Palladium Schiff Base Complexes: Potential Catalysts for C-C Bond Formation

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INTRODUCTION

The construction of new C-C bonds is of central importance in Organic Chemistry for the assembly of complex molecular frameworks with diversified interests and applications such as:

- Development of new Drugs,
- Industrial Chemical Processes,
- Synthesis of Pharmaceuticals,
- Biologically Active Compounds,
- Natural product synthesis and
- Material chemistry.

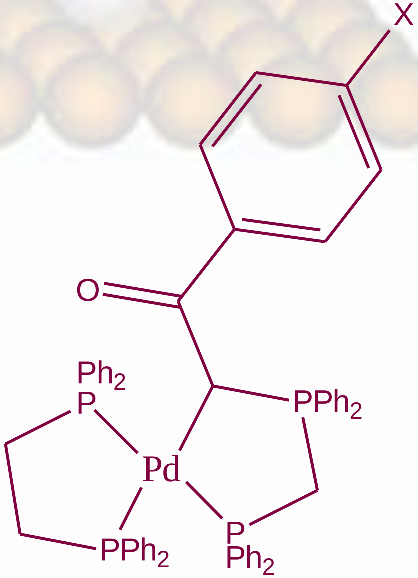
The emergence of cross-coupling as a popular method in synthesis arises from the diversity of transition metal complexes which have been developed and used successfully as catalysts in these reactions.

Among the ones used, Palladium occupy a unique position since:

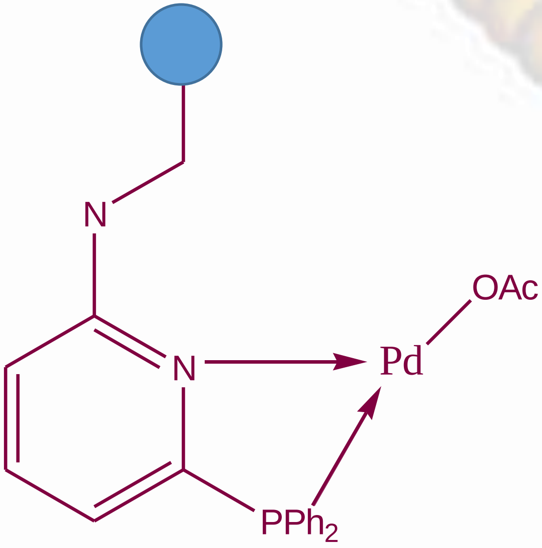
- Facile decomposition to Pd(0).
- Cheaper than platinum.
- High recovery of palladium catalyst.

Russell, M. J. H, *Platinum Met. Rev.* ***1989***, *33, 186*

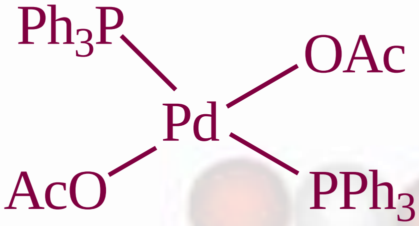
Palladium phosphine complexes that have been used in C-C bond formations (Heck & Suzuki):



(Sabounchei & Ahmadi, 2013)



(Liu et al, 2014)



(Amotore et al, 1994)

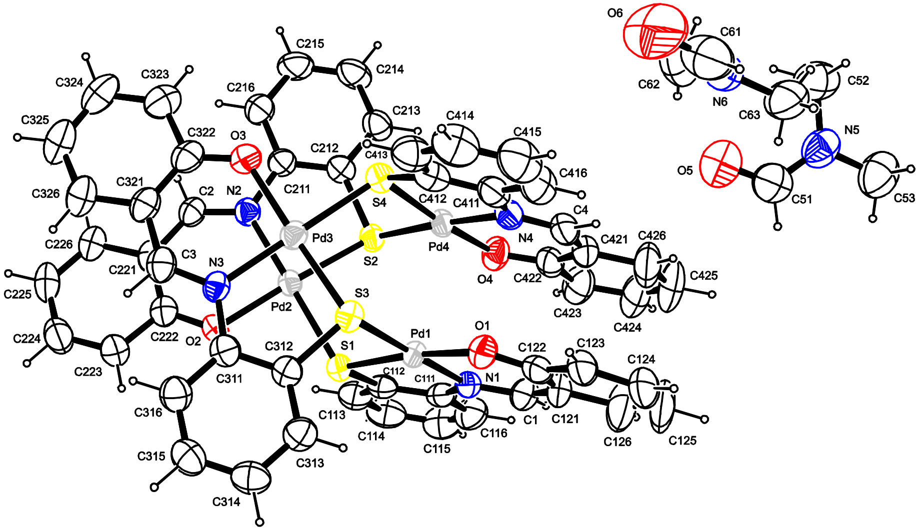
Drawbacks of palladium phosphine complexes:

- Expensive
- Air sensitive.
- Unstable.
- Sometimes precipitate.

