

Recent Applications of Phosphinite POCOP Pincer Complexes Towards Organic Transformations

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Abstract: Pincer complexes have represented a group of very important species in organometallic chemistry in the last decade. Among these, phosphinite POCOP pincer complexes have recently been used profusely in metal mediated organic transformations due to the easiness on their synthesis, high thermal stability and enhanced catalytic activity. This mini-review presents the evolution and recent advances in the chemistry and applications of this important group of compounds in different cross coupling reactions and other transformations relevant in organic synthesis.

Key Words: Cross coupling reactions, POCOP pincer complexes, POCOP pincer ligands, Phosphinite complexes, Platinum group metal complexes, C-C Coupling Reactions, catalysis, PCP pincer compounds.

1. INTRODUCTION

In 1976 Moulton and Shaw [1] reported for the first time a kind of compounds that later will receive the name of “Pincer Complexes or Pincer Compounds” due to the particular coordination that the ligand adopts around the metal center (Fig. 1). These compounds resulted particularly attractive due to their thermal properties, exhibiting melting points above 200 °C without any apparent decomposition. It was later proved that this thermal stability persisted even in solution being able to withstand continuous heating for prolonged periods of time. However, the relevance of these properties and the versatility of such a simple backbone was not exploited but recently, passing from being mere curiosity compounds to achieve the status of chemical players able to perform a wide variety of roles in different areas of chemistry [2], from chemical sensors [3] to extremely efficient catalyst for the activation of strong chemical bonds [4] and from their use as syntons for the synthesis of dendrimeric and nano materials [5] to complexes with potential pharmaceutical applications (Fig. 1) [6].

Thus, the development of the chemistry of pincer compounds has had a steadily growth (Fig. 2) due to the very rich variety of chemical motifs that have been included in their structures (e.g. NHCs heterocyclic carbenes, phosphines, thioethers, oxazolines and so forth) and the multiple applications that these complexes have found so far, this being particularly true in the case of homogeneous catalysis (Fig. 2) [7].

However, one of the caveats on the use of these complexes has been, sometimes difficult or tedious synthesis of the pincer ligands and their complexes. Thus, the independent reports by Morales-Morales & Jensen [8] and by Bedford [9] in 2000, concerning the synthesis of the first **POCOP** phosphinite palladium pincer complexes (Fig. 3), offered an answer to this problem.

These complexes exhibit the same characteristics of robustness and thermal stability and, as it will be shown later, enhanced reactivity compared with their phosphine counterparts and most importantly, *the ligands can be synthesized in a very facile manner.*

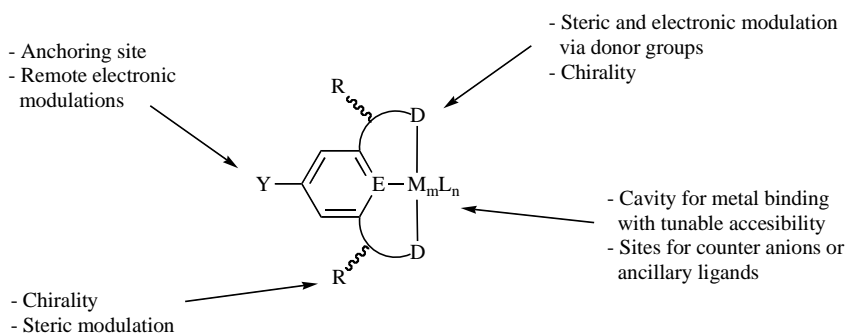


Fig. (1).

Thus, the present paper aims to present the evolution and recent advances on the chemistry of phosphinite POCOP pincer type ligands, their complexes and applications in different relevant organic transformations and catalysis.

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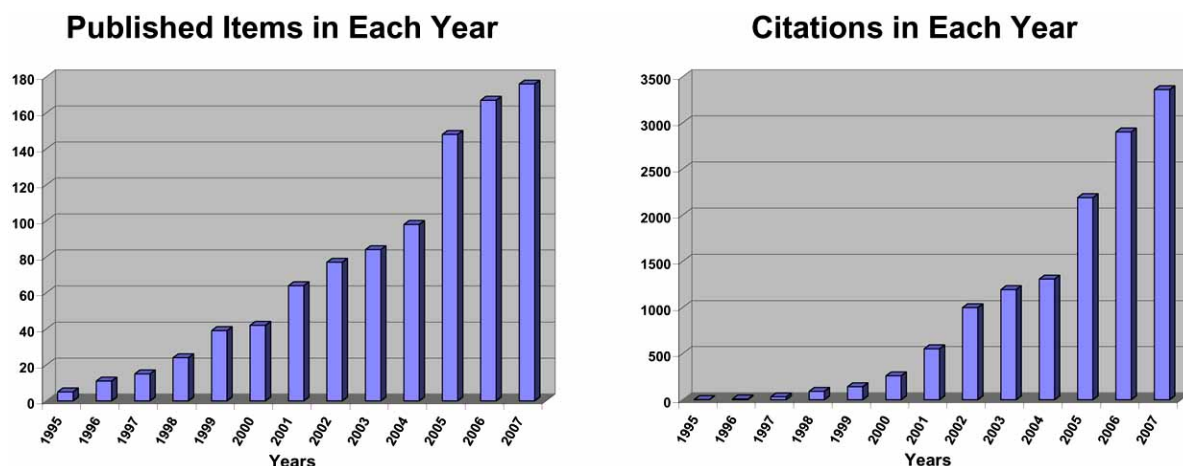


Fig. (2). The graphics illustrate the evolution that publications on Pincer compounds have had in the last decade, as well as the trend for citations to these papers in the same period of time.

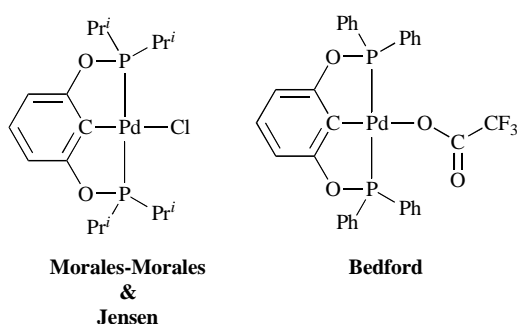


Fig. (3).

2. SYNTHESIS OF THE LIGANDS

In most of the cases, the synthesis of the ligands can be attained in a very facile manner from the corresponding chlorophosphine and resorcinol (for the most commonly known version of the POCOP phosphinite ligands) in the presence of a base (Fig. 4).

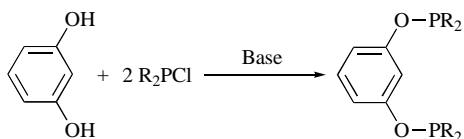


Fig. (4).

This procedure has been used successfully for the synthesis of a variety of POCOP phosphinite ligands (*vide infra*), and the same method has been probed adequate for the synthesis of other pincer ligands containing in their structures at least one phosphinite functionality [10].

