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NEWER ASPECTS IN THE SYNTHESIS OF ORGANOCHALCOGENIDES AS HYBRID LIGANDS

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ABSTRACT

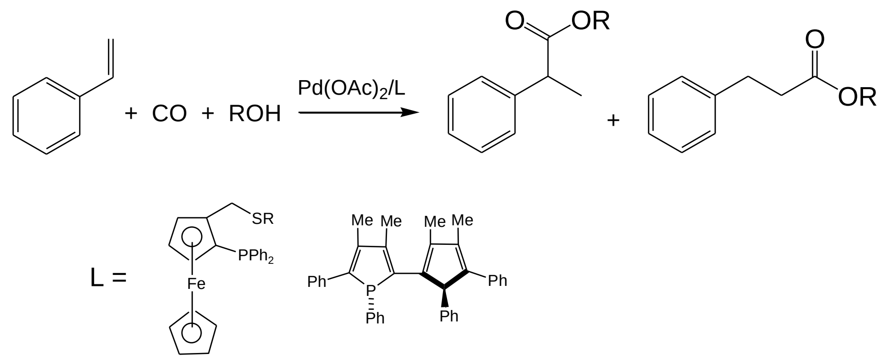
Heterolabile hybrid ligands are intensively studied and find wide applications in coordination as well as in organometallic chemistry. Organochalcogenides, R_2E_n (E = Se, Te and n = 1, 2) have received renewed interest as these compounds play an important role in organic synthesis as intermediates and in pharmaceutical industries for their potential biological activities such as antiviral, antihypertensive, antioxidant, antimicrobial and anticancer properties. These ligands are flexible species, wherein the distance between the chemically active functionalities can be modulated via reversible chemistry on metal centre coordinated to hemilabile ligands. The hemilabile bidentate ligands used to synthesize these systems employed strong-binding phosphine and weak-binding sites incorporating chalcoethers (O, S or Se).

Keywords: Chalcogenides, ligand, pyridine, phosphene, Selenium,

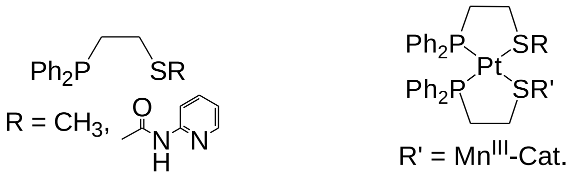
I. INTRODUCTION

Heterolabile hybrid ligands are intensively studied and find wide applications in coordination as well as in organometallic chemistry. Unique properties of the metal complexes and their ability to generate hemilabile systems often display enhanced reactivity [1], particularly soft/hard bases. Ligating systems containing P/N and P/O assemblies are able to coordinate reversibly to a metal center and provide/protect temporarily a vacant coordination site.

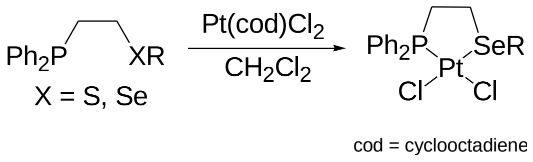
The methoxy carbonylation of styrene has been achieved using $Pd(OAc)_2$/L catalytic systems with L being a chiral ferrocene or biphosphole-based ligands.[2]



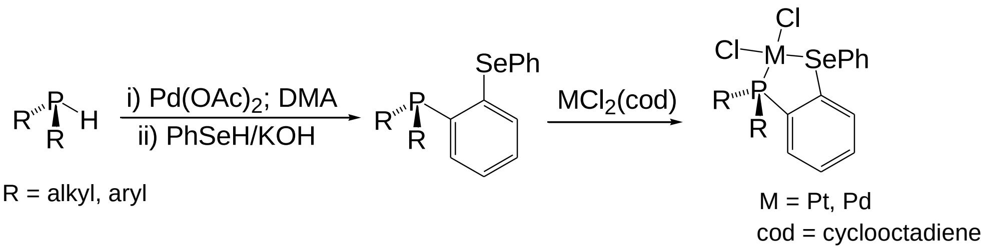
Schatz *et al.*, [3] described a heteroligated, hemilabile Pt (II)-P,S tweezer coordination complex that on combination with a Mn (III)-salen epoxidation catalyst, leads to an inversion of the major epoxide product.



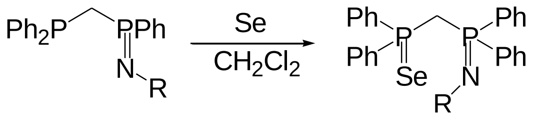
Bidentate phosphine-selenoether (P, Se) ligands have been synthesized and their heteroligated Pt(II) complexes studied by Rosen *et al*.[4]



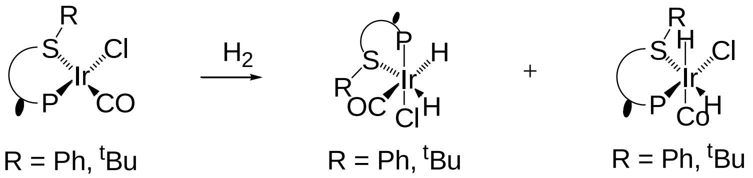
Tertiary phosphines based seleno-ethers functionalized with aryl or alkyl backbones have been recently reported.[5]



