GS4-3 Catalytic Carboxylation Reaction of Bis(π-allyl)palladium (Natsunori SUWA¹, Ryo AMEMIYA¹, Masahiko YAMAGUCHI²)

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The development of an efficient catalytic reaction for the carboxylation of organic compounds with carbon dioxide is desired. However, the problem with this method is difficulty in catalyst regeneration from metal

carboxylate. We considered that $bis(\pi-allyl)$ palladium is highly reactive to carbon dioxide, and allylation of the resulted metal carboxylate readily takes place. It was found that the efficient carboxylation of $bis(\pi-allyl)$ palladium (1) proceeded under ambient pressure of carbon dioxide.

Under a carbon dioxide atmosphere (1 atm), a mixture of 1 and tributylphosphine (1 eq.) in diethyl ether was

treated at 40°C for 12 h, and 3-butenoic acid (2) was obtained in 74% yield. Based on the result, a mixture of allyltributyltin, allyl chloride, and 50 mol% of tributylphosphine in THF was treated with a palladium catalyst (13 mol%) under carbon dioxide (1 atm) at 70 °C for 24 h, and allyl 3-butenoate (3) was obtained in 179% yield

THF, 70 °C, 24 h

mol%) under carbon dioxide (1 atm) at 70 °C for 24 h, and allyl 3-butenoate (3) was obtained in 179% yield based on Pd. It was found that the catalytic carboxylation of 1 took place under atmospheric carbon dioxide.

$$\frac{\langle Pd \rightarrow \rangle}{1} + \frac{CO_2}{1 \text{ atm}} \frac{P(n-Bu)_3}{Et_2O, 40 °C, 12 h} \frac{(1 \text{ eq.})}{2} \frac{Pd_2(dba)_3CHCl_3}{2} \frac{(13 \text{ mol}\%)}{2} + \frac{Pd_2(dba)_3CHCl_3}{2} \frac{(13 \text{ mol}$$

1 atm