3. SYNTHESIS AND APPLICATIONS OF TRANSITION METAL PHOSPHINITE POCOP Pincer COMPLEXES

Given the robustness of the POCOP pincer ligands, in general, all their transition metal derivatives have been synthesized in a very straightforward manner *via* aromatic C-H

activation. Hence, the usual experimental procedure involves thermal C-H activation *via* the reaction under reflux conditions (generally using toluene) of a transition metal salt e.g. $[M(\text{CH}_3\text{COO})_2]$ $M = \text{Ni}, \text{Pd}$ or organometallic e.g. $[\text{PdCl}_2(\text{COD})]$ or coordination e.g. $[\text{PtCl}_2(\text{SEt}_2)_2]$ compounds with the corresponding POCOP ligand or C-H activation *via* oxidative addition to a low oxidation state transition metal complex e.g. $[\text{Pd}(\text{PPh}_3)_4]$ of the corresponding POCOP ligand.

Due to the above mentioned physical properties, most of these complexes were initially synthesized and tested in C-C cross coupling reactions and hence most of the chemistry reported for these compounds has been dominated by the synthesis of several Pd(II) derivatives. Most recently, and due to the importance that their phosphine counterparts have had in the catalytic dehydrogenation of alkanes [11], attention has been placed in the synthesis of the corresponding iridium derivatives, and it has not been but in the last couple of years that the platinum, nickel, rhodium and ruthenium derivatives have been successfully synthesized and their chemistry, in many cases radically different from the phosphine counterparts, explored.

3.1. Palladium Complexes

3.1.1. Heck Reaction

The discovery of the Heck reaction in the 60's changed the way organic chemistry was made until then, becoming a real power tool and achieving nowadays the status of cornerstone in modern organic synthesis [12]. In general, the Heck reaction consists in the coupling of an α -olefin with a chloro, bromo or iodo derivative (Fig. 5). Most of the processes involving the Heck reaction are catalyzed by Pd(II) or Pd(0) derivatives in the presence of an auxiliary ligand in excess.

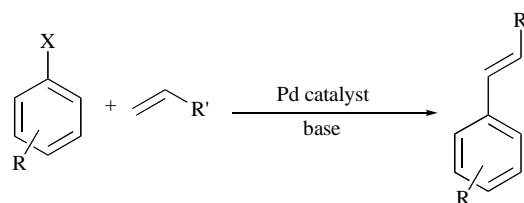


Fig. (5). General scheme of the Heck reaction

Unfortunately, the reaction intermediates formed during the catalytic reaction are sensitive to oxygen or thermally unstable, hampering the coupling process. In recent years several research groups have made important advances with the aim of getting the ideal catalyst with the adequate balance of reactivity and stability to carry out this process efficiently, the results of these experiments have lead researchers to the use of *ortho* metallated complexes, among which the PCP pincer type compounds represent one of the most important examples. In this sense, Milstein and co-workers were the first to employ Pd(II)-PCP pincer complexes (**1**, **2**) in the Heck coupling reaction [13] (Fig. 6).

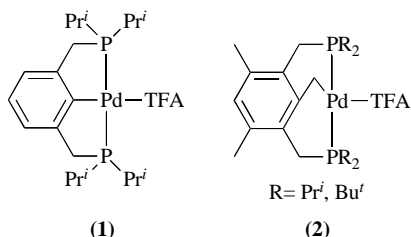


Fig. (6).

Milstein found these compounds to be active without decomposition at reaction temperatures as high as 140 °C, over reaction periods of 300 hours or higher. By using compounds **1** and **2** (Fig. 6), Milstein achieved full conversion in the couplings of iodobenzene with methylacrylate, employing *N*-methyl-pyrrolidine (NMP) as solvent and sodium carbonate as base to attain a maximum of 500,000 turnover numbers (TON) for iodobenzene and up to 132,900 for bromobenzene.

By the same time, Beller and Zapf [14] reported the use of electro-attractor phosphite ligands for the Heck couplings of activated chlorobenzenes (Fig. 7).

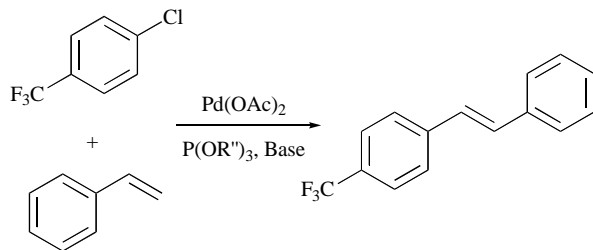


Fig. (7).

Inspired on these results, Morales-Morales & Jensen [8] synthesized an analogous POCOP pincer type ligand based on phosphinito fragments as *P* donors (Fig. 8). The palladium derivatives of this ligand **3** were shown to be efficient in the coupling of chlorobenzenes, being one of the few ex-

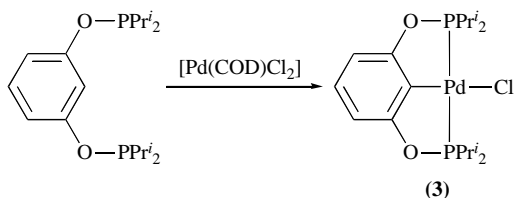


Fig. (8).

amples then known to activate, deactivated or sterically hindered chlorobenzenes [15]. Complex **3** showed to be as reactive as the PCP phosphine derivative reported previously by Milstein [13].

Most recently Ogo, *et al.* have reported the synthesis of water soluble phosphinite POCOP Pd(II) pincer complexes [16]. This compound being obtained by reaction of compound **3** with Ag₂SO₄ in water to afford complex **4** (Fig. 9).

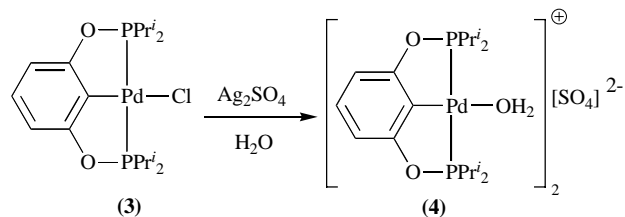


Fig. (9).

However, this species resulted inactive in the C-C Heck coupling reactions of 3-iodo and 3-bromo benzoic acids with 4-vinylbenzoic acid in water at a pH of 10.5.

It has to be noted that, the overwhelming majority of the reported PCP pincer complexes are based on the same structural principle, namely five membered bis-chelating metallacycles. Thus, with the exception of Venanzi's complexes [MBr{C₆H₃(CH₂CH₂PPh₂)₂-2,6}] (M=Pd, Pt) [17], the only reported examples of a PCP bis(phosphino)pincer complex with two six-membered metallacycles all other reported PCP pincer complexes are mainly five-membered metalocycles.

In 2007 Naghipour and Jensen [18] synthesized complex **5** (Fig. 10) in a similar manner as that of complex **3**. This compound resulted to be catalytically more efficient than their five-membered metalocycle counterparts **1** and **3**, even for the activation of chlorobenzene with high turnover numbers. The higher activity of these complex was rationalized in terms of the length of the pincer arms and the size of the palladacycle they generate, which in principle should provide a more flexible system by increasing the P-M-P bite angle.

