



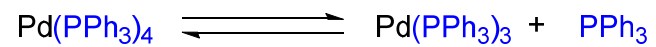
金属有机中的基元反应及应用

Peiyi Huang

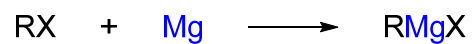
2022.4.22

基元反应的分类

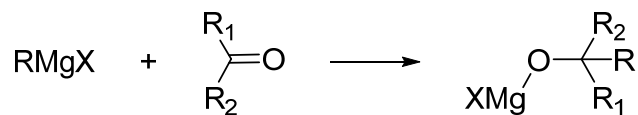
1. 配体的配位和解离



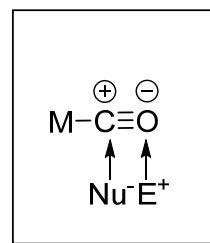
2. 氧化加成和还原消除



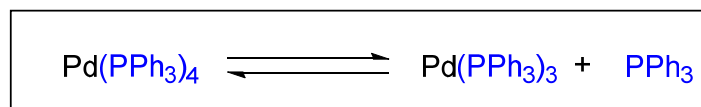
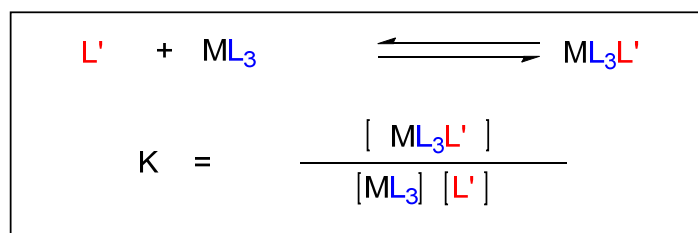
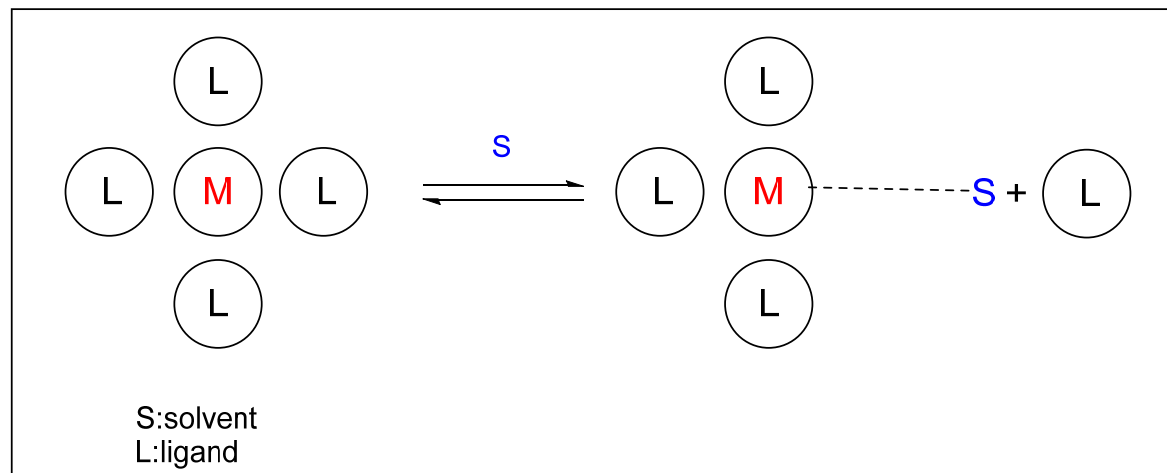
3. 插入与消除反应



