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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  $\text{CO}_2$  to form stannyl carboxylates (esters) is catalyzed by  $\text{Pd}(\text{PR}_3)_4$  complexes. Thus,  $\text{R}_3\text{SnCH}_2\text{CH}=\text{CH}_2$  [ $\text{R}=\text{Me}$  and  $\text{Ph}$ ] are converted to  $\text{R}_3\text{SnO}_2\text{CCH}_2\text{CH}=\text{CH}_2$  and  $\text{R}_3\text{SnO}_2\text{CCH}=\text{CHCH}_3$  under 33 atm of  $\text{CO}_2$  ( $70^\circ\text{C}$ , THF) in moderate to excellent yield in the presence of 8 mol%  $\text{Pd}(\text{PPh}_3)_4$ ; polycarboxylation of diallyldibutyltin and tetraallyltin also is effected, producing the respective di- and tetracarboxylates,  $\text{Bu}_2\text{Sn}(\text{O}_2\text{CCH}_2\text{CH}=\text{CH}_2)_2$  and  $\text{Sn}(\text{O}_2\text{CCH}_2\text{CH}=\text{CH}_2)_4$ , along with the corresponding isomeric crotyl derivatives. In the presence of allyl halides, allyl stannanes and  $\text{CO}_2$  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.