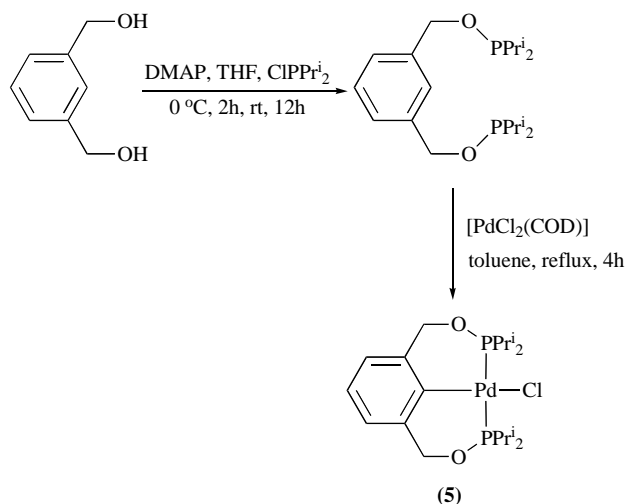


Fig. (10).

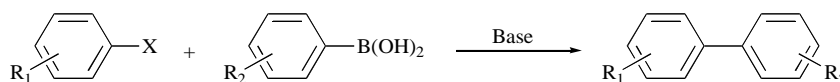
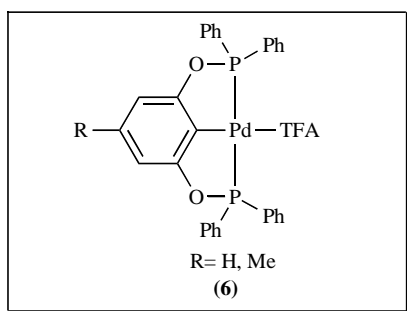


Fig. (11). General Scheme for the Suzuki type couplings.

3.1.2. Suzuki-Miyaura Coupling Reaction

The Suzuki or Suzuki-Miyaura C-C couplings [19] consist in the reaction of a halobenzene with arylboronic acids in the presence of a base (Fig. 11). This reaction proceeds by a similar reaction mechanism as that of the Heck reaction, thus most of the catalysts usually employed in Heck couplings have been successfully employed in the Suzuki reaction.

Complex **6** has been employed by Bedford *et al.* [9] in the couplings of aryl halides with phenyl boronic acid, exhibiting quantitative yields and turnover numbers of 92,000. Both complexes are also efficient in the couplings of deactivated and sterically hindered aryl bromides.



On the other hand, complex **4** (*vide supra*) was also evaluated by Ogo and co-workers in the Suzuki coupling of Ph₄BnA and 3-iodo and 3-bromo benzoic acids in water at a pH value of 10.5. Attaining turnover numbers of 123000 for the case of 3-iodobenzoic acid [16]. These results are very important since they clearly reflect, first, that the phosphinite ligand and their complexes are not sensitive to water and second, that they can withstand considerably basic reaction media.

Recent advances in the use of phosphinite POCOP pincer complexes in Suzuki couplings have been reported by Uozumi *et al.*, providing additionally a novel method for the synthesis of pincer complexes denominated the “*ligand introduction route*” being this method particularly useful for the synthesis of pincer complexes having bulky and/or chemically unstable ligand units [20]. This procedure con-

sists in the oxidative addition reaction of 2-iodoresorcinol to a Pd(0) complex [Pd(PPh₃)₄] (Fig. 12). Once the oxidative addition of 2-iodo resorcinol over the metal center has occurred the following step very much resembles the typical method for the synthesis of POCOP pincer ligands, involving the reaction of the Pd-resorcinol compound (Fig. 12) in a 1:2 molar ratio with the corresponding chlorophosphine in the presence of a base, to afford the POCOP pincer complex.

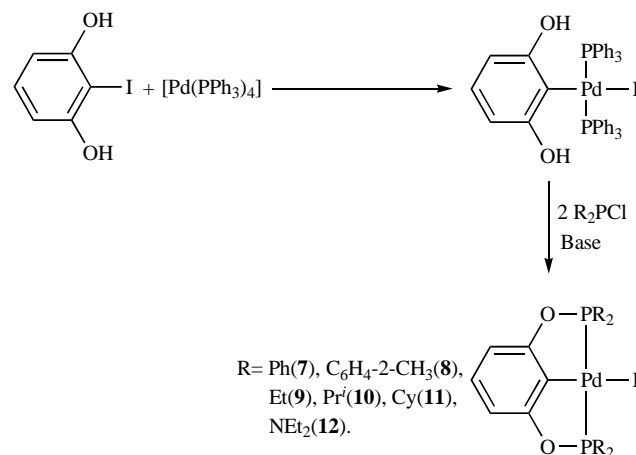


Fig. (12).

The series of complexes **7-12** synthesized by the “*ligand introduction method*” were tested in the Suzuki couplings of 4-bromoacetophenone and phenylboronic acid, exhibiting turnover numbers from 603 to 5790, the lower and higher values attained with complexes **12** and **7** respectively.

3.1.3. Stille Coupling Reaction

The Stille Coupling reaction [21] is a versatile C-C bond forming reaction between stannanes and halides or pseudo-halides, with very few limitations on the R-groups (Fig. 13). Well-elaborated methods allow the preparation of different products from all the combinations of halides and stannanes. The main drawback of this process is the toxicity of the tin compounds used, and their low polarity, which makes them poorly soluble in water. And, although stannanes are stable, boronic acids and their derivatives undergo much the same

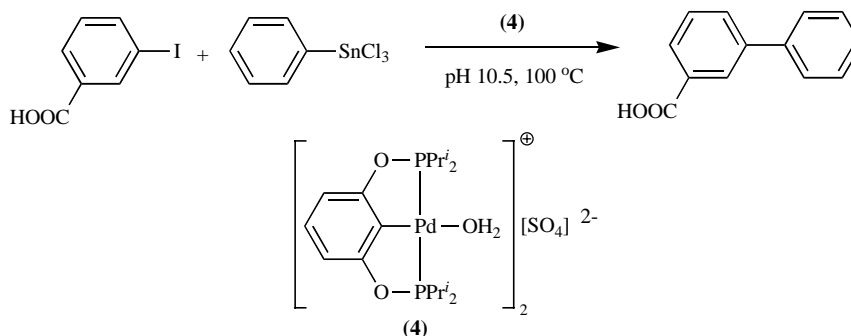


Fig. (13).

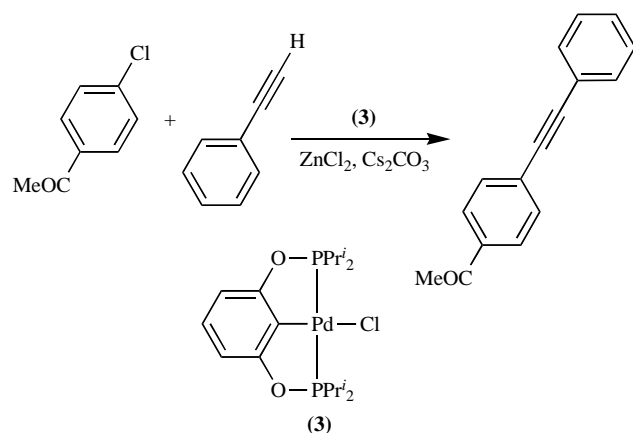


Fig. (14).

chemistry; Thus, in general the Suzuki Coupling reactions are preferred to the Stille couplings in order to avoid the drawbacks of using tin compounds. In fact, the only report of Stille coupling using pincer complexes of any type is provided by Ogo and co-workers [16], using compound **4** (*vide supra*) for the reaction of PhSnCl_3 with 3-iodobenzoic acid in water at a pH value of 10.5, achieving modest yields (42%) and turnover numbers of 2100 at 100 °C.

