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Revisión

Pincer Complexes. Applications in Catalysis

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Dedicated to the memory of Dr. Raymundo Cruz Almanza

Abstract. In the recent years the development of complexes having in its structure pincer type ligands has received considerable attention. Now a days these complexes are designed and synthesized not just for the mere structural interest, but for the great number of potential applications that these compounds may have, including their use as robust catalysts, motifs in molecules that exhibit self assembly arrangements, synthons for their employment in Medicinal Chemistry and as fundamental components in the synthesis of dendrimeric materials for their potential use in catalysis. Thus, the present review shows the multiple applications that the pincer complexes have had in particular in the area of catalysis and the future perspectives of applications of these compounds in chemistry.

Key words: PCP pincer ligands, SCS pincer ligands, NCN pincer ligands, pincer type complexes, catalysis.

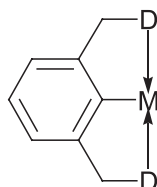
Resumen. En los últimos años el desarrollo de la Química de compuestos conteniendo ligantes tipo pincer (pinza para su traducción en español) ha tenido un gran avance, pasando de ser especies sintetizadas meramente por su interés estructural a formar parte hoy en día de uno de los motivos en Química mas utilizados por los químicos para el desarrollo de especies con diversas aplicaciones, que van desde su uso como precursores de catalizador, moléculas de interés en procesos de autoensamblado, sintones empleados en Química medicinal y el uso de estas moléculas como componentes fundamentales en la síntesis de materiales dendrimericos para usos múltiples entre los cuales resalta su profuso empleo en catálisis. De esta forma, la presente revisión representa una compilación de los múltiples y variados casos en los que compuestos tipo pincer han sido empleados en procesos catalíticos así como las perspectivas de desarrollo de esta área.

Palabras Clave: Ligandos tipo pinza PCP, Ligandos tipo pinza SCS, Ligandos tipo pinza NCN, complejos con ligantes tipo pinza, catálisis.

Introduction

In 1976 Moulton and Shaw [1] synthesized for the first time a pincer type ligand. In that point this ligand and its corresponding complexes only represented some very novel derivatives of a new diphosphine. These ligands and their complexes were forgotten for one decade. Then in the 80's a careful reexamination of the properties of these complexes revealed this compounds to have an extraordinary thermal stability, given their high melting points (they sublime without decomposition), property that could enable these complexes to be potentially used in homogeneous catalysis. Now a days these species have been motif of multiple studies beyond catalysis, ranging from application in nanoscience to the development of chemical sensors and chemical switches [2].

The pincer type complexes consist on a metallic center and of course a pincer type ligand containing in its structure the donor atoms being thus capable of coordinate in a tridentated manner to acquire the typical arrangement of the pincer like ligands.



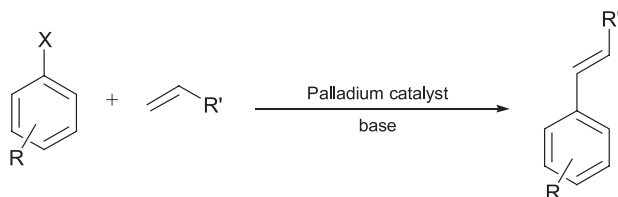
D = donor atom; O, S, N, P
M = metallic center

It is believed that is the σ metal-carbon bond the responsible for the unique stability of these complexes, thus avoiding the dissociation of the metal from the ligand and thus the decomposition of the complex, while the donor atoms and their corresponding substituents allow the fine tuning of the steric and electronic properties. Moreover, modification of these substituents has allowed in the recent years to incorporate stereochemical centers capable of induce chirality during a given process. Thus, depending of the donor atoms in the pincer ligands, these compounds are denominated as PCP pincer complexes for those compounds having phosphorus in their structures, SCS for those containing sulfur, etc.

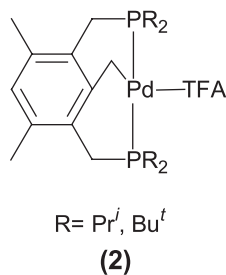
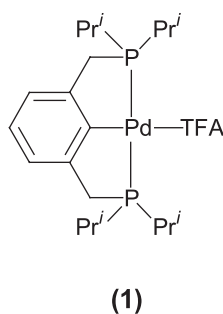
The facility to modify and tune the properties of these ligands and their complexes has been reflected in the profuse employment of these species in different areas of chemistry, particularly in catalysis [3].