4. 和金属络合物的配体反应

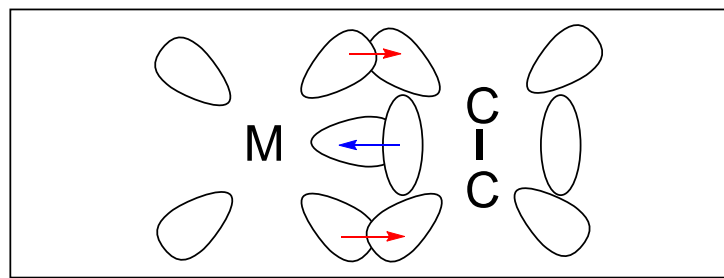


1.体的配位和解离



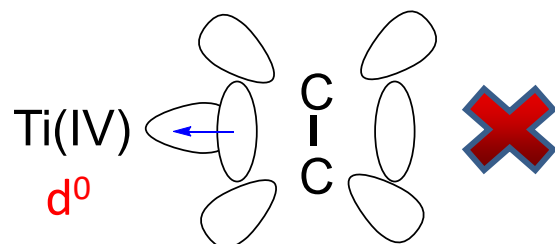
常用的金属络合物：Ni(cod)₂、Fe(CO)₅等

过度金属和烯烃配位



蓝箭头: σ 键, 烯烃供给金属电子成键

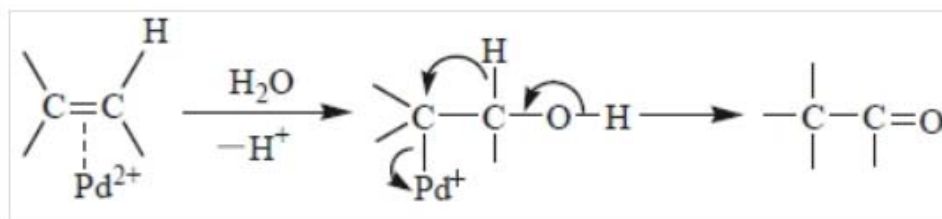
红箭头: π 键, 金属成键d轨道电子向烯烃反键 π^* 轨道反馈成键



单独依靠 σ 键不能使金属与烯烃成稳定络合物

与金属配位的烯烃被活化, 键长变长, 红外吸收光谱波数降低。

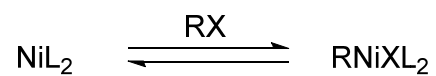
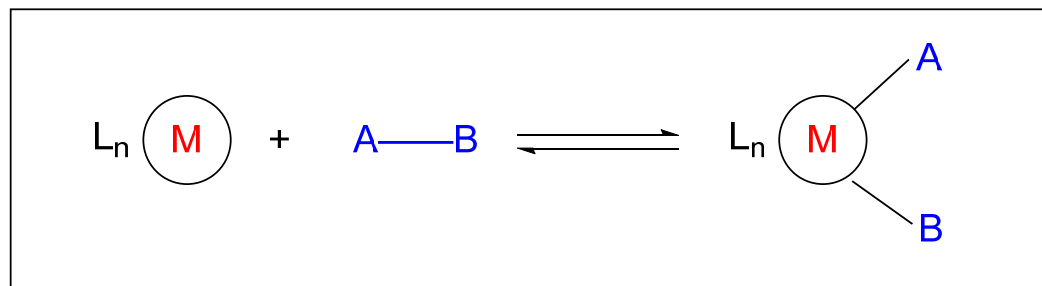
Wacker反应:



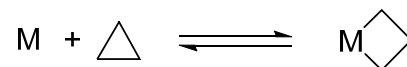
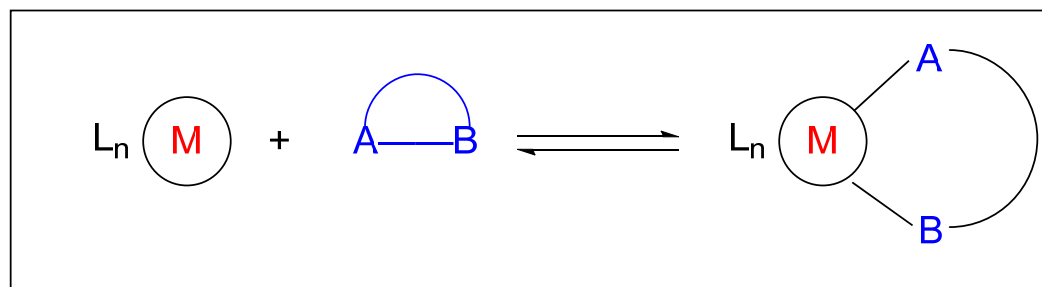
如CO, N₂, CO₂, SO₂, 等小分子都可以通过与过渡金属配位活化。

2.氧化加成和还原消除

第一类:

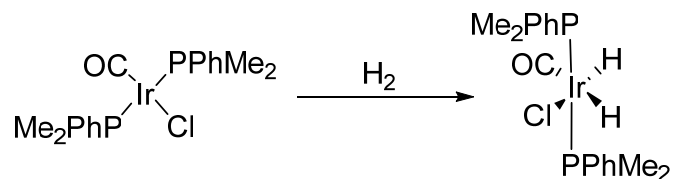


第二类:



