Efficient catalytic systems for olefins formation

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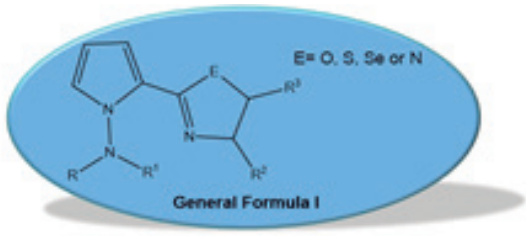
(Status: patent pending)

Abstract

This invention describes a synthesis method to produce functionalized styrenes with better yields and safer reaction conditions using a new family of pyrrole-based ligands (General Formula I), which enhances the Palladium catalytic activity.



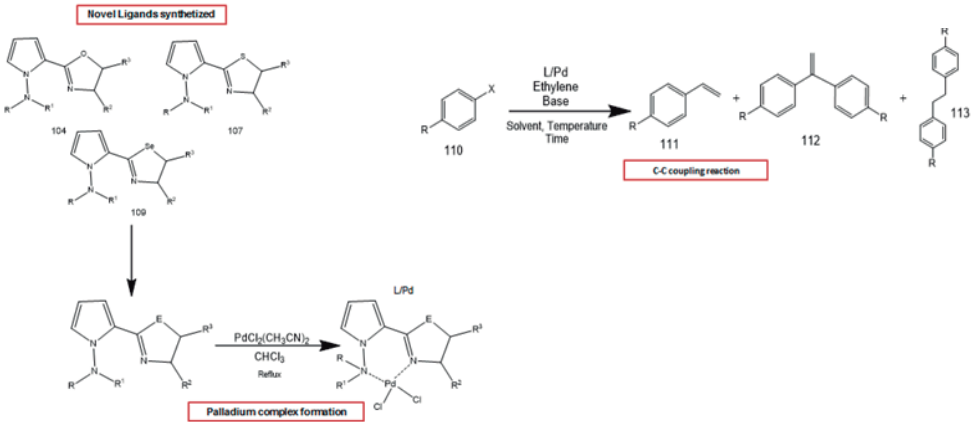
Background

The styrene is one of the most important chemical compounds in the plastic industry. Its synthesis is currently made by the ethylbenzene catalytic dehydrogenation, which uses inorganic oxides (like Fe_2O_2) as catalyst. These reactions are made under extreme conditions, such as high temperatures and pressures. Therefore, the current methods have huge disadvantages, like their reversible and endotherm character and their need of a great amount of water vapor, which is traduced into high costs.

In 2010, the novel prize of chemistry was given to Heck for the C-C coupling using Palladium (Pd) as catalyst. This reaction was used to produce styrene and has already been reported, but with yields from medium to good.

By adding ligand compounds it is possible to get better results in the Heck reaction, producing higher yields of styrene in safer conditions.

This invention describes the synthesis of pyrrole-based ligands that can be used to enhance the catalytic activity of the Palladium and produces functionalized styrenes.



Stage of research

The researchers have already synthetized three pyrrole-based ligands (compounds 104, 107 and 109). They also make these ligands react with Bis(acetonitril) dichloropalladium (II) to form a Palladium complex, later used as catalysts.

To form the terminal olefins, it was used the C-C coupling reaction between different aryl halides (Structure 110, in which the R-functional group and the position on the aromatic ring vary) and ethylene in the presence of the palladium complexes synthesized.