Heck Reaction

Since its discovery in the 60's, the Heck reaction has turned into a real power tool in organic synthesis, now a day reaching the status of angular stone in the modern organic synthesis [4]. In general the Heck reaction consists in the coupling of an α -olefin with a bromo or iodo derivative. Most of the processes involving the Heck reaction are catalyzed by Pd(II) or Pd(0) derivatives in the presence of PPh_3 in excess.

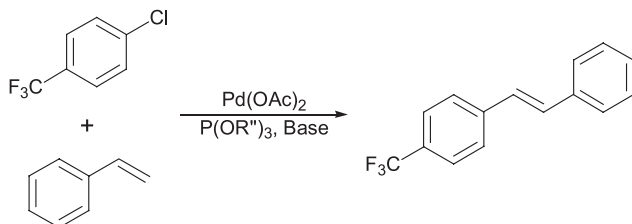


Unfortunately, the reaction intermediates formed during the catalytic reaction are sensitive to oxygen or thermally unstable, hampering the coupling process. In the recent years several research groups have done important advances with the aim of getting the ideal catalyst with the proper characteristics of reactivity and stability to carry out this process, the result of these experiments has lead to the researchers to the use of ortho metallated complexes, among which the pincer type ligands represent one of the most important examples. Milstein and coworkers were the first to employ Pd(II)-PCP pincer complexes (**1**, **2**) in the Heck coupling reaction.

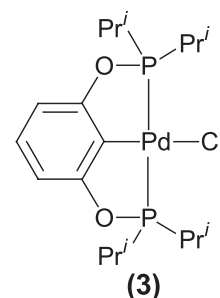


Milstein found that these complexes were active without decomposition at reaction temperatures as high as 140 °C, over reaction periods of 300 hours or higher. By using these catalysts (**1**, **2**) Milstein achieved full conversion in the couplings of iodobenzene with methylacrylate, using *N*-methylpyrrolidine (NMP) as solvent and sodium carbonate as base with a maximum of 500,000 turnover numbers for iodobenzene and up to 132,900 for bromobenzene.

By the same time, Beller and Zapf [6] reported the use of electro-attractor phosphite ligands for the Heck couplings of activated chlorobenzenes.

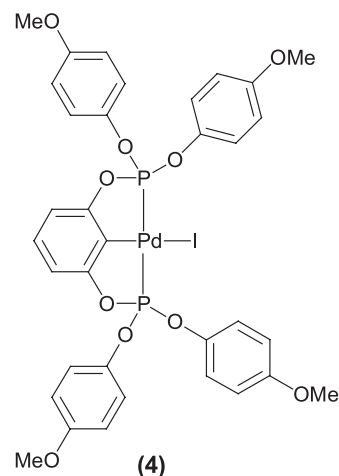


Based on these results Jensen [7] *et. al* synthesized an analogous PCP pincer type ligand based on phosphinito fragments as *P* donors. The palladium derivatives of this ligand (**3**) where shown to be efficient in the coupling of chlorobenzenes, being one of the few examples then known to activate, deactivated or sterically hindered chlorobenzenes.

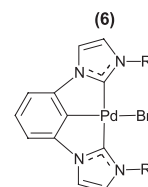
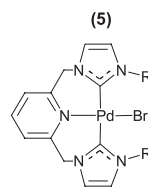


This complex (**3**) showed to be as reactive as the PCP phosphino derivative reported previously by Milstein.

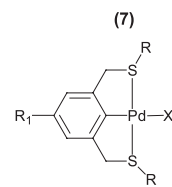
A similar approach lead to Shibasaki [8] *et. al*, to the synthesis of complex (**4**), this compound was able to provide turnover numbers higher than 980,000.



Several other pincer type complexes and their palladium derivatives have been synthesized and used in the Heck reaction, including CNC ligands where *C* represents a carbon from a heterocyclic carbene [9] (**5**, **6**) and SCS ligands (**7**) [10].