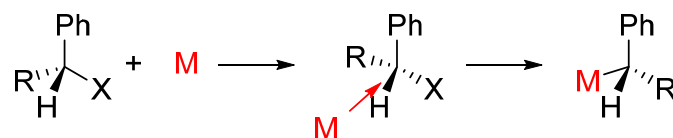
氧化加成

1. H₂的氧化加成



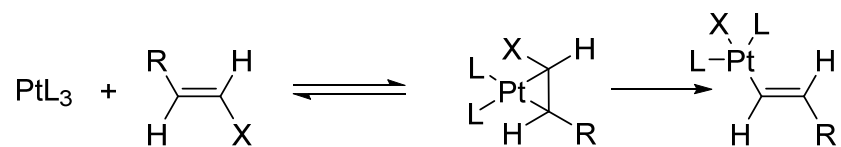
顺式加成

2. C-X的氧化加成



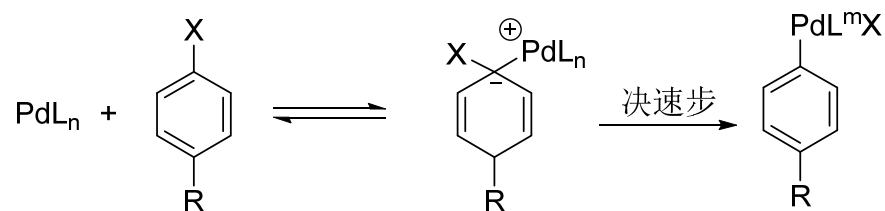
S_N2机理，反式加成

3. 卤代烯烃的氧化加成



构型保持

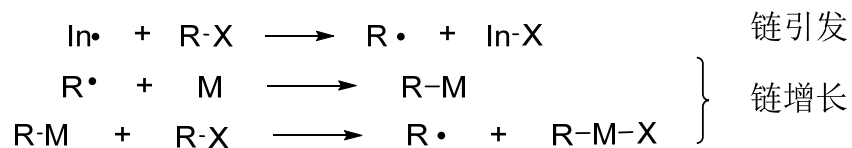
4. 卤代芳烃的氧化加成



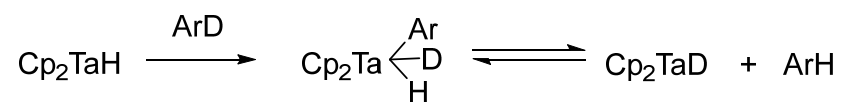
碘代物反应活性最高
吸电子取代基加快反应速率

氧化加成

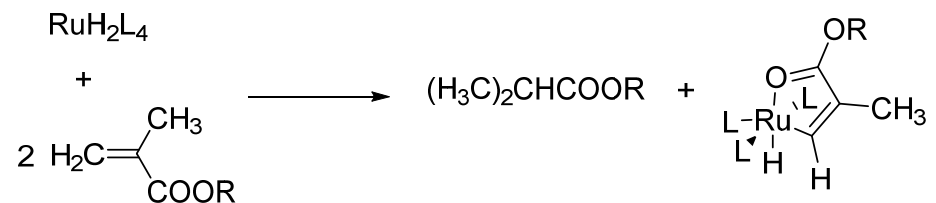
5. 自由基机理的氧化加成



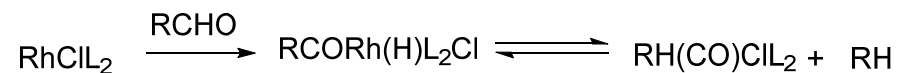
6. 芳烃碳氢键的氧化加成



7. 烯烃碳氢键的氧化加成



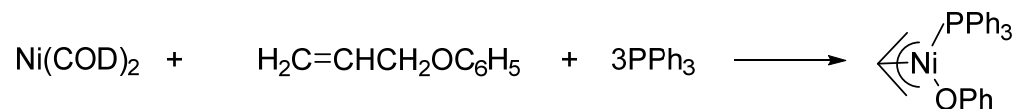
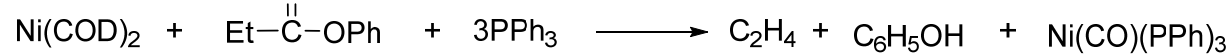
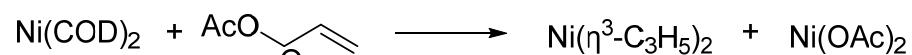
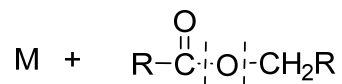
8. 醛碳氢键的氧化加成



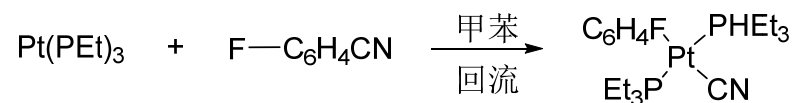
具有活泼氢的化合物如丙酮、乙酸酯等也可以与金属络合物发生氧化加成

氧化加成

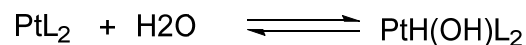
9. 碳氧键的氧化加成



10. 碳碳键的氧化加成

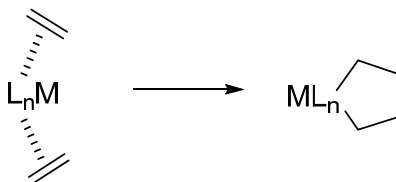


11. 其它化学键的氧化加成



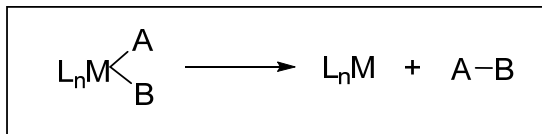
C-N、C-P、N-H、均可以与低价金属发生氧化加成

12. 环金属化反应



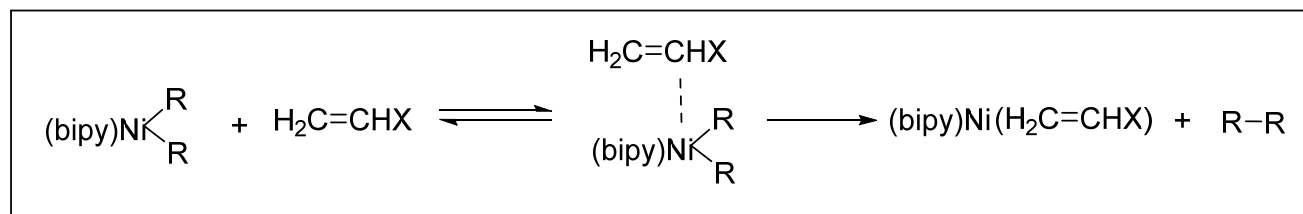
还原消除

基本途径:



促进还原消除的因素:

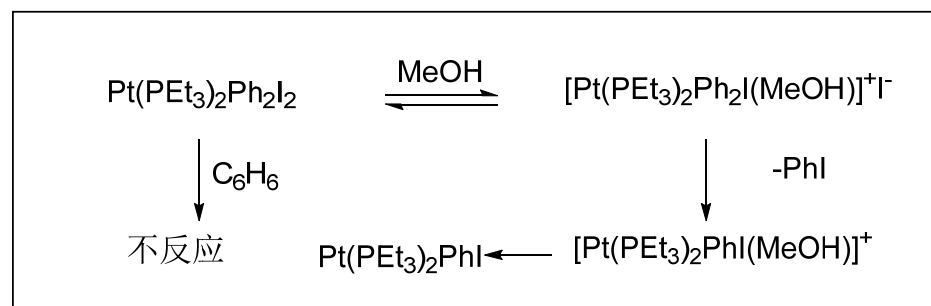
1. 吸电子烯烃



2. CO

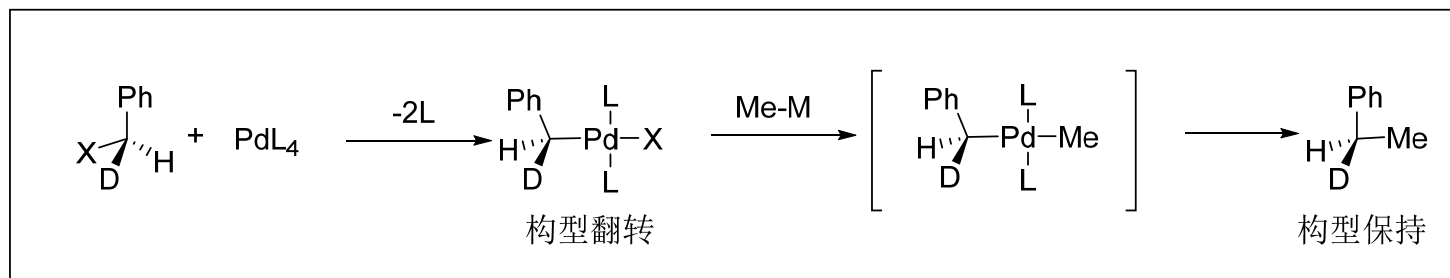
3. 加热

4. 正电荷



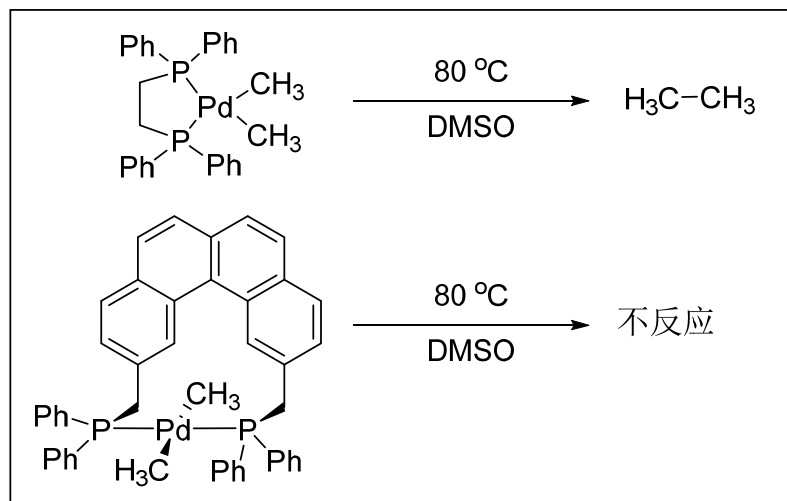
还原消除

还原消除的立体化学:



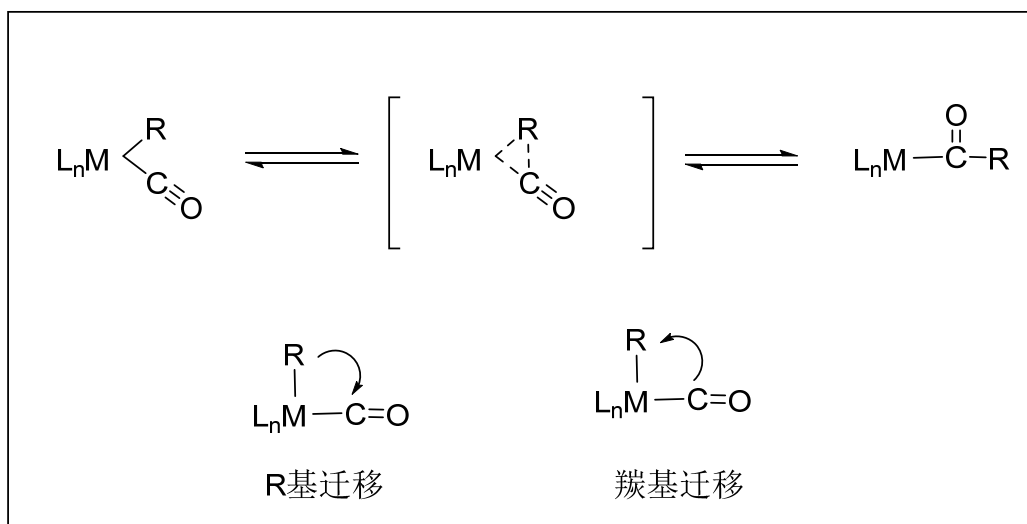
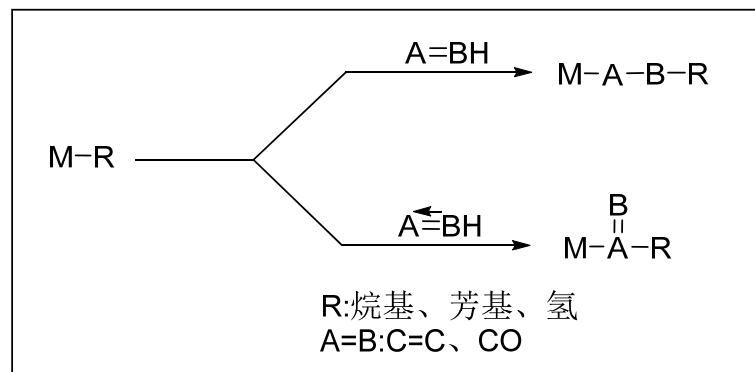
还原消除中构型是保持的

还原消除的立体要求:



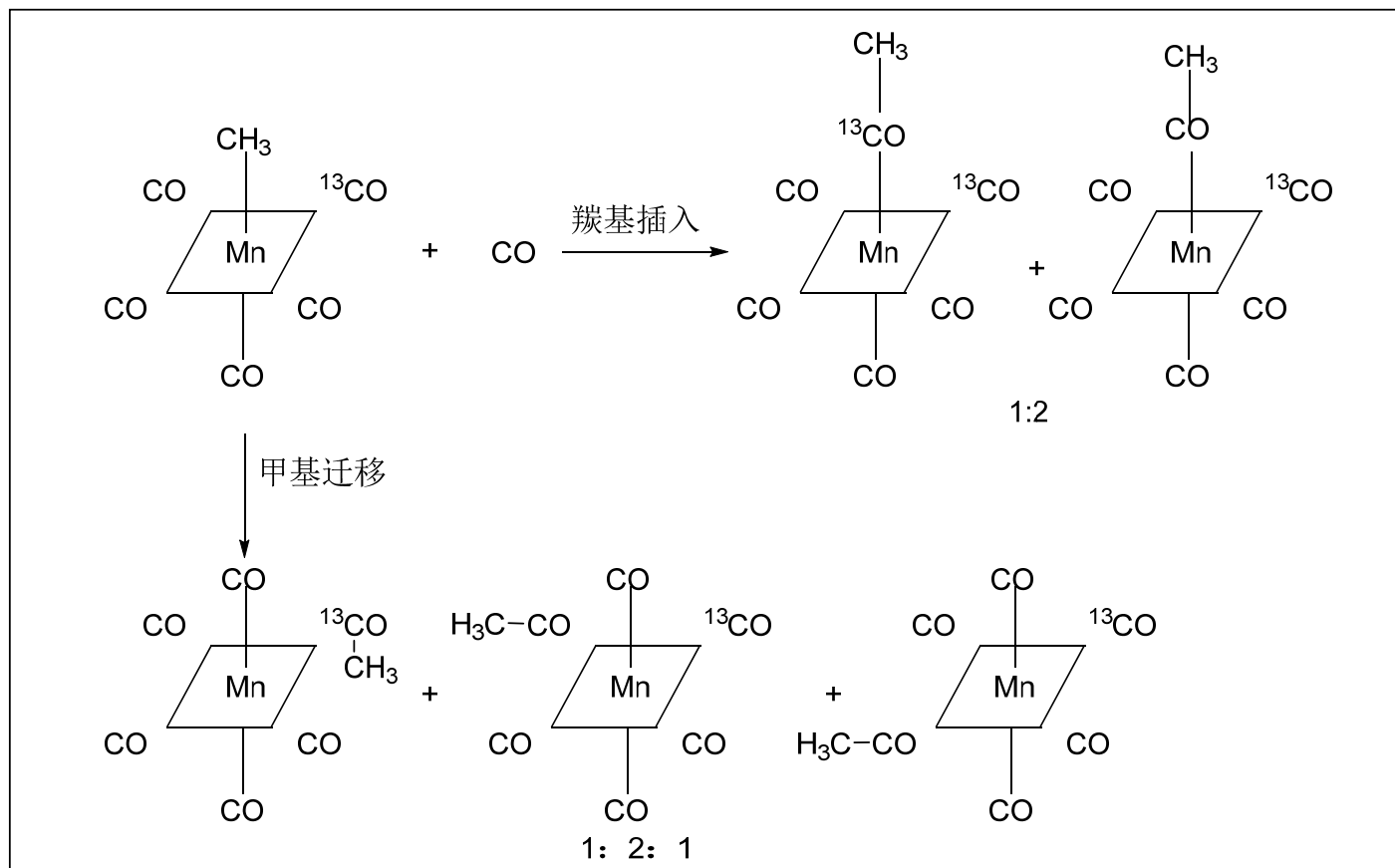
3.插入与消除反应

CO的插入反应:



插入反应

机理验证:

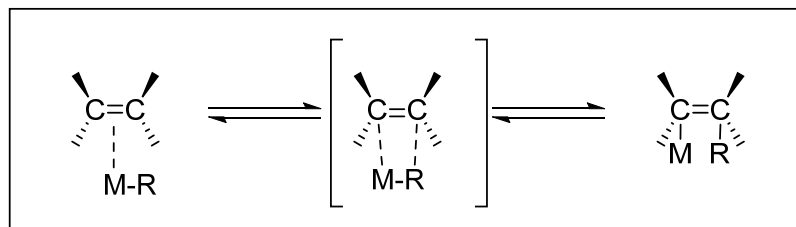


反应机理是按照烷基迁移进行的

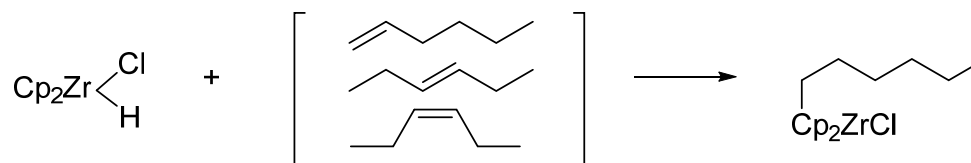
烷基位移的一般次序：烷基>苄基>>H、全氟烷基与酰基
金属活性：原子序数小的金属烷基化合物更容易迁移

烯烃的插入与 β -H消除

反应机理:



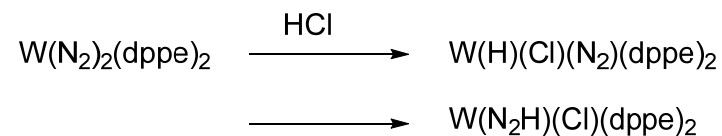
反应实例:



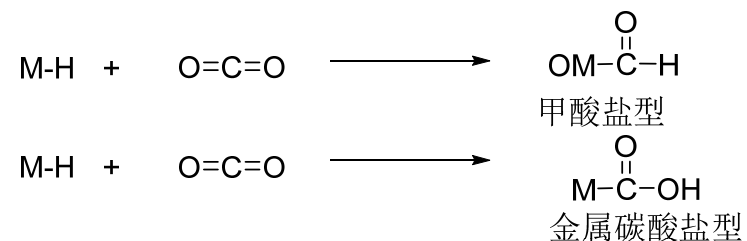
烷基位移的一般次序：烷基>苄基>>H、全氟烷基与酰基
金属活性：原子序数小的金属烷基化合物更容易迁移

