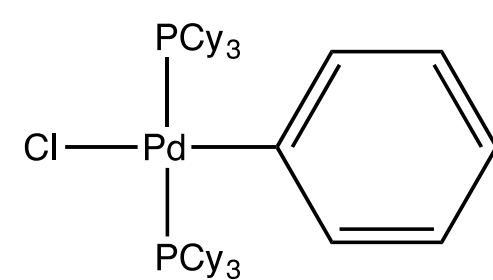


Activation of Carbon Chlorine Bonds Using Palladium (II) Catalysts

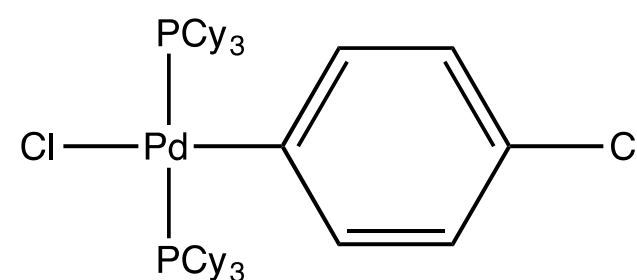
Briana Goddard and Derk A. Wierda, Ph.D
Saint Anselm College, Manchester NH

Abstract

Chlorophenylbis(tricyclohexylphosphine)palladium(II) (**1**) and chloro(p-chlorophenyl)bis(tricyclohexylphosphine)palladium(II) (**2**) showed catalytic activity capable of activating carbon chlorine bonds in chlorobenzene, para-dichlorobenzene, and meta-dichlorobenzene. Activation of ortho-dichlorobenzene was unsuccessful. The successful catalytic cycles produced benzene and hydrochloric acid, which was neutralized with the base triethylamine. Successful activation of ortho-chlorotoluene was achieved with catalyst (**1**) to produce toluene. The activation of meta-chlorotoluene, para-chlorotoluene, 1,3,5, trichlorobenzene and 1,3,5-trichloro-2,4,6-trimethylbenzene are currently being explored.



(**1**) Chlorophenylbis-(tricyclohexylphosphine)palladium(II)



(**2**) Chloro(p-chlorophenyl)bis-(tricyclohexylphosphine)palladium(II)

Introduction

Polychlorinated biphenyls (PCBs) shown in *Figure 1*, are stable organic molecules, consisting of two phenyl rings substituted with one to ten chlorine atoms. Due to their being flame-resistant, having low thermal conductivity, and other properties, PCBs were used in various industrial equipment, including transformers, capacitors, and adhesives. However, PCBs have carcinogenic properties, and are now known to be an environmental hazard. In order to safely dispose of these chemicals, the inert carbon to chlorine bond must be activated.

