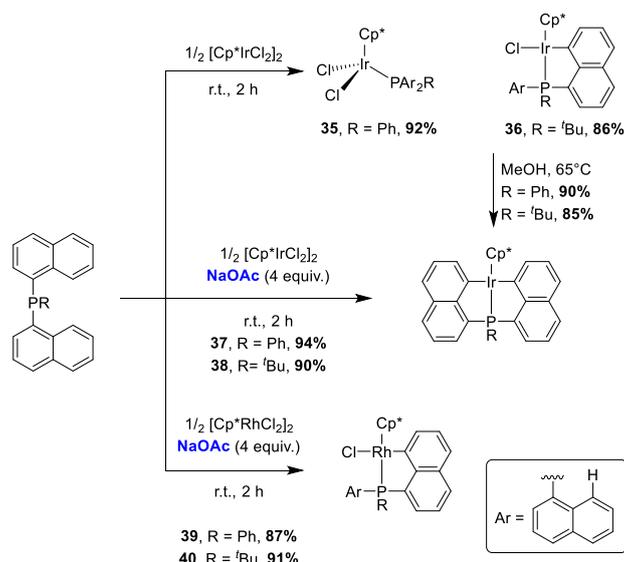
In 2017, the group of Zhu studied in detail the cyclometalation of diphenyl 1-naphthyl phosphine by $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{M} = \text{Ir}, \text{Rh}$) in the presence of sodium acetate (Scheme 7).¹⁷ The reactions were performed in methanol at room temperature for 4 h. The cyclometalated complex $[\text{Np}(\text{Ph}_2\text{P,C})\text{IrCl}(\text{Cp}^*)]$ **30** was thereby obtained in 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 the cyclometalation (an independent experiment actually confirmed the 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 $\text{C}_{\text{sp}^2}\text{-H}$ bond activation was observed with both iridium and rhodium.



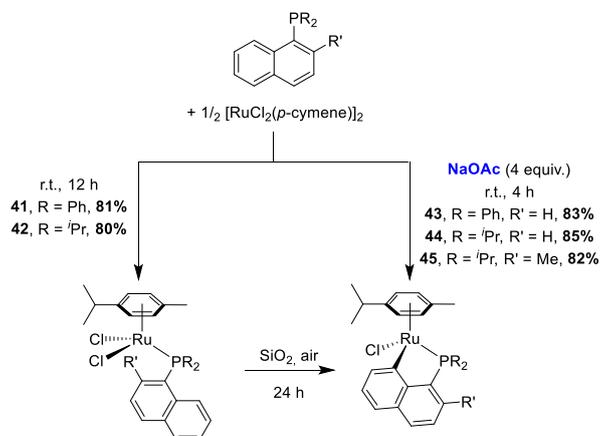
Scheme 7. Synthesis of $[\text{Np}(\text{P,C})\text{Ir}(\text{III})]$ and $[\text{Np}(\text{P,C})\text{Rh}(\text{III})]$ complexes via base-assisted C–H activation, selectivity for $\text{C}_{\text{sp}^2}\text{-H}$ over $\text{C}_{\text{sp}^3}\text{-H}$ bonds.

The cyclometalation of bis-1-naphthyl phosphines was then investigated (Scheme 8).¹⁸ With $[\text{Cp}^*\text{IrCl}_2]_2$, very different outcomes were observed at room temperature depending on the substituent at phosphorus ($\text{R} = \text{Ph}, \text{}^t\text{Bu}$). Indeed, only P-coordination without cyclometalation was observed for the phenyl phosphine, whereas the *tert*-butyl phosphine directly afforded the cyclometalated complex $[\text{Np}(\text{}^t\text{Bu}_2\text{P,C})\text{IrCl}(\text{Cp}^*)]$. 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 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 $\text{}^t\text{BuOK}$.

Zhu also applied the C–H activation route to prepare $[\text{Np}(\text{P,C})\text{Ru}(\text{II})]$ complexes (Scheme 9).¹⁹ Most convenient was to react 1-naphthyl phosphines with $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ at room temperature in methanol in the presence of sodium acetate (4 eq.). Alternatively, the non-cyclometalated phosphine complexes could be first prepared in dichloromethane without base, and then stirred over silica gel under air to induce cyclometalation. An analogous complex $[\text{Np}(\text{Ph}_2\text{P,C})\text{RuCl}(\text{C}_6\text{Me}_6)]$ was prepared soon after by Ishii starting from $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$.²⁰ 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 $\text{C}_{\text{sp}^3}\text{-H}$ activation was assessed by Zhu.¹⁹ As with iridium and rhodium, the 1-naphthyl phosphine featuring a methyl group adjacent to phosphorus was found to react with $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2 / \text{NaOAc}$ exclusively at the *peri* $\text{C}_{\text{sp}^2}\text{-H}$ site.



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



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

Using the NaOAc-assisted conditions, Grabulosa prepared in 2019 a series of $[\text{Np}(\text{P,C})\text{Ru}(\text{II})]$ 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).²¹ 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 the ^tPr-substituted phosphine, good phosphorus to ruthenium chiral induction was apparently achieved, with the formation of a single diastereoisomer according to ³¹P NMR spectroscopy.

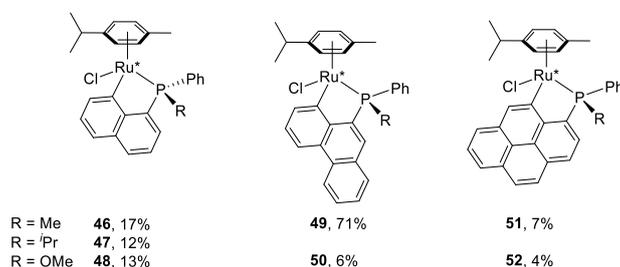
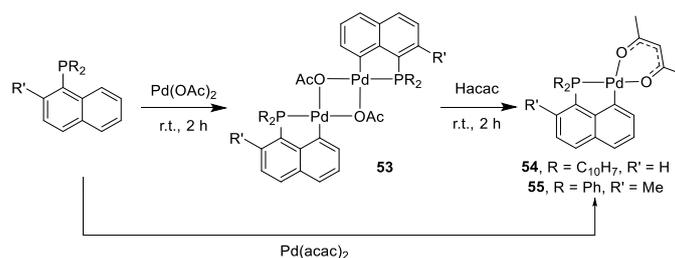


Chart 2. (P,C)-cyclometalated Ru(II) complexes deriving from optically pure 1-naphthyl, 9-phenanthrenyl and 1-pyrenyl phosphines.

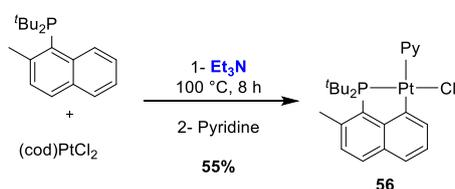
Base-assisted C–H activation has also been applied to prepare (P,C)-cyclometalated naphthyl complexes with group 10 metals. The first examples were reported by Shaw in 1998.²² Starting from the tri-1-naphthyl phosphine, a series of palladacycles was prepared as a result of mono cyclometalation. With $\text{Pd}(\text{OAc})_2$, a dimeric acetate-bridged complex was obtained (Scheme 10). Subsequent treatment with acetyl-acetone gave the corresponding mononuclear acac complex $[\text{Np}(\text{Np}_2\text{P,C})\text{Pd}(\text{acac})]$ which can be

alternatively prepared by reacting PNp_3 with $[\text{Pd}(\text{acac})_2]$. The analogous complex $[\text{Np}(\text{Np}_2\text{P,C})\text{Pd}(\text{acac})]$ featuring an 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.²³ 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.



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

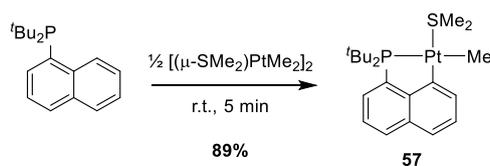
Finally, Vigalok and Vedernikov prepared in 2013 a Pt(II) complex using triethylamine as a base (Scheme 11).²⁴ The naphthyl phosphine featured a methyl group adjacent to phosphorus and again, complete chemoselectivity for $\text{C}_{\text{sp}^2}\text{-H}$ over $\text{C}_{\text{sp}^3}\text{-H}$ bond activation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



Scheme 11. C_{sp^2} -selective base-assisted C–H activation with a Pt(II) precursor.

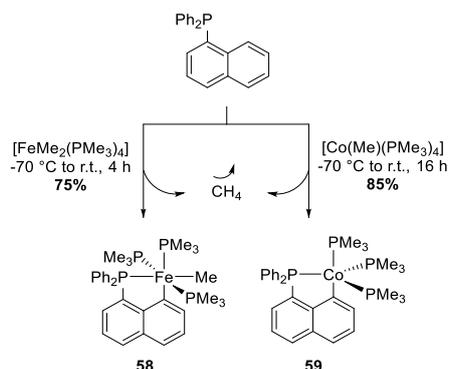
c. C–H activation by a metal-alkyl precursor

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.² $[\text{Np}(\text{Me}_2\text{P,C})\text{Pt}(\text{II})]$ complexes were prepared 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).²⁵ Here, gas evolution, most likely methane, was observed right after mixing at room temperature. The cyclometalated complex $[\text{Np}(\text{tBu}_2\text{P,C})\text{Pt}(\text{SMe}_2)\text{Me}]$ was quickly (5 minutes) and efficiently obtained (89% isolated yield). The presence of a single phosphine *per* metal and the steric demand of the *t*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.



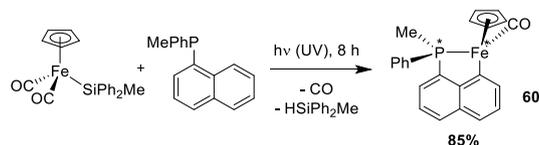
Scheme 12. Synthesis of a $[\text{Np}(\text{P,C})\text{Pt}(\text{II})]$ complex upon C–H activation by a Pt–Me precursor.

In the 2000's, Klein and Beck extended the approach to first-row metals, namely cobalt and iron (Scheme 13).²⁶ The diphenyl 1-naphthyl phosphine was found to react smoothly with trimethylphosphine $\text{Fe}(\text{II})\text{Me}_2$ and $\text{Co}(\text{I})\text{Me}$ 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 the cyclometalation.



Scheme 13. Synthesis of $^{Np}(P,C)$ -cyclometalated complexes of first row metals by methane elimination.

