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ALKYL GROUP ISOMERIZATION IN THE REACTION OF σ-ARYL PALLADIUM COMPLEXES WITH ALKYLLITHIUM COMPOUNDS

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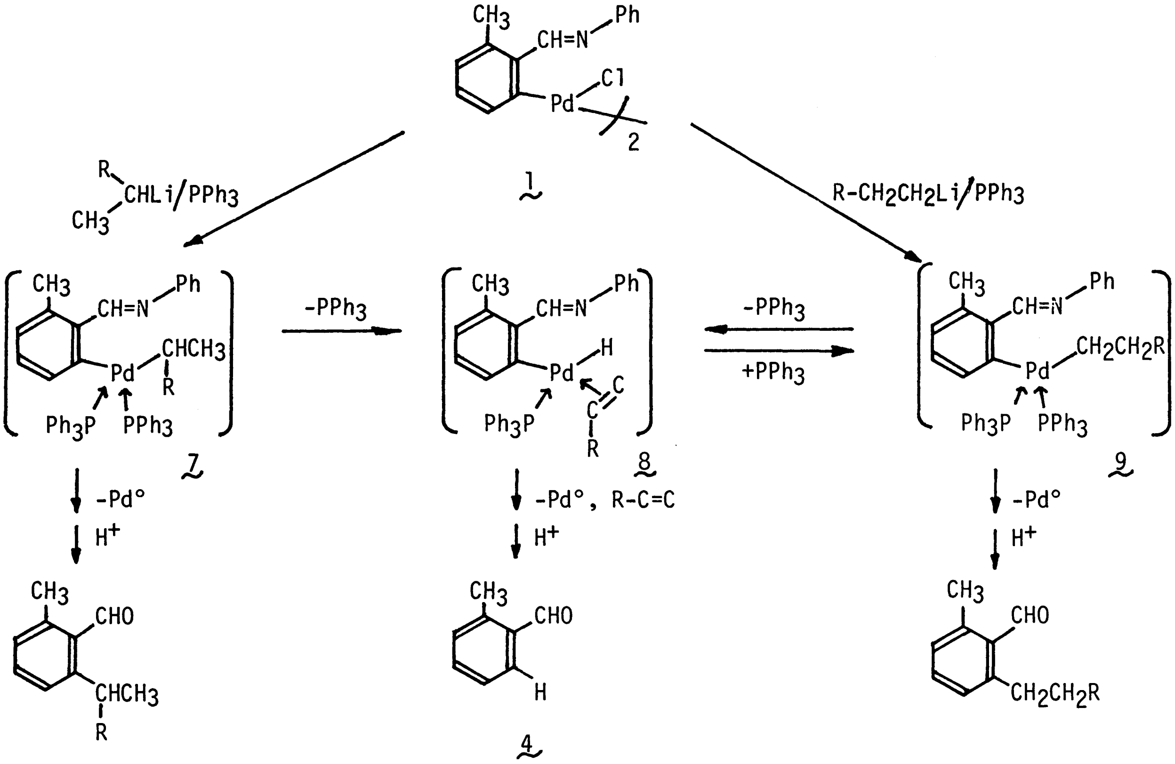
Reaction of di-μ-chlorobis[2-(N-phenylformimidoyl)-3-tolyl]dipalladium (1) with secondary alkyllithium compounds provides evidence indicating that a secondary alkyl-palladium isomerizes to the primary *via* a hydrido-olefin intermediate.

We recently reported that the reaction of di-μ-chlorobis[2-(N-phenylformimidoyl)phenyl]dipalladium with alkyllithium compounds followed by acid-hydrolysis provides a convenient method for selective synthesis of ortho-alkyl substituted benzaldehydes which are hardly accessible, and showed that an alkylarylpalladium is involved as an intermediacy.1)

We now wish to report that secondary alkyllithium reagents also undergo the carbon-carbon bond formation by utilizing of the σ-arylpalladium complexes, but the coupling reaction is accompanied by alkyl group isomerization from secondary to primary. Reaction of complex 12) with i-propyllithium in the presence of two molar amounts of PPh_3 followed by hydrolysis with aq HCl solution gave 2-methyl-6-i-propylbenzaldehyde2)(2, 5 %), 2-methyl-6-propylbenzaldehyde2)(3, 6 %), and 2-methylbenzaldehyde (4, 80 %). Likewise, reaction of complex 1 with 1-methylpropyllithium afforded 2-methyl-6-(1-methylpropyl)benzaldehyde2)(5, 6 %), 2-methyl-6-butylbenzaldehyde2)(6, 10 %), and 4 (70 %). Formation of secondary alkyl substituted benzaldehydes, 2 and 5 can be rationalized by initial formation of the σ-complex (7) containing $Pd-CH(CH_3)R$ bond and subsequent reductive coupling reaction.1) On the other hand, formation of primary-alkyl substituted benzaldehydes, 3 and 6, can be rationalized by assuming rapid isomerization of 7 to n-alkyl-palladium (9) *via* a hydrido-olefin intermediate (8), from which the major reductive product 4 is derived, as shown in Scheme 1. When complex 1 was reacted with propyllithium under the same condition, 3 and 4 were obtained in 37 % and 45 % yields, respectively, but alkyl-isomerization product 2 could not be detected among the products. These results indicate the higher stability of a primary alkyl palladium complex 9 in comparison with the secondary 7. This may be due to the release of steric strain rather than the electronic effect. An increase in the electron density on palladium owing to the electron donating ligand seems not to facilitate the σ-π conversion, since the yield of 3 in the reaction of 1 with i-PrLi did not depend upon the ligands used [PPh$_3$ (6 %), PBu$_3$ (4 %), P(OPh$_3$)$_3$ (6 %)].

This is the first example of direct observation that the secondary alkyl-palladium isomerizes to the primary. Although numerous examples of palladium-induced isomerizations of olefins have been shown, there has been no direct evidence of an alkyl-palladium isomerization because of facile β-elimination of palladium hydride species.3,4,5) Recently, analogous alkyl group isomerizations have been demonstrated in alkyliridium6) and alkylnickel.7)



2, R=CH$_3$
5, R=CH$_2$CH$_3$

Scheme 1

3, R=CH$_3$
6, R=CH$_2$CH$_3$

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