3.1.4. Negishi Coupling Reaction

In 2002 Jensen *et al.* [22], reported a modified Negishi coupling reaction protocol for the one-pot coupling of a wide array of aryl chlorides with phenylacetylene in the presence of ZnCl_2 using complex **3** as catalyst, achieving yields of 91% for the reaction of 4-chloroacetophenone with phenylacetylene at 160 °C in 24 hours (Fig. 14).

Based on this report, Siegel and co-workers [23] designed an efficient method for the synthesis of pentasubstituted corannulenes from **13** (Fig. 15).

3.1.5. Allylic Alkylation

Further efforts by Jensen's group lead them to the synthesis of a new class of unsymmetric POCOP phosphinite pincer ligand and its palladium derivatives (Fig. 16) [24].

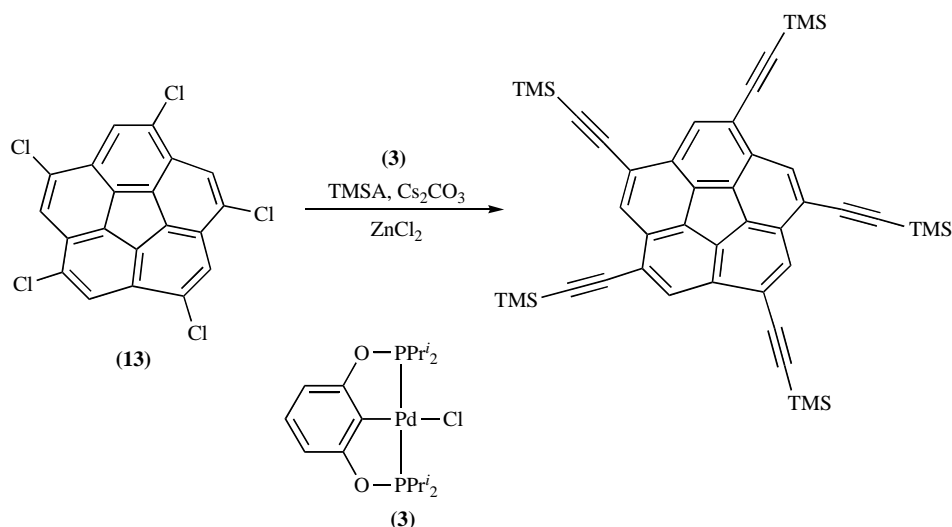


Fig. (15).

Compounds **14-16** were found to be active in the allylic alkylation of cinnamyl acetate with sodium dimethyl malonate, affording exclusively the linear product (Fig. 16). The enhancement in reactivity of these species as compared with compound **3**, being a consequence of the introduction of a six-membered palladacycle into the pincer complex structure, thus making these species more flexible and increasing the P-M-P bite angle. Moreover, the catalytic activity resulted to be strongly dependent of the anion, the more active specie having the less coordinating ligand (OAc⁻) complex **16**.

3.1.6. α -Arylation of Ketones

As it has been for the previously discussed reactions, the palladium catalyzed α -arylation of ketones has become in recent years a useful and general synthetic method in organic chemistry [25]. In this process, an enolate is generated from a ketone and a base in the presence of an aryl halide, then a palladium catalyst couples this enolate with the aryl halide (Fig. 17).

In this context, San Martín *et al.* have recently reported the use of *p*-alcoxy carbonylated POCOP-Pd(II) phosphinite pincer type complexes **17** and **18** for the α -arylation of ketones (Fig. 18) [26].

The procedures developed allow both the regioselective monoarylation and diarylation of hindered and unhindered ketone enolates with a wide variety of aryl bromides with no formation of phenyl-aryl exchange by-products, using significantly low catalysts loadings, achieving yields up to 99% using **17** as catalyst.

3.1.7. Allylation of Electrophiles

In recent years, Szabó and co-workers have directed their attention to explore processes involving the palladium catalyzed allylation of electrophiles. Through several recent publications [27] they have shown that Palladium pincer complexes can efficiently catalyze the electrophilic allylation of aldehyde and imine substrates and the allylation of sulfonimines with potassium trifluoro(allyl)borate. Moreover, the fact that some pincer complexes react very slowly, if at all,

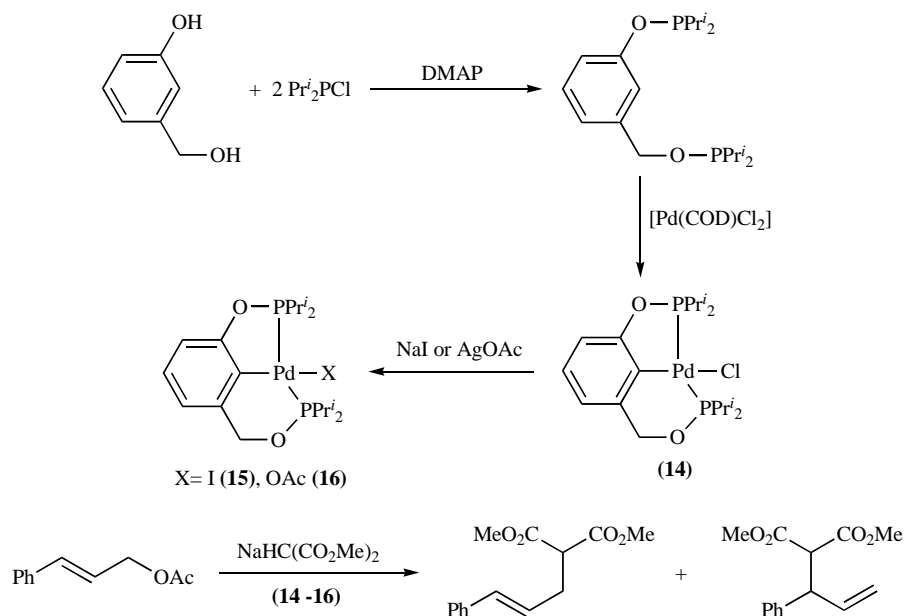


Fig. (16).

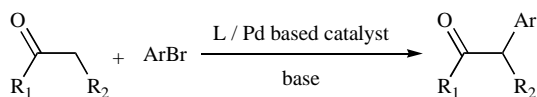


Fig. (17).