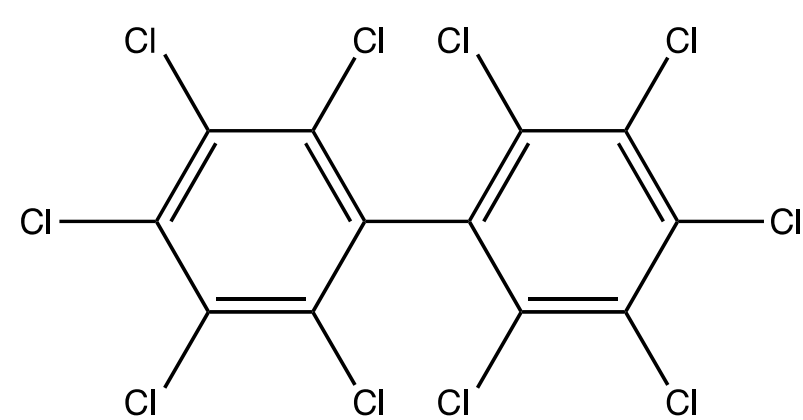
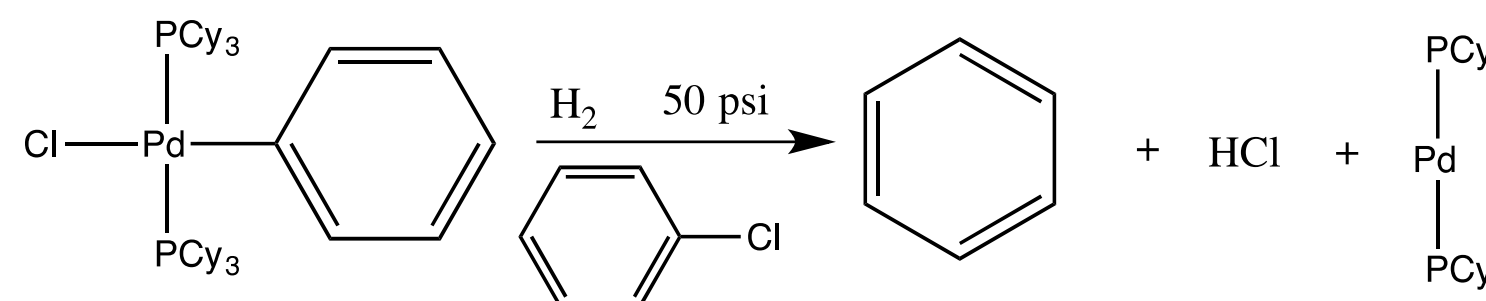


Figure 1: An Example of a PCB

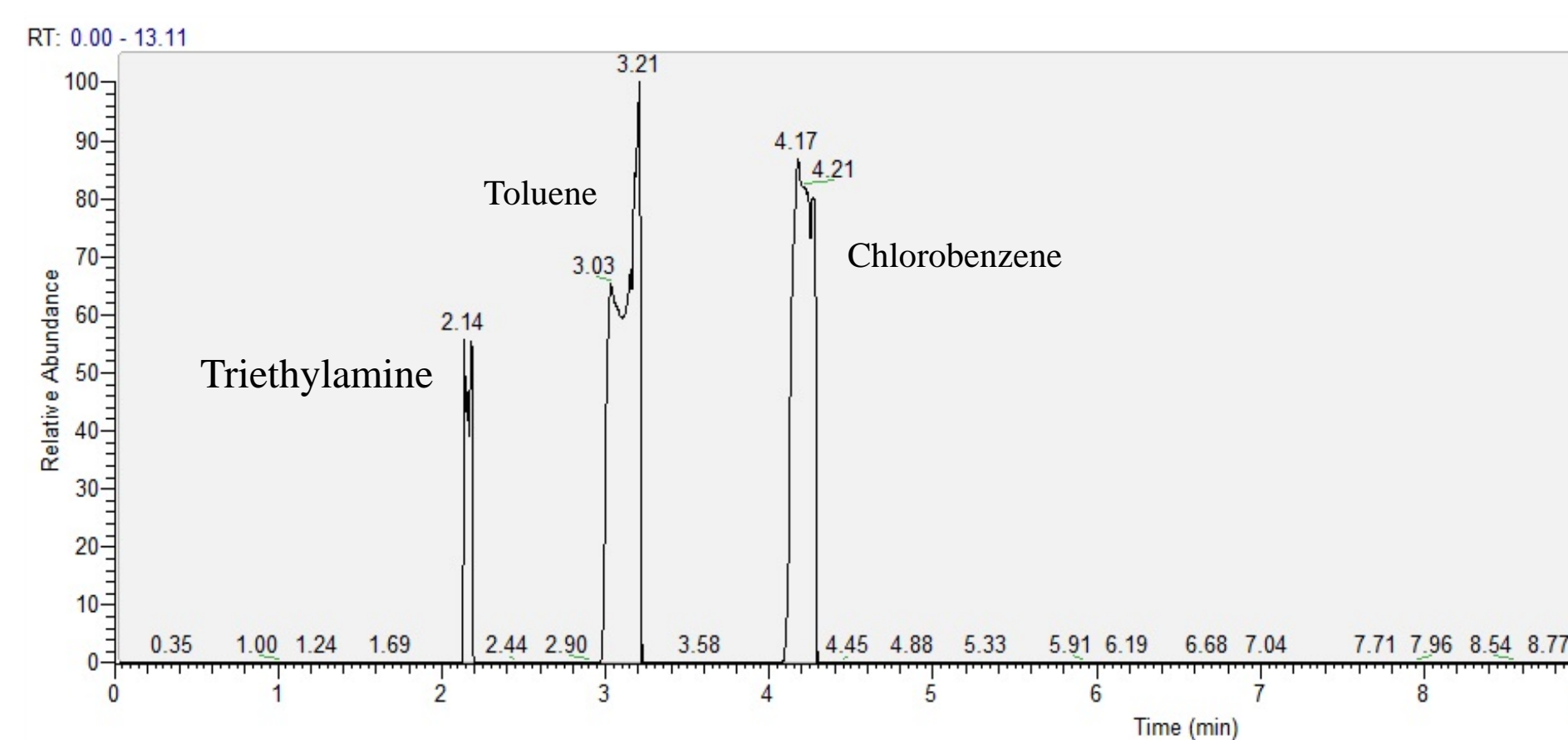
The current and most widely used method to dispose of PCBs is high temperature incineration, occurring at a temperature of 1200°C. When the PCBs are incinerated, they are oxidized, producing a harmful dioxin species.¹ This method is environmentally hazardous and not cost effective. Two other methods to dispose of PCBs are gamma radiation from a Co-60 source, and chemical dechlorination though a chemical reaction^{1,2}.