Therefore the need to develop cheaper and more stable palladium-based catalysts.

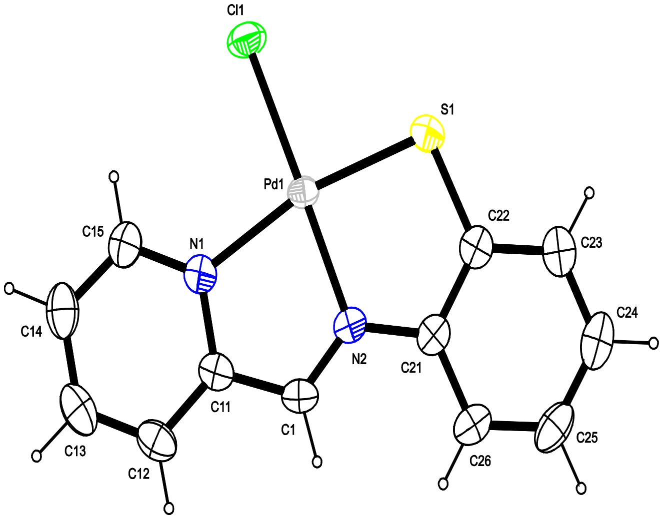
The C-C coupling reactions that have been studied in this work:

- Heck,
- Suzuki and
- Michael Addition reactions.



$[\mathrm{Pd}_4(\mathbf{dbbs})_4]$ (**1**)

$(\mathbf{dbbs})_2$ = *N,N'*-(1,1'-dithio-bis(phenylene))bis(salicylideneimine)



$[\mathrm{Pd}(\mathbf{dpds})\mathrm{Cl}]$ (**2**)

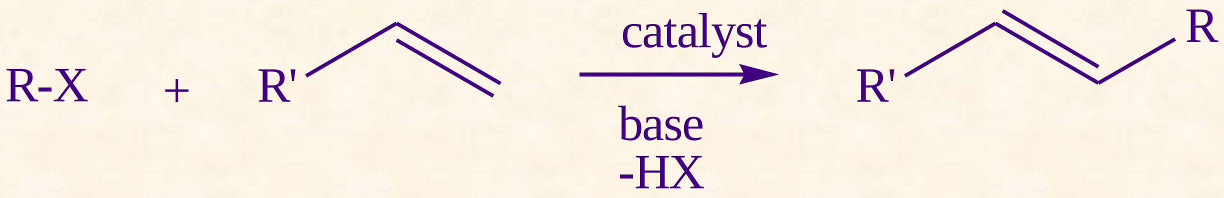
$(\mathbf{dpds})_2$ = *o,o'*-(*N,N'*-dipicolinyldene)diazadiphenyl disulfide)

In this work, palladium complexes (**1**) and (**2**) derived from Schiff Base ligands have been used as catalyst for cross coupling reactions

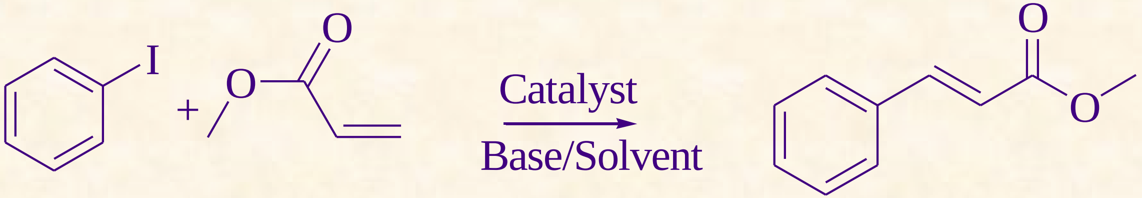
Moosun, S. B., Bhowon, M. G., Hosten, E. C., Jhaumeer-Laulloo, *S. J. Coord. Chem*. **2016**

Heck Reactions

It involves the coupling of an aryl, vinyl halide or sulfonate with an alkene.



The cross coupling of iodobenzene with methyl acrylate was investigated.



