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THE REACTIONS OF ortho-CARBON σ-BONDED AROMATICS-PALLADIUM COMPLEXES WITH ALKYLLITHIUM. SELECTIVE SYNTHESES OF ortho-ALKYL SUBSTITUTED AROMATIC COMPOUNDS

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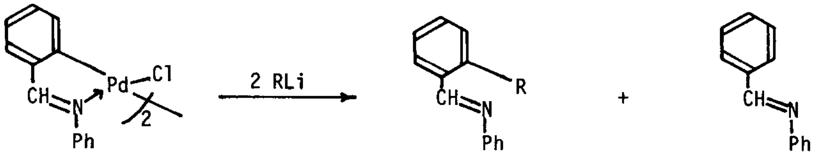
Syntheses and structural studies of five-membered palladium complexes (1) which are formed by internal metallation of alkyl or aryl groups of co-ordinated ligands including amines (1), Schiff bases (2), azo-compounds (3) have received wide-spread attention; however, few studies have been carried out concerning to using these complexes for organic synthetic reactions (4).

We wish to report facile carbon-carbon bond formation by the reaction of 1 with either alkyllithiums or Grignard reagents. This process provides a convenient method for selective syntheses of some ortho-alkyl substituted aromatic compounds which are difficult to be prepared (5) and gives important mechanistic insight into the carbon-carbon bond formation via palladium complexes.

Reaction of di-μ-chlorobis[o-(N-phenylformimidoyl)phenyl]dipalladium (2), prepared from N-benzylideneaniline (4) in 95% yield (2), with methyllithium in ether gave N-(o-methylbenzylidene)aniline (3a) and 4 in 76% and 21% yields, respectively. Further reaction of 2 with t-butyllithium gave 3b (28%) and 4 (34%). This reaction promises to provide a convenient method for synthesis of ortho-alkyl substituted aromatic compounds. Indeed, for synthesis of t-butylbenzaldehyde, six steps are required from t-butylbenzene, and its yield is extremely low (6).