The oxidative addition of chlorobenzene has been achieved with nickel, platinum, and palladium³ complexes. In each case, the reaction proceeded through the same intermediate form, M(PR₃)₂, the unsaturated complex. If this catalytic cycle can be optimized to work with multiply chlorinated species, it could then be developed into a safe, inexpensive, and environmentally friendly method to neutralize PCBs.

Example Gas Chromatography Data



Before the Reaction



After the Reaction

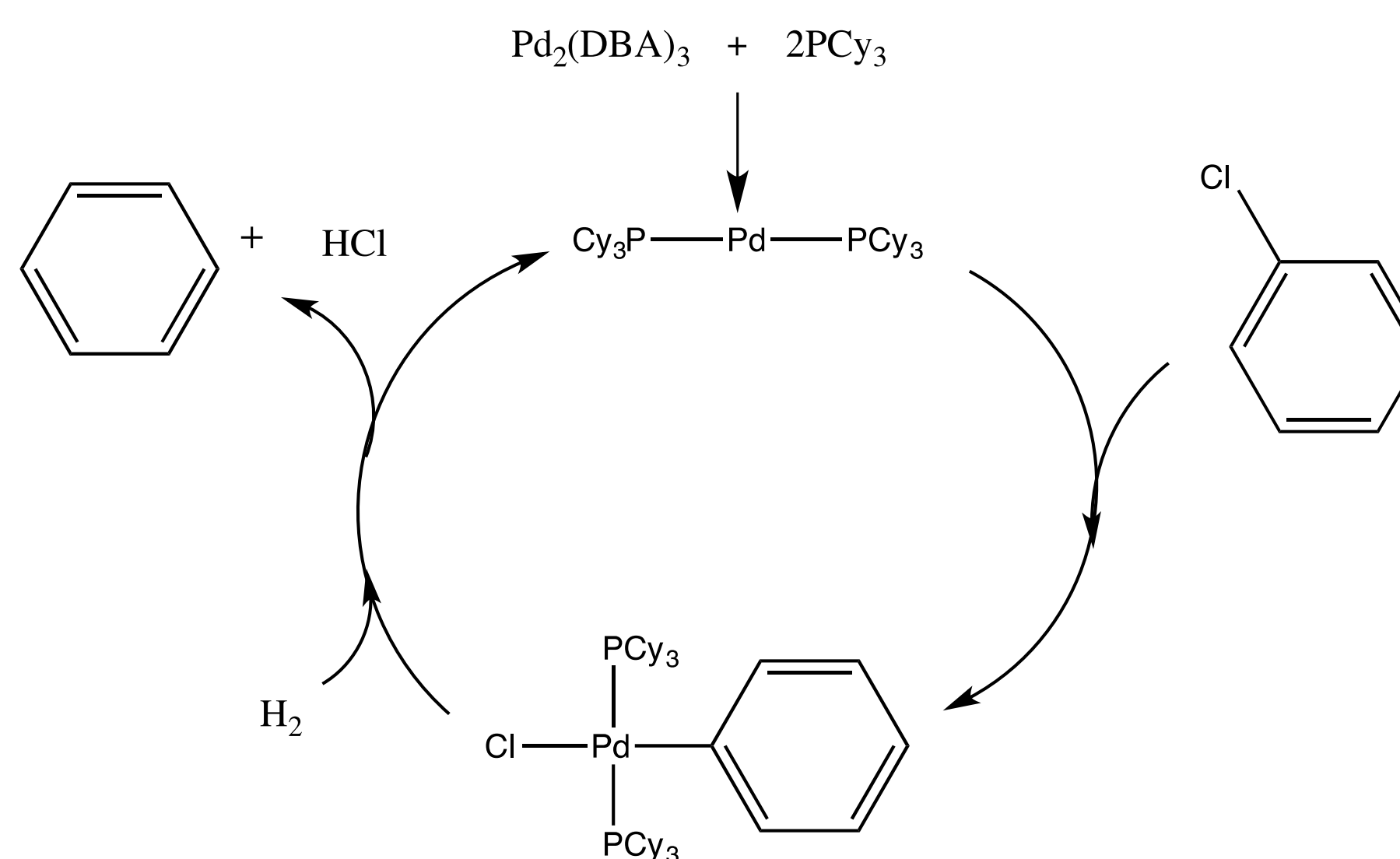
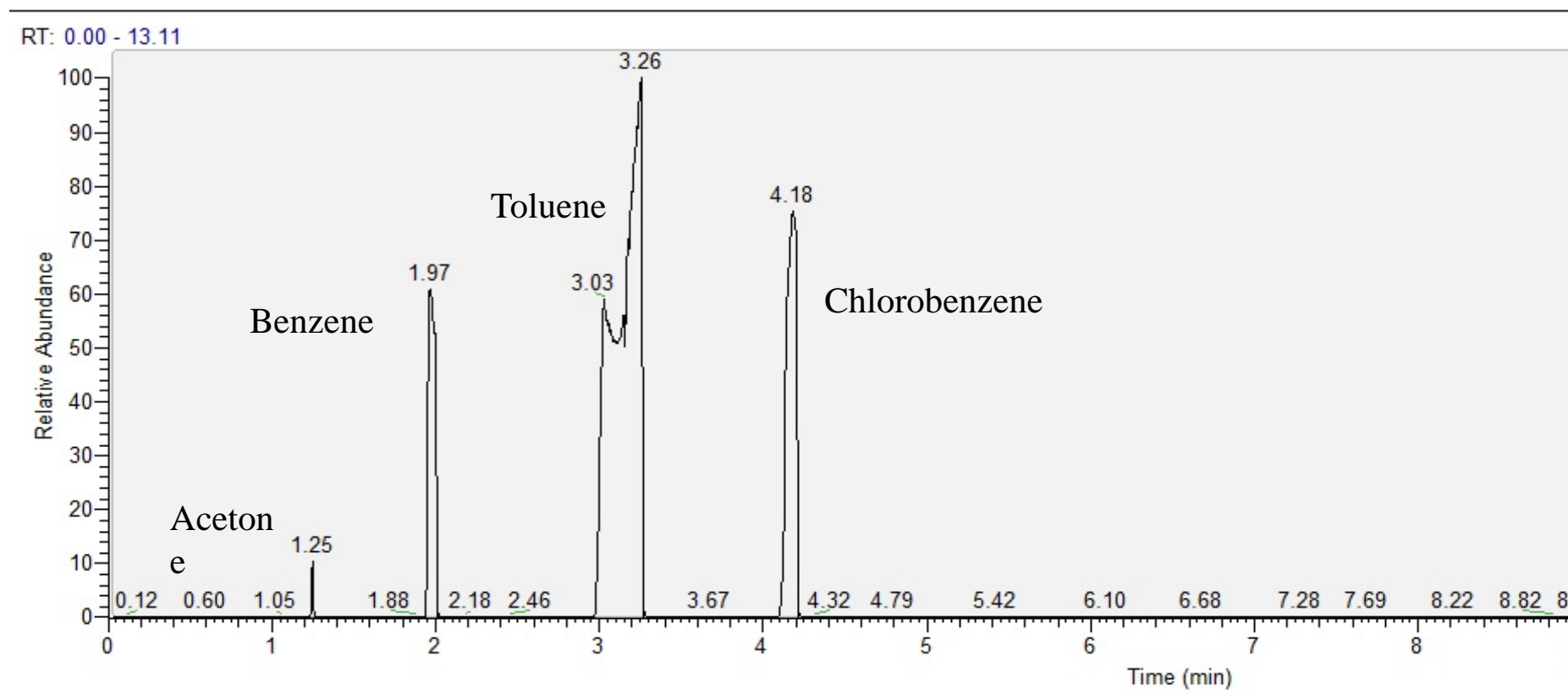