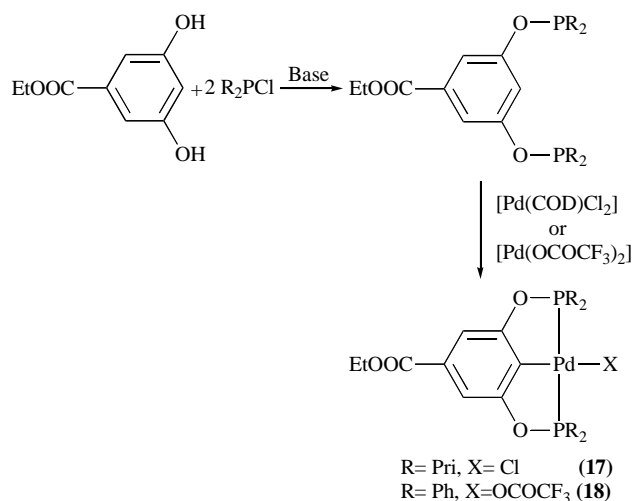


Fig. (18).

with allylstannanes and allylboranes and the possibility for an efficient and fine tuning of the substituents in the donor atoms and therefore the potential reactivity of these pincer complexes, makes them ideal catalysts for the synthesis of reactive organometallic compounds with allyl, allenyl, and propargyl functionalities. Thus, the use of various dimetallic compounds comprising Sn-Sn, Sn-Si, Sn-Se and B-B bonds allows the synthesis under mild conditions of allylstannanes, allylboronates, allenylstannanes, allenylsilanes and to perform in an efficient manner the phenylselenation of organohalides.

From this set of reactions, palladium phosphinite POCOP pincer complexes have been employed successfully in the electrophilic allylation of aldehyde and imine substrates [28] and in the allylation of sulfonimines with potassium trifluoro(allyl)borate (Fig. 19) [29].

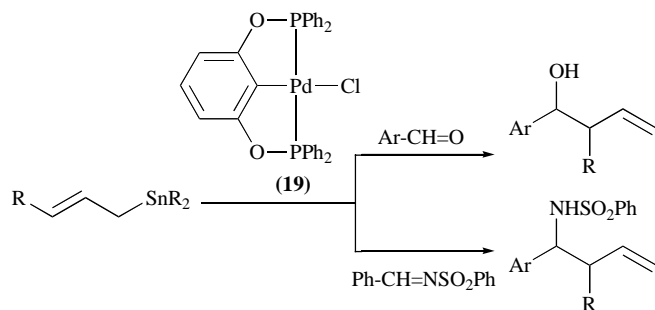


Fig. (19).

This chemistry has been motif of a recent review [30].

3.2. Iridium Compounds

3.2.1. Transfer Dehydrogenation of Alkanes

The first reports regarding transfer dehydrogenation of alkanes using Iridium phosphinite POCOP pincer complexes, were published by Morales-Morales & Jensen [31] and Brookhart *et al.* [32] in 2004. Morales-Morales & Jensen reported on the use of the iridium phosphinite POCOP pincer complex **21** (Fig. 20) for both the transfer dehydrogenation of cyclooctane in the presence of *tert*-butylethylene (TBE) and the acceptorless dehydrogenation of *n*-undecane, finding the reactivity of these complex to be slightly superior to that found for the analogous PCP phosphine derivative $[\text{IrH}_2\{\text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{P}^i\text{Bu}'_2)_2\}_2]$ with similar yields and TONs, exhibiting the same problems of product inhibition and isomerization to internal alkenes (Fig. 21).

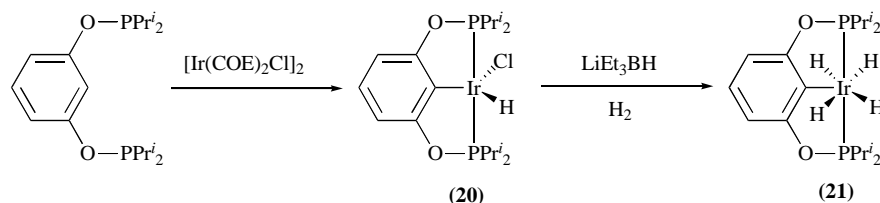


Fig. (20).

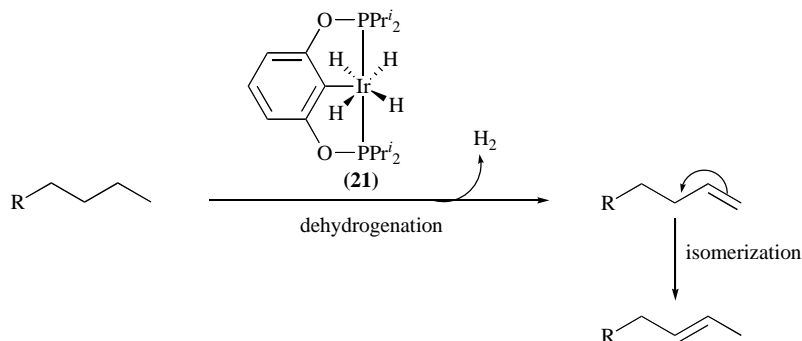


Fig. (21).

On the other hand Brookhart and co-workers [32], synthesized a series of new phosphinite *p*-XPOCOPIrHCl pincer complexes (Fig. 22).

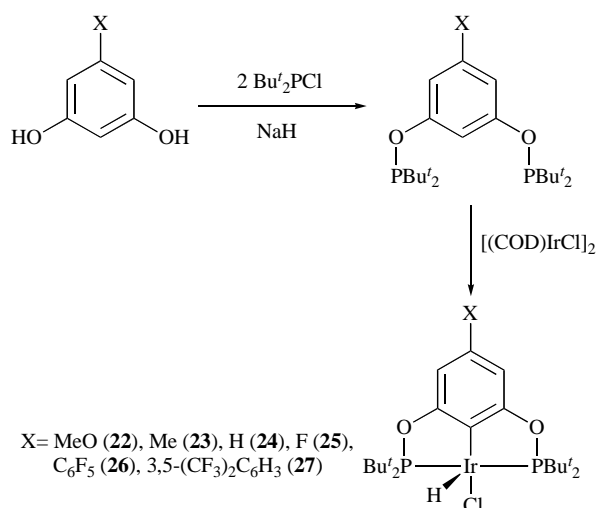


Fig. (22).

Interestingly, in comparison with their phosphine counterparts, where the air and moisture sensitive hydrido-chloride compound has to be converted into the even more sensitive dihydride species by treatment with LiBHET₃ under hydrogen atmosphere. In this case, the generation of the catalytically active species is made *in situ* by reacting complexes 22 to 27 with NaOBu^t (Fig. 23).

Thus, the transfer dehydrogenation of cyclooctane (COA) with *tert*-butylethylene (TBE) to form cyclooctene (COE) and *tert*-butylethane (TBA) was easily accomplished. Under comparable conditions, compounds 22-27 are about 1 order of magnitude more active in terms of TOFs, TONs and substrate conversion than the benchmark catalyst [IrH₂{C₆H₃-2,6-(CH₂PBu^t₂)₂}₂] (28). A further dehydrogenation of COE to form 1,3-COD was accomplished by transfer dehydrogenation

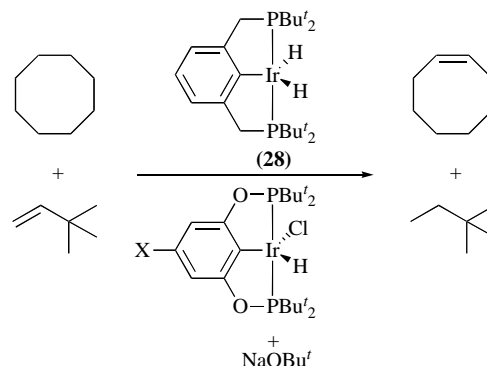


Fig. (23).

in the presence of TBE at high COE concentration. Moreover, in the absence of another hydrogen acceptor, COE itself serves as hydrogen acceptor giving rise to disproportionation of COE into COA and 1,3-COD, which is further transformed into *o*-xylene and ethylbenzene at temperatures as low as 200 °C. However disproportionation of COE into 1,3-COD and COA at 200 °C is only operative at relatively low COE to catalyst ratios (*ca.* 450:1).