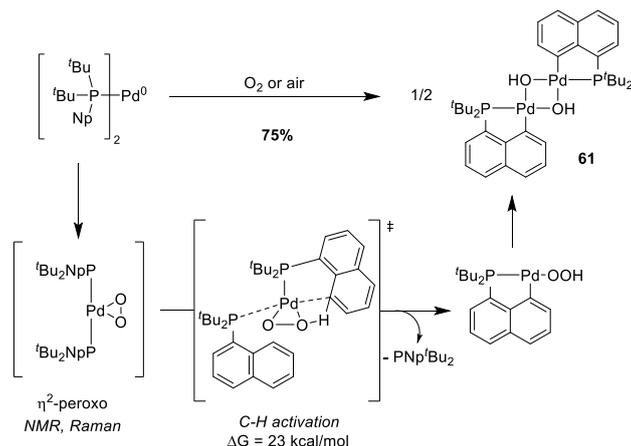
Metal-silyl precursors may also be used to cyclometalate 1-naphthyl phosphines, as substantiated by Corriu in 1981 (Scheme 14).²⁷ Under UV irradiation, the di-carbonyl silyl iron complex $[CpFe(CO)_2SiPh_2Me]$ was found to cleanly react with the P-stereogenic phosphine $MePhP(Np)$. The cyclometalated complex $[^{Np}(PhMeP,C)FeCp(CO)]$ was obtained in 85% yield as a 1:1 mixture of diastereomers. The silane $HSiPh_2Me$ was concomitantly released (90% yield) and no deuterium incorporation was observed when the reaction was performed in deuterated benzene, suggesting 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 non-racemic mixture, but sadly, phosphorus epimerization was faster than coordination/cyclometalation under UV irradiation.



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

d. O_2 -promoted C–H activation

In 2014, the group of Goldberg reported a peculiar route to a dinuclear hydroxy-bridged $[^{Np}(P,C)Pd(II)]$ complex (Scheme 15).²⁸ The di-phosphine $Pd(0)$ complex $[(^tBu_2Np)_2Pd]$ was found to readily react with dioxygen with concomitant cyclometalation of the *peri* C–H bond and O–O cleavage. Reaction monitoring at low temperature enabled to authenticate an η^2 -peroxo palladium complex as key intermediate. Based on DFT calculations, the authors proposed a plausible path for the C–H activation, by addition across one of the Pd–O bond with concomitant release of a phosphine. The resulting Pd –OOH species would then lose an oxygen atom to give the dimeric hydroxy-bridged complex $[^{Np}(^tBu_2P,C)Pd(\mu-OH)]_2$.

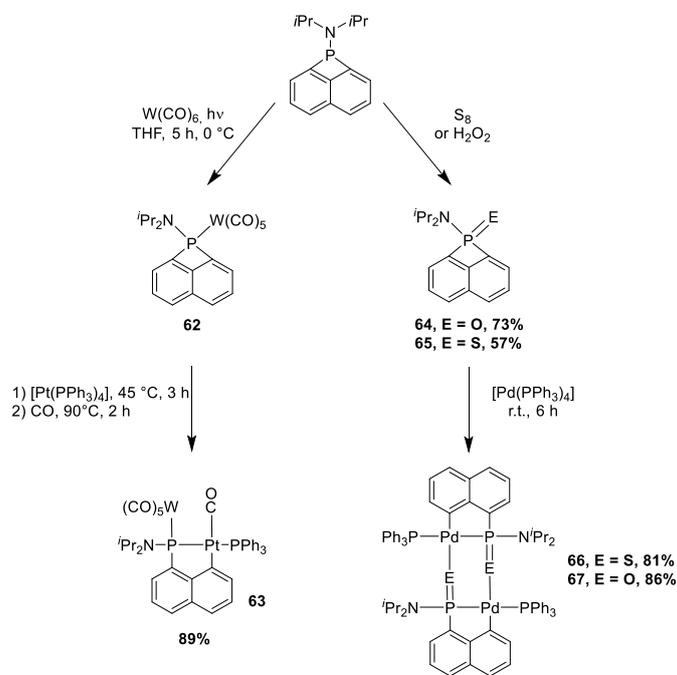


Scheme 15. Synthesis of a dinuclear hydroxy-bridged $[^{Np}(P,C)Pd(II)]$ complex by O_2 -promoted C–H activation.

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 $[^{Np}(P,C)Pt(II)]$ complex.^{29,30} The phosphorus lone pair was first masked with a $W(CO)_5$ fragment. Upon treatment with $[Pt(PPh_3)_4]$, one of the P–C bond oxidatively added to platinum

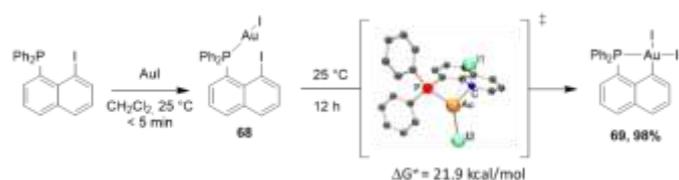
and one of the PPh₃ co-ligand at platinum was then displaced by CO. Related [^{Np}(P,C)Pd(II)] complexes were then synthesized by the same group using a similar strategy, with [Pd(PPh₃)₄] as palladium(0) precursor.³¹ The phosphorus atom of the strained four-membered phosphacycle was preliminarily oxidized 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 insertion of low valent metals into the strained four-membered ring of phosphorus *peri*-bridged naphthalenes, but the generality and practical utility of this approach is limited by the access to the starting P compounds.



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

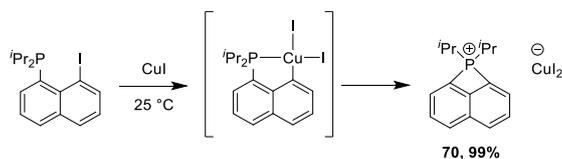
Naphthyl phosphines with an halogen in the *peri* position are readily available from 1,8-dihalogenonaphthalenes.³² They are predisposed to undergo P-chelation assisted oxidative addition, as first demonstrated by our group in 2014 with gold.³³ In the context of a lively debate about the feasibility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

P-Chelation assistance was clearly substantiated by the spectroscopic characterization of the instantaneously formed gold(I) complex, followed by progressive build-up of the [^{Np}(P,C)Au(III)]₂ complex. Kinetic and computational studies shed light into the intramolecular and unimolecular character 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 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, compared to 32.1 kcal/mol for C–Br and 21.9 kcal/mol for C–I). Furthermore, in this case, the formation of the gold(III) complex is uphill in energy (+0.3 kcal.mol⁻¹) in contrast to the oxidative additions of the C–I and C–Br bonds (–9.1 and –7.2 kcal/mol, respectively). Analogous [^{Np}(P,C)AuI₂] were subsequently prepared using the same approach with *i*Pr and Cy substituents at phosphorus.^{34,35}



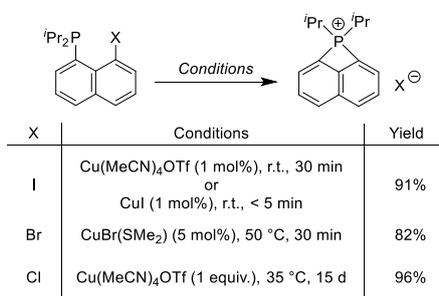
Scheme 17. Synthesis of a [^{Np}(P,C)Au(III)] complex by P-chelation assisted oxidative addition of a *peri*-iodo naphthyl phosphine to Au.

We also studied the behaviour of copper in such a process and reacted *peri*-halo naphthyl phosphines with various Cu(I) complexes (Scheme 18).^{36,37} P-chelation was found to efficiently assist 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 a 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 kcalmol⁻¹ in DCM, respectively). The formation of the *peri*-bridged phosphonio naphthalene compound is exergonic by 12.3 kcal/mol.



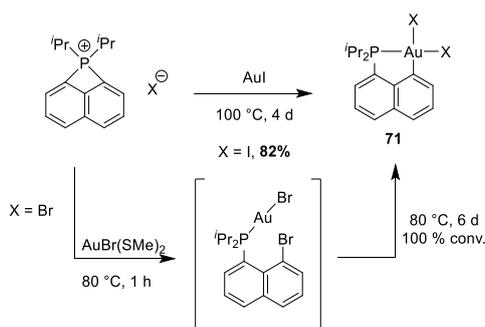
Scheme 18. Formation of a *peri*-bridged naphthyl phosphonium by P-chelation assisted C–I oxidative addition to Cu, followed by P–C reductive elimination.

The generality of the reaction was then examined. Replacing the *i*Pr substituents at phosphorus either by a diamino (*i*Pr)NCH₂CH₂N(*i*Pr) moiety or Ph groups led to similar results. The halogen atom in 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 the *peri*-bridged naphthyl-phosphonium using only 1-5 mol% of copper(I) starting from the *peri* iodo- or bromo-naphthyl phosphines (Scheme 19).³⁸



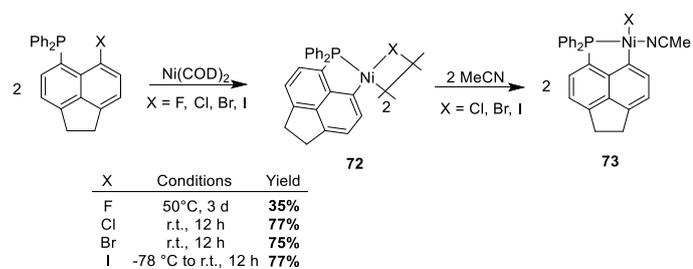
Scheme 19. Copper-catalyzed/mediated formation of *peri*-bridged naphthyl phosphoniums.

The ring strain of the *peri*-bridged phosphonio naphthalenes is apparent from the acute $C_{peri}PC_{peri}$ (77.34°) and $PC_{peri}C_{bridge}$ (86.99° & 86.57°) 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 [N^δ(P,C)Au(III)] complexes. This proved indeed feasible, although it required relatively harsh conditions (Scheme 20).



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

In 2021, Beckmann extended the P-chelation strategy and prepared [AcNp(Ph₂P,C)Ni(II)] complexes (AcNp refers to acenaphthyl) *via* oxidative addition of C–X bonds (X = F, Cl, Br, I) *peri* to phosphorus (Scheme 21).³⁹ Once again, the halide was observed to have a major impact on the rate of the C–X bond activation. Indeed, oxidative addition of the C–I bond proceeded at –78°C and that of the C–Br / C–Cl bonds at room temperature, while heating at 50°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 = Cl, Br, I but not for X = F.