Figure 2: Proposed Catalytic Cycle

Results and Discussion

The catalytic activity of both (**1**) and (**2**) were tested in the presence of various monochlorinated and dichlorinated species. The base triethylamine was used to trap the hydrochloric acid generated and precipitated out of solution. The resulting solutions were analyzed using gas chromatography and mass spectroscopy. As expected, (**1**) was active with chlorobenzene, and yielded benzene.

When in the presence of ortho-dichlorobenzene, both of the catalysts were inactive. However, in the presence of para-dichlorobenzene or meta-dichlorobenzene, both produced a majority of chlorobenzene and minority of benzene.

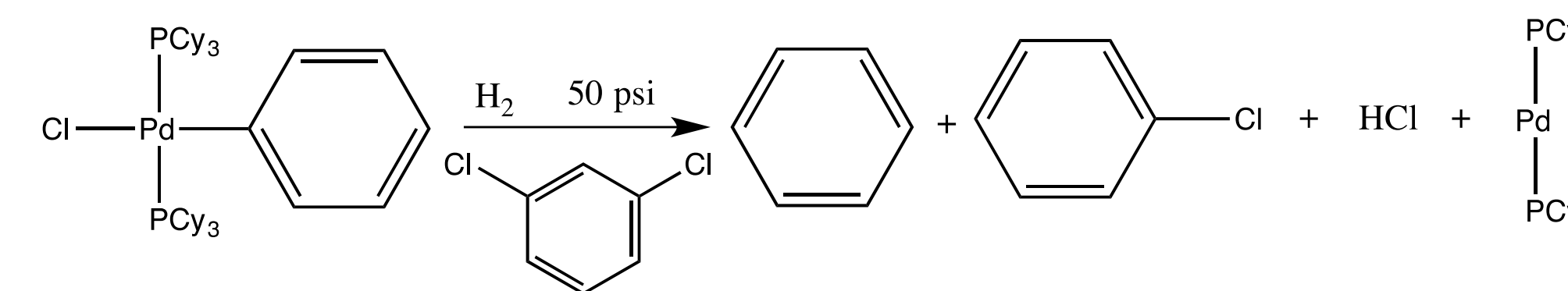


Figure 3: Reaction of Catalyst 1 with meta-dichlorobenzene

Catalyst (**1**) reacted with ortho-chlorotoluene to yield toluene. It is possible the ortho position was activated in this case due to the weakly activating effects of the methyl group.

