Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions

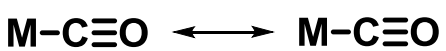
- **Carbon monoxide as ligand**
  - **Complexes are available by direct synthesis**

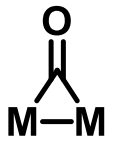
$$Ni + CO \longrightarrow Ni(CO)_4$$

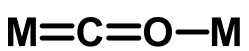
  - **Complexes are available by reductive carbonylation**

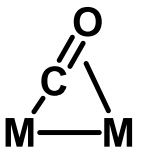
$$WCl_6 + CO + Et_3Al \longrightarrow W(CO)_6$$

  - **CO binding modes**

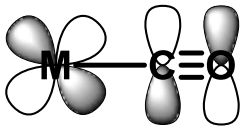




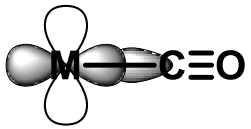




π-backbonding



σ-donation



Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions

- **Carbon monoxide as ligand**
  - **Carbon monoxide as a tool to determine the scope of π-backbonding**

CO	$Ph_3P(Cl)Ir(CO)PPh_3$	$Ph_3P(Cl)Pt^{\oplus}(CO)PPh_3$	$Ni(CO)_4$	$Co(CO)_4^{1-}$	$Fe(CO)_4^{2-}$
ν_{CO} = 2143	ν_{CO} = 1860	ν_{CO} = 2100	ν_{CO} = 2057	ν_{CO} = 1886	ν_{CO} = 1785
		decreased π-backbonding		increased π-backbonding	

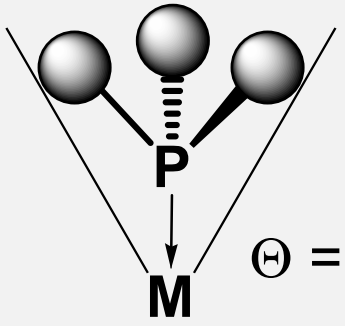
  - **Carbon monoxide and electronic properties of *P*-ligand**

$Ni(CO)_3L$ CO ν_{CO} = 2143 $Ni(CO)_4$ ν_{CO} = 2057

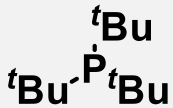
$P(t\text{-Bu})_3$	$P(Cy)_3$	$P(Me)_3$	$P(Ph)_3$	$P(4\text{-}OMeC_6H_4)_3$	$P(OMe)_3$	$P(OPh)_3$	PF_3
ν_{CO} = 2056	ν_{CO} = 2056	ν_{CO} = 2064	ν_{CO} = 2069	ν_{CO} = 2069	ν_{CO} = 2079	ν_{CO} = 2085	ν_{CO} = 2110 weakest donor

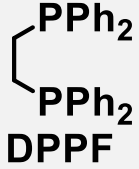
Basic Mechanisms in Organometallic Chemistry

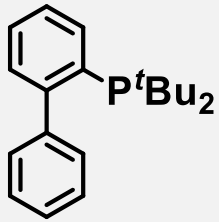
➢ Tolman cone angle (Bite angle)

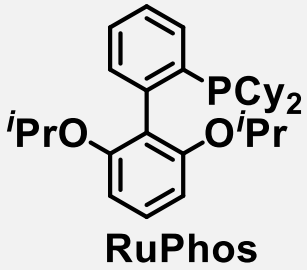


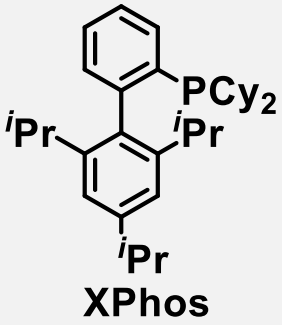
Θ = Cone angle

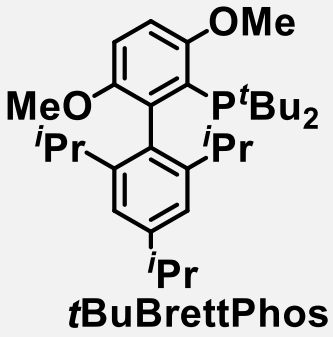


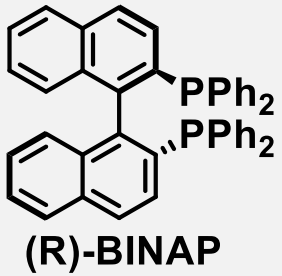


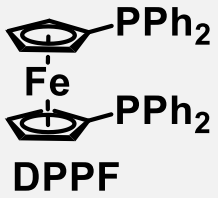


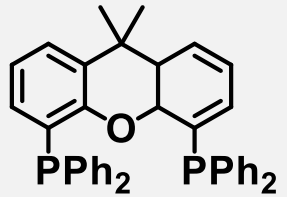








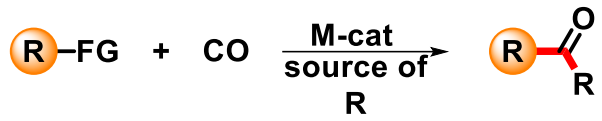




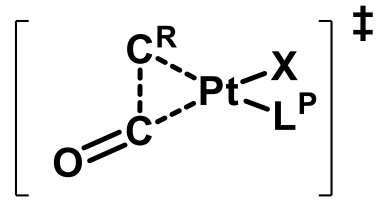
Phosphorus ligand	Cone angle (°)
PH_3	87
$P(OMe)_3$	107
PMe_3	118
PPh_3	145
PCy_3	170
P^tBu	182
$P(mesityl)_3$	212

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

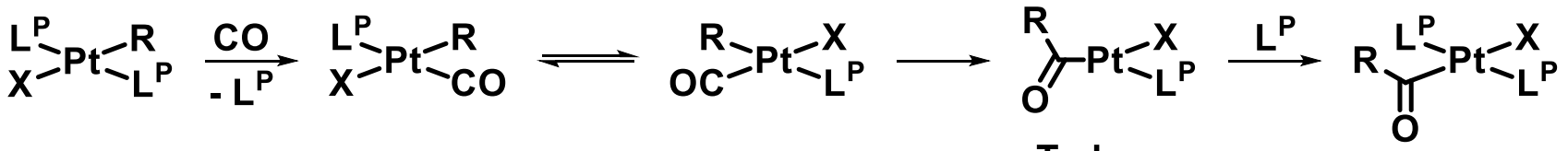
➢ Carbonylation reactions



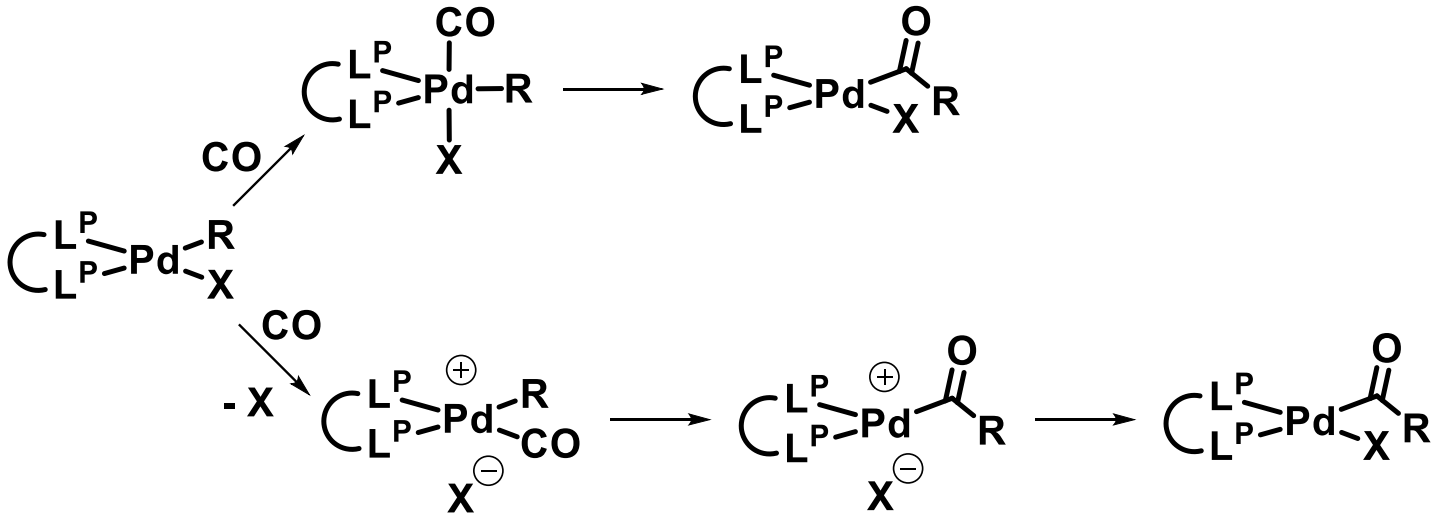
- Insertion of carbon monoxide for 16-electrons d^8 complexes