Methyl cinnamate

The formation of the methyl cinnamate was confirmed by ^{1}H NMR and GC/MS data

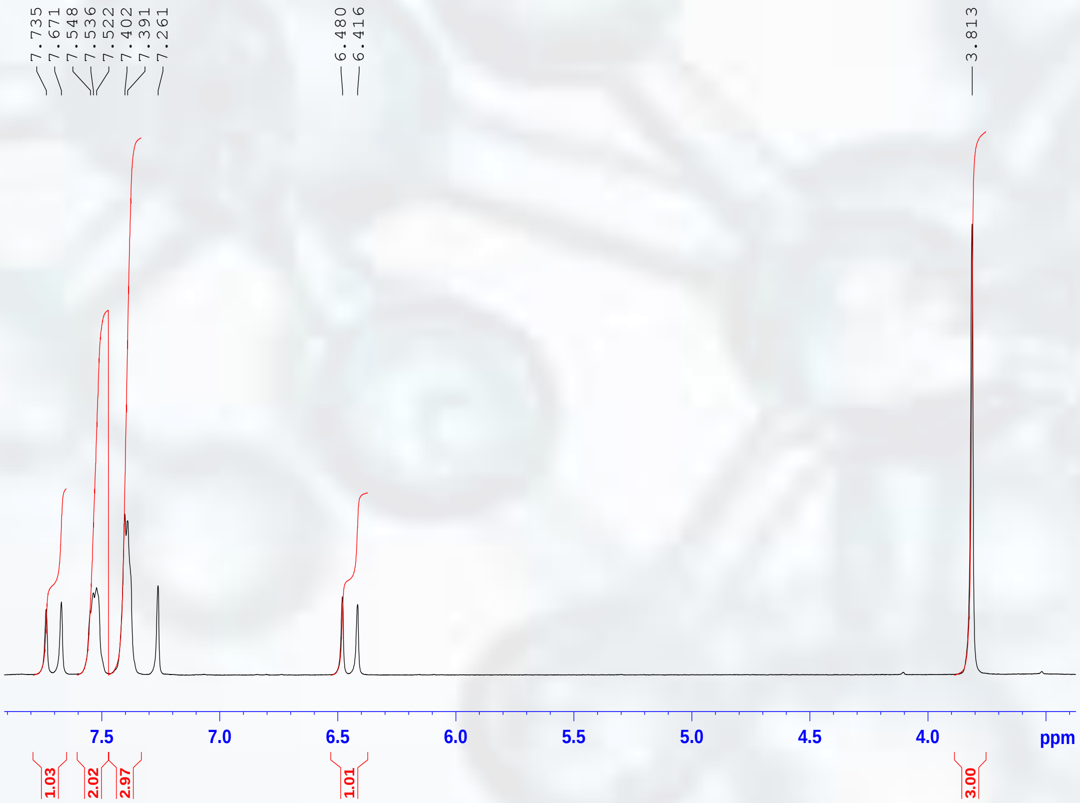


Fig. 1.0: ^{1}H NMR spectrum of methyl cinnamate

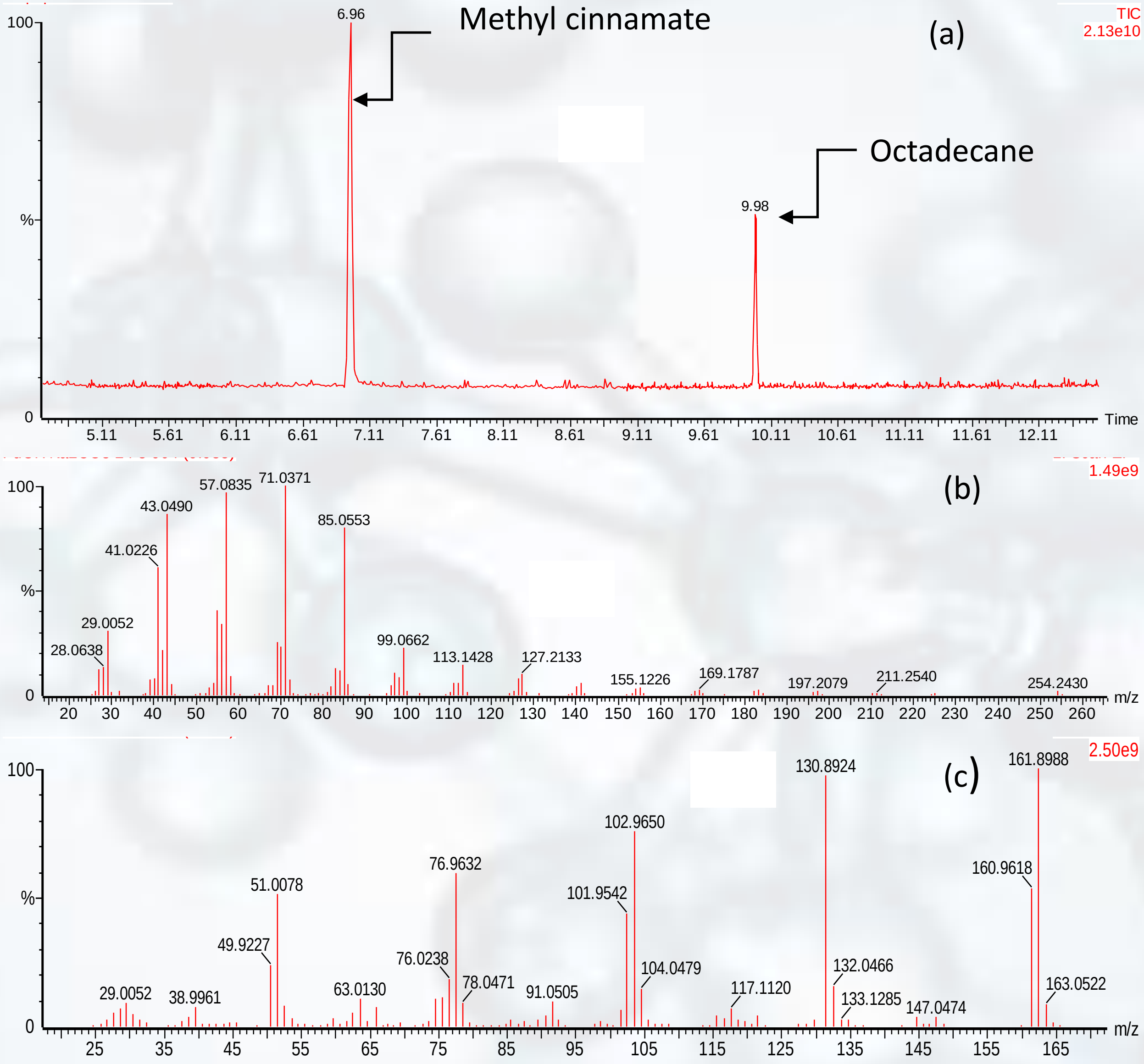
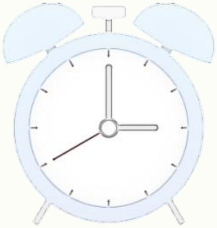


Fig. 2.0: (a) GC chromatogram of methyl cinnamate and octadecane; (b) Mass spectrum of octadecane; (c) Mass spectrum of methyl cinnamate.



Optimization of reaction conditions