Two main problems of the systems presented above are the product inhibition of the catalyst and the isomerization processes. Having this in mind, a catalyst or a combination of catalysts able to consume the newly formed α -olefin would, in principle, avoid both problems. The idea would be even more interesting and profitable if the dehydrogenation process could be carried out in tandem with another process capable to convert the initially formed α -olefins in other high value products. An answer to this problem has been given recently by Goldman and Brookhart, they reported the combined application of an iridium phosphinite POCOP pincer complex with a Schrock-type metathesis catalyst [33]. The idea resulted very simple, to have a catalyst able to acceptorless dehydrogenate linear alkanes for the production of the corresponding α -olefin and once the α -olefin is formed to

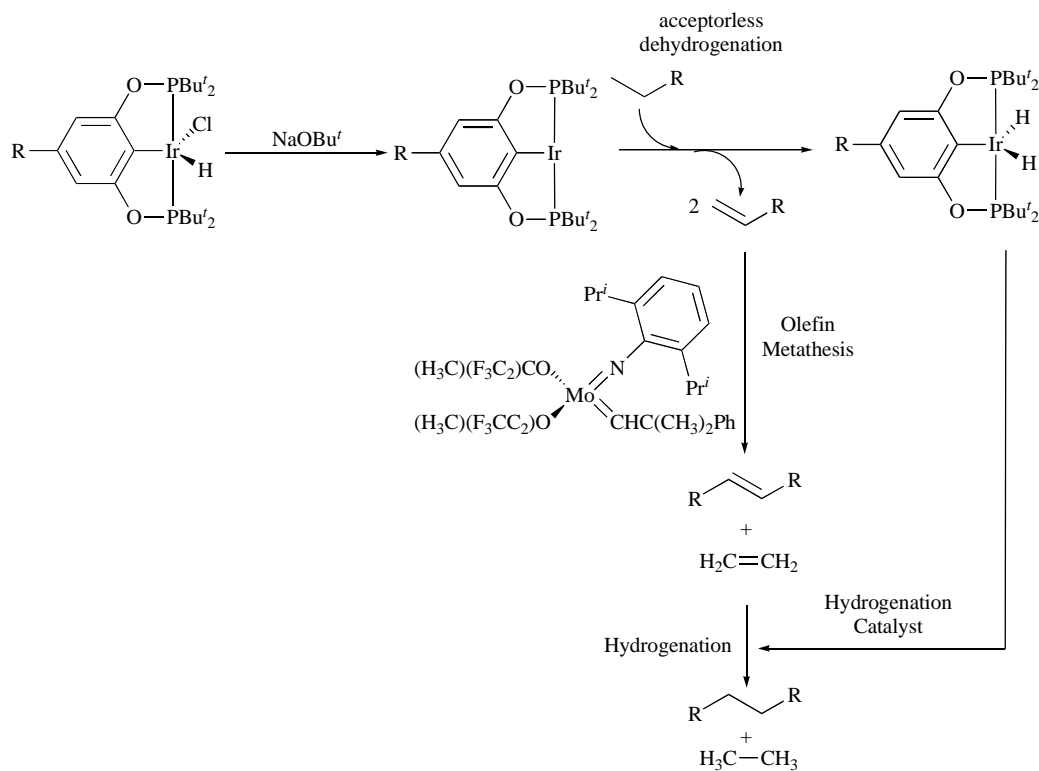


Fig. (24).

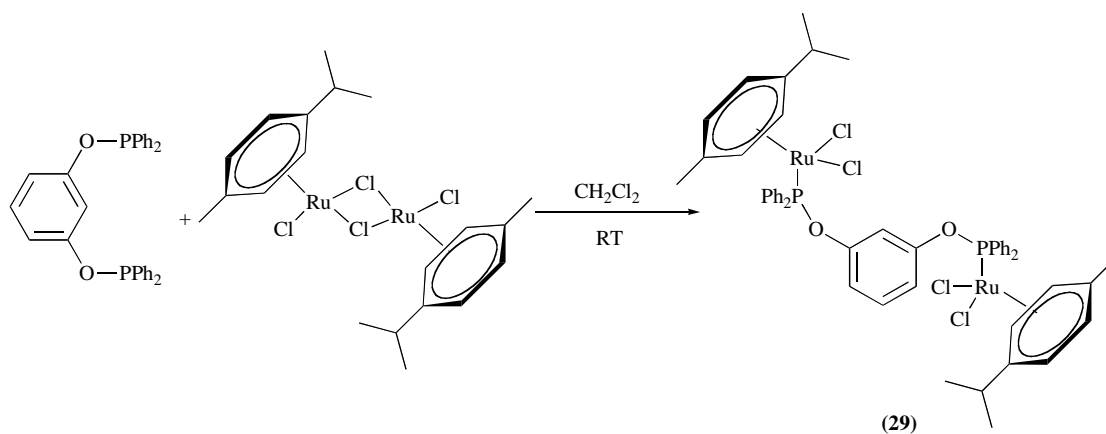


Fig. (25).

undergo olefin metathesis catalyzed by the Schrock-type metathesis catalyst. Thus, the continuous consumption of the formed α -olefin would cause the dehydrogenation catalyst to keep performing its function while the metathesis catalyst will consume any of the α -olefin produced creating a synergic system (Fig. 24). However, in this particular case the PCP phosphine analogue **28** resulted to be more effective than the POCOP phosphinite derivatives, due to faster isomerization reactions to internal olefin using the later catalyst. The present system is completely selective for the linear product (n -alkane). Although the exposed process is promising, the decomposition of the olefin metathesis catalyst appears to limit the conversion, so it is expected that more robust and compatible olefin metathesis catalysts will yield higher turnover numbers.

3.3. Ruthenium Complexes

The first attempts to explore the chemistry of ruthenium phosphinite POCOP pincer complexes did not start until very

recently. Thus, independently Morales-Morales [34] and Bedford [35] reported the first reactions of ruthenium starting materials with phosphinite POCOP pincer ligands in 2006.

Reactions of different ruthenium starting materials with the ligand $[\text{C}_6\text{H}_4-1,3-(\text{OPPh}_2)_2]$ lead to Morales-Morales and co-workers [34] to the formation of intractable mixtures of compounds. However, the compound $[(\eta^6-p\text{-cymene})\text{RuCl}_2]_2$ reacts smoothly with the POCOP phosphinite ligand at room temperature in CH_2Cl_2 to afford the dinuclear complex **29** without the formation of the orthometallated compound (Fig. 25).

Although compound **29** is not necessarily a pincer complex, this specie was tested in the hydrogen transfer of ketones, showing similar results as to those reported by van Koten with the PCP pincer complex $[(\text{C}_6\text{H}_3-2,6-(\text{CH}_2\text{PPh}_2)_2)\text{RuCl}(\text{PPh}_3)]$ **30** for benzophenone and acetophenone (Fig. 26) [36].