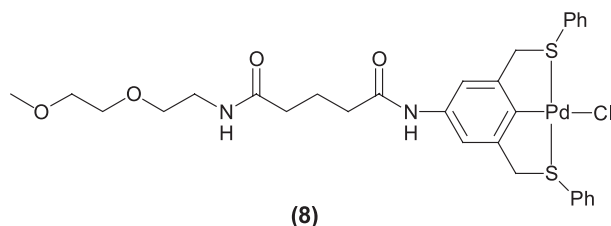


$R = \text{alkyl, aryl}$

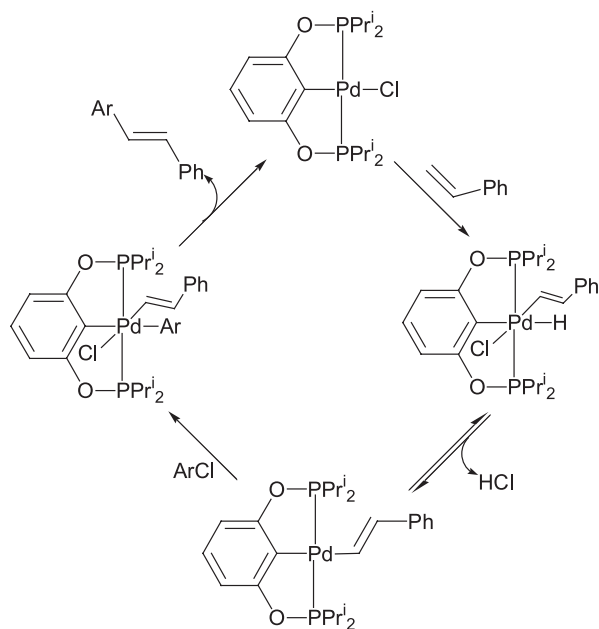


$R_1 = \text{H, CH}_3\text{CONH, PhCH}_2\text{O}$
 $R = \text{Bu}^i, \text{Ph}$
 $X = \text{Cl, CF}_3\text{CO}_2$

These complexes have demonstrated analogous reactivities and stabilities as their phosphinated counterparts. However, an interesting characteristic of the SCS pincer ligands is the facile functionalization of the aromatic backbone to attach tails that in turn can be linked to polyethylene glycol supports (**8**), thus generating highly stable and highly active catalyst that can be easily separated, isolated and then used again for at least three cycles without decrease in activity [10].



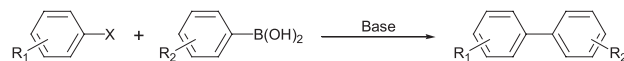
Thus, characteristics like the supreme activity and superior thermal stability that the palladium pincer complexes have shown in the C-C coupling reactions (Heck type reactions), has lead to Jensen and Morales-Morales [7] to propose an alternative reaction mechanism involving Pd(II)/Pd(IV) [5,7] species instead of the traditionally accepted mechanism involving Pd(0)/Pd(II) species. This reaction mechanism is still under debate.



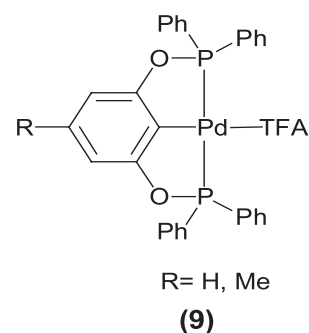
Suzuki-Miyaura Couplings

The Suzuki or Suzuki-Miyaura C-C couplings [11] consist in the reaction of a halobenzene with arylboronic acids in the presence of a base. This reaction proceeds by a similar reaction mechanism as that of the Heck reaction, thus most of the

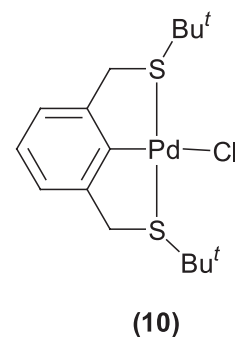
catalysts usually employed in the Heck coupling reactions have been successfully employed in the Suzuki reaction too.



Thus, Pd(II) complexes having phosphinito PCP pincer ligands (**9**) have been successfully used by Bedford *et. al* [12] in the couplings of aryl halides with phenyl boronic acid, exhibiting quantitative yields and turnover numbers in the order of 92,000. These complexes are also efficient in the couplings of deactivated and sterically hindered aryl bromides.



On the other hand, Pd(II) SCS pincer complexes (**10**) have also been employed in the Suzuki type couplings, however their application has been limited being only active in the reaction of *p*-bromotoluene with phenyl boronic acid to a maximum of 69% yield of the corresponding biphenyl [13].