The reaction conditions were systematically optimized in the standard reaction of iodobenzene with methyl acrylate using catalyst **1**. The parameters that were being investigated are:

- Time,

- Solvent,

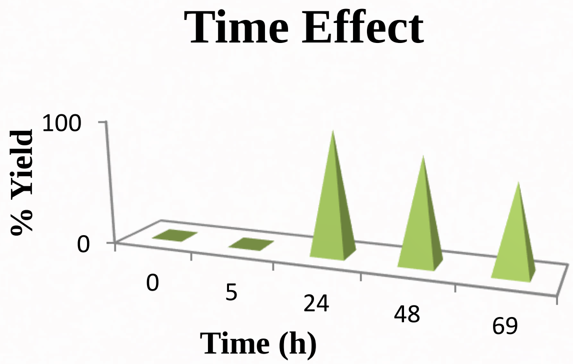
- Base

- Catalyst loading.

Optimization of reaction conditions between iodobenzene and methyl acrylate:

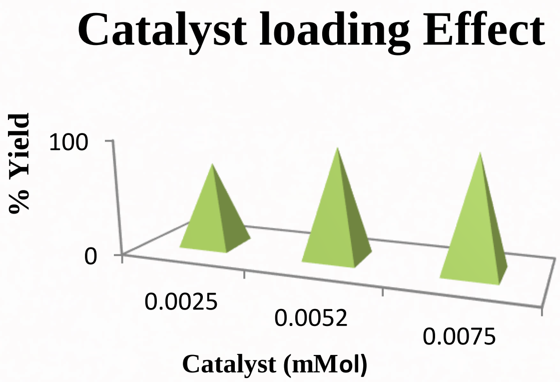
120 °C, **1**, DMF (10 mL), Na_2CO_3. % Yield was determined by GC-MS.