其它分子插入

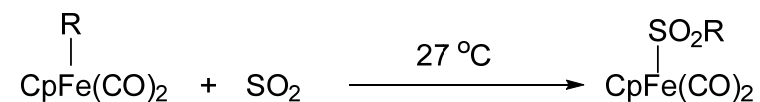
1. N₂插入



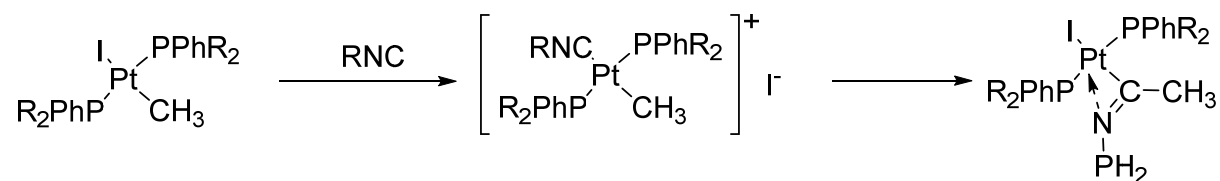
2. CO₂插入



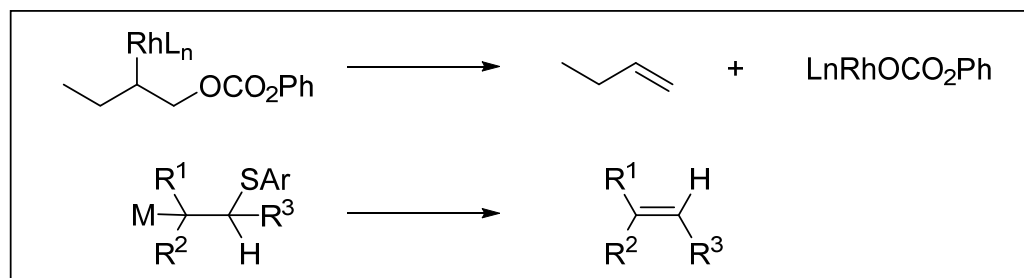
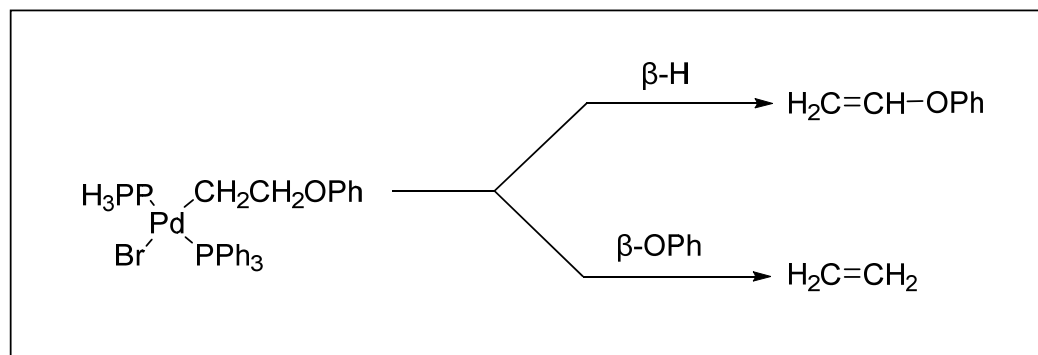
3. SO₂插入



