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Russell J. Franks

Stephen F Austin State University, [rjfranks@sfasu.edu](mailto:rjfranks@sfasu.edu)

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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<sub>2</sub> to form stannyl carboxylates (esters) is catalyzed by Pd(PR<sub>3</sub>)<sub>4</sub> complexes. Thus, R<sub>3</sub>SnCH<sub>2</sub>CH=CH<sub>2</sub> [R=Me and Ph] are converted to R<sub>3</sub>SnO<sub>2</sub>CCH<sub>2</sub>CH=CH<sub>2</sub> and R<sub>3</sub>SnO<sub>2</sub>CCH=CHCH<sub>3</sub> under 33 atm of CO<sub>2</sub> (70°C, THF) in moderate to excellent yield in the presence of 8 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>; polycarboxylation of diallyldibutyltin and tetraallyltin also is effected, producing the respective di- and tetracarboxylates, Bu<sub>2</sub>Sn(O<sub>2</sub>CCH<sub>2</sub>CH=CH<sub>2</sub>)<sub>2</sub> and Sn(O<sub>2</sub>CCH<sub>2</sub>CH=CH<sub>2</sub>)<sub>4</sub>, along with the corresponding isomeric crotyl derivatives. In the presence of allyl halides, allyl stannanes and CO<sub>2</sub> 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.