Octadecane was used as internal standard.



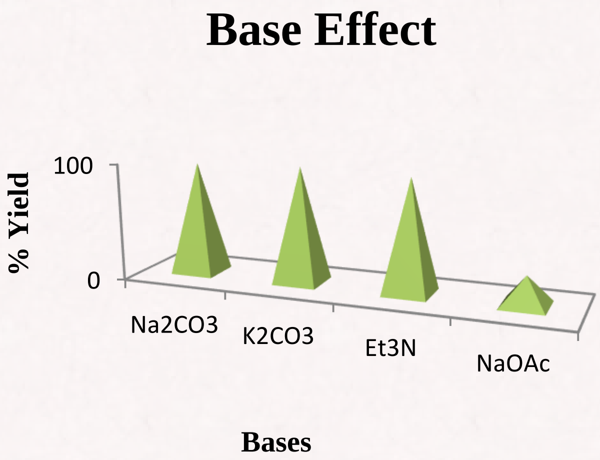
Time (h)	% Yield
0	0
5	0
24	99
48	84
69	70

- Time Effect: Maximum conversion was obtained at 24h. A steady decrease in yield was observed after 24h.



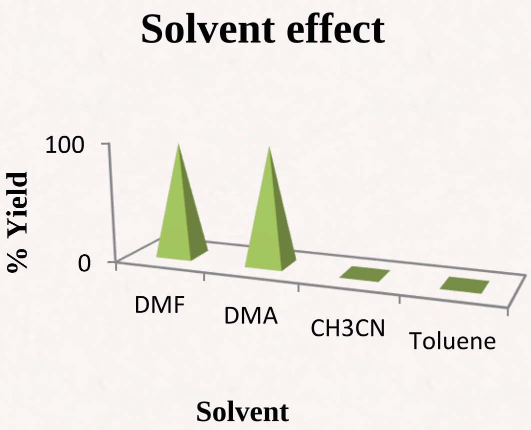
Catalyst (mMol)	% Yield
0.0025	74
0.0052	96
0.0075	99

- Catalyst loading effect: > 99 % conversion achieved with 0.0075 mMol.



Base	% Yield
Na_2CO_3	96
K_2CO_3	99
Et_3N	97
NaOAc	25

C–C Base effect: Both organic and inorganic bases were found to be very efficient except NaOAc. K_2CO_3 was used for further studies.

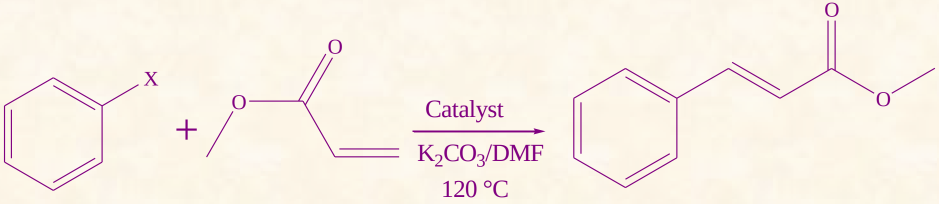


Solvent	% Yield
DMF	96
DMA	87
CH_3CN	0
Toluene	0

C–C Solvent effect: CH_3CN and toluene were inefficient. DMF was used for further reactions.

The scope of the reaction was further evaluated using various aryl halides and catalysts.

Evaluation of halide groups and catalyst in Heck reactions



Entry	X	Catalyst	% Conversion
1	I	1	> 99
2	Cl	1	Trace
3	Br	1	Trace
4	I	-	-
5	I	$PdCl_2$	3
6	I	2	98