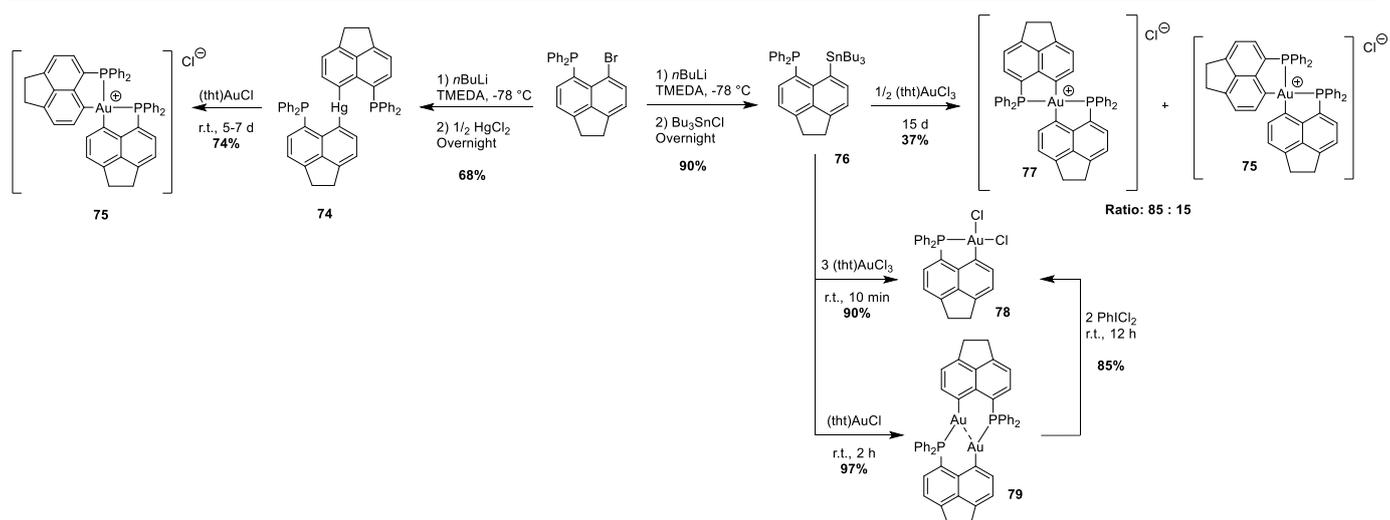


Scheme 21. Synthesis of $[\text{AcNp}(\text{P,C})\text{Ni}(\text{II})]$ complexes by P-chelation assisted oxidative addition of *peri*-halo naphthyl phosphines to Ni.

3. Via Transmetalation

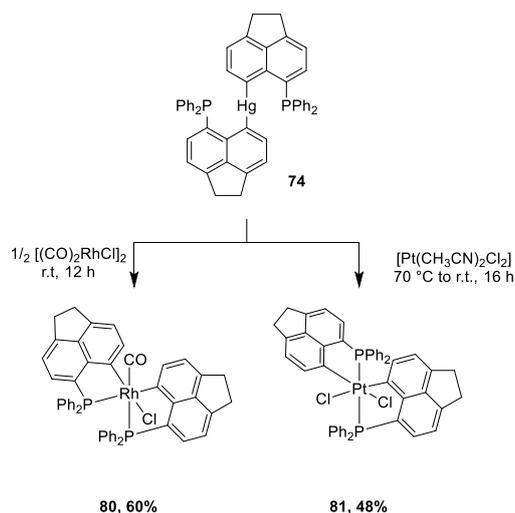
Recently, Beckmann has developed a complementary transmetalation route (Scheme 22). Accordingly, the $[\text{AcNp}(\text{Ph}_2\text{P,C})]$ group was transferred from mercury or tin to group 9-11 transition metals (Rh, Ir, Ni, Pd, Au). Transmetalation from gallium to copper was also observed once, leading to a Cu cluster.⁴⁰ 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.⁴¹ The $[\text{AcNp}(\text{Ph}_2\text{P,C})]_2\text{Hg}(\text{II})$ derivative slowly reacted with (tth)AuCl (tth = tetrahydrothiophene) to give the cationic *cis*- $[\text{AcNp}(\text{Ph}_2\text{P,C})]_2\text{Au}^+$ complex along with mercury(0). Note that the same gold(III) complex was obtained later on in mixture with its *trans* isomer (*cis/trans* ratio = 15:85) upon reaction of the $[\text{AcNp}(\text{Ph}_2\text{P,C})\text{Sn}^n\text{Bu}_3]$ derivative with half an equivalent of (tth)AuCl₃.⁴² The factors controlling the *cis/trans* stereochemistry of the gold(III) complexes remain unknown. When reacted with an excess of (tth)AuCl₃, the tin derivative afforded the neutral $[\text{AcNp}(\text{Ph}_2\text{P,C})\text{AuCl}_2]$ 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 PhICl₂.



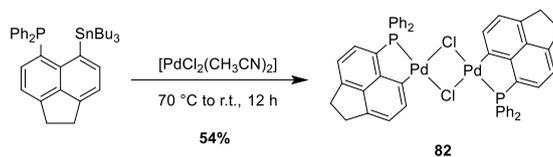
Scheme 22. Synthesis of $[\text{AcNp}(\text{P,C})\text{Au}(\text{III})]$ complexes *via* mercury and tin to gold transmetalation.

Besides gold(III) complexes, the transmetalation/redox strategy was applied to the preparation of bis-(P,C)-cyclometalated rhodium(III) and platinum(IV) complexes by reacting $[\text{AcNp}(\text{Ph}_2\text{P,C})]_2\text{Hg}(\text{II})$ with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$, respectively (Scheme 23).⁴³



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

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



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

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 supporting information, Table S1) so as to analyse the geometric constraints and distortions. The 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_{peri} distances were compared with the sum of the corresponding covalent radii,⁴⁴ referring to the *r* parameters (Charts 3a and 3b). None of the structurally characterized complex shows a *r*(P–M) 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 ± 0.05 range. The (P,C)-naphthyl backbone is thus very suited and very well accommodate all 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*(M–C_{peri}) values that marginally deviate from 1.00 (87% fall in the 1.00 ± 0.05 range).

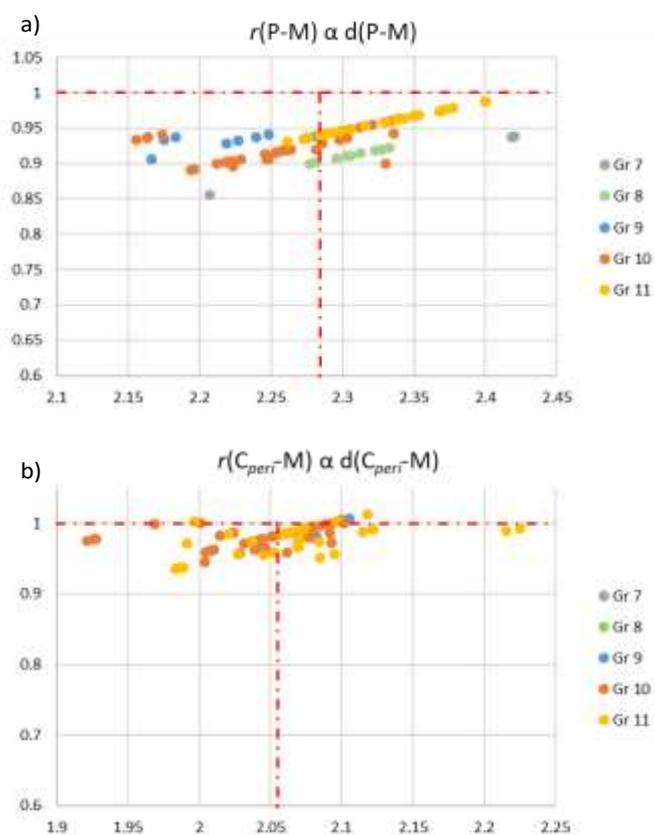
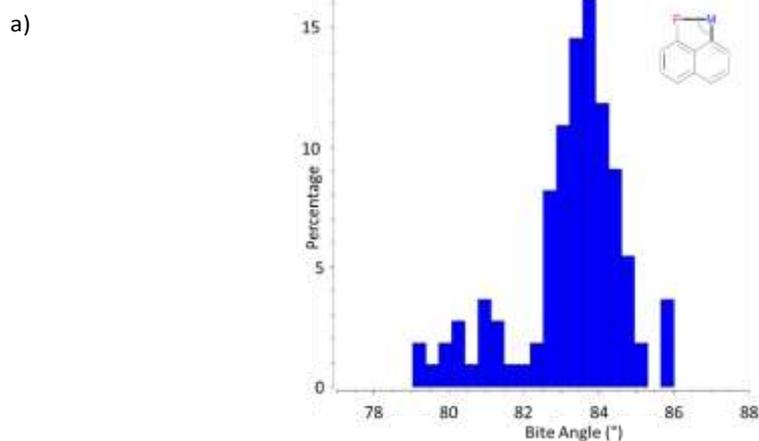
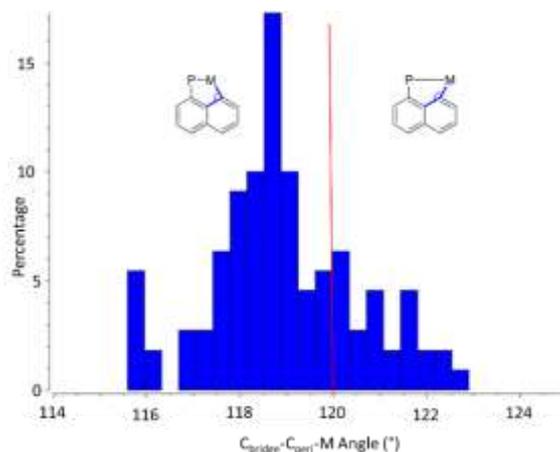


Chart 3. a) Plot of the $r(\text{P-M})$ factor [$r(\text{P-M}) = d(\text{P-M}) / (r_{\text{cov}}(\text{P}) + r_{\text{cov}}(\text{M}))$] against the P-M bond distance for Gr 7 to 11 transition metals, the average P-M bond distance (2.284 Å) is indicated by a vertical red dotted line. b) Plot of the $r(\text{C}_{\text{peri}}\text{-M})$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

As for bond angles, the bite angle ($\text{P-M-C}_{\text{peri}}$) varies very little, regardless 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 $\text{C}_{\text{bridge}}\text{-C}_{\text{peri}}\text{-M}$ and $\text{P-C}_{\text{peri}}\text{-C}_{\text{bridge}}$ bay angles (Charts 4b and 4c). While the $\text{C}_{\text{bridge}}\text{-C}_{\text{peri}}\text{-M}$ bay angle does not deviate much from the ideal 120° value (by 2° at most), the $\text{P-C}_{\text{peri}}\text{-C}_{\text{bridge}}$ 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 $\text{C}_{\text{peri}}\text{-P}$ bond.



b)



c)

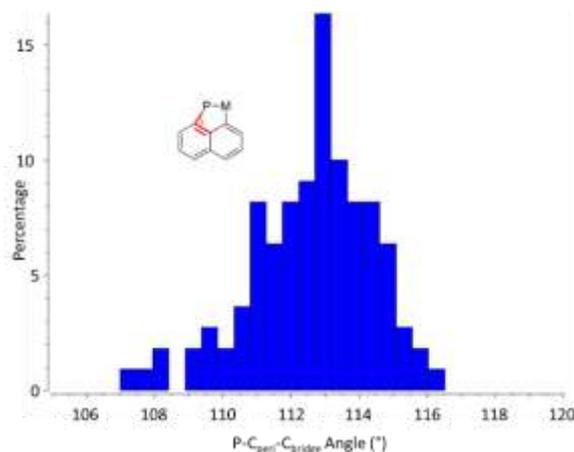
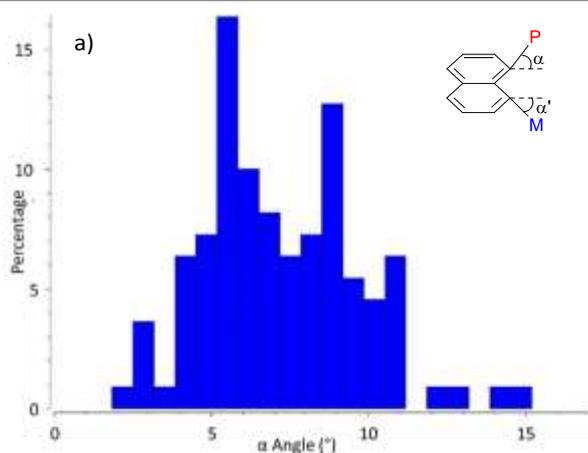


Chart 4. Histograms showing the distribution (in percentage) of the bite angle (a), the $C_{\text{bridge}}-C_{\text{peri}}-M$ bond (b) and the $P-C_{\text{peri}}-C_{\text{bridge}}$ bond angle (c) among crystallographically characterized $[M^{\text{II}}(P,C)M]$ complexes.