○ Mechanism for complexes with monodentate ligands

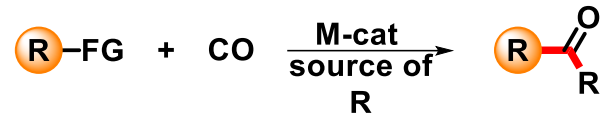


○ Mechanism for complexes with bidentate ligands

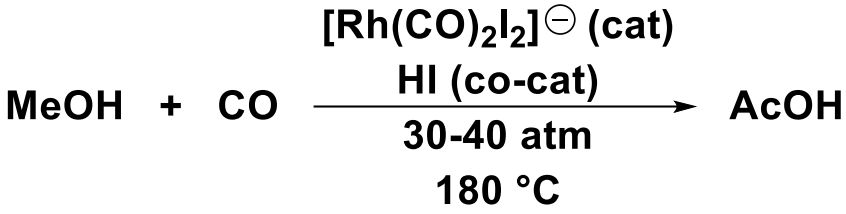


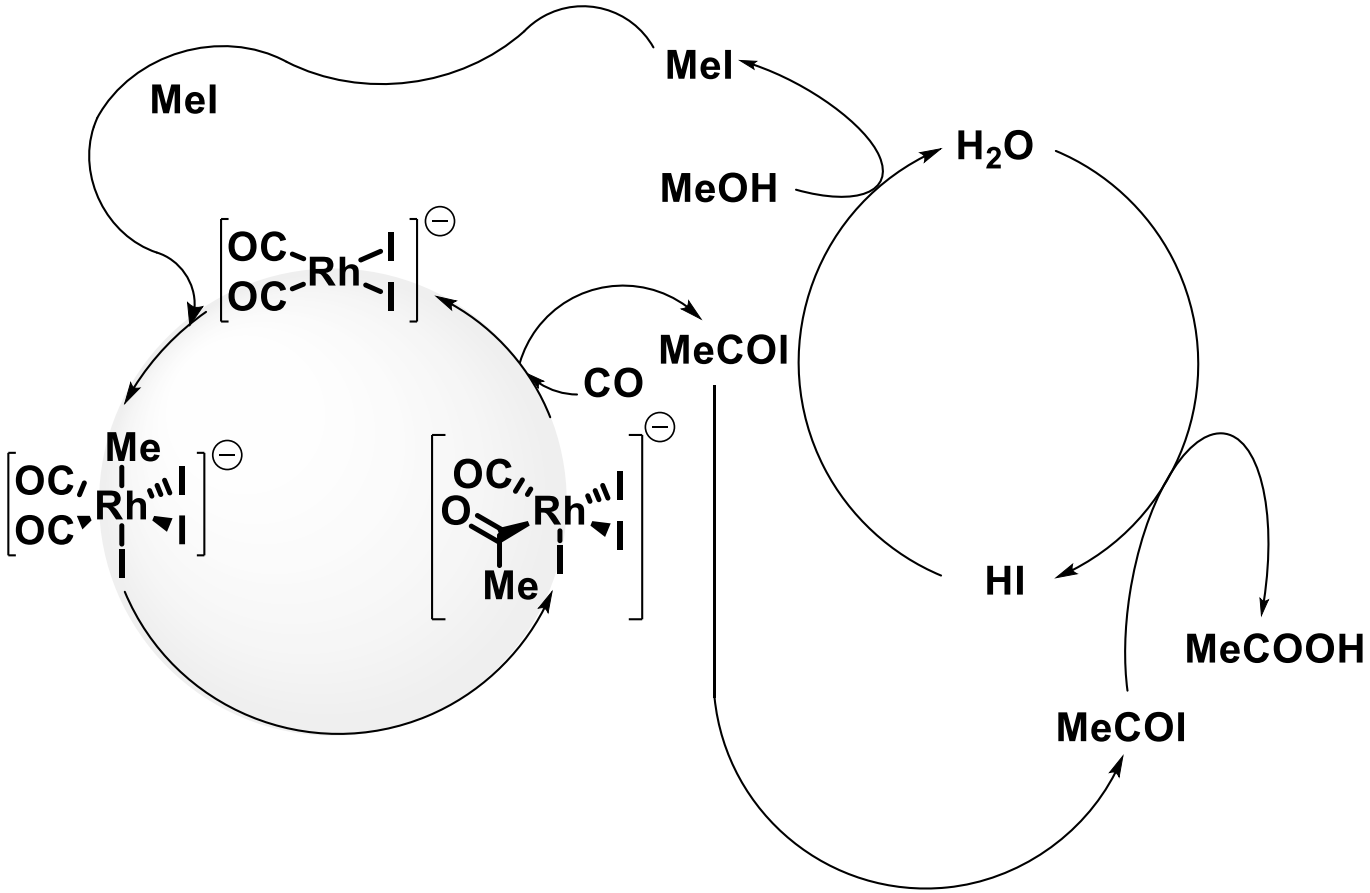
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions



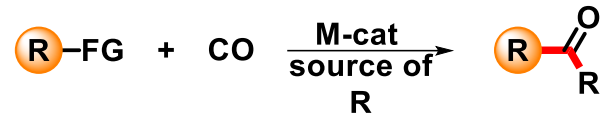
- **Industrial applications**
  - **Monsanto proces for acetic acid synthesis**