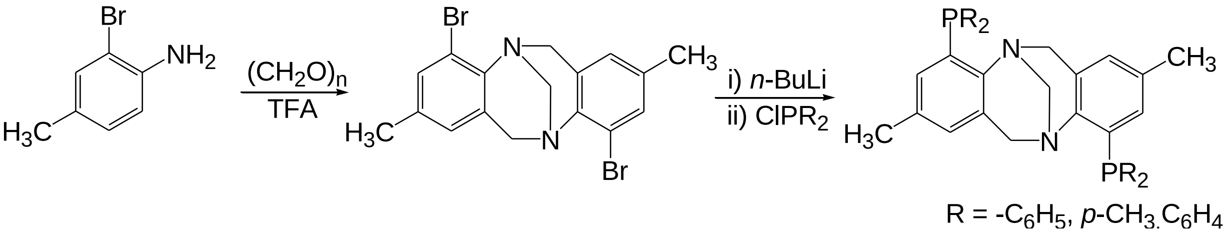
A family of mixed ligands have been synthesized by the oxidation of $Ph_2PCH_2P(=NR)Ph_2$ with elemental selenium.[6]



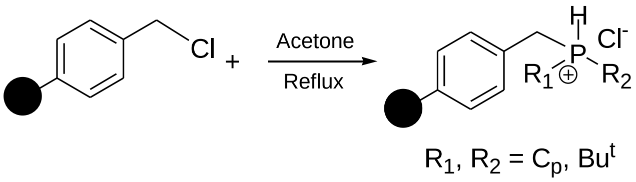
Iridium carbonyl complexes containing P, S ligands undergo H_2 addition across the S-Ir-CO axis to form two distinct diastereo isomeric products.[7]



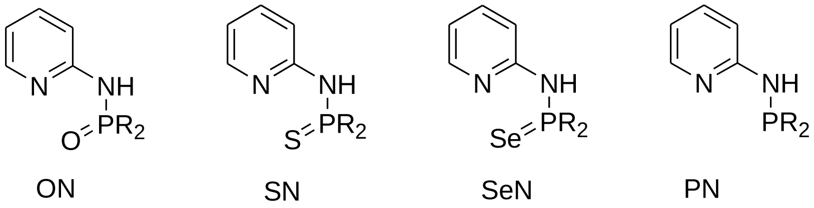
Pereira *et al.*,[8] have achieved concise two step synthesis of novel C_2-symmetric PN ligands.



A simple, efficient one-step route to polystyrene-supported trialkyl phosphine ligands is reported by Robertson and coworkers.[9]



A series of cationic palladium allyl complexes with several hetero difunctional EN (E= P, O, S, Se) ligands based on N-(2-pyridyl) amino phosphines containing O, S and Se have been prepared recently.[10]



II. RESULT AND DISCUSSION

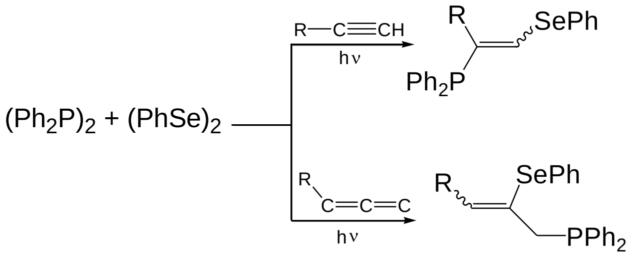
Organoseleneium compounds are attractive molecules due to their biological activities and selective reactions. Interest in the synthesis of these compounds have increased in previous years due to their applicability in material sciences and in catalysis.

Coordination chemistry based approaches for constructing supramolecular assemblies are well established with three general sub-strategies emerging namely the directional bonding[11], symmetry interaction[12] and weak-link approaches[13]. The former two approaches result in rigid structures. The later weak-link approach, WLA is unique and yields flexible species wherein the distance between the chemically active functionalities can be modulated via reversible chemistry on metal centre coordination to hemilabile ligands. Metals that have explored in the WLA approach include Pd(II)[14], Pt(II)[15] and Cu(I)[16] The hemilabile bidentate ligands used to synthesize WLA systems employed strong-binding phosphine and weak-binding sites incorporating chalcoethers (O, S or Se). The diverse tool box of metals and ligands explored has resulted in the synthesis of increasing sophisticated molecular architectures including tweezers[14], triangular prisms [17], macrocycles and triple layer complexes.[18]