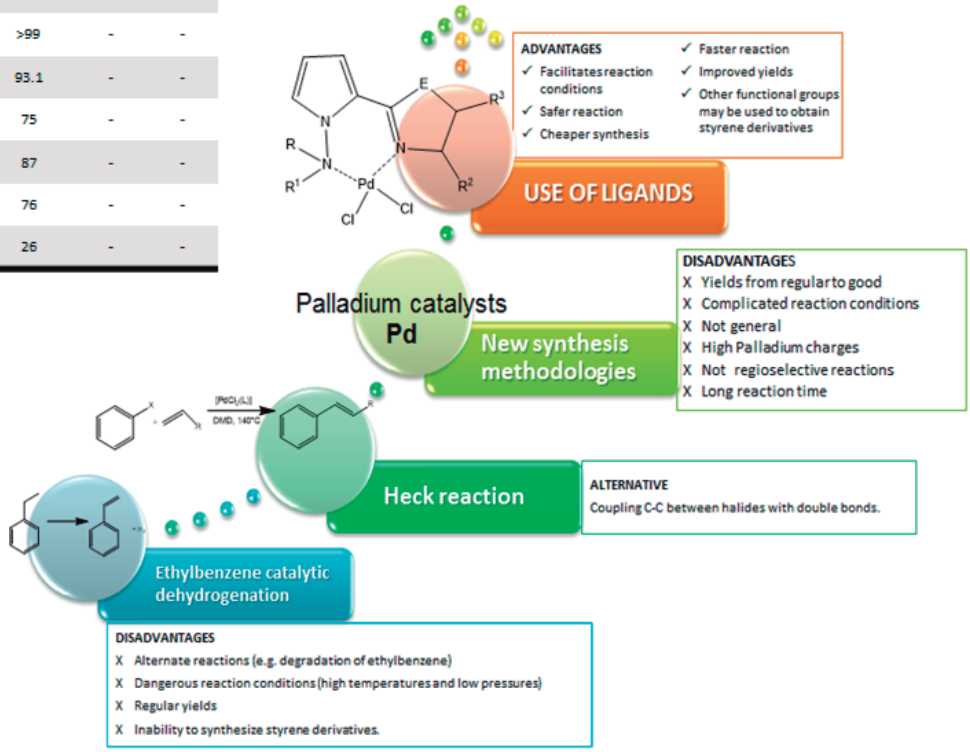
Under optimum conditions (usage of the synthesized binders (104, 107 and 109), correct temperature, pressure, base and time of reaction), it is obtained exclusively the product of the mono coupling, shown in structure 111. This means that it is a regioselective reaction under the right conditions.

#	R	Time (h)	110 (%)	111 (%)	112 (%)	113 (%)
1	(1a)p-NH3	2	-	-	-	-
2	(1b)p-OCH3	2	6.2	93.8	-	-
3	(1c)p-CH3	2	6.1	93.9	-	-
4	(1d)H	2	16	80.3	-	3.7
5	(1e)p-Br	2	13	81.6	5.3	-
6	(1f)p-COCH3	1	37.7	62.3	-	-
7	(1f)p-COCH3	2	4.8	95.2	-	-
8	(1g)p-COOCH3	1	17.8	82.2	-	-
9	(1g)p-COOCH3	2	4.3	95.7	-	-
10	(1h)p-CF3	1	23.9	63.1	-	-
11	(1h)p-CF3	2	12.3	87.7	-	-
12	(li)p-NO2	1	-	>99	-	-
13	(lj)p-CN	2	6.9	93.1	-	-
14	(lk)m-CH3	2	25	75	-	-
15	(ll)o-CH3	2	13	87	-	-
18	(lm)p-NHCOCH3	2	-	76	-	-
19	(ln) Fc-I	2	74	26	-	-

Table No. 1 Yields obtained from the final olefins

Applications

This invention application goes to the plastic industry, giving the option to improve the current methods of styrene (and its derivatives) synthesis. With these novel ligands, the reaction conditions change into safer and faster conditions, which could be traduced in more economic processes and industrial security.



Advantages

The use of these novel ligands improve the C-C coupling reaction, obtaining better yields and allowing us to syntheses styrene derivatives, not only styrene, something that cannot be done with the traditional ethylbenzene catalytic dehydrogenation.

How do they do this? These ligands modulate the Palladium electro density, stimulating the C-C coupling.

Expectations

- Improvement of this invention at an industrial scale is being developed.
- Potent ligands can be further developed.
- The application of this invention in the industry could lead to the improvement of the current synthesis used.
- The application of styrene derivatives obtained with this method could be applied in many fields.