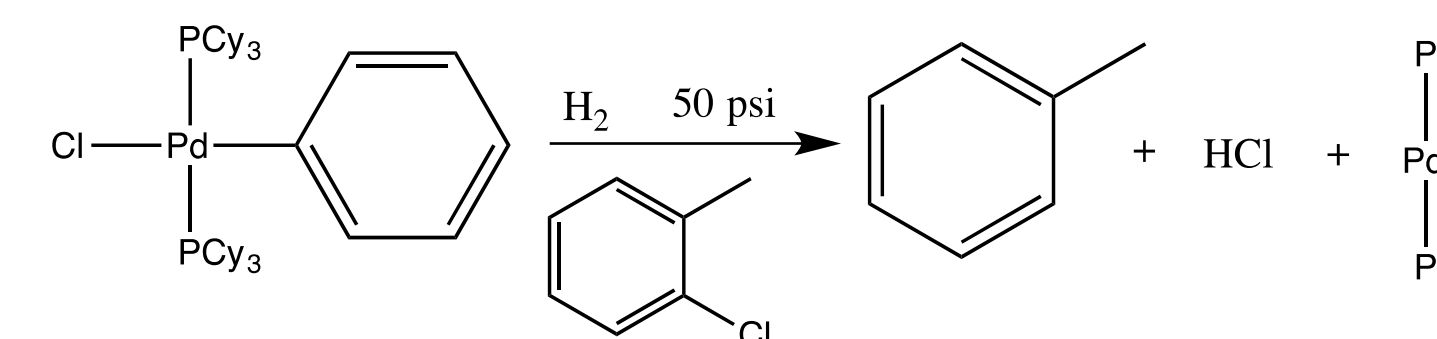


Figure 4: Reaction of Catalyst 1 with ortho-chlorotoluene

Conclusion

Chlorophenylbis(tricyclohexylphosphine)palladium(II) and chloro(p-chlorophenyl)bis(tricyclohexylphosphine)palladium(II) each underwent a reductive elimination reaction to yield the fourteen valence electron reactive species bis(tricyclohexylphosine)palladium(0), which readily participated in oxidative addition reactions to activate carbon chlorine bonds. Both catalysts activated monochlorinated and dichlorinated species, but not when the dichlorinated species were in the ortho position. Catalyst (**1**) reacted with ortho-chlorotoluene. The reaction of catalyst **2** with ortho-chlorotoluene is still being explored, as well as the reaction of both catalysts with meta-chlorotoluene, para-chlorotoluene, 1,3,5-trichlorobenzene, and 1,3,5-trichloro- 2,4,6- trimethylbenzene.

References

1. Singh, R; Khandal, R; Singh, G. Destruction of Polychlorinated Biphenyls (PCBs) In Waste Electronic Capacitor Oil Using Gamma Radiation. *Poll Res.* **2009** 28, 2, 271-27
2. Ryoo, K; Byun, S; Choi, J; Hong, Y; Ryu, Y; Song, J; Lee, D; Lee, H. Destruction and Removal of PCBs in Waste Transformer Oil by a Chemical Dechlorination Process. *Bull Korean Chem Soc* **2007**, 28, 4, 520-528.
3. Osborne, J; Huser, M; Youinou, M. Chlorocarbon Activation:Catalytic Carbonylation of Dichloromethane and Chlorobenzene. *Angew. Chem. Int. Engl.* **1989**, 28, 10, 1386-1388