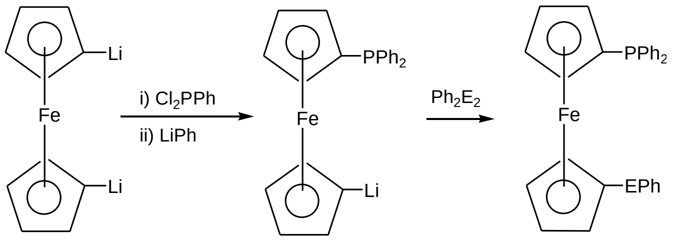
Tertiary phosphines continue to remain an integral tool in the design and synthesis of new metal based complexes. Hybrid tertiary phosphines, bearing additional donor atoms such as oxygen and nitrogen have frequently been described as hemilabile by virtue of their soft/hard donor atom combination[19]. Considerable recent interest has focused on mixed P,O– and P,S– ligands for their fascinating coordination chemistry [20] including water-soluble macrocyclic complexes using a weak-link approach [21] and catalytic applications. [22] Tertiary phosphines with an additional selenium donor centre have been very poorly developed in comparison to their lighter group 16 counterparts.[23]

Synthesis of heterodifunctional ligands, carried out recently deserve a special attention.

A novel combination of tetra-phenyl diphosphine and diphenyl diselenide under photo-irradiation conditions resulted in simultaneous introduction of diphenyl phosphino and phenyl seleno groups into carbon-carbon unsaturated bonds regio-selectively.[24]

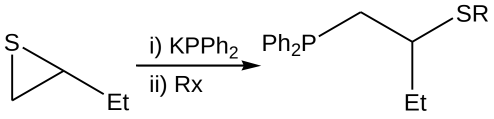


The reaction of unsymmetrical ligands, 1-diphenyl-phosphino-1-(phenyl sulfanyl/selanyl)ferrocene with several group 11 metal derivatives leads to the synthesis of following complexes.[25]

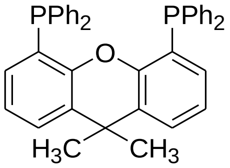


E = S or Se

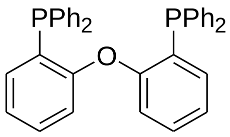
Dervisi *et al.*,[26] have reported the synthesis of the benzyl phosphino thio-ether derivatives and their corresponding palladium complexes.



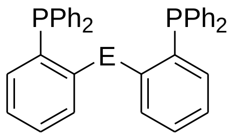
Weller and co-workers [27] have reported a catalyst for inter-molecular hydroacylation of alkenes and alkynes using β- substituted aldehydes.



Xantphos

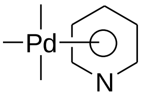


Dpephos

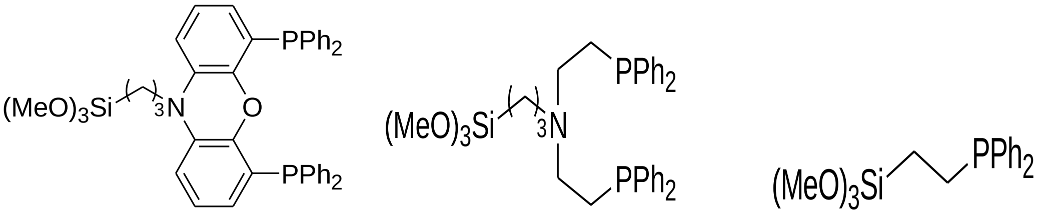


E = S, CH_2

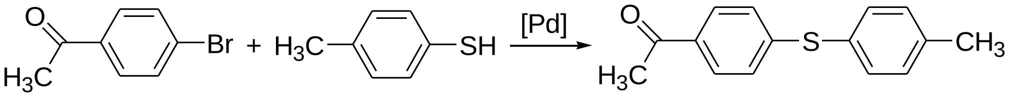
The pyridyl complexes containing triphenyl phosphine can act as catalysts for cross coupling reaction of bromo-pyridines.[28]



Both bidenate and monodentate phosphine ligands form stable palladium catalysts. Immobilisation of palladium phosphine complexes on silica has been demonstrated to be a viable method for the recovery without catalyst deterioration and metal leaching.[29]

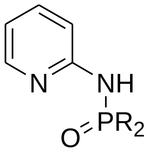


N-Heterocyclic carbenes, NHCs have proved to be useful ligands for palladium-complex catalysis in Pd-catalysed, C-S cross coupling reactions to produce the functionalized sulfides in good yields.[30]

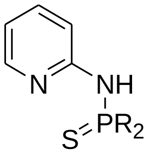


[Pd] = Palladium complex

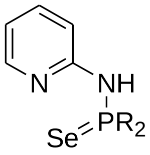
Synthetically useful cationic palladium allyl complexes containing several heterodifunctional EN (E = P, O, S, Se) ligands based on N-(2-pyridyl)amino phosphines and oxo, thio and seleno derivatives are well documented.[31]



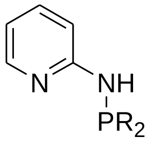
ON



SN



SeN



PN

III. CONCLUSION

In brief, the present investigation deals with study of the synthesis and characterization of Hemilabile hybrid ligands. Importance of these hybrid ligands is due to their mixed donor characterstic of soft chalcogen, phosphorus and hard nitrogen atom which provide a significant insight into the competitive coordinating behaviour towards the same central metal ion.

IV. ACKNOWLEDGEMENT

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