Journal of Organometallic Chemistry, 74 (1974) C21—C22

Preliminary communication

INTERACTION OF h^3-ALLYL(CROTYL)PALLADIUM CHLORIDE WITH ALLYL HALIDES

L.F. SHELOHNEVA, I.A. POLETAYEVA, N.A. KARTSIVADZE and V.A. KORMER
S.V. Lebedev All-Union Scientific Research Institute of Synthetic Rubber, Leningrad (U.S.S.R.)
(Received May 6th, 1974)

Reactions of h^3-allylic palladium complexes with allyl(alkyl) halides have not been reported. In studying these reactions we found that in the presence of allyl iodide h^3-crotylpalladium chloride undergoes transformation to give h^3-allylpalladium iodide and h^3-crotylpalladium iodide (molar ratio 2/1). The conversion in a toluene solution at 20°C after a period of 20 h amounts to 50 %. The formation of h^3-allylpalladium iodide was revealed by NMR study of the system h^3-perdeuteropalladium chloride—allyl iodide. This fact as well as the formation of h^3-crotylpalladium iodide is also supported by the composition of the organic products formed in the reaction. Using gas-liquid chromatography the following compounds were found in solution: allyl chloride, 3-chloro-1-butene and 1-chloro-2-butene (see Table 1). An increase in the reaction temperature and the replacement of toluene by dimethylformamide (DMF) lead to a higher total yield of the exchange products with simultaneous increase in the extent of the exchange reaction in which chloro-anion is replaced by iodo anion (see Table 1).

When h^3-allylpalladium chloride is treated with crotyl iodide in a toluene solution the only reaction to occur is the exchange of acido ligands. In the

TABLE 1

INTERACTION OF h^3-CROTYL(ALLYL)PALLADIUM CHLORIDES WITH ALLYL(CROTYL) IODIDES

Products	Yield in mole % based on the initial complex		
	toluene at 20°C	DMF at 20°C	toluene at 50°C
	$[h^3\text{-}C_4H_7PdCl]_2 + C_3H_5I$		
Allyl chloride	14	53	44
3-Chloro-1-butene	14	16	9
1-Chloro-2-butene	22	31	8
	$[h^3\text{-}C_3H_5PdCl]_2 + C_4H_7I$		
Allyl chloride	—	7	—
3-Chloro-1-butene	50	10	—
1-Chloro-2-butene	38	42	—

dimethylformamide medium, small amounts of allyl chloride are formed along with chlorobutenes.

Allyl chloride does not react with h^3-crotylpalladium chloride.

Thus, the reaction of h^3-crotyl(allyl)palladium chlorides with allyl(crotyl) iodides consists in the exchange of ligands, while nickel complexes under similar conditions give predominantly the products of cross-coupling [1, 2].

References

1 E.G. Corey, M.F. Semmelhack, J. Amer. Chem. Soc., 89 (1967) 2755.
2 L.F. Shelohneva, I.A. Poletayeva, N.A. Kartsivadze and V.A. Kormer, in press.