Out-of-plane distortions were also examined through the deviations of the P and M atoms in *peri* positions from the naphthalene plane (tilt angles α/α' , Charts 5a and 5b). In general, only minor deviations are observed. No correlation was found between the variations of α , α' and $r(P-M)$ (Chart S1 & S2). The largest deviations concern the P atom (with out-of-plane distortions α up to 10° 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 α' values between 1 and 5°). 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.



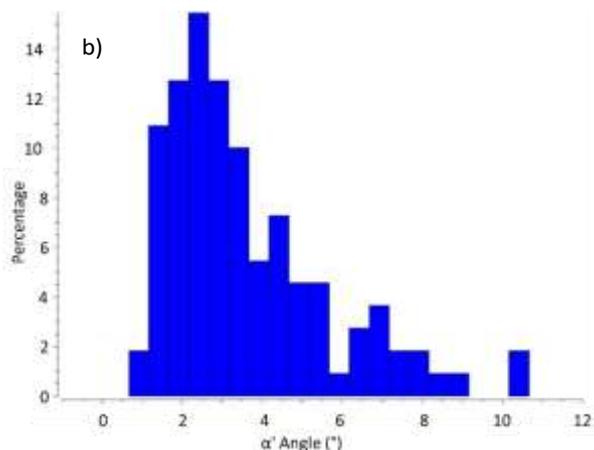


Chart 5. Out-of-plane deviations of the P and M atoms in *peri* positions from the naphthalene plane illustrated by the distribution of the tilt angles α (a) and α' (b).

The bonding situation within $[\text{N}^p(\text{P},\text{C})\text{M}]$ complexes has been occasionally assessed by computational means. Mebs, Hupf and Beckmann performed Atom-In-Molecules, Electron Localizability Indicator and Non-Covalent Interaction analyses on rhodium, nickel, palladium, platinum and gold complexes.^{39,42,43} 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 than in the C–M bonds.

III. Applications of $[\text{N}^p(\text{P},\text{C})\text{M}]$ cyclometalated complexes: stoichiometric reactivity and catalytic transformations

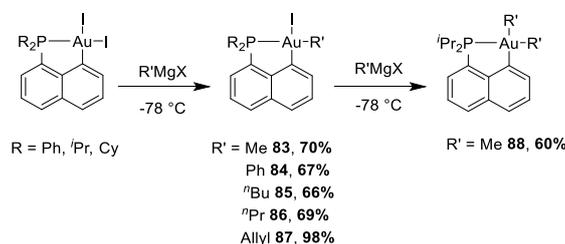
In this section, the stoichiometric reactivity and catalytic application of cyclometalated naphthyl (P,C) complexes will be presented. It is organized *per* metal, starting from gold(III), then palladium(II), platinum(II/IV), iron(II) and ruthenium(II). In most cases, the metalacyclic structure is retained and these reactions are reported first. Finally, miscellaneous examples involving cleavage of the M–C bond are discussed.

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

In the previous section, we presented the easy access to cyclometalated (P,C)-Au(III) complexes *via* chelate-assisted oxidative addition of 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, β -H elimination...) 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 the cyclometalated (P,C)-Au₂ giving easily access to (P,C)-AuR'₂ complexes by reaction with the corresponding Grignard reagent (Scheme 25).^{34,45,46} In presence of one equivalent of 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 the methyl in *cis* position in $[\text{N}^p(\text{P},\text{C})\text{AuMe}_2]$ and in line with *trans* effects.

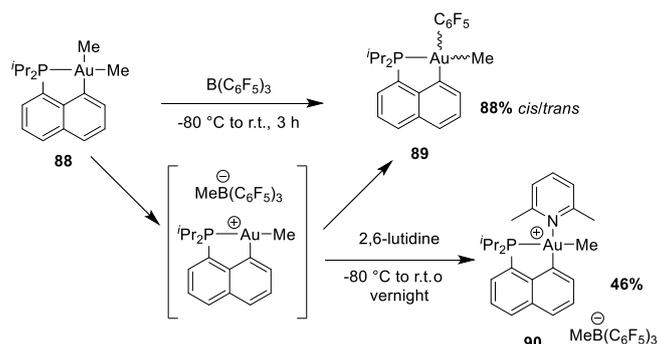


Scheme 25. Synthesis of mono- and dialkyl $[\text{N}^p(\text{P},\text{C})\text{Au(III)}]$ complexes using Grignard reagents.

a. Migratory insertion of alkenes in Au(III)–C bonds

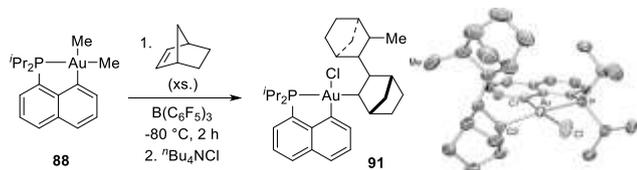
In 2015, we took advantage of the robustness of the $[\text{N}^p(\text{P},\text{C})\text{AuMe}_2]$ complex to demonstrate the feasibility of migratory insertion of alkenes into Au(III)–C bonds (Scheme 26).³⁴ The 3-coordinated cationic gold(III) complex was generated by methyl abstraction with tris(pentafluorophenyl)borane. Due to its high electrophilicity, it proved highly unstable and spontaneously grasped a pentafluorophenyl group from the borate counter-anion to give the neutral $[\text{N}^p(\text{P},\text{C})\text{AuMe}(\text{C}_6\text{F}_5)]$ 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.



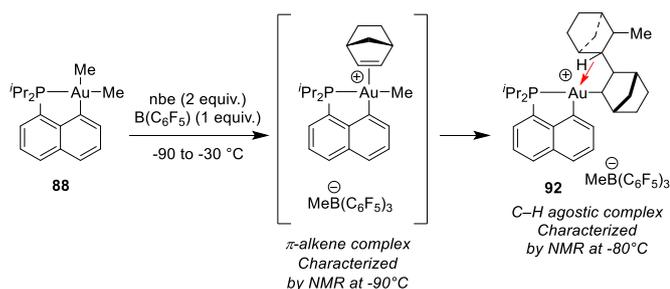
Scheme 26. Generation and rearrangement/trapping of the 3-coordinate cationic Au(III) complex $[\text{N}^p(\text{P},\text{C})\text{AuMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ complex.

The reaction of $[\text{N}^p(\text{P},\text{C})\text{AuMe}_2]$ with $\text{B}(\text{C}_6\text{F}_5)_3$ was then carried 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 gold(III) complex was isolated and fully characterized (HRMS, NMR, 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).



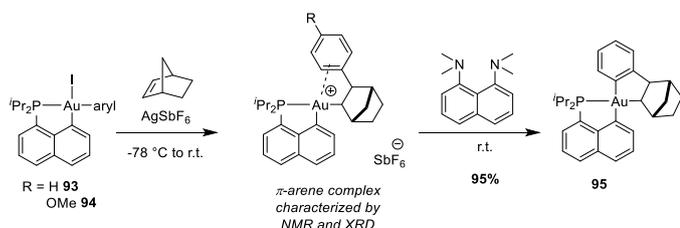
Scheme 27. Double insertion of norbornene into a Au(III)–Me bond.

The mechanism of this reaction was thoroughly investigated by computational and experimental means (Scheme 28).^{34,47} Accordingly, it classically involves coordination-insertion of the 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, respectively), in line with the observation of double insertion. Low-temperature monitoring by NMR spectroscopy enabled to detect two key intermediates: the first π -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 γ C–H bond of the bis-norbornyl moiety to gold was apparent from the reduced $^1J_{\text{CH}}$ coupling (97 Hz) as well as NBO and AIM analyses.⁴⁸



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

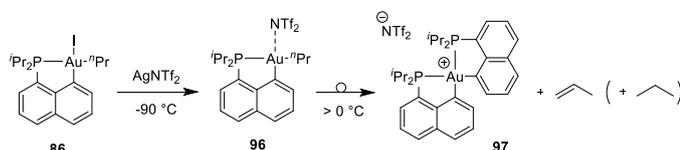
We then envisioned to extend the migratory insertion of alkenes to gold(III) aryl complexes, with the idea to access and characterize π -arene gold(III) complexes (Scheme 29).^{49,50} Such species were proposed as the initial stage of C–H activation of arenes at gold(III). The $[\text{N}^p(\text{P},\text{C})\text{Au}(\text{Ph})\text{I}]$ complex was reacted with AgSbF_6 in the presence of norbornene. Here, mono-insertion took place rapidly and cleanly to give a π -arene gold(III) complex. According to NMR spectroscopy, XRD analysis (of the *p*-methoxy derivative) and DFT calculations, the arene moiety is η^2 -coordinated to gold. The reaction profile of nbe insertion into the Au(III)–Ph bond was analysed by DFT. Coordination-insertion was found to be facile (with an even lower activation barrier than for the Au(III)–Me complex, 10.7 vs 18.7 kcal/mol). Then *cis/trans* isomerization proceeds readily to give the π -arene gold(III) complex obtained. Of note, the auration of the π -coordinated arene could be triggered easily by adding a base such as the proton sponge. This demonstrates the relevance of such π -arene complexes to the electrophilic metalation of arenes at gold(III).