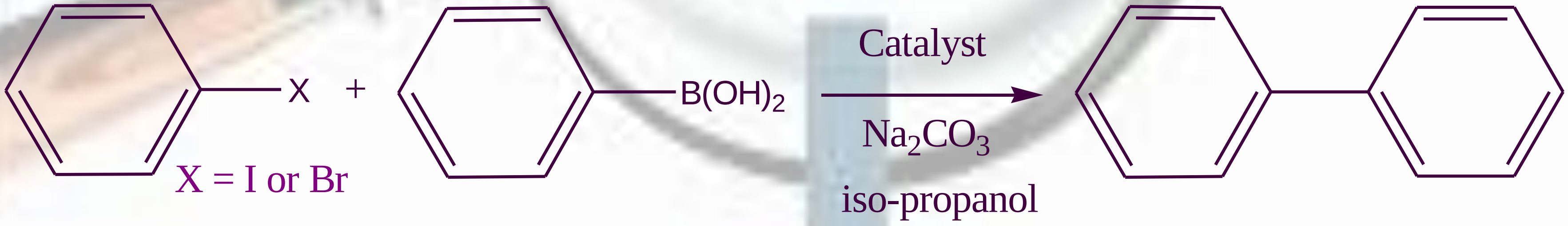
Aryl halide: 3.0 mmol; methyl acrylate: 8.32 mmol, catalyst: 0.0052 mmol, base: 4.5 mmol; time: 24 h. Octadecane was used as internal standard. % conversion was determined by GC-MS as an average of two injections.

- With chloro and bromo benzene, trace amount of product was obtained.
- With iodo benzene- in absence of catalyst, no Heck product formed while with $PdCl_2$ only, trace amount obtained.
- Complexes **1** and **2** showed comparable yields,

Suzuki Reactions

Suzuki reaction is the cross-coupling of an aryl or vinyl boronic acid with aryl or vinyl halide or triflate and allows the synthesis of conjugated olefins, styrenes, and biphenyls.

Preliminary studies were carried out using complexes **1** and **2** and further investigation is still under process.



Biphenyl

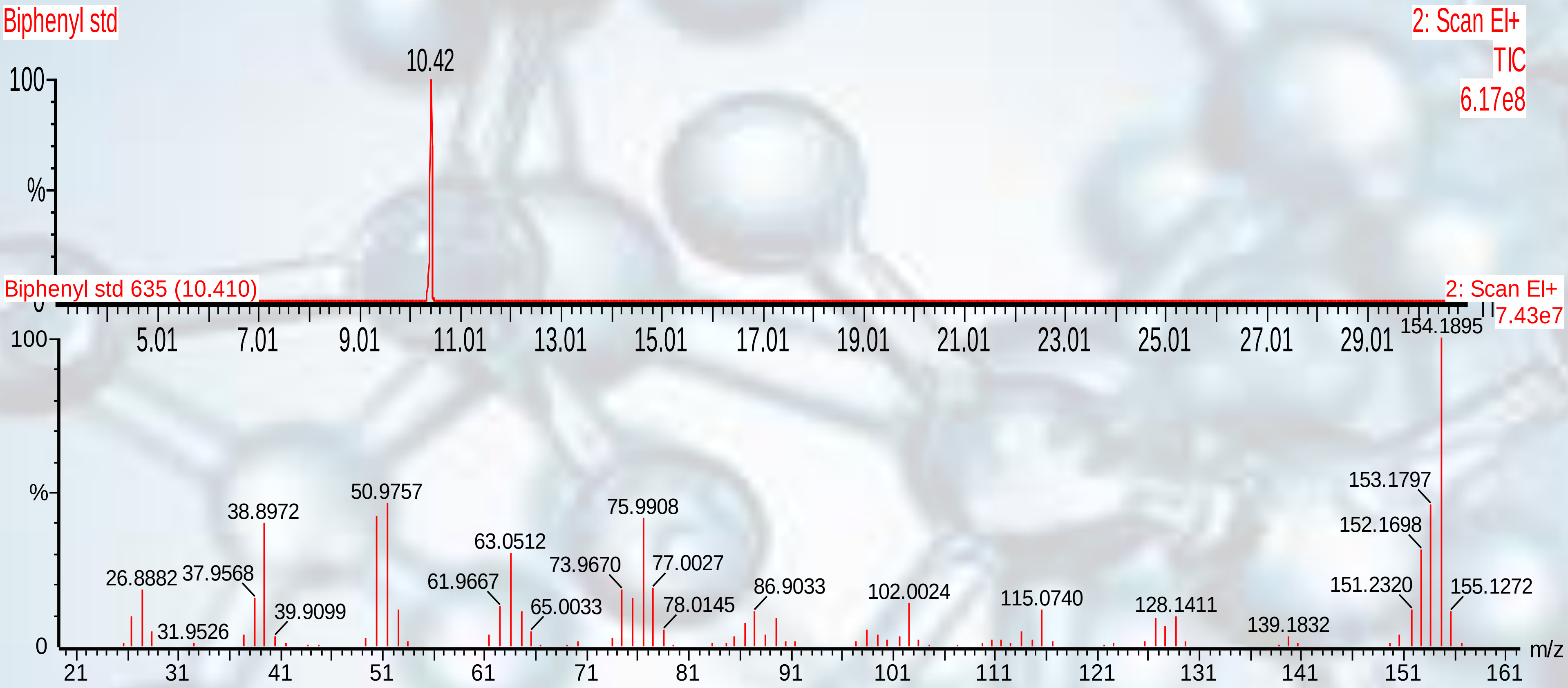


Fig. 3.0: (a) GC chromatogram of biphenyl; (b) Mass spectrum of biphenyl.