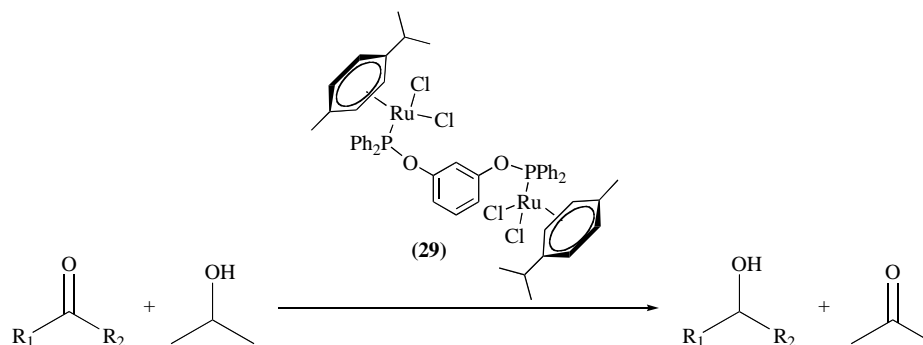
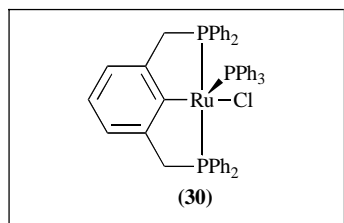


Fig. (26).

Interestingly, complex **29** resulted a much faster catalyst, at least in the case of benzophenone, affording yields up to 84% in only 10 hours whereas van Koten's catalyst **30** affords 98% but only after 108 hours of reaction [36]. Other ketones like propiophenone and 3-heptanone were also tested, however the yields under the same reaction conditions and reaction times were only of 34% and 58% respectively. An interesting result occurred when the transfer hydrogenation of chalcone was attempted, affording the hydrogenation of the alkene C=C bond, without any detectable (GC-MS) amount of alcohol as hydrogenated products, which in fact may favor the use of this catalyst in the regioselective hydrogenation of conjugated enones. It is noteworthy that, extension of the reaction times up to 40 hours afforded quantitative yields in all cases.



Independently, Bedford and co-workers [35], reached similar results as those exposed above, however careful elec-

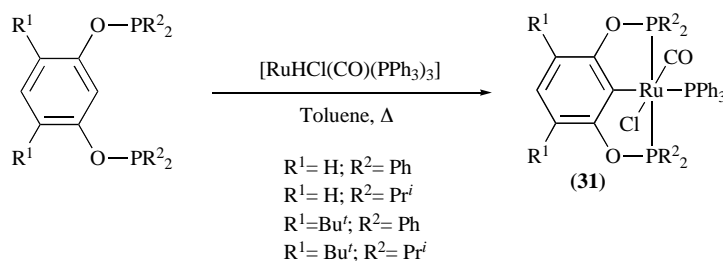


Fig. (27).

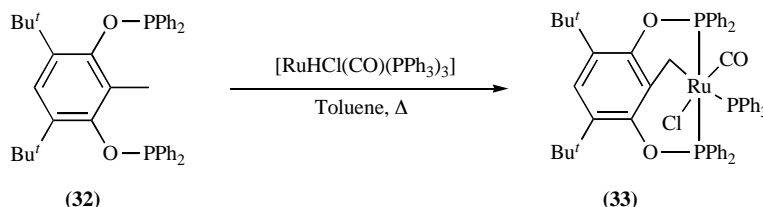


Fig. (28).

tion of the ruthenium starting material and reaction conditions lead them to the desired orthometallated POCOP pincer complexes **31** by reacting $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ with the POCOP phosphinite ligand $[\text{C}_6\text{H}_4\text{-1,3-}(\text{OPPh}_2)_2]$ under reflux conditions in toluene albeit in low yields (Fig. 27).

Phosphinite POCOP pincer complexes can also be synthesized in a straight-forward manner *via* alkyl activation of the ligand **32** with the same ruthenium starting material to produce complex **33** (Fig. 28). These results indicate that ruthenium POCOP phosphinite pincer complexes can be readily synthesized particularly when steric bulk is introduced onto the resorcinol backbone, in which case the C-H activation rate is significantly accelerated. The potential application of these species in both catalysis or metal mediated organic synthesis was not explored.

3.4. Platinum Complexes

The chemistry of platinum phosphinite POCOP pincer complexes has only been reported recently and is limited to a single report by Morales-Morales & Jensen [37]. The novel phosphinite POCOP pincer Pt(II) complex, $[\text{PtCl}\{\text{C}_6\text{H}_3\text{-2,6-}(\text{OPPr}^i)_2\}]$ (**34**) was prepared from the reaction of the ligand $[\text{C}_6\text{H}_4\text{-1,3-}(\text{OPPr}^i)_2]$ and $[\text{PtCl}_2(\text{SEt}_2)_2]$ in good yields (Fig. 29) and the molecular structure of **34** determined through a single crystal X-ray diffraction study. The pincer-ligated platinum complex **34** was tested as catalysts for the hydroxy-

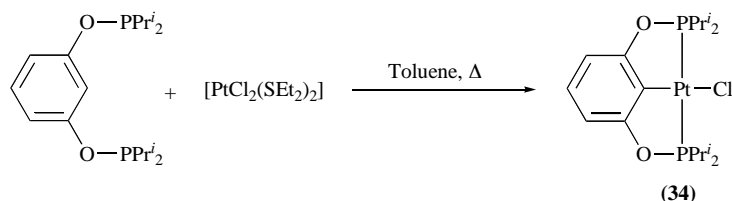
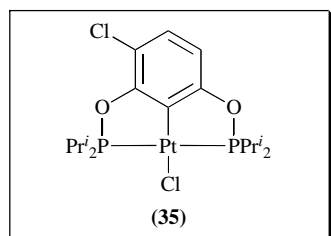


Fig. (29).

lation of 1-propanol to 1,3-propanediol under mild conditions, attaining product ratios and turnover numbers comparable to those obtained with $[\text{PtCl}_4]^{2-}$. However, the pincer complex **34** catalyzes this transformation even upon replacement of PtCl_4 by the more economical CuCl_2 as the requisite stoichiometric oxidant.

Further, analysis of the reaction mixtures by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy following the hydroxylation of 1-propanol by **34** in the presence of CuCl_2 revealed that **34** is partially converted to the ring substituted complex, $[\text{PtCl}\{3\text{-Cl-C}_6\text{H}_2\text{-2,6-(OPPr}^i\text{)}_2\}]$ (**35**). The molecular structure of **35** was also determined through a single crystal X-ray diffraction study.



3.5. Nickel Complexes

Finally, Morales-Morales and co-workers have recently reported the synthesis and applications in catalysis of the Ni(II) phosphinite POCOP pincer complex **36** [38]. This compound was obtained in a very facile manner *via* C-H activation from the reaction of the POCOP ligand $[\text{C}_6\text{H}_4\text{-1,3-(OPPh}_2\text{)}_2]$ with NiCl_2 under reflux conditions in toluene in good yields (Fig. 30). The green compound (**36**) is both air and moisture stable.