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

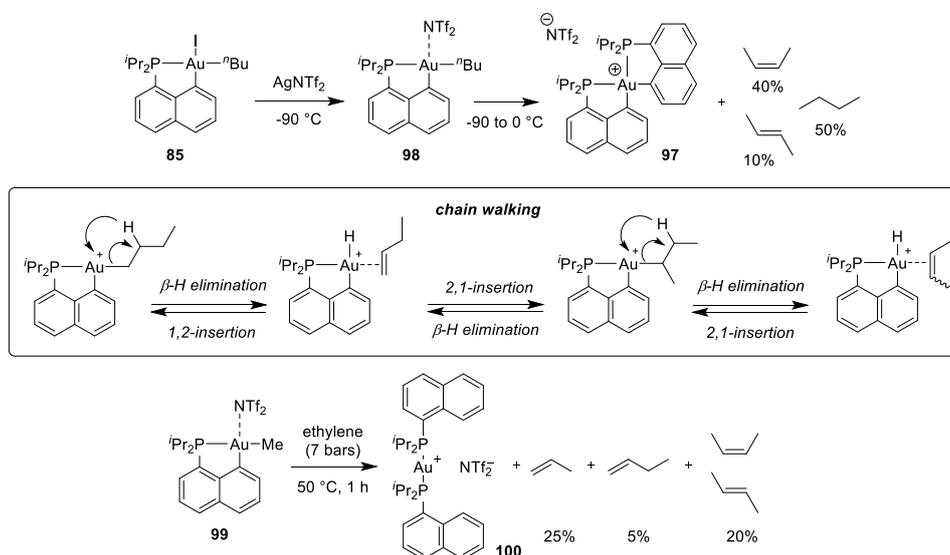
b. β -Hydride elimination

As pointed out by Köppel and Hashmi in 2013, β -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 β -H elimination, although direct experimental evidence was long lacking. Taking advantage of the stability of $[\text{N}^p(\text{P},\text{C})\text{Au}(\text{III})]$ complexes, we carried out in 2016 a comprehensive study on 3-coordinated cationic gold(III) *n*-alkyl complexes (Scheme 30).⁴⁵ The target compounds (^{*n*}Pr, ^{*n*}Bu) were easily generated by reacting the corresponding neutral iodide complexes with AgNTf₂ 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 concomitant release of propylene as a result of β -hydride elimination (propane is also formed by a bimolecular pathway).



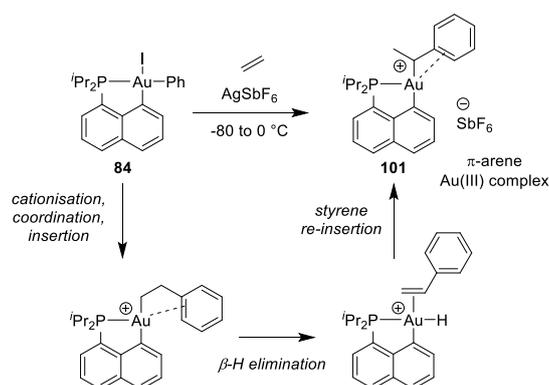
Scheme 30. β -Hydride elimination from the cationic $[\text{N}^p(\text{P},\text{C})\text{Au}(\text{III})]$ *n*-propyl complex.

A similar process was observed from the corresponding *n*-butyl gold(III) complex, with 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 a chain walking process. Computational studies have estimated the activation barriers for such β -H eliminations to 8–14 kcal/mol (compared to <2 kcal/mol for the olefin re-insertion into the Au(III)–H bond). In addition, reacting the corresponding $[\text{N}^p(\text{P},\text{C})\text{Au}(\text{III})]$ methyl complex with ethylene (7 bars) at 50 °C afforded a mixture of propene and butenes. Here, slow insertion of ethylene into the Au(III)–Me bond is followed by rapid β -H elimination.



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

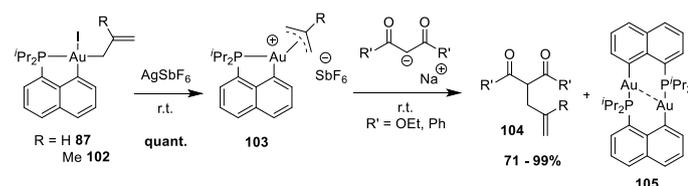
A reaction sequence involving coordination-insertion and β -hydride elimination was also observed by reacting the $[\text{N}^p(\text{P},\text{C})\text{Au}(\text{III})\text{Ph}]$ complex with ethylene (Scheme 32).⁴⁹ In this case, styrene re-insertion is very facile, much more than its dissociation. As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



Scheme 32. Formation of a $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ π -arene complex by a coordination-insertion/ β -hydride elimination/isomerisation sequence.

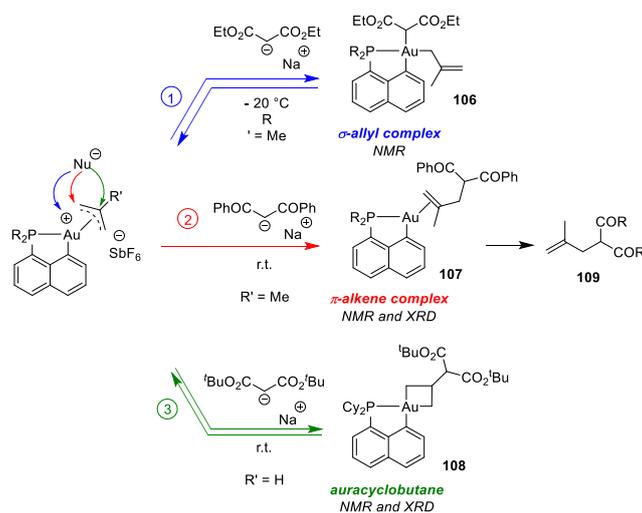
c. π -Allyl gold(III) complexes

While palladium(II) π -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 $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ platform to prepare and study π -allyl gold(III) complexes (Scheme 33).⁴⁶ They were readily prepared from the corresponding neutral σ -allyl precursors, by iodide abstraction with AgSbF_6 . Thorough analysis of the bonding situation by NMR, XRD and DFT revealed static and highly symmetric η^3 -coordination of the π -allyl moiety to gold. Of note, related (N,C)-cyclometalated gold(III) π -allyl complexes prepared simultaneously and independently by Tilset proved to adopt highly fluxional and unsymmetric $\sigma+\pi$ structures instead.⁵¹ To draw parallel with palladium(II) complexes, we reacted the $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ π -allyl complexes with β -dicarbonyl carbanions. The corresponding C–C coupling products were obtained in good to excellent yields, as the result of nucleophilic addition to the π -coordinated allyl moieties.



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

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

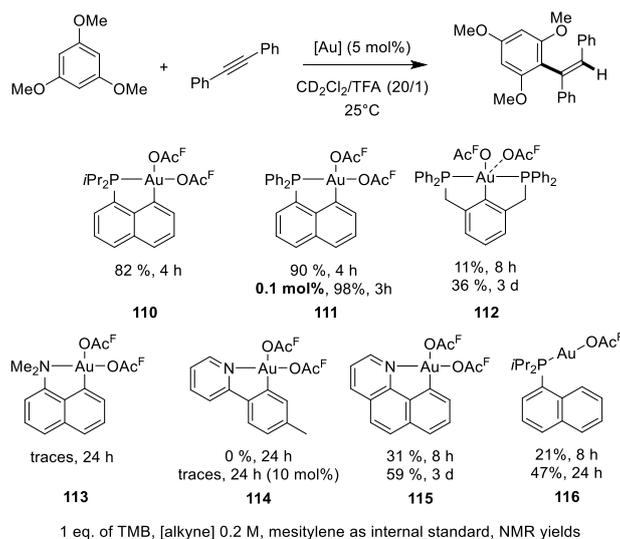


Scheme 34. The three reactive sites for the addition of β -dicarbonyl nucleophiles to $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ π -allyl complexes and the ensuing products authenticated experimentally.

Of note, π -allyl gold(III) complexes were amenable to catalytic allylation. Using a P^N hemilabile ligand, we could cross-couple allyl acetates and alcohols with indoles with complete selectivity for the branched C3-allylated products.⁵²

d. Hydroarylation of alkynes catalysed by $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ complexes

The ability of $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ complexes to engage into migratory-insertion, C–H activation and β -H elimination prompted us to consider their possible use as catalysts in the intermolecular hydroarylation of alkynes.⁵³ This transformation, pioneered by Fujiwara with platinum and palladium complexes,^{54,55} 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 pre-functionalization of the arene substrate. (P,C)-Cyclometalated gold(III) complexes **110**, **111** with labile trifluoroacetate OAc^{F} co-ligands were readily prepared. Using trifluoroacetic acid (TFA) as co-solvent facilitates OAc^{F} dissociation and enables to operate under silver-free conditions. Using the addition of 1,3,6-trimethoxybenzene (TMB) to diphenylacetylene (DPA) as test reaction, the (P,C)-cyclometalated gold(III) complexes proved extremely active, while related (N,C)-cyclometalated complexes showed no or low activity (Scheme 35). Poor results were also observed with a (P,C,P) gold(III) complex as well as a non-cyclometalated gold(I) complex. The $[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ complexes are thus unique to show high robustness and activity in this transformation. Substituting the phosphorus atom by a Ph instead of an ⁱPr 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 98% yield at 0.1 mol% loading within 3 h!



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

$[\text{Np}(\text{P,C})\text{Au}(\text{III})]$ 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 dialkoxy-benzenes, durene and mesitylene. In all cases, the hydroarylation is fully regioselective, and it is generally fully stereoselective, affording the *anti* addition product.

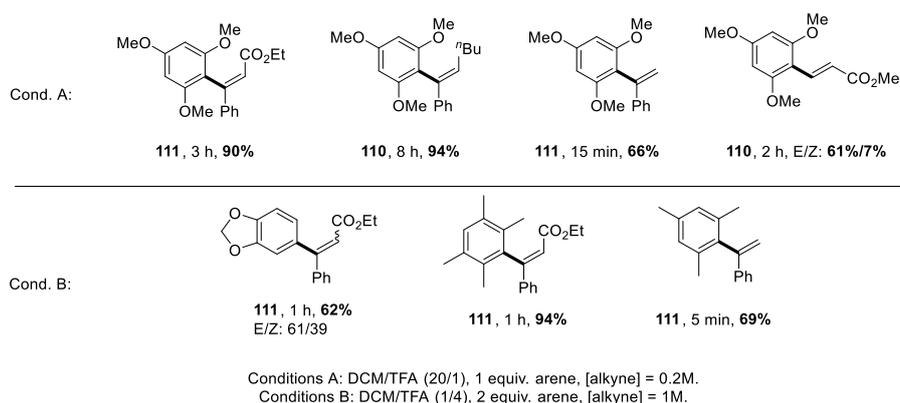
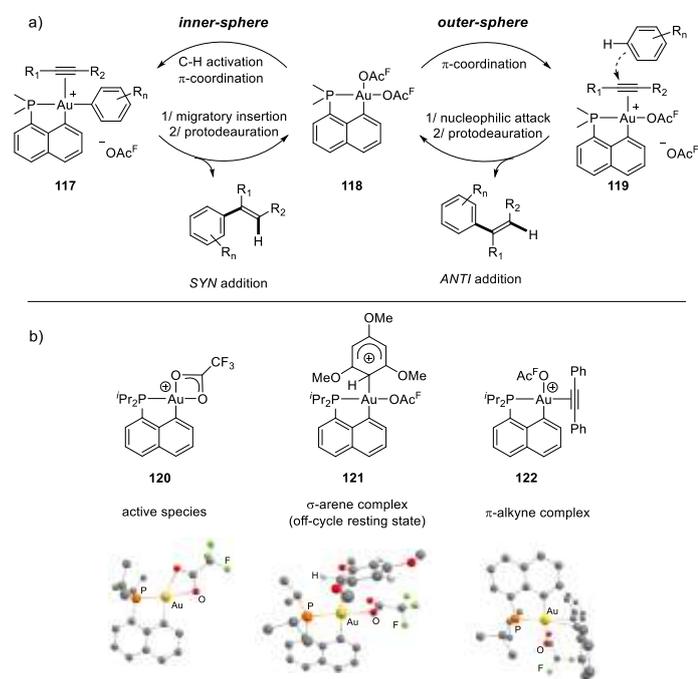


Chart 6. Selected examples of intermolecular hydroarylation of alkynes catalysed by $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$ complexes.