Dehydrogenation of alkanes

Saturated hydrocarbons represent one of the most abundant and accessible feedstocks in our planet [14]. However, their use has been limited due to the intrinsic lack of reactivity of these compounds [15]. An interesting alternative to this problem has been the use of transition metal complexes able to activate C-H bonds under mild reaction conditions [16]. Some

dehydrogenation of linear alkanes to their corresponding terminal alkenes (α -olefins), being this the kinetically favored process. However, the same complex slowly catalyzes the isomerization of the terminal alkene to internal alkenes, being this the thermodynamic product [22].

The reaction scheme illustrates the catalytic cycle for the isomerization of 1-alkynes to 1-alkenes. The catalyst, labeled (13), is a 1,2-bis(isobutyl)phthalate-iridium complex. The cycle begins with the coordination of a 1-alkyne to the iridium center, forming a π-alkyne complex. This is followed by a dehydrogenation step, which involves the transfer of a hydride from the alkyne to the iridium, resulting in an alkynyl-iridium hydride intermediate. The subsequent isomerization step leads to the formation of a vinyl-iridium species, which then undergoes a final dehydrogenation to yield the 1-alkene product and regenerate the catalyst.

Diagram illustrating the central iridium complex (13) coordinated by two PBu_2^t ligands and two hydride ligands (H). The complex is surrounded by various substrates, including cycloocta-1,5-diene, 1,3-butadiene, styrene, benzene, furan, cyclohexene, cyclopentadiene, and cyclohepta-1,3-diene.

The diagram illustrates the catalytic cycle for the hydrogenation of 1,3-butadiene to 2-butene using an iridium complex. The cycle involves several intermediates and reaction steps:

- Top Left:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands and a hydride ligand (H).
- Top Right:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a CMe_3 ligand.
- Middle Left:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a $\text{CH}_2\text{CH}_2\text{CMe}_3$ ligand.
- Middle Right:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a $\text{H}_3\text{CCH}_2\text{CMe}_3$ ligand.
- Bottom Left:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a $\text{CH}_2\text{CH}_2\text{R}$ ligand.
- Bottom Center:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a $\text{CH}_2\text{CH}_2\text{R}$ ligand.
- Bottom Right:** A 1,5-cyclooctadiene-iridium complex with two PBu'_2 ligands, a hydride ligand (H), and a $\text{H}_3\text{CCH}_2\text{R}$ ligand.

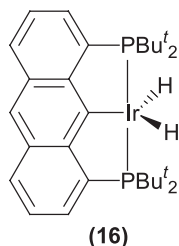
The reaction steps are as follows:

- Top Left to Top Right:** Reaction with $\text{H}_2\text{C}=\text{CHCMe}_3$.
- Top Right to Middle Left:** Reaction with H_2 (slow).
- Middle Left to Middle Right:** Reaction with $\text{H}_3\text{CCH}_2\text{CMe}_3$.
- Middle Right to Bottom Right:** Reaction with $\text{H}_3\text{CCH}_2\text{R}$.
- Bottom Right to Bottom Center:** Reaction with H_2 (slow).
- Bottom Center to Bottom Left:** Reaction with $\text{H}_2\text{C}=\text{CHR}$.
- Bottom Left to Top Left:** Reaction with $\text{H}_2\text{C}=\text{CHR}$ (slow).

The cycle is labeled with "acceptor pathway" and "acceptorless pathway".

Recently, Kaska and coworkers [27] have reported a rigid PCP pincer system based on anthracene backbone (**16**), the iridium derivative of this ligand has demonstrated catalytic activity in the dehydrogenation of alkanes at temperatures as high as 250 °C without decomposition. Although even at this reac-

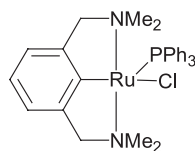
tion temperature the system do not match the performance of the complexes **13** and **14**, nor in yield of the terminal olefin or in the turnover numbers previously discussed.



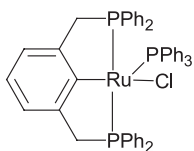
(16)

Hydrogen Transfer Reactions

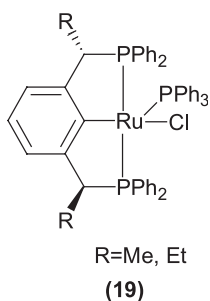
van Koten and coworkers have employed successfully ruthenium NCN (**17**) and PCP (**18**) pincer complexes to perform hydrogen transfer reactions to reduce ketones to their corresponding alcohols using *iso*-propanol as source of hydrogen and KOH as co-catalyst [28].