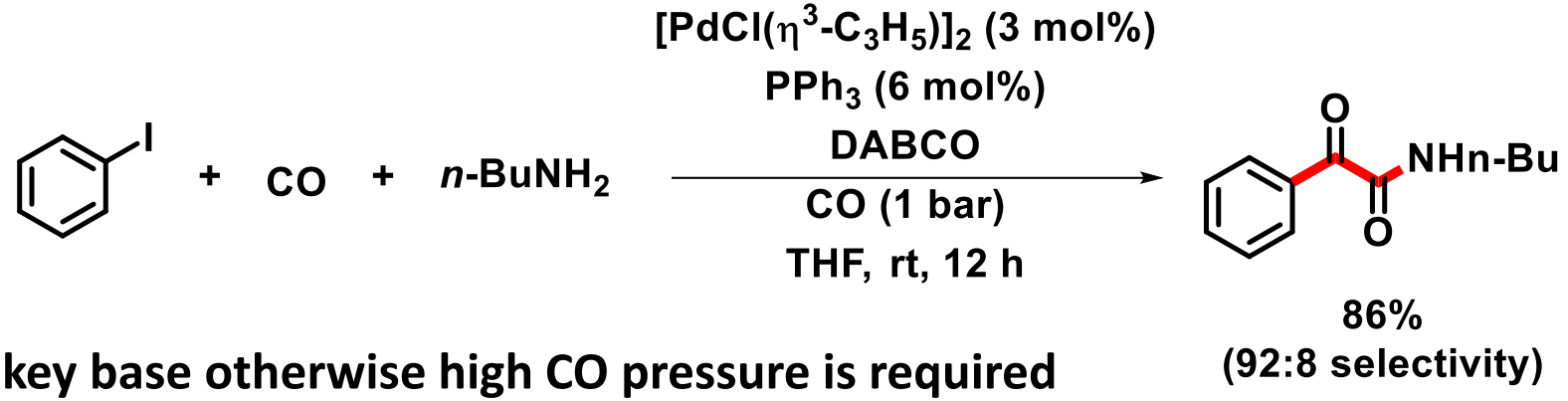


Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions

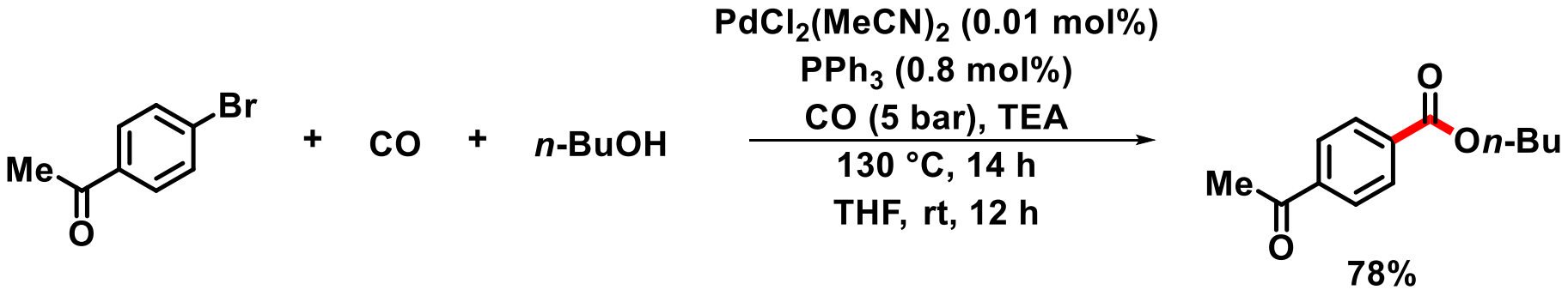


- **Synthetic applications – transition-metal-catalyzed carbonylation of substrates with C–halogen bonds**



✓ **DABCO is the key base otherwise high CO pressure is required**

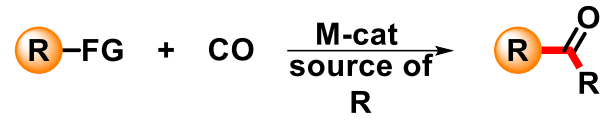
J. Org. Chem. **2001**, *66*, 5272



- *J. Mol. Catal. A: Chem.* **2000**, *156*, 213

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions



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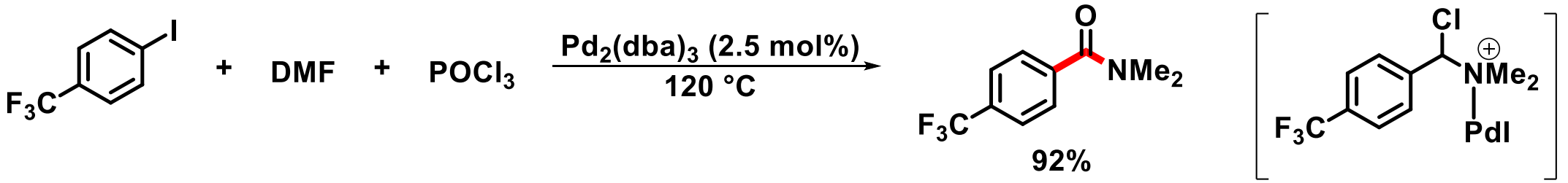
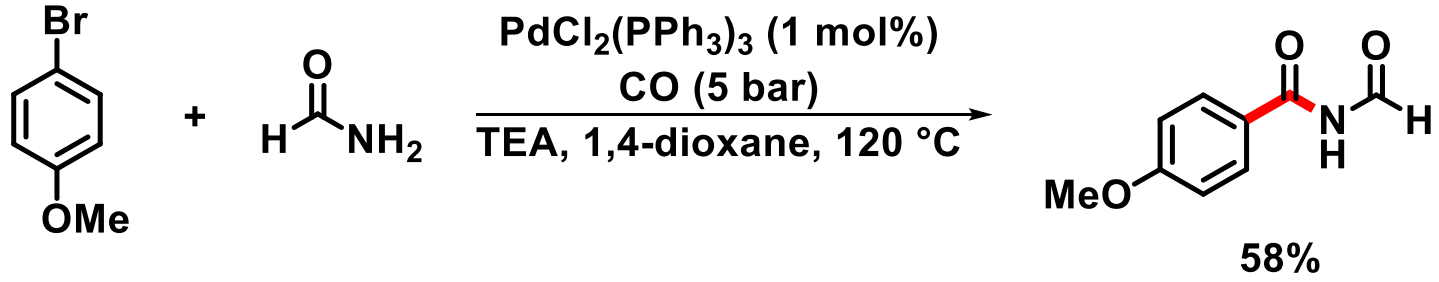


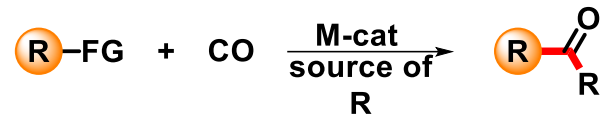
Org. Lett. **2002**, *4*, 2849



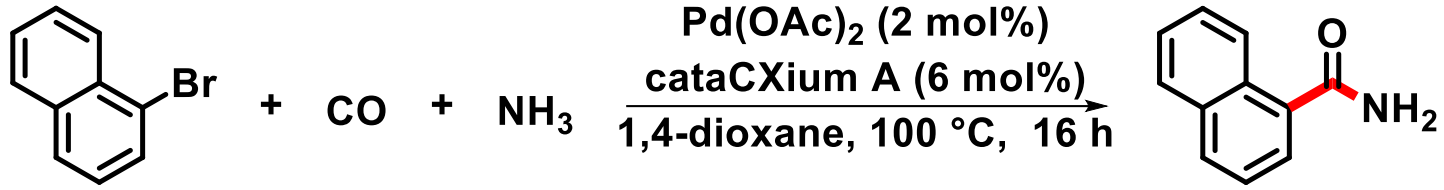
J. Org. Chem. **2002**, *67*, 594

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions

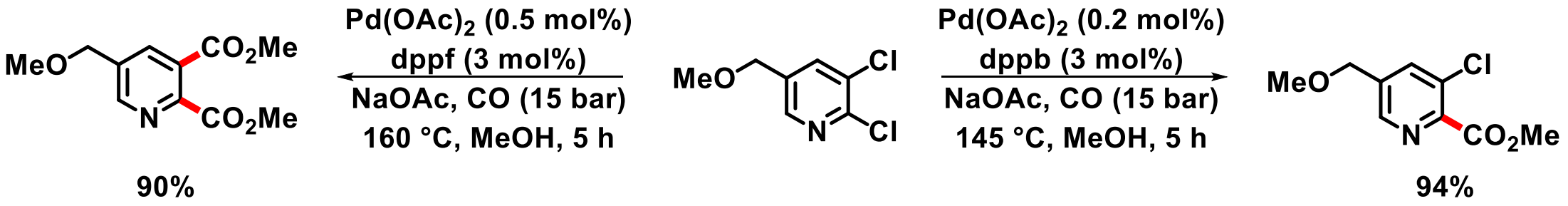


- **Synthetic applications – transition-metal-catalyzed carbonylation of substrates with C–halogen bonds**