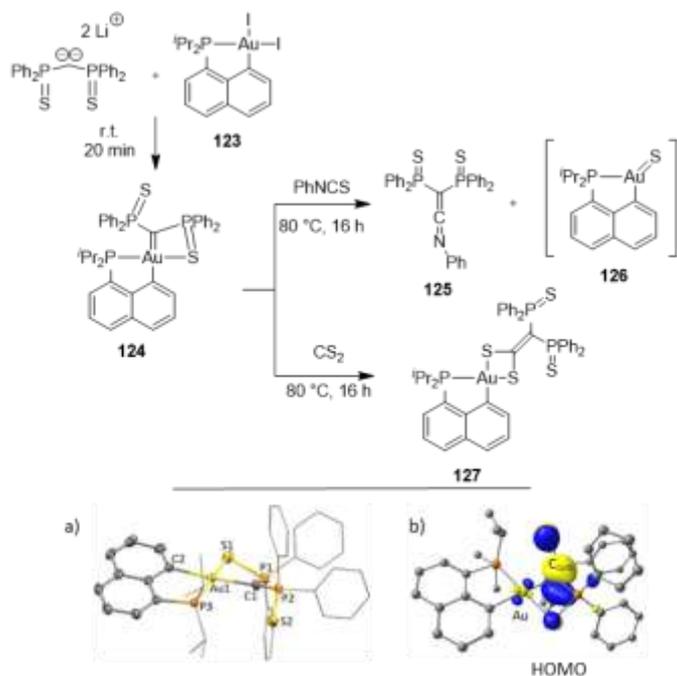
A priori, two paths are conceivable to account for such Au(III)-catalyzed arene/alkyne coupling (Scheme 36). One involves π -coordination of the alkyne to gold yielding **119**, outer-sphere nucleophilic addition of the arene and finally protodeauration. The other one starts by C–H activation of the arene affording **117**, followed by 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,⁵⁶ to track reactive intermediates and better understand the factors at play. Accordingly, using $\text{B}(\text{C}_6\text{F}_5)_3$ as co-catalyst instead of TFA as co-solvent enabled us to characterize by low temperature NMR spectroscopy the cationic complex $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{OAc}^{\text{F}})]^+$, the active species easily shifting from κ^2 to κ^1 -OAc^F coordination, as well as its TMB adduct $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{OAc}^{\text{F}})(\text{TMB})]^+$, an off-cycle resting state and actually the first Wheland-type σ -arene complex of Au(III) to be authenticated. The key π -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.



Scheme 36. a) Schematic representation of the inner- and outer-sphere mechanisms conceivable for the hydroarylation of alkynes catalyzed by $[\text{N}^{\text{P}}(\text{P},\text{C})\text{Au}(\text{III})]$ complexes, b) Related intermediates authenticated experimentally and optimized geometry computed at the SMD(CH_2Cl_2)-B97D/SDD+f(Au)/6-31G** (other atoms) level of theory.

e. A Schrock-type nucleophilic Au(III) carbene complex

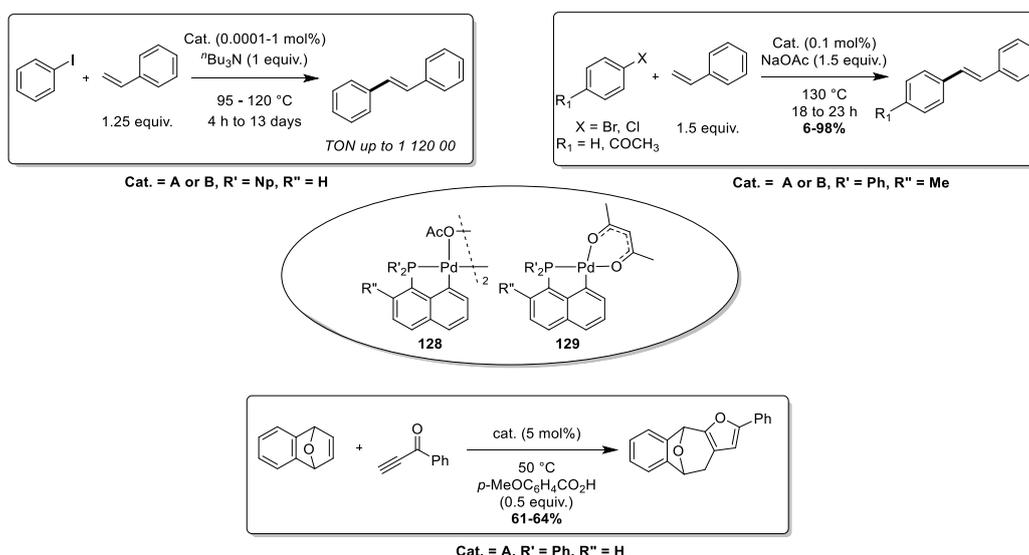
In contrast with electrophilic Fischer-type gold(I) carbene complexes, which are now relatively well-established and understood species, gold(III) complexes with a reactive carbene moiety were elusive until recently. In 2017, the groups of Mézailles and Bourissou combined a geminal dianion stabilized by electron-withdrawing P^V substituents with a $[N^p(P,C)Au(III)]I_2$ complex to prepare an original gold(III) carbene complex (Scheme 37).⁵⁷ 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 $P(=S)Ph_2$ side-arm is coordinated to gold, the other remains pendant. Variable-temperature ^{31}P NMR indicated a dynamic situation, with rapid exchange of the two $P(=S)Ph_2$ moieties at room temperature. The ^{13}C NMR signal for the carbene center was found at δ 18.2 ppm, very much shielded compared to those of electrophilic cationic Au(I) carbene complexes (δ 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 CS_2 .



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

2. $[N^p(P,C)Pd(II)]$ complexes

In 1998, Shaw demonstrated the high catalytic activity and robustness of $[N^p(P,C)Pd]$ acetate and acetylacetonate complexes **128** and **129** in the Heck reaction (Scheme 38).²² 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 $95^\circ C$) to reach TON as high as 1,120,000. Of note, related cyclometalated complexes deriving 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 $130^\circ C$ and 0.1 mol% catalyst loading.²³ Under these conditions, the Heck coupling products could be obtained in high yields from bromo-arenes (with TON up to 1,000) but not chloro-arenes (29% at best).

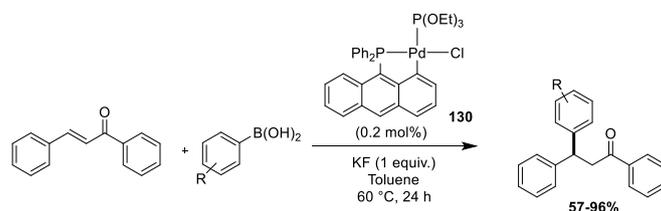


Scheme 38. Catalytic applications of $[\text{N}^{\text{p}}(\text{P,C})\text{Pd}]$ complexes **128** and **129**.

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

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

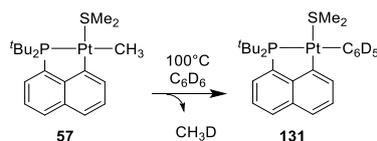
Recently, Yamamoto applied 9-(diphenylphosphino)anthracene-based phosphapalladacycles as catalysts for the conjugate addition of arylboronic acids to electron-deficient alkenes (Scheme 39).⁵⁹ *In situ* tests using $\text{Pd}(\text{OAc})_2$ and phosphines showed the higher performance of the anthracenyl phosphine (95% yield in coupling product from phenylboronic acid and $\text{PhCH}=\text{CHC}(\text{O})\text{Ph}$) over the corresponding naphthyl phosphine (Ph_2PNp , 53%) and triphenylphosphine (<5%). Using the preformed $[\text{A}^{\text{n}}(\text{P,C})\text{Pd}]$ complex with $\text{P}(\text{OEt})_3$ as co-ligand, the catalytic loading could be decreased to 0.2-0.5 mol% keeping high reactivity over a large substrate scope.



Scheme 39. Catalytic application of an $[\text{A}^{\text{n}}(\text{P,C})\text{Pd}]$ complex in the conjugate addition of arylboronic acids to electron-deficient alkenes.

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

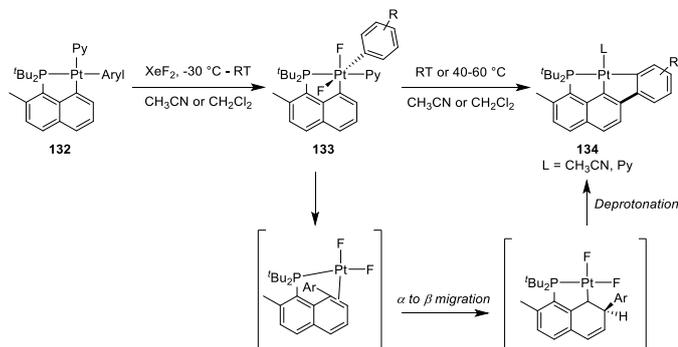
In 2011, Goldberg reported C–H activation of benzene upon thermolysis (100°C) of a cyclometalated $[\text{N}^{\text{p}}(\text{P,C})\text{Pt}(\text{II})]$ methyl complex in C_6D_6 (Scheme 40).²⁵ Methane was identified as co-product (with CH_3D as the major isotopomer) and addition of an excess of SMe_2 was found to inhibit the C–H activation. The authors thus proposed a mechanism involving the displacement of SMe_2 by benzene- D_6 at platinum, followed by oxidative addition of a C–D bond/reductive elimination of CH_3D or a σ -bond metathesis process.



Scheme 40. C–H bond activation of benzene by a $[\text{N}^{\text{p}}(\text{P,C})\text{Pt}(\text{II})]$ methyl complex.