(17)

X = Cl, H, OSO₂CF₃
(18)

Although both complexes are active catalysts in this process, the best yields and turnover numbers were obtained with the PCP pincer derivatives, for instance, for cyclohexanone, under reflux conditions, yields of 98% and turnover numbers of 27,000 were obtained, being these numbers the best so far obtained, compared with mono phosphine ruthenium complexes like [RuCl₂(PPh₃)] or [RuCl(H)(PPh₃)] [29]. Given these results, several attempts have been done with the aim of interpolate this process to obtain enantiomerically pure alcohols, among these the use of chiral ruthenium PCP pincer complexes (**19**) [30]. However, despite of the fact that com-

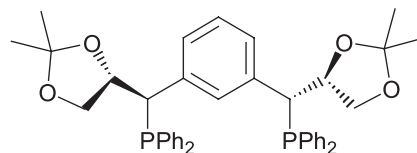
R = Me, Et
(19)

plex **19** exhibits catalytic activity comparable to the non-chiral counterparts, the reaction of *iso*-PrOH and acetophenone only affords 14% ee [31].

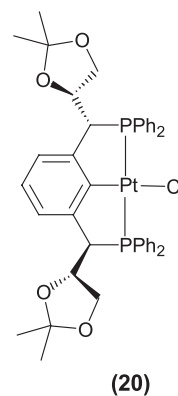
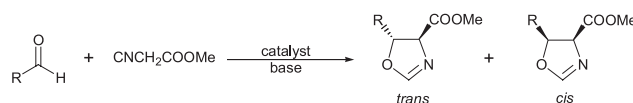
Aldolic Condensations

The synthesis of enantiomerically pure oxazolines can be conveniently done through the gold catalyzed [32] aldolic condensation reactions between an aldehyde or a ketone with an isocyanate. These compounds are very important, since the consecutive hydrolysis of the oxazolines obtained by this procedure, offers a simple and efficient route for the synthesis of β -hydroxyaminoacids.

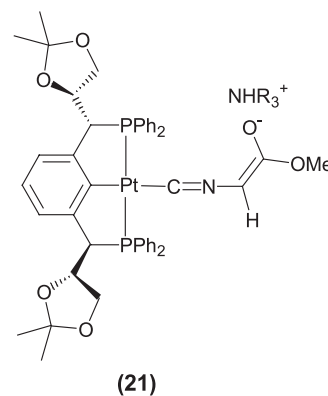
It is noteworthy that the first enantiomerically pure PCP pincer complexes were evaluated in this process. Venanzi and coworkers [33] designed these compounds by introducing chiral acetals in the benzylic positions of the PCP ligands, the reaction being achieved by the Sharpless type enantioselective epoxydation.



The platinum derivative of this ligand (**20**) has shown to be active in the asymmetric aldolic addition of methyl- α -isocyanoacetate with aldehydes to yield moderated enantiomeric yields of 32% and 65% ee for the corresponding *cis* and *trans* oxazolines respectively. This reaction is carried out in the presence of a base that acts as cocatalyst for the formation of the metal-isocyanoenolate intermediate (**21**).

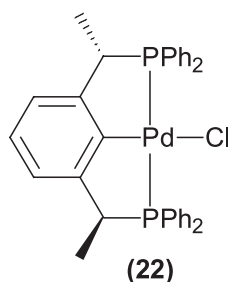


(20)



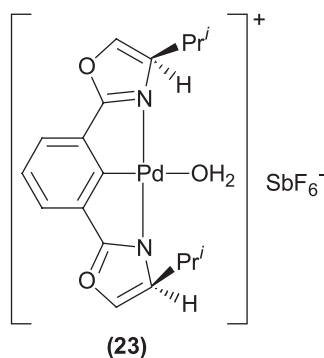
(21)

However, the synthesis of these compounds is difficult and tedious, thus its potential application has been limited. Recently, Zhang and coworkers [34] have reported an easier and efficient route for the synthesis of enantiomerically pure PCP pincer ligands and their Pd(II) complexes (**22**).



