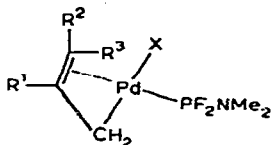


compounds the NMR spectra of the species in solution just prior to halogen migration are consistent with the existence of (II) and the complex (II) ($R^1 = R^2 = H$, $R^3 = CH_3$, $X = Br$) has been isolated and characterised (Found C, 20.65; H, 3.77; N, 4.03. $C_6H_{13}BrF_2NPPd$ calcd.: C, 20.33; H, 3.67; N, 3.95%). Further addition of the fluorophosphine at -78° affords the zerovalent palladium complex, 86% of the primary halide $CH_3CH=CHCH_2Br$ and only 14% of the isomer $CH_2=CHCHBrCH_3$. Essentially the same isomer distribution is observed when the reaction is conducted at room temperature. The dimethylallyl complex (II) ($R^1 = H$, $R^2 = CH_3 = R^3$; $X = Br$) affords the primary halide $(CH_3)_2C=CHCH_2Br$.



(III) ($R^1 = H$, $R^2 = Me$, $R^3 = H$ or Me)

Details of the changes observed in the 1H NMR spectra of the π -allyl dimers on addition of the fluorophosphine ligands at various temperatures will be reported in full later¹¹, but are comparable with the limited observations made in systems containing bis(2-methylallyl)palladium chloride) and carbon monoxide^{10, 12} where, however, evaporation of the solution regenerates the starting palladium dimer. The fluorophosphine induced migration of halogen mainly from the metal to the least substituted carbon atom parallels previous observations⁶⁻⁹ on the insertion of carbon monoxide into palladium-carbon bonds in unsymmetrical allyl complexes. In the fluorophosphine reactions the ligand preferentially stabilises the zerovalent state of the metal and thus assists the transfer of the halogen atom from the π -allyl halogeno complex where the metal formally is in the divalent state. In analogous systems using carbon monoxide insertion of CO into the metal-carbon bond (allyl migration) may or may not precede halogen migration⁶⁻¹⁰. Studies on mixed carbonyl-fluorophosphine π -allyl-metal complexes are currently under way.

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