- Suzuki reactions were carried out for 6 h under refluxing conditions with iodo and bromo as aryl halides. % conversion was determined after isolation of products.

Table 2: Evaluation of halide groups and catalyst in Suzuki reactions

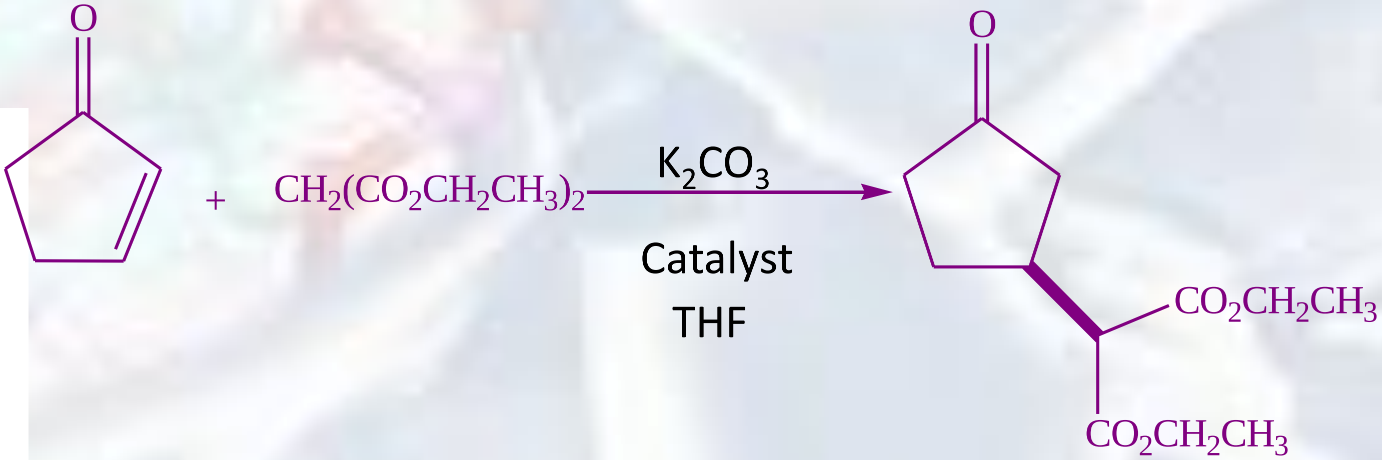
Entry	X	Catalyst	% Conversion
1	I	1	97
2	Br	1	60
3	I	2	99
4	Br	2	64

Aryl halide: 0.01 mol; acid: 0.01 mol, catalyst: 0.1 mmol, base: 0.2 M; time: 6 h.

- Moderate to excellent yields were obtained.
- Both catalysts were very efficient since high % conversion were obtained (entry 1 and 3).
- The bond strength of C-X influences the yield of the reaction.

Michael Addition Reactions

It involves a nucleophilic attack of carbanions to α,β-unsaturated carbonyl compounds under basic (for deprotonation of donor) or acidic medium (activation of acceptor) in organic solvents. In the base catalysed reactions, the donor is first deprotonated forming an enolate anion which then reacts with the acceptor in a 1,4-fashion.