In the context of the electrophilic fluorination of arenes with high valent transition metals, Vigalok and Verdernikov investigated the oxidation of $[\text{N}^{\text{p}}(\text{P,C})\text{Pt}(\text{II})]$ aryl complexes with XeF_2 (Scheme 41).²⁴ The ensuing platinum(IV) complexes showed

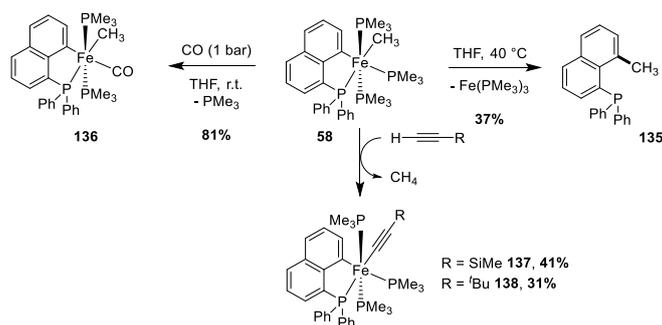
moderate stability and evolved at 20-60°C *via* an 1,3-aryl migration from the platinum center to the β-carbon of the naphthyl fragment to yield (P,C,C)Pt(II) pincer complexes. Based on DFT calculations, the authors proposed a stepwise mechanism for this unprecedented C_{sp2}-C_{sp2} coupling. Following pyridine dissociation and C-C coupling, the aryl group would migrate from the α to the β-position of the naphthyl ring to generate a naphthylidene complex. Finally, deprotonation of the naphthyl ring would restore the aromatic naphthalene system.



Scheme 41. Electrophilic fluorination of [N^p(P,C)Pt(II)] aryl complexes leading to (P,C,C)Pt(II) pincer complexes.

4. [N^p(P,C)Fe(II)] complexes

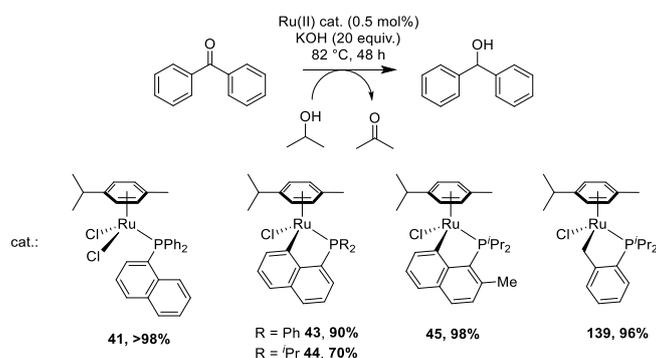
The [N^p(P,C)Fe(II)] methyl complex was found by Beck and Sun to be unstable thermally (Scheme 42).⁶⁰ The iron center is in octahedral geometry with the Me group in *cis* position to the carbon atom of the (P,C)-cyclometalated ligand. Upon gentle heating (40°C, 4 h), reductive elimination took place to give the corresponding C-methylated naphthyl diphenylphosphine. Nonetheless, some stoichiometric reactions with retention of the cyclometalated N^p(P,C) framework were also reported. With carbon monoxide, 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 42. Stoichiometric reactions of a [N^p(P,C)Fe(II)] methyl complex.

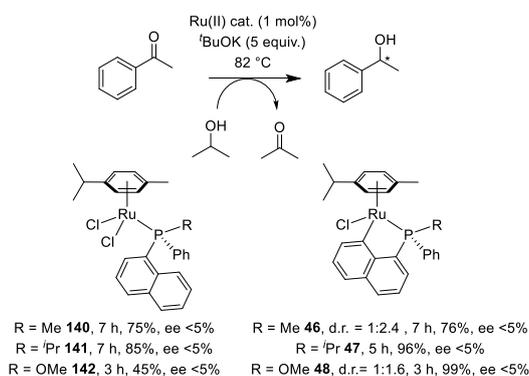
5. [N^p(P,C)Ru(II)] complexes

[N^p(P,C)Ru(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*PrOH), 48 h, KOH (20 equiv.) (Scheme 43).¹⁹ Whatever the substituent at phosphorus (Ph or *i*Pr), the [N^p(P,C)Ru(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 yield was observed upon introducing a methyl group in the *o*-position of phosphorus of the [N^p(*i*Pr₂P,C)Ru] complex (from 70 to 98%).



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

Two years later, Grabulosa envisioned to develop an asymmetric version by chirality transfer from a P-stereogenic center to the ruthenium center (Scheme 44).²¹ 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*-Pr-substituted phosphine induced full control of the ruthenium chiral center, but unfortunately, the cyclometalated complex was formed in very low yield (15%). Evaluation of these [N^p(P,C)Ru(II)] complexes in asymmetric transfer hydrogenation of acetophenone reveals very low, if any, enantioselectivity (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).



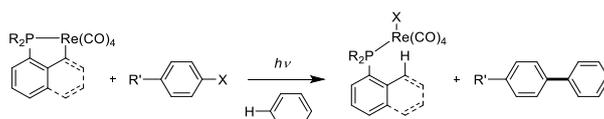
Scheme 44. Attempts for Ru-catalyzed asymmetric hydrogenation of acetophenone with P-chiral naphthyl phosphine complexes.

6. Miscellaneous examples involving M–C cleavage

The [N^p(P,C)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 happen in a few cases, presented hereafter.

a. [N^p(P,C)Re] complexes

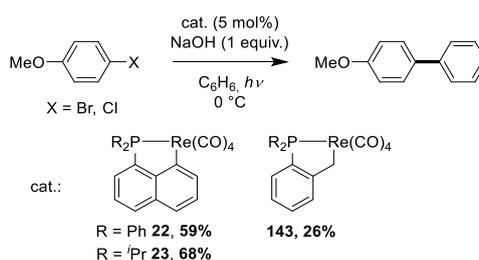
In 2017, the group of Zhu investigated the decyclometalation of [N^p(P,C)Re] complexes¹¹ inspired by the work of Lu on homologous N,C-cyclometalated complexes.⁶¹ The cleavage of the Re–C bond was achieved under UV irradiation at room temperature in chloroform or bromoform to yield the corresponding rhenium 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).



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

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 solvent) was then possible under catalytic conditions, in the presence of 1 equivalent of

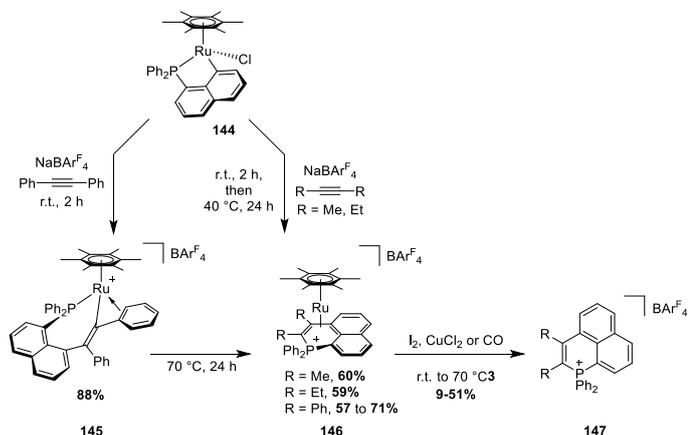
sodium hydroxide (Scheme 46). Of note, the ancillary $N^p(P,C)$ ligand was found to outperform its more flexible C_{sp^3} variante (59 vs 26% yield) and replacing the Ph groups at phosphorus for iPr led to an increase in stability of the rhenium catalyst (no free ligand observed with iPr) and thus better yield in coupling product (68%).



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

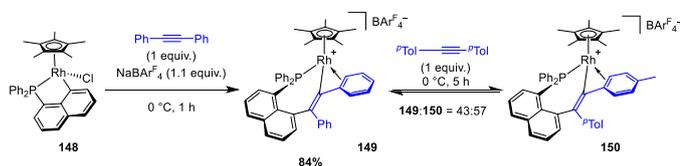
b. $[N^p(P,C)Ru]$ and $[N^p(P,C)Rh]$ complexes

In the course of their work on insertion/remote rearrangement of internal alkynes in ruthenium complexes, the group of Ishii reported a rare example of P–C reductive elimination at ruthenium (Scheme 50).²⁰ When exposed to an halide abstractor and an internal alkyne, the $[N^p(P,C)Ru]$ complex undergoes 1,2-insertion of the alkyne ($R = \text{alkyl or aryl}$) in the $Ru-C$ bond followed by P–C reductive elimination to provide the sandwich complex **146**. This mechanism was supported by the isolation of intermediate **147** resulting from the 1,2-insertion of diphenylacetylene in presence of NaBAR_4^F at room temperature. Heating at 70°C for 24 hours allows the P–C reductive elimination to take place. The phosphalenium salts can then be released using oxidants (I_2 , CuCl_2) or CO .⁶²



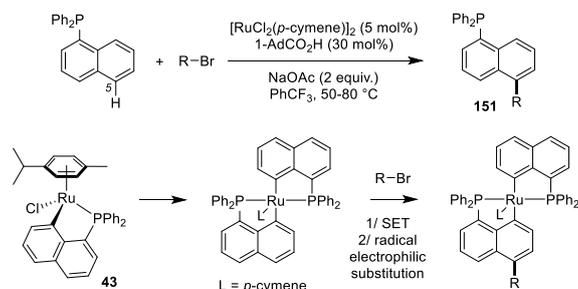
Scheme 50. Reaction of a $[N^p(P,C)Ru(II)]$ complex with internal alkynes leading to phosphalenium salts.

Recently, Ishii synthesized the analogous alkenyl rhodium(III) complex coordinated with pentamethylcyclopentadienyl (Cp^*) by 1,2-insertion of diphenylacetylene in presence of NaBAR_4^F (Scheme 51).⁶³ 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* β -carbon elimination, for which the activation barrier was estimated computationally to be accessible (15.6 kcal/mol). This represents one of the rare examples of β -carbon elimination from an alkenyl complex (*i.e.* the reverse process of alkyne insertion).



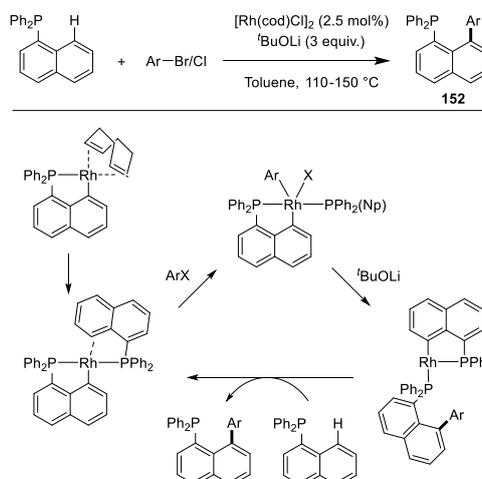
Scheme 51. Synthesis of complex **149** by alkyne insertion in the $\text{Cp}^*en\text{-Ru}$ bond and exchange reaction of alkenyl moiety using di-*p*-tolylacetylene.