98%

Chem. Eur. J. **2010**, *16*, 9750

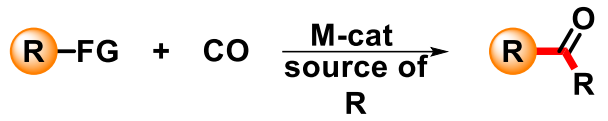


90% 94%

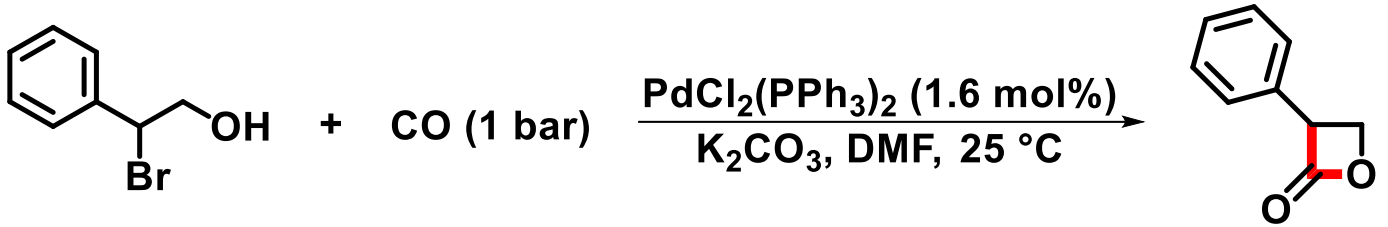
Tetrahedron **1999**, *55*, 393

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

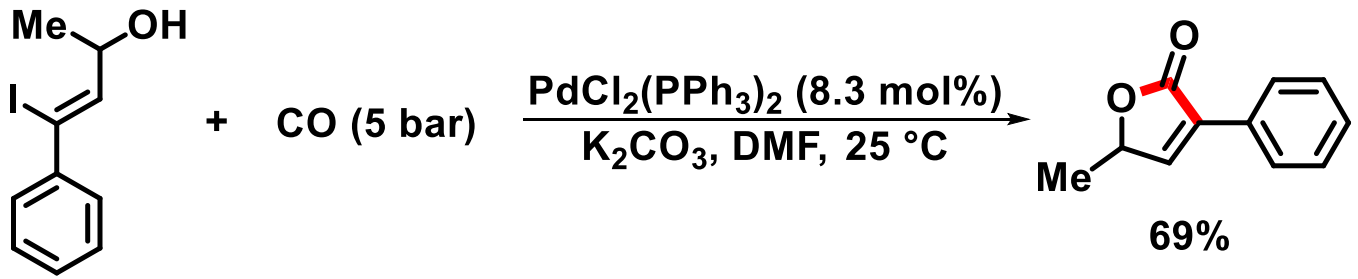
➢ Carbonylation reactions



- **Synthetic applications – transition-metal-catalyzed carbonylation of substrates with C–halogen bonds**



