Synthesis of Tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$)

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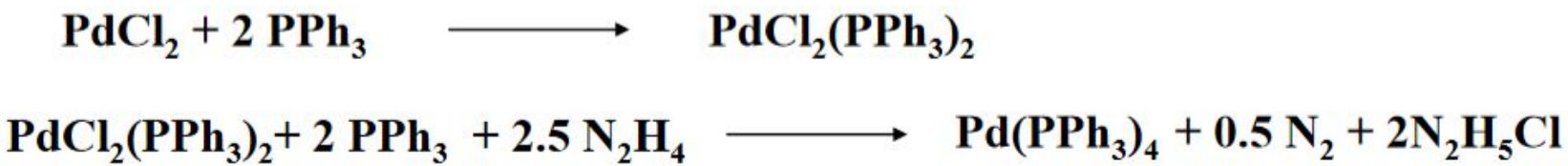
Purpose

The purpose of this experiment is to synthesize tetrakis(triphenylphosphene)palladium(0), an important organometallic catalyst used in coupling reactions in organic synthesis.

Overall Reaction



Reagents/MSDS

Name	M.W.	Density	Amount	Moles	Hazards/Precautions and MP/BP	Role
Palladium (II) dichloride	177.33	4 g/cm^3	0.44 grams	0.00248	Harmful if swallowed. Causes serious eye damage. May cause an allergic skin reaction. MP: 678-680°C	Reactant
Hydrazine hydrate	32.05	1.029 g/cm^3	0.62 grams	0.0193	Toxic if swallowed or in contact with skin. Causes severe skin burns and eye damage. MP: -52°C BP: 120°C	Reactant
Triphenyl phosphene	262.29	1.07 g/cm^3	3.28 grams	0.0125	Harmful if swallowed. Causes serious eye damage. May cause an allergic skin reaction. MP: 80°C BP: 377°C	Reactant
Dimethyl sulfoxide	78.13	1.100 g/cm^3	30 mL	0.422	Combustible liquid. Can carry dissolved chemicals through skin. May cause eye, skin, and respiratory tract irritation. MP: 18.4°C	Solvent
Nitrogen	28.01	0.97 g/cm^3	--	--	May displace oxygen and cause suffocation. MP: -210°C BP: -196°C	Product
$Pd(Ph_3)_4$	1155.58	--	--	--	Harmful if swallowed. May form combustible dusts. MP: 105°C	Product

Procedure

1. Dissolve 0.44 g of fine palladium dichloride, 3.28 g of triphenylphosphine in 30 mL of dimethylsulfoxide with stirring and heating to 140°C in closed RBF flushed with argon or nitrogen.
2. When all of the palladium dichloride is dissolved stop the heating and add slowly 0.62 g of hydrazine hydrate over the course of 1 minutes.
3. Cool the solution in a water bath until the mixture becomes turbid and remove it from the ice bath. Continue the stirring in a room temp for 20 minutes and further cool down 10°C.
4. Filter and wash with 10 ml of ethanol and with some diethyl ether. Dry in a vacuum.

Flow Chart

$PdCl_2$ (brown)

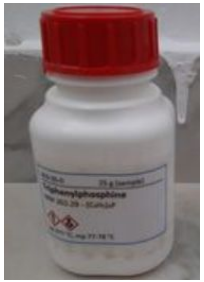
↓ $2PPh_3$

$PdCl_2(PPh_3)_2$ (yellow/orange)

↓ $2PPh_3 + 2.5N_2H_4$

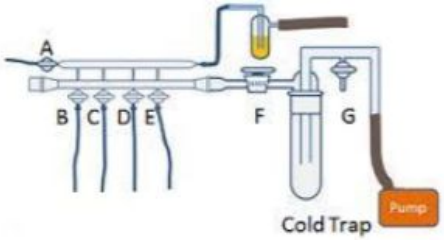
$Pd(PPh_3)_4$ (bright yellow) + $0.5N_2$ + $2N_2H_5Cl$

0.44 palladium chloride, 3.28 g triphenylphosphine, 30 mL dimethylsulfoxide in round-bottomed flask



Flushed w/ argon

Stir and heat to 140℃ until palladium chloride dissolves



Stop heating, added 0.62 g hydrazine hydrate

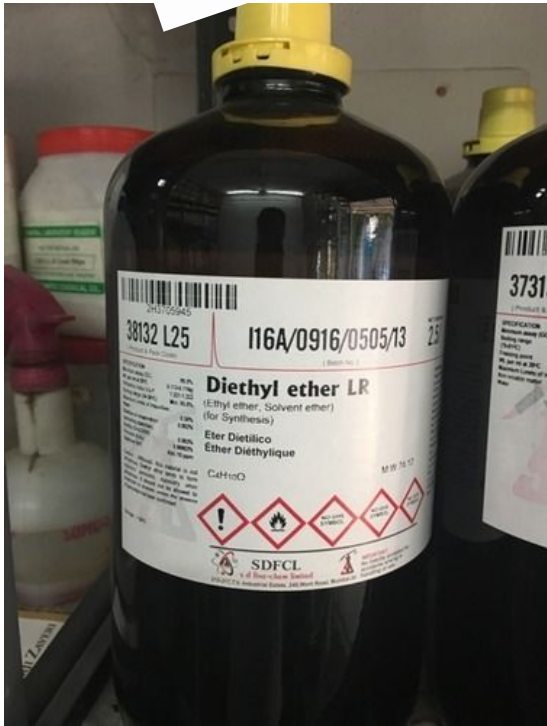
Cool in water bath until mixture becomes turbid

Continue stirring at room temp and cool down to 10℃

Filter the product using a Schlenk flask and cannula

Wash with 10 ml ethanol

Wash with diethyl ether



Vacuum line

Dry product in high vacuum

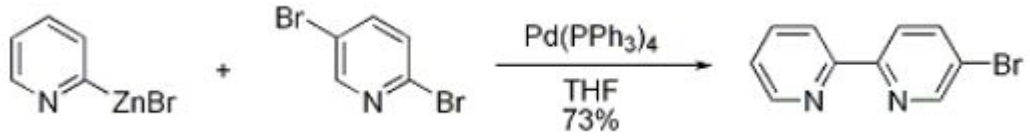
Conclusion

In this lab, we accomplished synthesis of the important organometallic catalyst tetrakis(triphenylphosphene)palladium(0). We learned about use of the Schlenk flask to conduct reactions in inert environments, as oxygen prevents synthesis of the product. We also learned about important techniques when using the Schlenk funnel, such as using cannula to perform filtration. There were no issues and future recommendations, as this experiment was conducted remotely. This is an important reaction to create the catalyst, as the catalyst is used in Suzuki, Heck, and Negishi coupling reactions to form many important organic compounds.

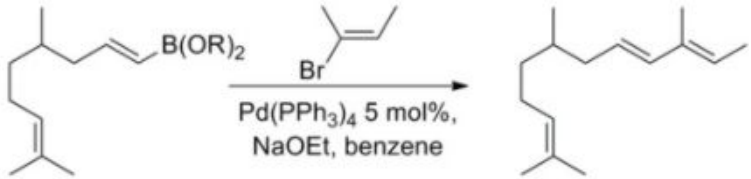
Post Lab Questions

(1) Given one example of each of the following reactions utilizing Pd(PPh3)4.

Negishi coupling:



Suzuki coupling:



(2) Given one example another Palladium catalyst other than Pd(PPh3)4. Give example of one reaction using that catalyst.

The reaction below shows the formation of a lactone compound using the $Pd(OAc)_2$ catalyst (palladium (II) acetate)