Recently, Zeng reported an original Ru -catalyzed alkylation of naphthyl phosphines occurring selectively on the remote C5 position (Scheme 45).⁶⁴ The transformation proceeds under relative mild conditions ($50\text{--}80^\circ\text{C}$) with bromo-alkanes as alkylating reagents. It takes advantage of the facile and reversible formation of $[N^p(P,C)Ru]$ complexes by phosphine-directed cyclometalation / protodemetalation. The bromo alkanes is 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 $N^p(P,C)Ru$ metallacycle.



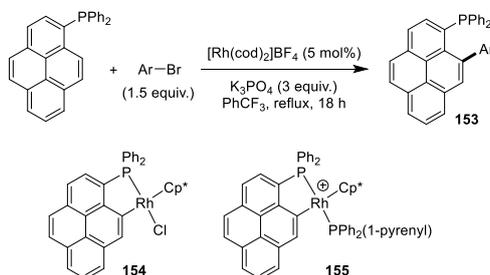
Scheme 45. Ru-catalyzed C5-selective alkylation of naphthyl phosphines involving $[\text{N}^p(\text{P},\text{C})\text{Ru}(\text{II})]$ complexes.

In 2018, Yu and Che described jointly the Rh-catalyzed *peri* arylation of naphthyl phosphines (Scheme 46).⁶⁵ 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 bromo-arenes (within 24 h at 110°C) as well as chloro-arenes (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-arenes as well. Mechanistic studies by mass spectrometry suggest a Rh(I)/Rh(III) catalytic cycle. The bis-phosphine complex $[\text{N}^p(\text{P},\text{C})\text{Rh}(\text{PPh}_2\text{Np})]$ was proposed to be the active species.



Scheme 46. Rh-catalyzed C–H arylation of 1-naphthyl diphenylphosphines involving $[\text{N}^p(\text{P},\text{C})\text{Rh}]$ complexes.

Very recently, Hierso and Roger extended this methodology to polycyclic aromatic hydrocarbons, in particular 1-pyrenyl diphenylphosphine (Scheme 47).⁶⁶ 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 was 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.



Scheme 47. Rh-catalyzed C–H arylation of 1-pyrenyl diphenylphosphine involving $[\text{N}^p(\text{P},\text{C})\text{Rh}]$ complexes.

IV. Luminescence properties and optoelectronic applications of $[N^p(P,C)M]$ complexes

1. $[N^p(P,C)Pt(II)]$ complexes

In 2009, Yip reported an interesting study on (P,C)-cyclometalated platinum complexes deriving from pyrene.¹⁰ 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 was envisioned as a mean to introduce Pt on the pyrene ring and benefit from internal heavy-atom effect to enhance phosphorescence. Accordingly, the mono and dimetallic platinum complexes **18,20** showed phosphorescence at λ_{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 μ s (Figure 2). The heavy-atom effect of Pt was supported by the very weak phosphorescence of the related Pd dinuclear complex under the same conditions (λ_{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.⁶⁷ The related complexes with dangling (non-cyclometalated) Pt centers showed very weak if any phosphorescence.

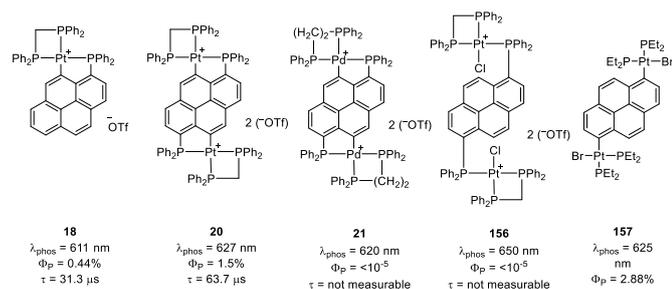


Figure 2. Phosphorescence properties of (P,C)-cyclometalated and non-cyclometalated pyrene derivatives.

Note that the same authors performed a similar photophysical study on analogous anthracene-derived complexes two years before.⁹ The bis-cyclometalated complexes were found to emit at λ_{em} ~ 460–510 nm in dichloromethane solution at room temperature, with quantum yields of 1–6% and short half-lifetimes < 2 ns (Figure 3). Only weak fluorescence was observed in this case, with no apparent enhancement of phosphorescence due to heavy-atom effect. Comparison of the *syn* and *anti* isomers revealed little changes, while the corresponding mono-cyclometalated complex showed weaker fluorescence (0.16% quantum yield) with a too-short lifetime to be measured.

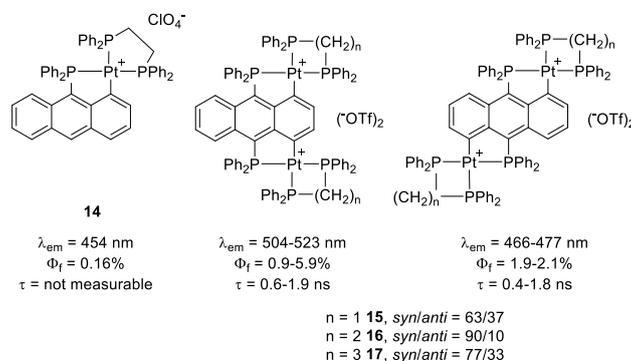


Figure 3. Fluorescence properties of (P,C)-cyclometalated Pt complexes deriving from anthracene (similar data were observed with dpmp and dppp instead of dppe as ancillary diphosphines).

2. $[N^p(P,C)Ir(III)]$ complexes

Cyclometalated iridium(III) complexes such as [(phenyl-pyridyl)₃Ir] 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^N and one P^AC cyclometalated ligands (Figure 4).¹⁵ Attempts to prepare analogous complexes from benzyldiphenylphosphine failed, preventing the authors to assess the influence of the naphthyl ring on the luminescence properties. Whatsoever, complexes **26,27** proved robust (as long as the N^AC ligand is equipped with a fluorine atom) and phosphorescent in oxygen-free dichloromethane solution at room temperature with λ_{em} 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^AC 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^AC ligand. In particular, the (P,C)-naphthyl

ligand was proposed to act as CT acceptor when iridium is ligated by the phenyl-pyridine ligand. Of note, the proof of feasibility of incorporating such complexes in devices was substantiated. Orange-red emitting OLEDs with decent quantum efficiencies (up to 12.5% at 500 cd/m² brightness) were prepared.

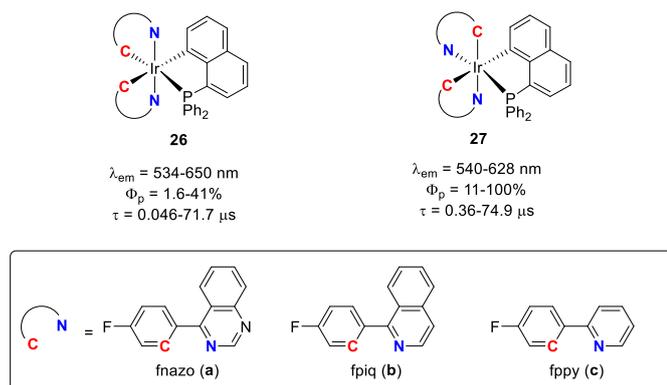


Figure 4. Phosphorescence properties of heteroleptic tris-cyclometalated Ir(III) complexes.

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

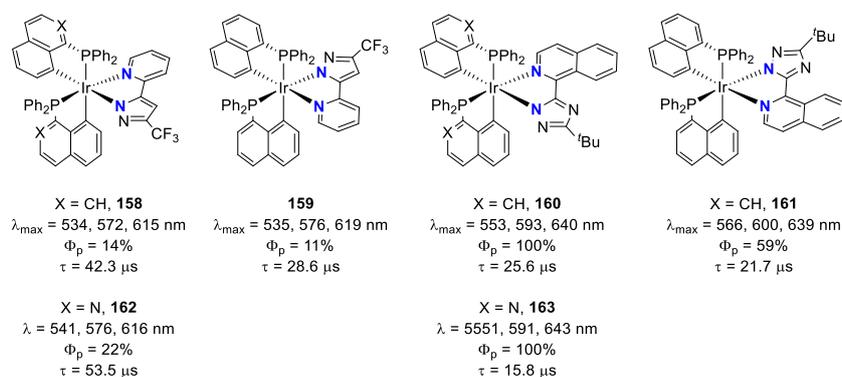


Figure 5. Structural modulation of the phosphorescent heteroleptic cyclometalated Ir(III) complexes: naphthalene and isoquinoline-derived phosphines, N^N azolate ligands.

Conclusions

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

The historical P-chelation assisted C–H activation route pioneered by Shaw 50 years ago remains the most straightforward and general way to prepare $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ complexes. It shows complete selectivity for the $\text{C}_{\text{sp}^2}\text{--H}$ bond in *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 $\text{C}_{\text{sp}^2}\text{--X}$ oxidative addition to a single gold(I) center, it has been then extended to nickel. A third complementary route applied to group 7-11 metals relies on transmetalation from stable mercury or tin *peri*-metalated naphthyl phosphines.

From a structural viewpoint, the $[\text{N}^{\text{p}}(\text{P,C})]$ framework is well suited and nicely accommodates metals from group 7 to 11, as apparent from the P–M and $\text{C}_{\text{peri}}\text{--M}$ 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 $\text{C}_{\text{peri}}\text{--P}$ bond toward the metal and out of the naphthalene plane.

Reactivity studies on $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ 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...). $\text{N}^{\text{p}}(\text{P,C})$ -cyclometalation turned to be particularly fruitful in gold(III) chemistry, where it has opened new reactivity paths (migratory insertion, $\beta\text{--H}$ elimination, nucleophilic addition to π -allyl) and has enabled to authenticate many new bonding situations (C–H agostic, π and σ -arene, π -allyl, Schrock-type nucleophilic carbene complexes), resulting ultimately in unique catalytic activity in the intermolecular hydroarylation of alkynes. $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ complexes have also been shown recently to be key intermediates in the Ru-catalyzed alkylation of the remote C5 position of naphthyl phosphines and in the Rh-catalyzed arylation of the *peri* position of naphthyl/pyrenyl phosphines.

Very little is known yet about the photophysical properties of $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ complexes. Interesting phosphorescence properties have been occasionally pointed out but further studies are certainly needed to better understand the very influence of $\text{N}^{\text{p}}(\text{P,C})$ -cyclometalation and develop its use in opto-electronic systems.

It is likely that the chemistry of $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ complexes will keep developing and new facets will be discovered in near future. Although not all transition metals may form stable $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ 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, 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 $[\text{N}^{\text{p}}(\text{P,C})\text{Au}(\text{III})]$ 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 $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ 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, $[\text{N}^{\text{p}}(\text{P,C})\text{M}]$ complexes may well complement and eventually outperform the commonly used rigid (N,C)-cyclometalated complexes.

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