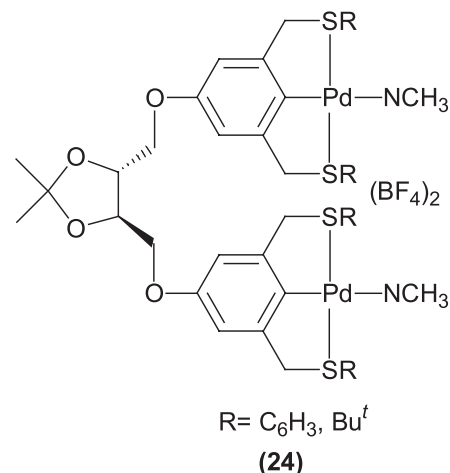
The use of the palladium derivatives of this ligand (**22**) in the same reaction reported by Venanzi, affords the formation of oxazolines in high yields, with high enantioselectivity for the formation of the *cis*-oxazolines. This example once more illustrates the importance of the proper selection of the ligand and metal for a particular transformation.

Other chiral pincer type complexes have also been employed. For instance, ligands including oxazolines in their backbones afford modest results in the synthesis of oxazolines [35].

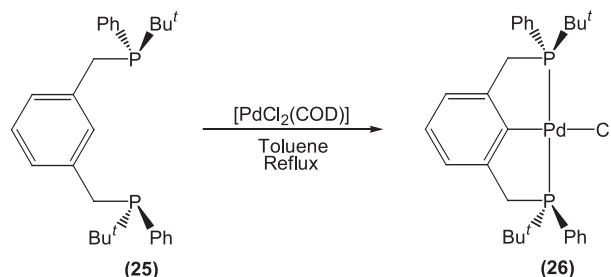


In addition, SCS pincer ligands including chiral groups have also been employed in this reaction. Unfortunately, the chiral induction using this kind of complexes resulted to be zero, this being probably due to the fact that the chiral centers are located too far from the metal center to have a significant effect in the chiral discrimination during the reaction [36].

Most recently Morales-Morales and coworkers [37] have synthesized a PCP pincer ligand (**25**) and its palladium derivatives (**26**) having the chiral centers at the phosphorus atoms and used them in the same reaction with poor enantiomeric excesses in the order of 6%. In this case it does seem that the R groups at the *P** chiral centers are too similar in size to lead

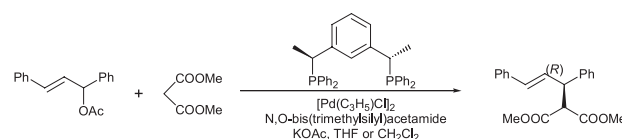


to a good chiral discrimination, thus efforts pointing to the design of similar ligands with bulkier requirements are under way.



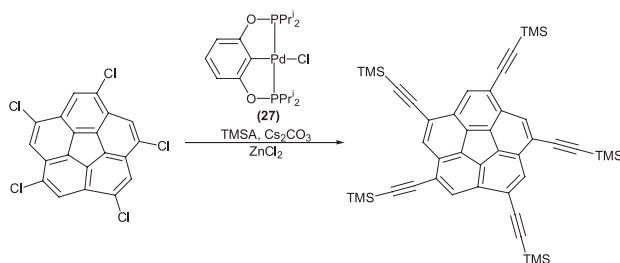
Asymmetric allylic alkylation

In the recent years, the allylic alkylation reaction in its asymmetric fashion has received considerable interest; proof of this is the tremendous number (more than a 1000) of chiral diphosphines that have been synthesized for this particular reaction. In the field of the pincer ligands Zhang and coworkers [38] have used the PCP pincer chiral ligand **22**, previously employed in the aldolic condensation reaction, in the reaction of dimethyl malonate with 1,3-diphenyl-2-propenyl acetate using $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}_2]_2$ as a source of palladium, attaining yields in the order of 50 to 94%. This particular reaction proceeds at room temperature; however decreasing of the reaction temperature increases considerably the enantiomeric yields to a maximum of 79% *ee* for the enantiomer (*R*).

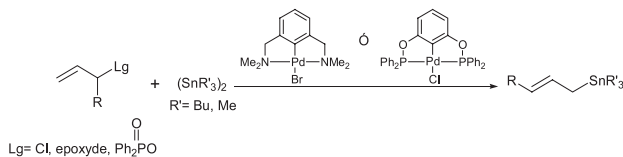


Recent advances

As it can be noted from the above, the pincer ligands and their metallic derivatives represent in many cases the ideal examples to carry out catalytic processes otherwise difficult or impossible to be carried out with conventional diphosphine ligands. The versatility of these species to be modified and modulated both sterically and electronically, makes these compounds and their corresponding transition metal derivatives attractive complexes to be continuously used in different challenging catalytic processes. Thus, around the world several important research groups maintain as priority research lines the design of new pincer ligands, their complexes and their potential applications, while other research groups have foreseen the potential of these complexes by use them as catalyst in different organic transformations. It is noteworthy the use of the palladium-phosphinito PCP pincer complex **27** [39] in the synthesis of corannulenes in high yields recently reported by Siegel and coworkers [40].