63%

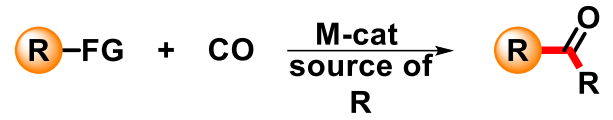


69%

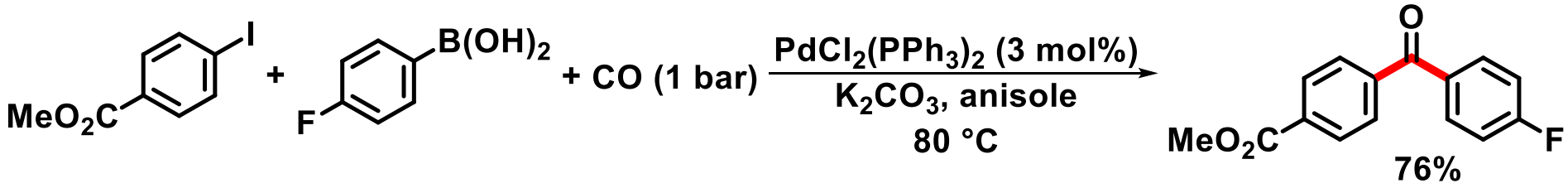
J. Am. Chem. Soc. **1980**, *102*, 4193

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

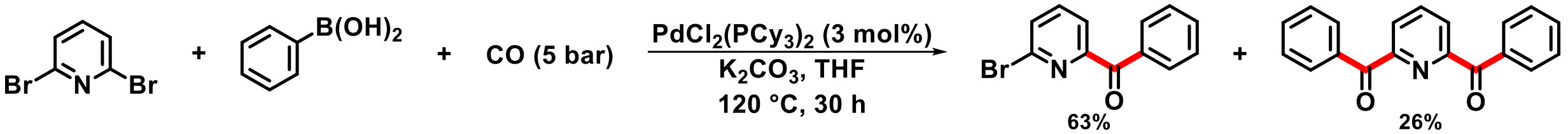
➢ Carbonylation reactions



- **Carbonylative coupling in the presence of organometallic reagents**



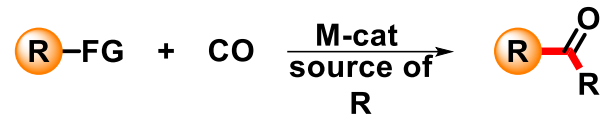
Tetrahedron Lett. **1993**, *34*, 7595



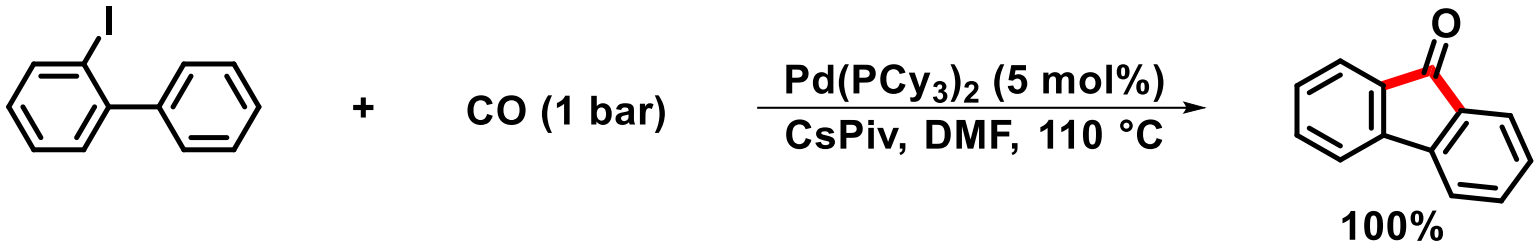
Tetrahedron Lett. **2001**, *42*, 3689

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

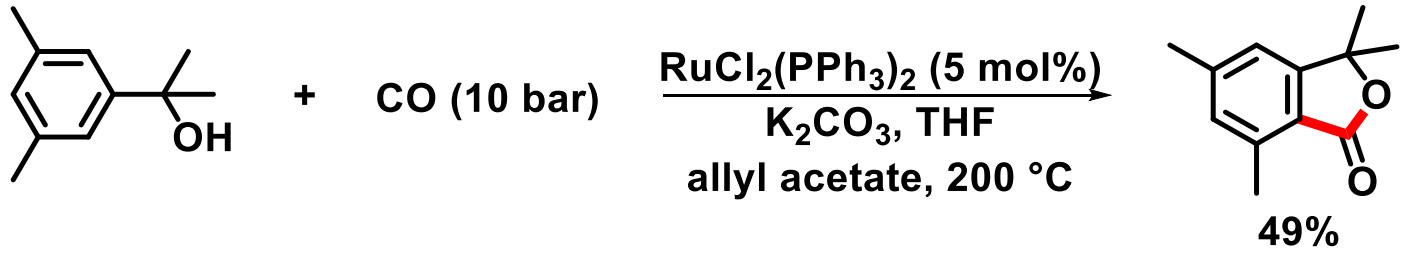
➢ Carbonylation reactions



- **Carbonylative C–H activation**



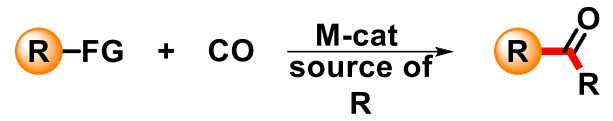
J. Org. Chem. **2002**, *67*, 5616



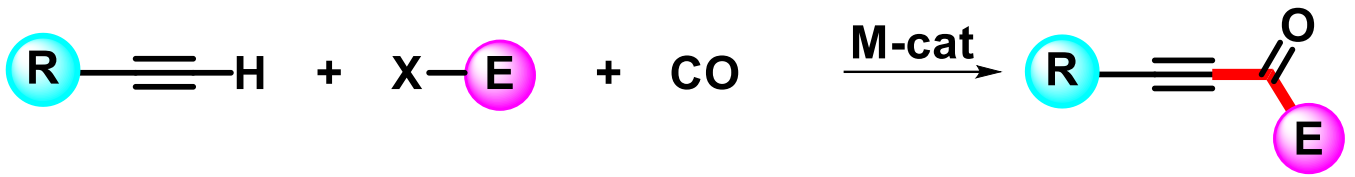
Chem. Lett. **2003**, *32*, 24,

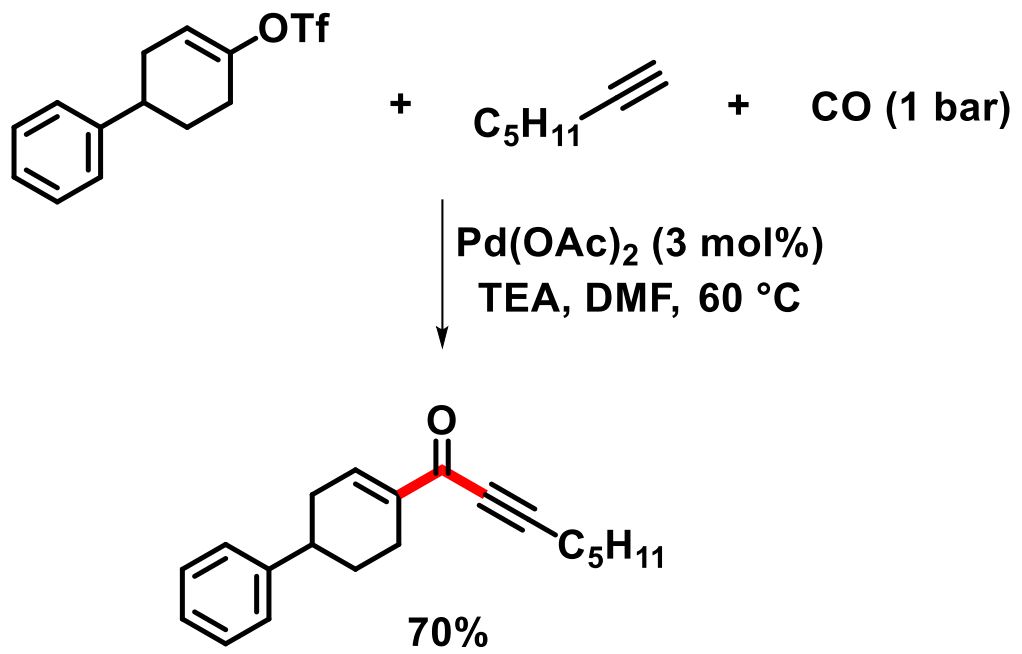
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions



- **Carbonylative Sonogashira reaction**

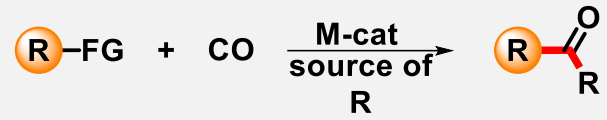




Tetrahedron Lett. **1991**, *32*, 6449

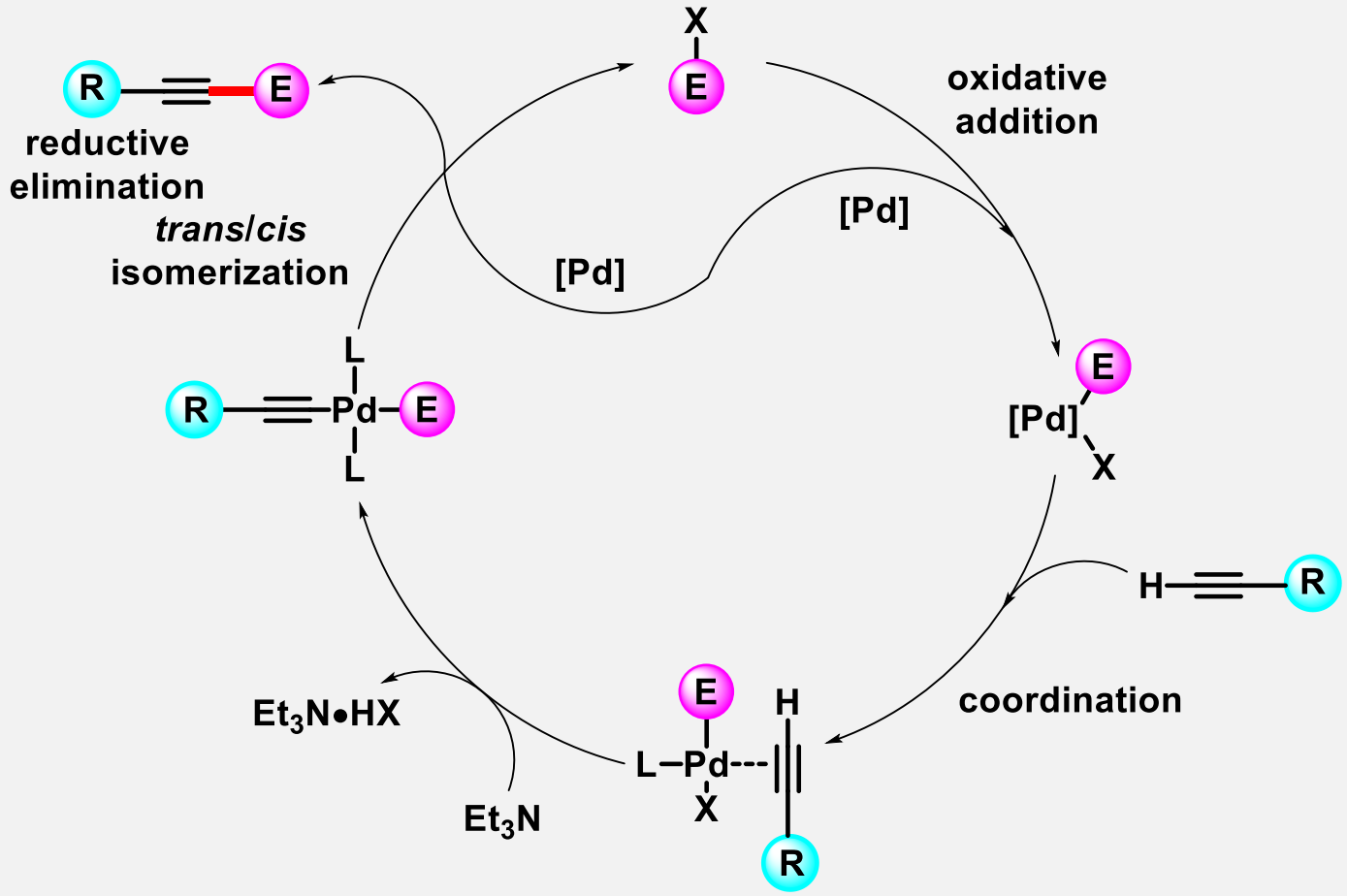
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions



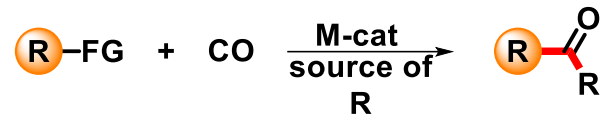
- **Carbonylative Sonogashira reaction**