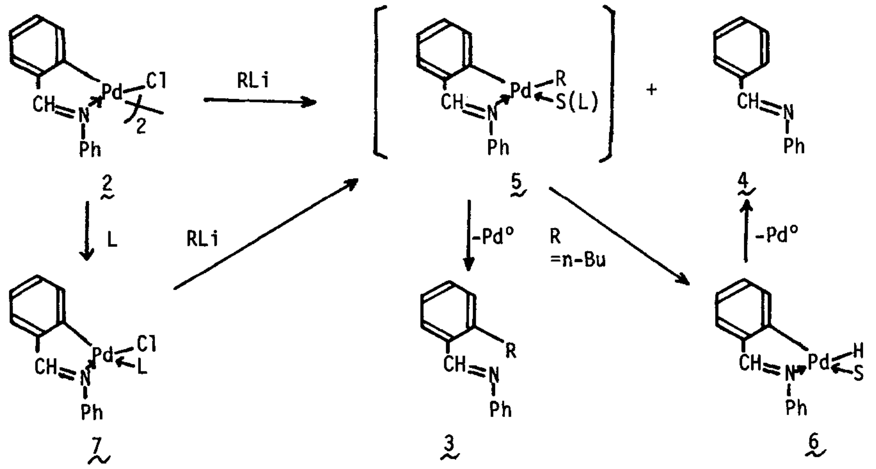


2

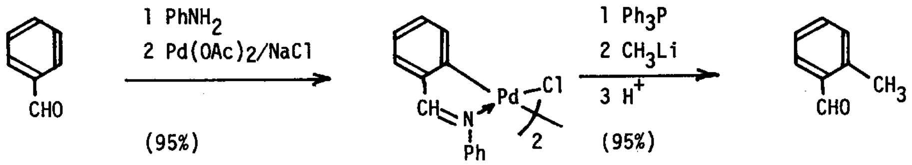
3a R=Me
3b R=Bu^{-t}
3c R=Bu^{-n}

4

For accomplishing of the complete retardation of the liberation of one part of N-benzylideneaniline in 2 unchanged, the scheme of the reaction of 2 with alkyllithium was examined. The first step is the substitution of the Pd-Cl bond with alkyllithium giving the intermediate 5 accompanied with splitting the bridged structure of 2 to give 4. The second step is the reductive coupling of 5 leading to 3. It is noteworthy that when 2 was treated with n-butyllithium, 4 was formed in 91% yield along with small amount of 3c(5%). The result is consistent with this scheme, indicating the initial formation of the palladium alkyl bond yielding 5. Facile β-elimination of the palladium hydride species from the intermediate 5 would lead to the hydride complex 6 which subsequently couples to give 4 reductively. If it is the case, addition of a certain ligand let the dimer 2 splitt into two ligand co-ordinated monomer complex 7, and subsequent reaction of 7 with alkyllithium would lead to the ligand-co-ordinated 5, therefore 3 can be prepared exclusively. Indeed, when the complex 2 was treated with alkyllithium compounds in the presence of two equivalent of triphenylphsphine (7), the desired products 3 were obtained in excellent yields as shown in Table 1 (8). Therefore, the reaction provides a convenient method for synthesis of ortho-alkyl substituted compounds (5-6).

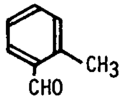
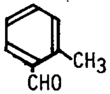
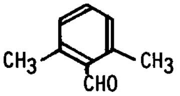
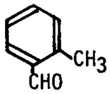
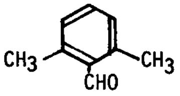
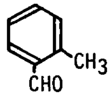
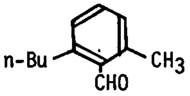
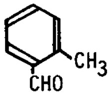
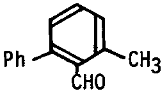
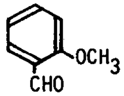
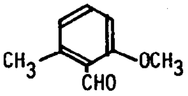


A typical procedure is as follows. To a suspension of the complex 2 (5 mmole) in dry benzene (40 ml) was added triphenylphsphine (10 mmole) with stirring. After additional stirring for 30 min the etheral solution of methyllithium (10 mmole) was added, and it kept stirring for 1 hr. Then, the reaction mixture was hydrolyzed by treatment with diluted hydrochloric acid solution. Usual work-up and distillation gave 3a in 95% yield.



When this process is utilized twice to benzaldehyde, ortho-dialkylsubstituted benzaldehyde can be prepared highly selectively by simple treatment. Thus, 2,6-dimethylbenzaldehyde was synthesized from o-methylbenzaldehyde in 80% yield, and from benzaldehyde in 72% yield, respectively. Grignard reagents can be also utilized for this reaction.

Table 1 The Reactions of the Palladium complexes of Shiff Bases with either Alkyllithium or Grignard Reagents in the Presence of Triphenylphosphine

Compounds[a]	RLi(RMgI)	Products(Yields %)[b]	
	CH_3Li		(95)
	CH_3Li		(86)
	CH_3MgI[c]		(70)
	n-BuLi		(75)[d]
	PhLi		(60)
	CH_3Li		(85)

a) The aldehydes can be quantitatively converted into the corresponding Shiff bases whose palladium complexes can be readily prepared in >95% yields (8). b) The isolated yields based on the palladium complexes of the Shiff bases. c) Four equivalent moles of CH_3MgI and PPh_3 were reacted with the corresponding palladium complex. d) Four equivalent moles of PPh_3 was used. Another product of this reaction was o-tolualdehyde (4%).

This reaction can be applied to the other palladium complex of 1. Thus, reaction of di-μ-chloro-bis[o-(phenylazo)phenyl]dipalladium (3) and di-μ-chlorobis[α-(dimethylamine)-o-tolyl]-dipalladium (1) with methyllithium in the presence of triphenylphosphine gave the corresponding ortho-methyl substituted aromatic compounds in 91% and 99% yields, respectively. Attempts to extend the reaction to softer anions such as malonate anion failed. This fact is in contrast to the results of the reaction of π-allyl palladium chloride complexes with carbanions where only soft bases react and have been suggested to attack not at the chlorine of the Pd-Cl bond of the complex but at the carbon of the π-allyl group initially (9).

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7) Triphenylphosphine is the best ligand for this reaction among other ligand such as $P(OPh)_3$, $P(n\text{-}Bu)_3$, $(Ph_2PCH_2)_2$.

8) Satisfactory analytical and spectral data have been obtained for all of the products.

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