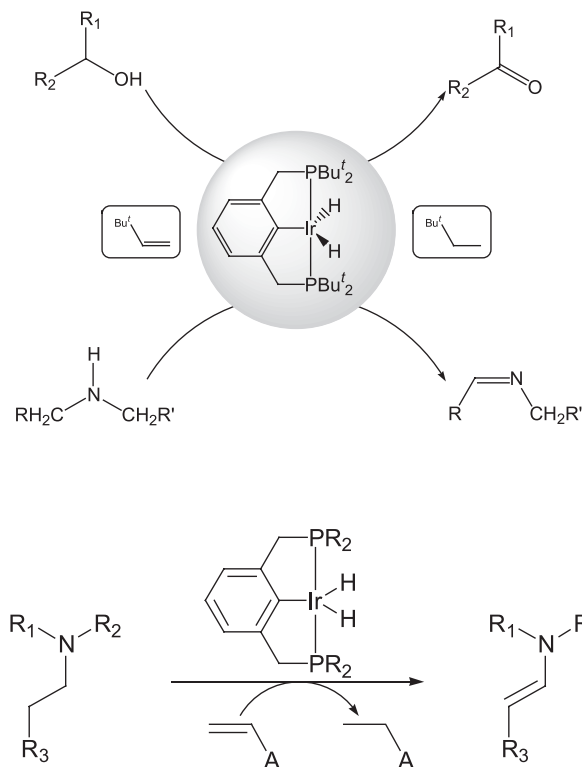
Moreover, Zsabó and coworkers [41] have found the palladium derivatives of NCN and PCP pincer complexes to be active catalysts in the allylic stannylation reaction with high yields.



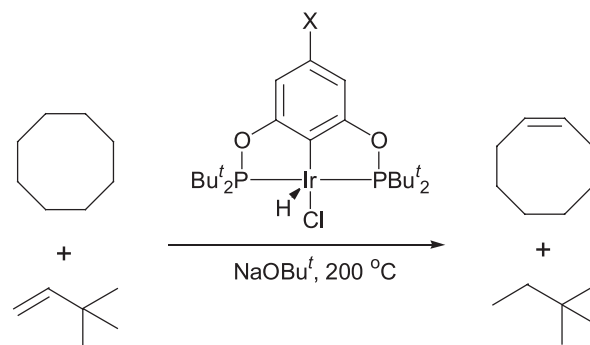
Recently, Morales-Morales and coworkers have extended the application of the iridium pincer complexes $\text{IrH}_2\{\text{C}_6\text{H}_3-2,6-(\text{CH}_2\text{PR}_2)_2\}$ ($\text{R} = \text{Bu}^t, \text{Pr}^i$) for their application in the catalytic dehydrogenation of amine [42] and alcohols [43], providing alternative high yield methods for the synthesis of imines and ketones and aldehydes.

Additionally, Goldman *et al.* [44] has recently reported the use of these same species for the catalytic dehydrogenation of tertiary amines to enamines in good yields.