○ **Catalytic scheme for Sonogashira reaction**



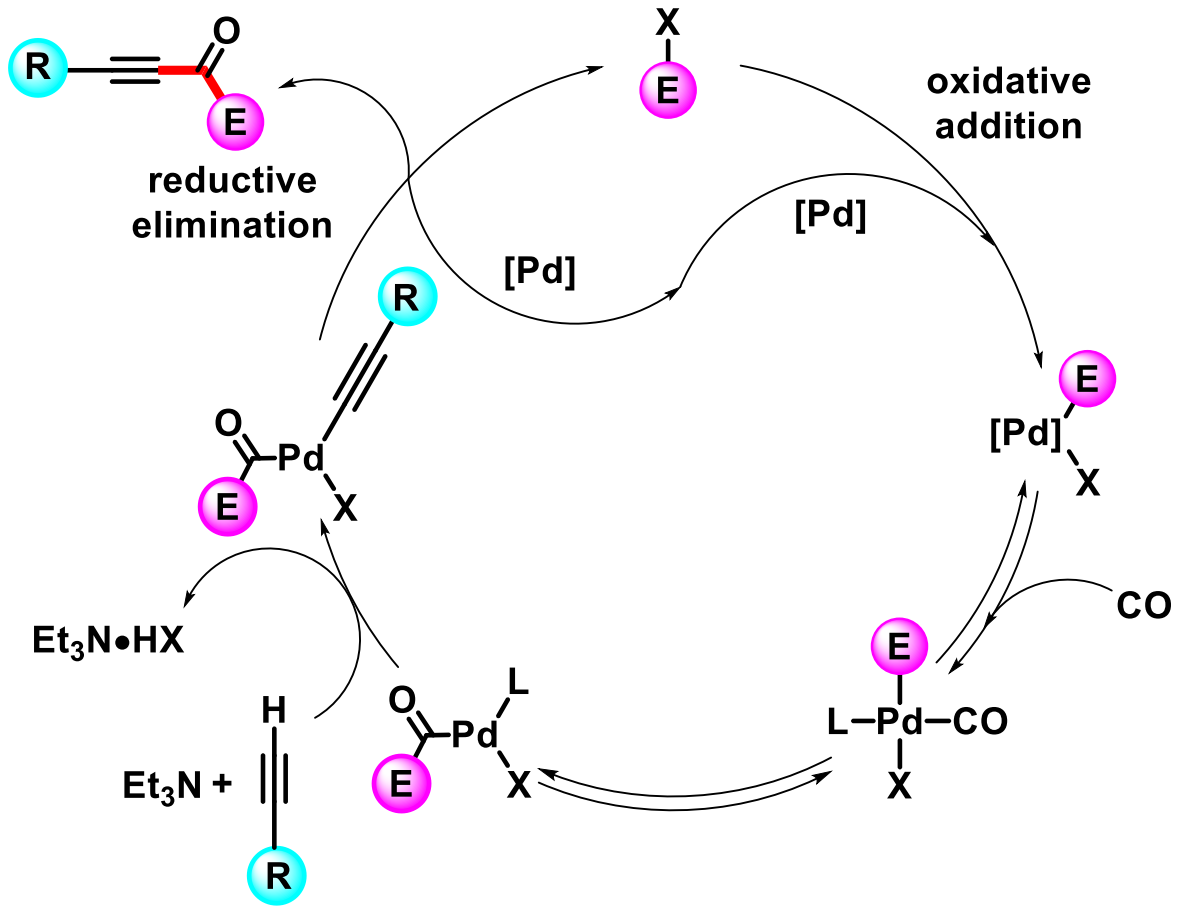
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carbonylation reactions



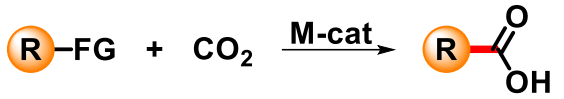
- **Carbonylative Sonogashira reaction**

○ **Catalytic scheme for carbonylative Sonogashira reaction**

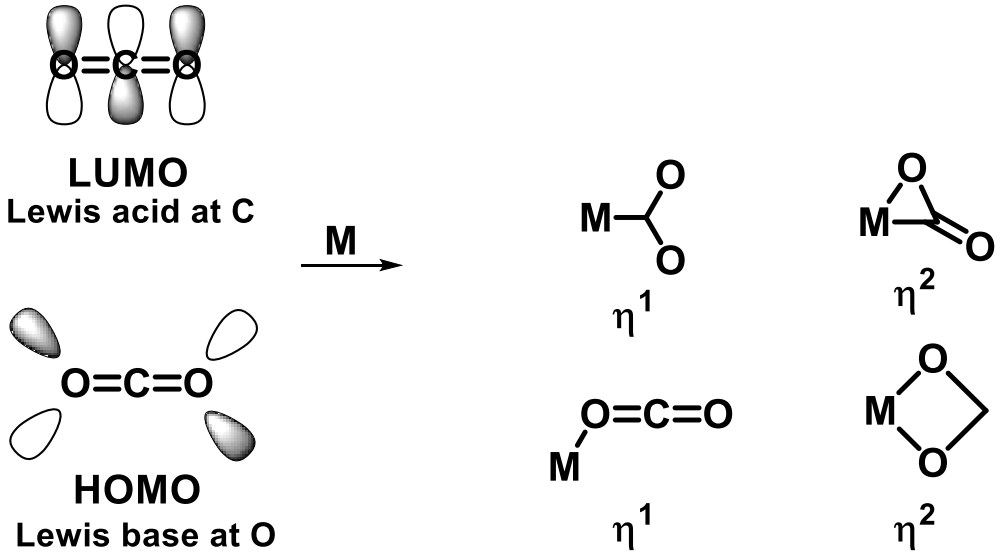


Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

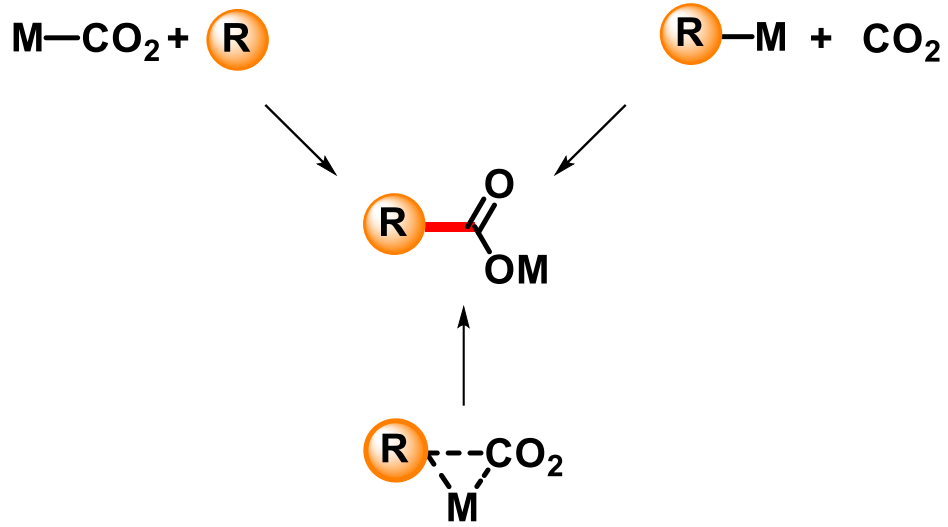
➢ Carboxylation reactions with carbon dioxide



- **Binding modes for carbon dioxide**



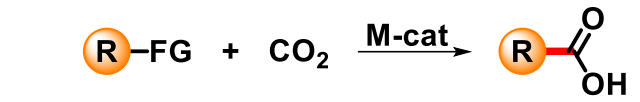
- **Pathways for carboxylation with CO_2**



