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Palladium-Catalyzed Carboxylation of Allyl Stannanes and Carboxylative Coupling of Allyl Stannanes and Allyl Halides [Abstract]

The reaction of allyl stannanes with CO$_2$ to form stannyl carboxylates (esters) is catalyzed by Pd(PR$_3$)$_4$ complexes. Thus, R$_3$SnCH=CH$_2$ [R=Me and Ph] are converted to R$_3$SnO$_2$CCH=CH$_2$ and R$_3$SnO$_2$CCH=CHCH$_3$ under 33 atm of CO$_2$ (70°C, THF) in moderate to excellent yield in the presence of 8 mol% Pd(PPh$_3$)$_4$; polycarboxylation of diallyldibutyltin and tetraallyltin also is effected, producing the respective di- and tetracarboxylates, Bu$_2$Sn(O$_2$CCH=CH$_2$)$_2$ and Sn(O$_2$CCH=CHCH$_3$)$_4$, along with the corresponding isomeric crotyl derivatives. In the presence of allyl halides, allyl stannanes and CO$_2$ undergo carboxylative coupling to produce allyl esters. Under these conditions other Sn-C (Sn-alkyl, -aryl, -vinyl) and Si-C (Si-allyl, -alkyl, -aryl, -vinyl) bonds are inert to carboxylation and carboxylative coupling with allyl halides. A tentative mechanism is proposed to account for this catalytic carboxylation of a main group metal-carbon bond.