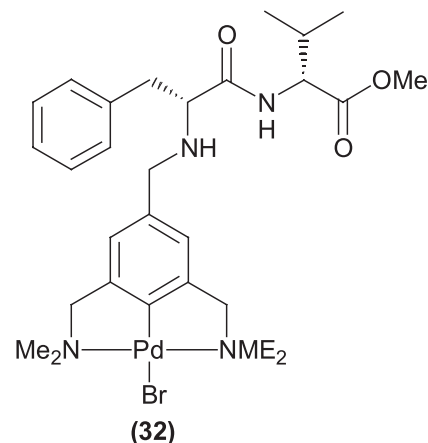
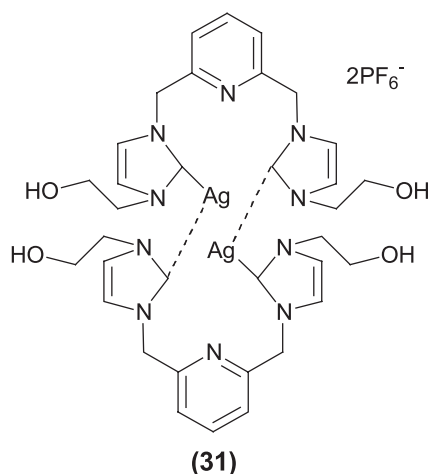
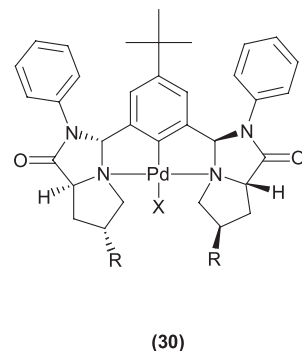
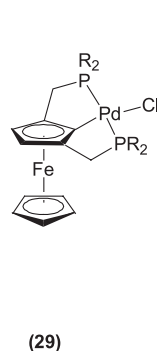
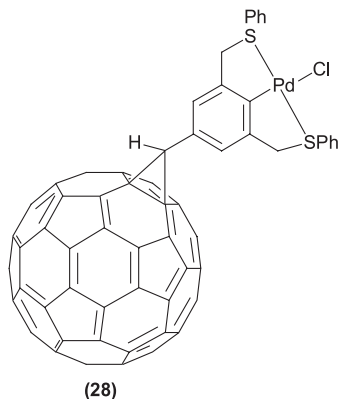
Furthermore, Brookhart *et al.* [45] and Morales-Morales *et al.* [46] have recently reported, independently, the use of Iridium-Phosphinito PCP pincer type complexes in the catalytic dehydrogenation of alkanes, thus matching the yields and



performance of the previously reported phosphino analogues. However, these complexes exhibit additional advantages compared to their phosphino counterparts, such as the fact that the phosphinito PCP pincer ligands can be obtained in an easier manner and in higher yields; and, second, that the hydrido species are not necessary, since this complex can be formed *in situ* by plain addition of a strong base, like NaOBu^t .



The continuous search for more specific ligands [47], has taken several research groups to the synthesis of more complex ligands as well as their transition metal complexes, with more elaborated structures including fullerene (**28**) [48] or ferrocene (**29**) [49] backbones or very sterically hindered ligands (**30**) that have allowed to block, in a very specific way, partic-

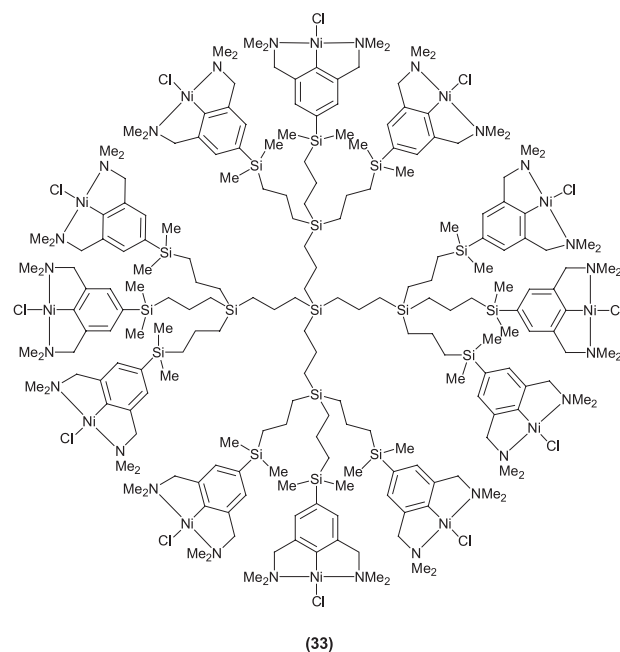


ular quadrants in the complex and thus make them able to provide exceedingly good enantiomeric excess values in, for instance, asymmetric Michael additions [50].

It results easy to forecast that the chemistry of pincer ligands would continue to grow and evolve in the following years, to be included in new and emerging areas of chemistry. Now a days silver(I) systems having the pincer motif in their structure have been considered for their application in Medicinal Chemistry as antimicrobial agents (**31**) [51], bioorganometallic chemistry (**32**) [52], and more recently used in the design of nanostructured and dendrimeric systems for their application in catalytic heterogeneized systems and supramolecular chemistry (**33**) [53].

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