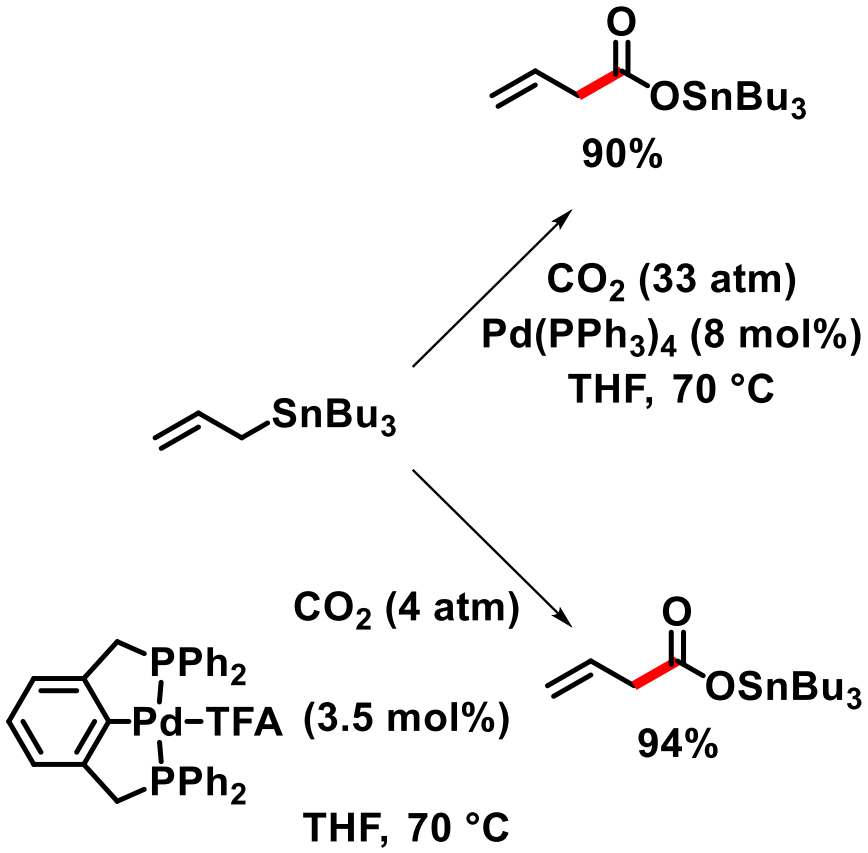
- **Binding lowers down the activation energy for CO_2 activation.**

Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

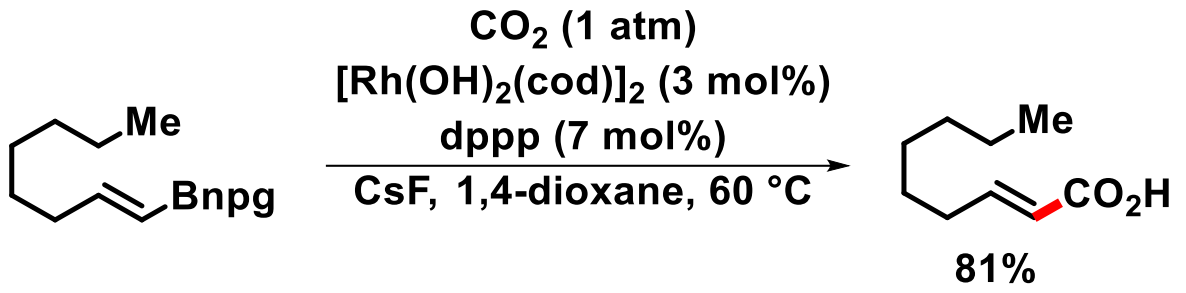
➢ Carboxylation reactions with carbon dioxide



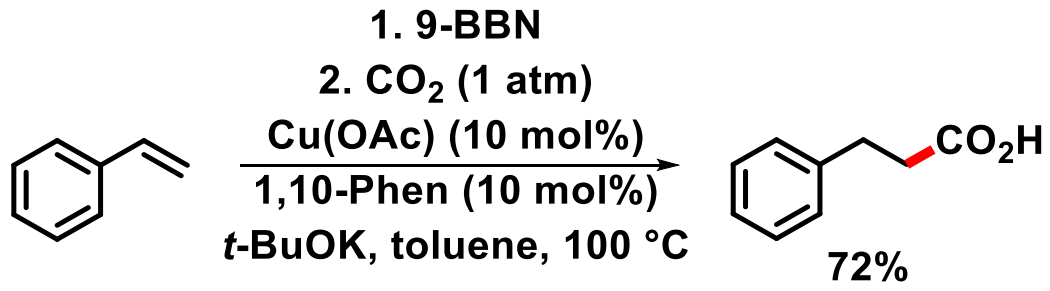
• Carboxylation of organometallic reagents



J. Am. Chem. Soc. **1997**, *119*, 5057



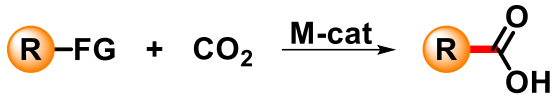
J. Am. Chem. Soc. **2006**, *128*, 8706



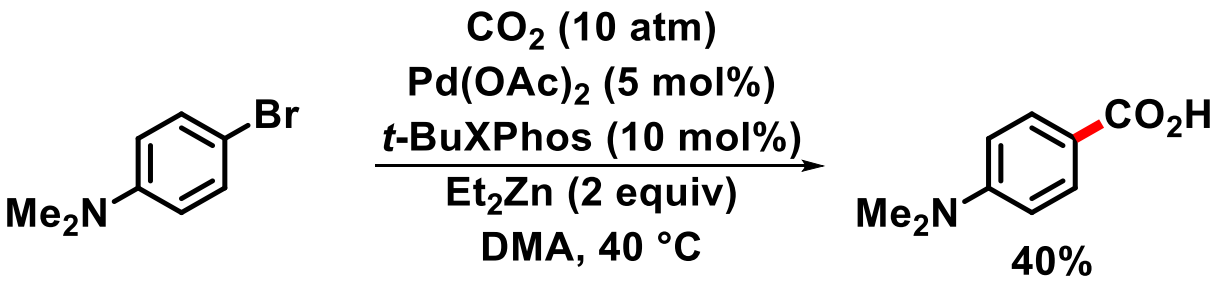
Org. Lett. **2011**, *13*, 1086

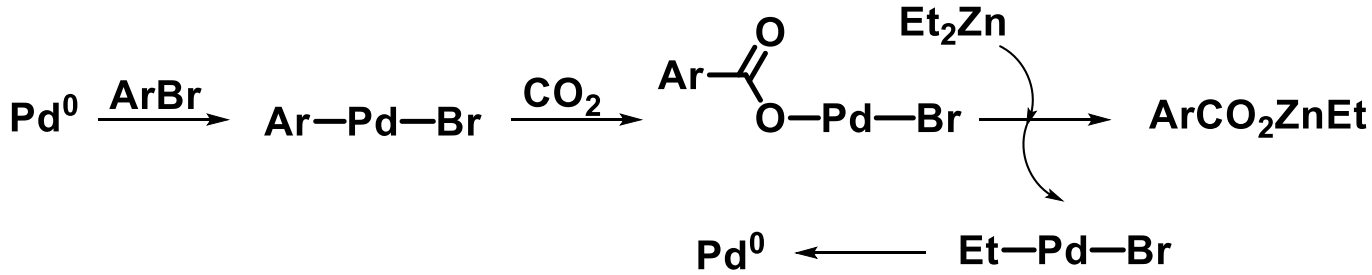
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carboxylation reactions with carbon dioxide