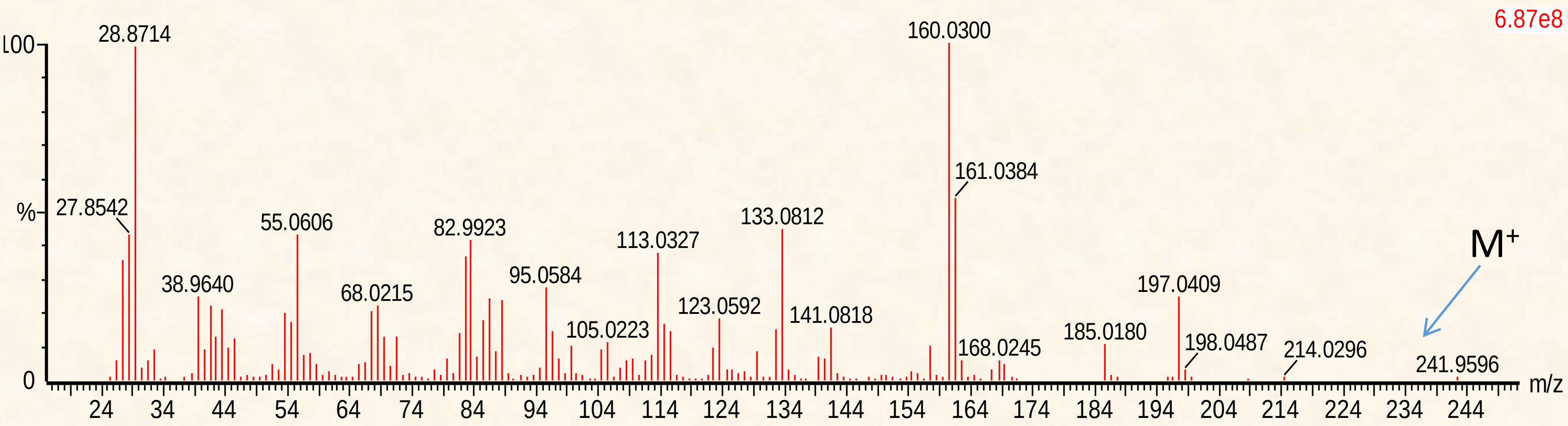


Fig. 4.0: Mass spectrum of Michael adduct

The use of catalysts of **1** and **2** in the Michael reactions of cyclopentenones with diethymalonates in THF at different temperatures (24-60 °C) did not gave the desired product as confirmed by the mass spectrum below.

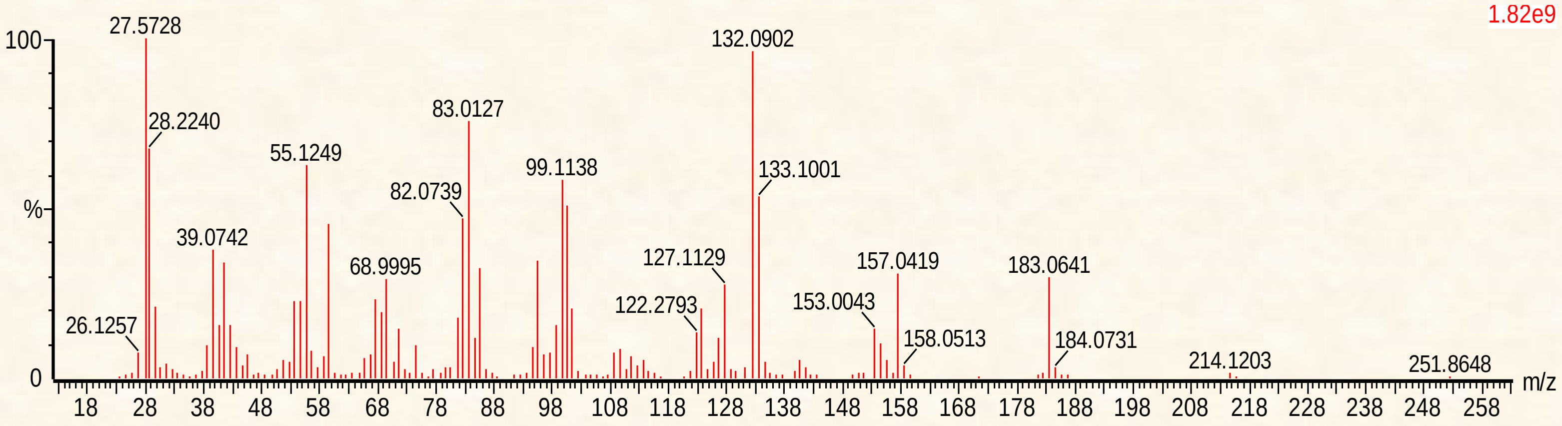


Fig. 5.0: Mass spectrum of Michael adduct using catalysts 1 and 2

CONCLUSIONS

- Both palladium complexes were found to be efficient catalysts in promoting the Heck and Suzuki reactions.
- The products were obtained in excellent yields even at a very low catalyst loading.
- The yields of the product were highly dependent on parameters such as time, solvent, base and substrate.
- Both catalysts gave comparable yields, however catalyst **2** was better than **1**, considering its lower palladium content.
- The complexes were inefficient as catalysts in Michael addition reactions.

THANK YOU