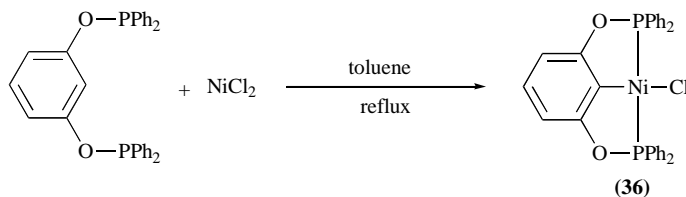


Fig. (30).

The phosphinite POCOP pincer complex $[\text{NiCl}\{\text{C}_6\text{H}_3\text{-2,6-(OPPh}_2\text{)}_2\}]$ (**36**) catalyzes the high yield C-S cross couplings (thiolation reaction) of a broad scope of disulfides using zinc as necessary reducing agent (Fig. 31). The reactivities of a variety of disulfides were examined under optimized conditions and uniformly showed >99 % selective for the corresponding asymmetric sulfide, except for the cases of di-*tert*-butyldisulfide and diphenyldisulfide where the yields for the desired product were reduced by the formation of

biphenyl, product of the C-C homo-coupling of iodobenzene. This fact was explained to probably being due to steric effects due to the larger size of the substituents in these disulfides.

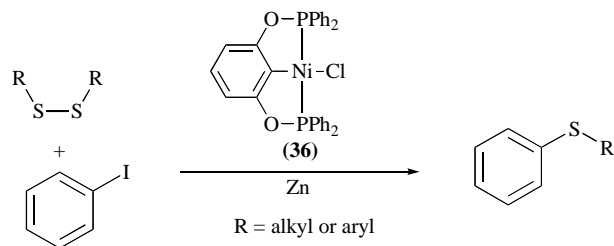


Fig. (31).

A mechanistic proposal for the formation of the products was also formulated (Fig. 32).

Analogous species to **36** have been recently reported by Zargarian and Pandarus [39], including the aliphatic analogs **38** (Fig. 33).

Compounds of the type **38** were oxidized in a controlled manner to their Ni(III) derivatives **39** and proved efficient in Kharasch additions (Fig. 34a), while the cationic acrylonitrile derivative of **37** promoted in good yields Michael additions (Fig. 34b).

4. CONCLUSIONS

The chemistry of phosphinite POCOP pincer compounds has had a steadily growing in the last 7 years. Given the

relevance that these species have reached during this time and based on their facile synthesis it can be anticipated that its chemistry will develop even further by presenting new derivatives with other transition metals and ligands and based on the ingeniousness of the chemistry community other applications of considerable importance in a wide variety of areas in Chemistry, particularly in metal mediated organic synthesis and homogeneous catalysis.

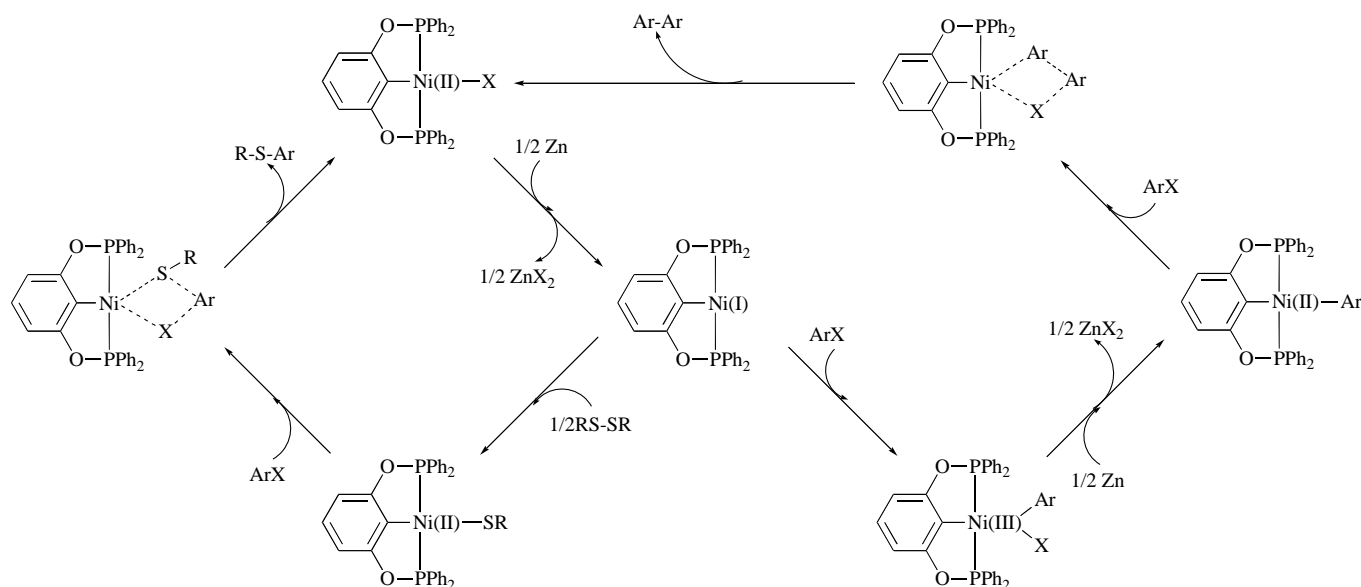


Fig. (32).

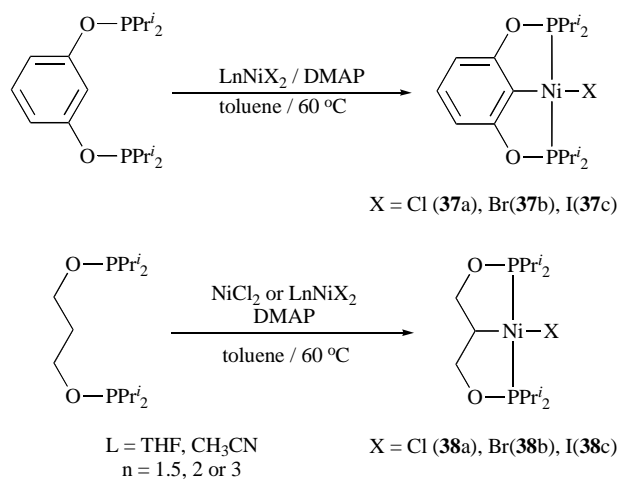


Fig. (33).

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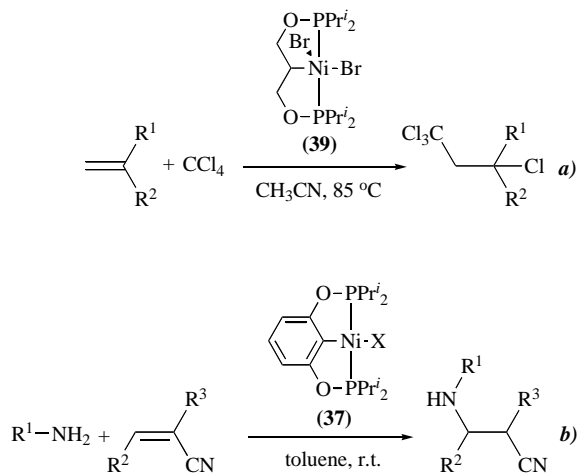


Fig. (34).

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