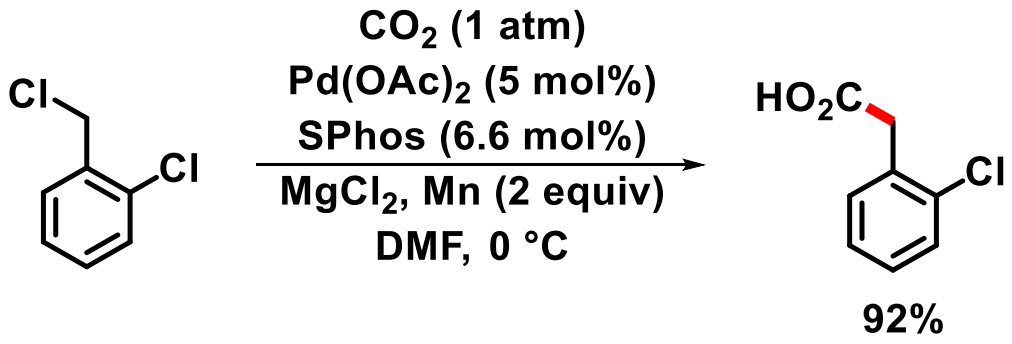


• Reductive carboxylation





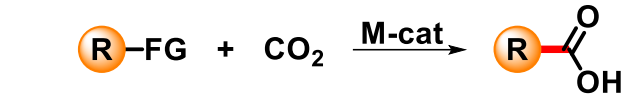
J. Am. Chem. Soc. **2009**, *131*, 15974



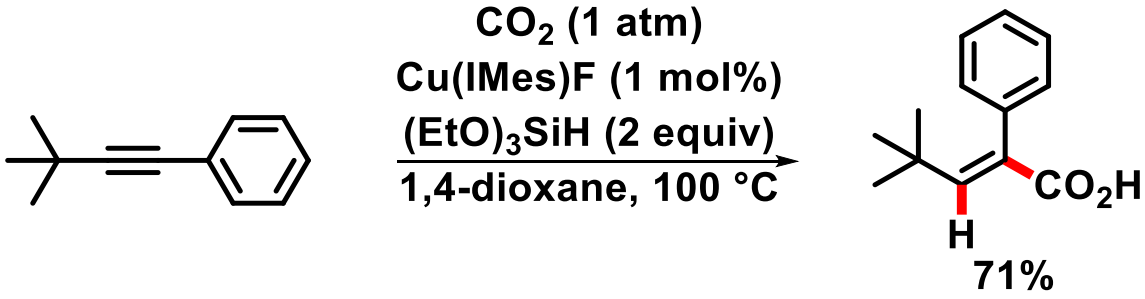
ChemCatChem **2015**, *7*, 3972

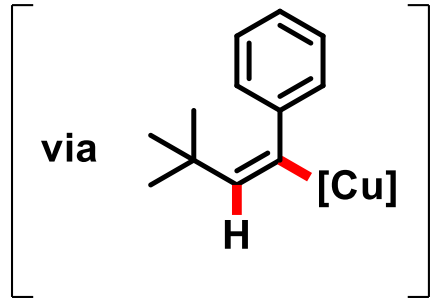
Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carboxylation reactions with carbon dioxide

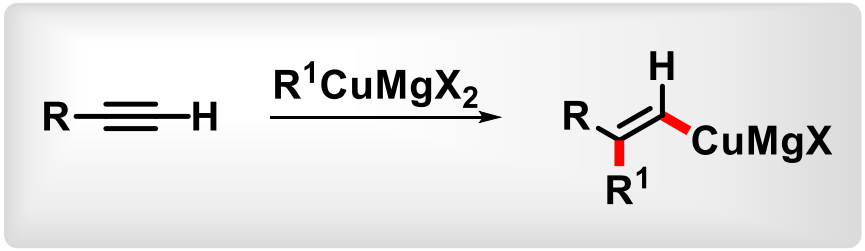


- **Catalytic hydrocarboxylation of alkynes**



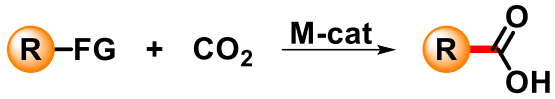


Angew. Chem. Int. Ed. **2011**, *50*, 523

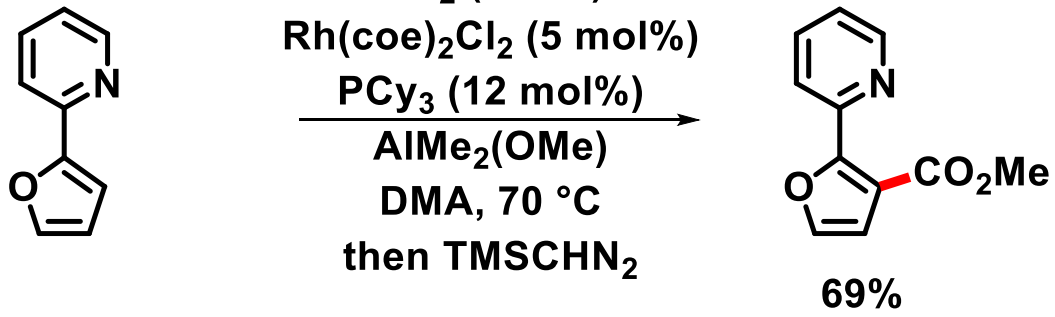


Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

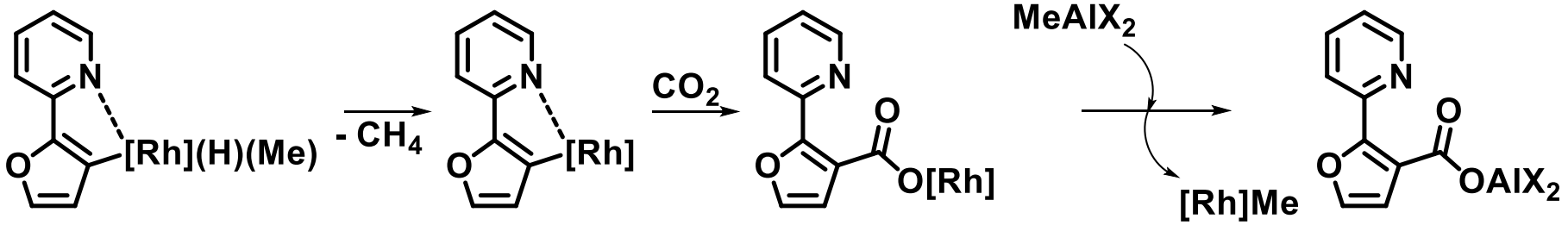
➢ Carboxylation reactions with carbon dioxide



- **C–H carboxylation**

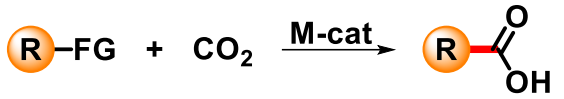


J. Am. Chem. Soc. **2011**, *133*, 1251

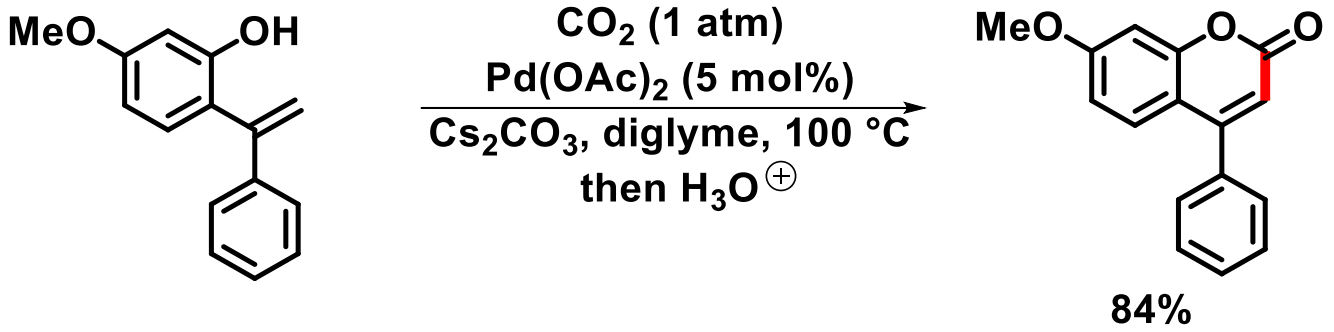


Transition-Metal-Catalyzed Carbonylation and Carboxylation Reactions

➢ Carboxylation reactions with carbon dioxide



- **C–H carboxylation**



J. Am. Chem. Soc. **2013**, *135*, 10954