4. 异腈

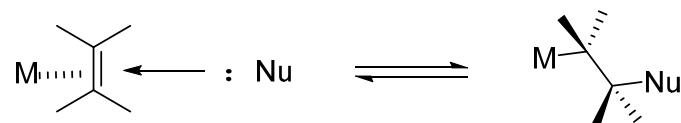


氢以外的β-攢取反应

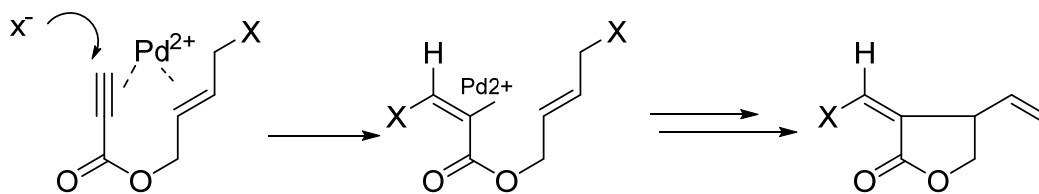


4.和金属络合物的配体反应

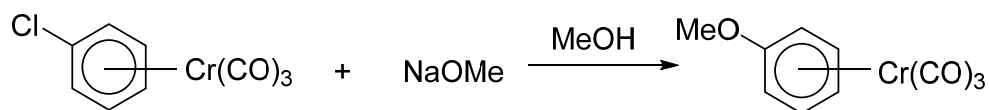
1.配位的烯烃反应



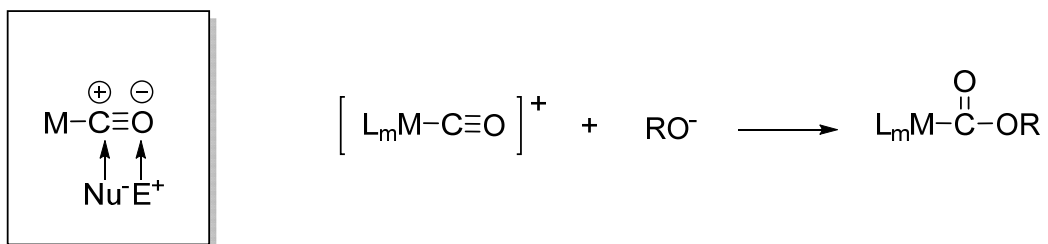
2.配位的炔烃反应



3.配位的苯环反应



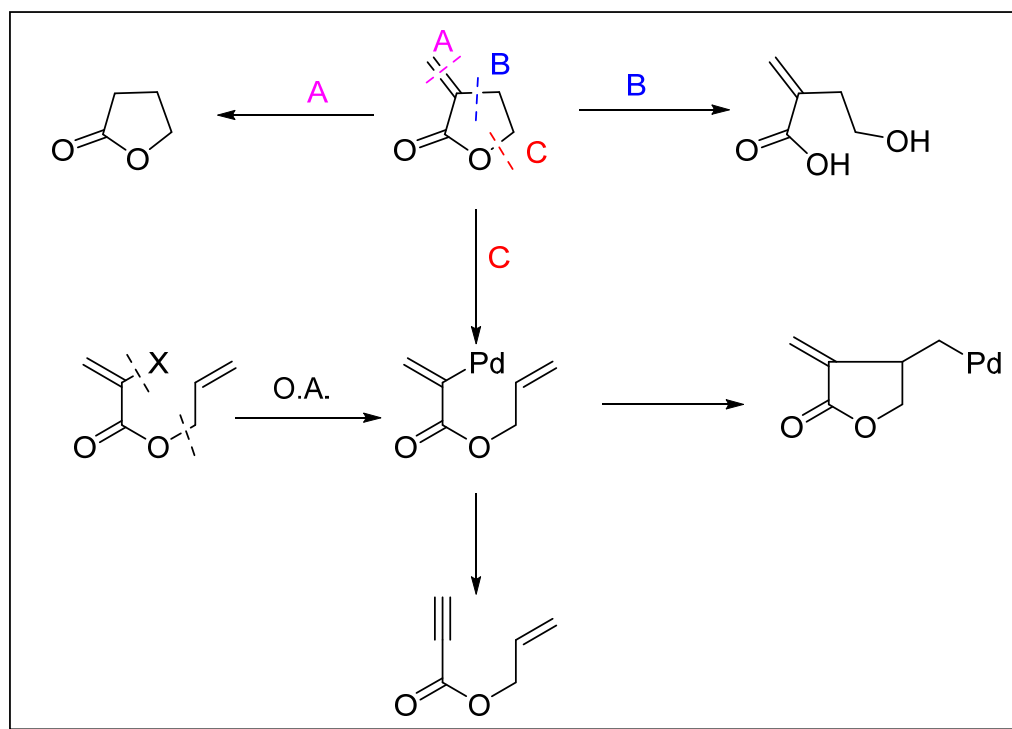
4.配位的CO反应



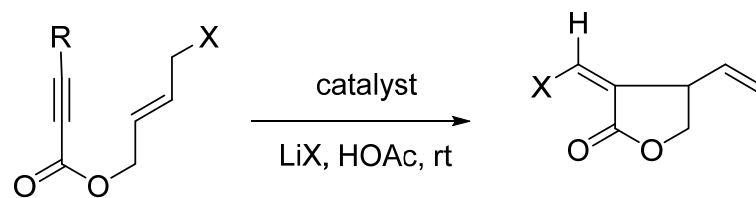
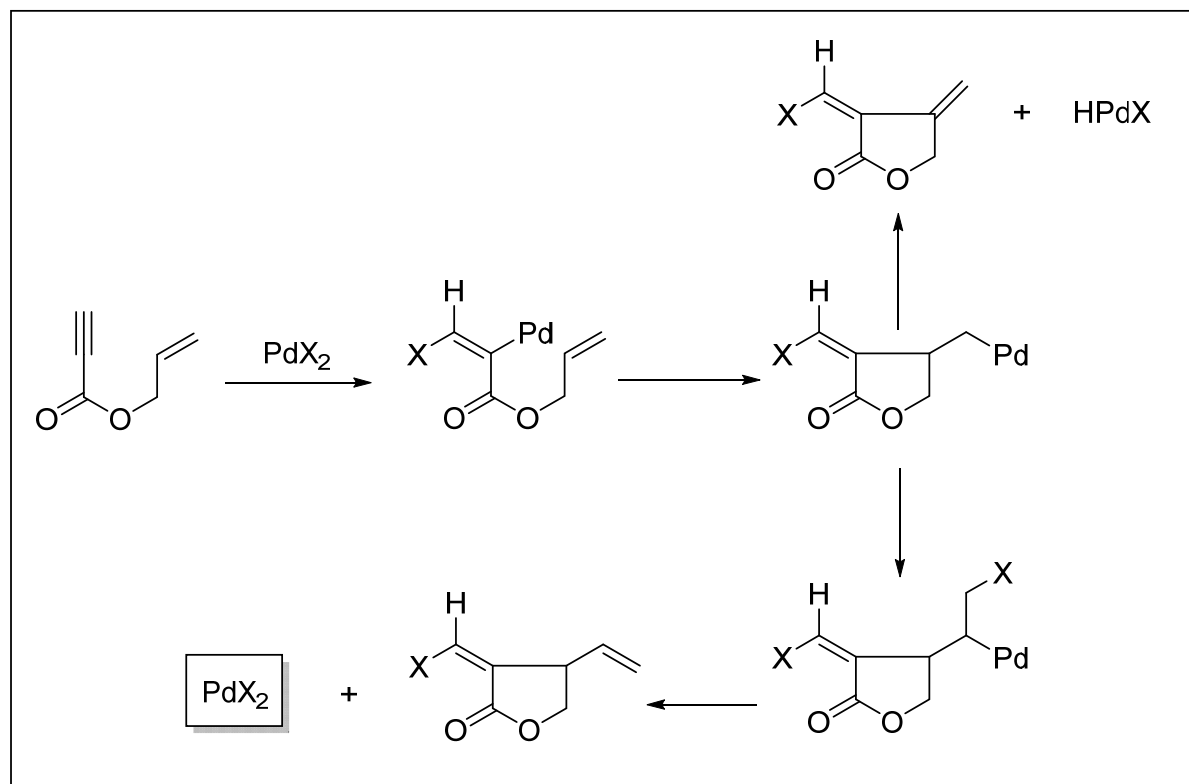
金属有机化学基元反应设计新的有机合成

重点:

1. 金属有机中间体的生成—碳-金属键第一次生成
2. 金属有机中间体的反应—新的碳-金属键生成
3. 碳-金属键的猝灭—目标产物生成

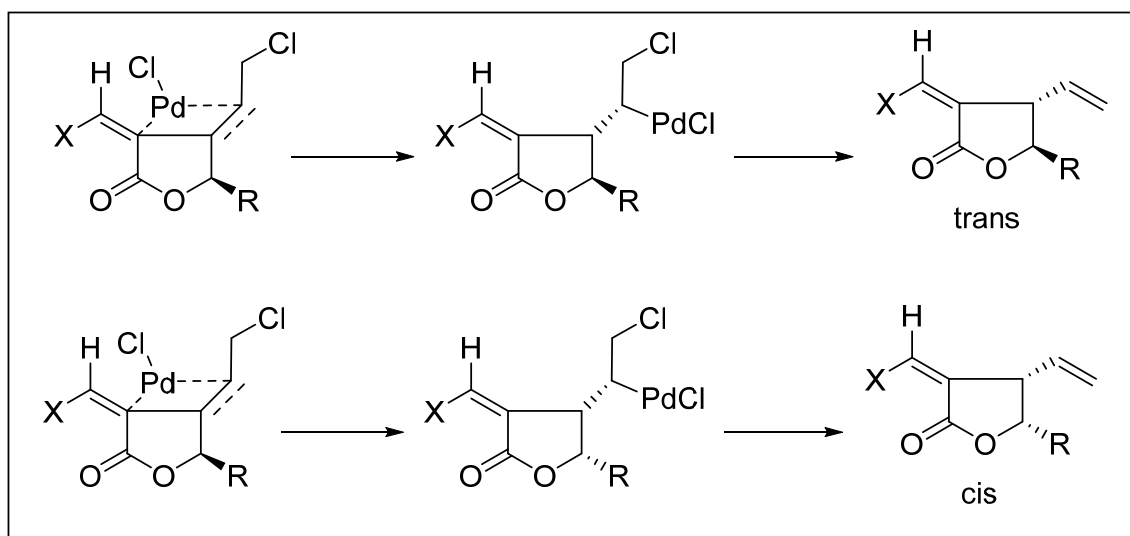
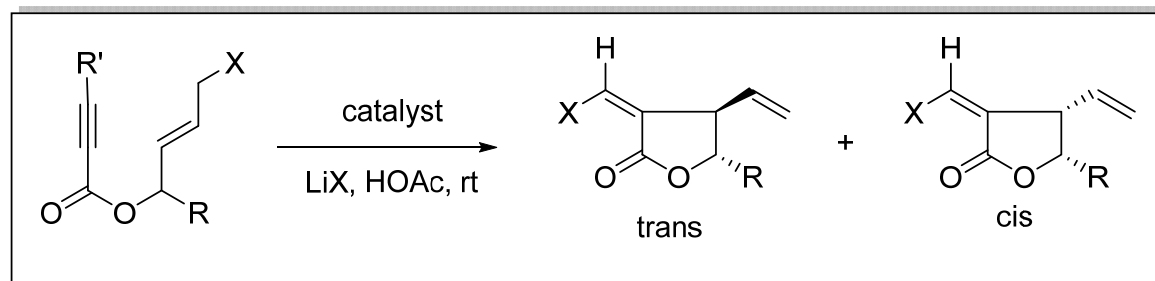


金属有机化学基元反应设计新的有机合成

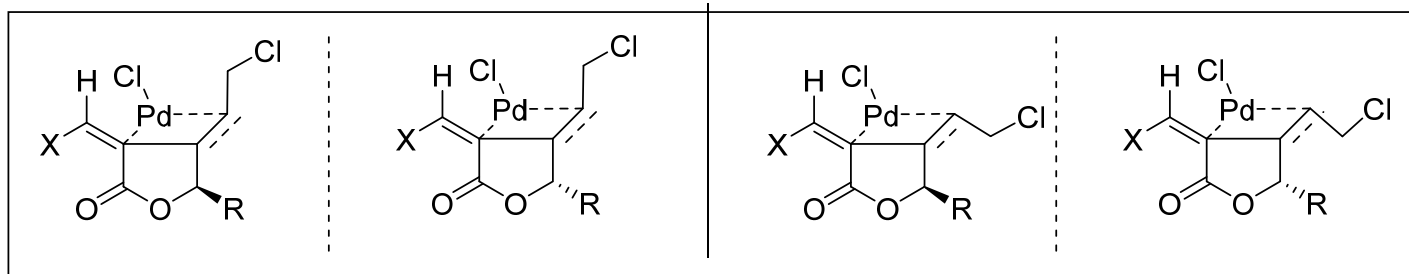


金属有机化学基元反应设计新的有机合成

$R' = H$

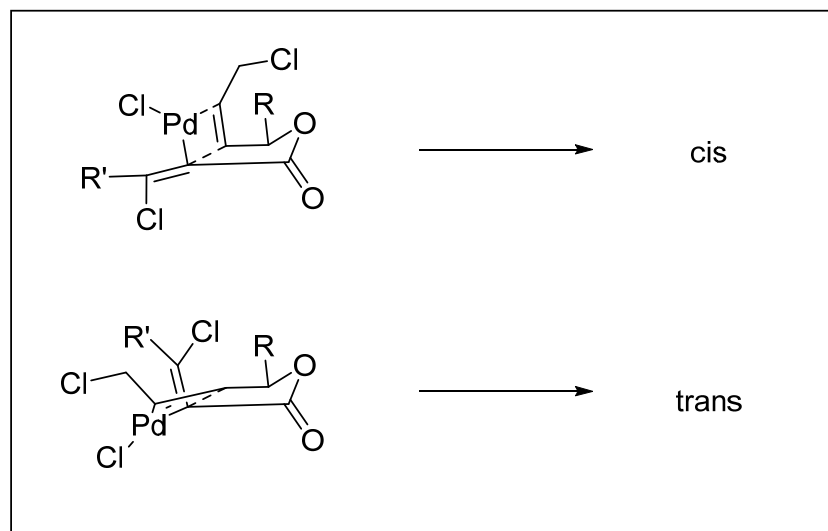


由于反式结构取代基处于反式位置，热力学稳定，主要产物有为反式异构体同时 R 取代基越大，诱导效应越好

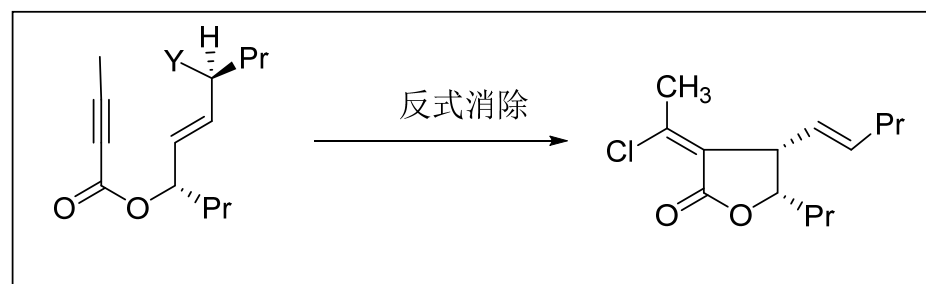


金属有机化学基元反应设计新的有机合成

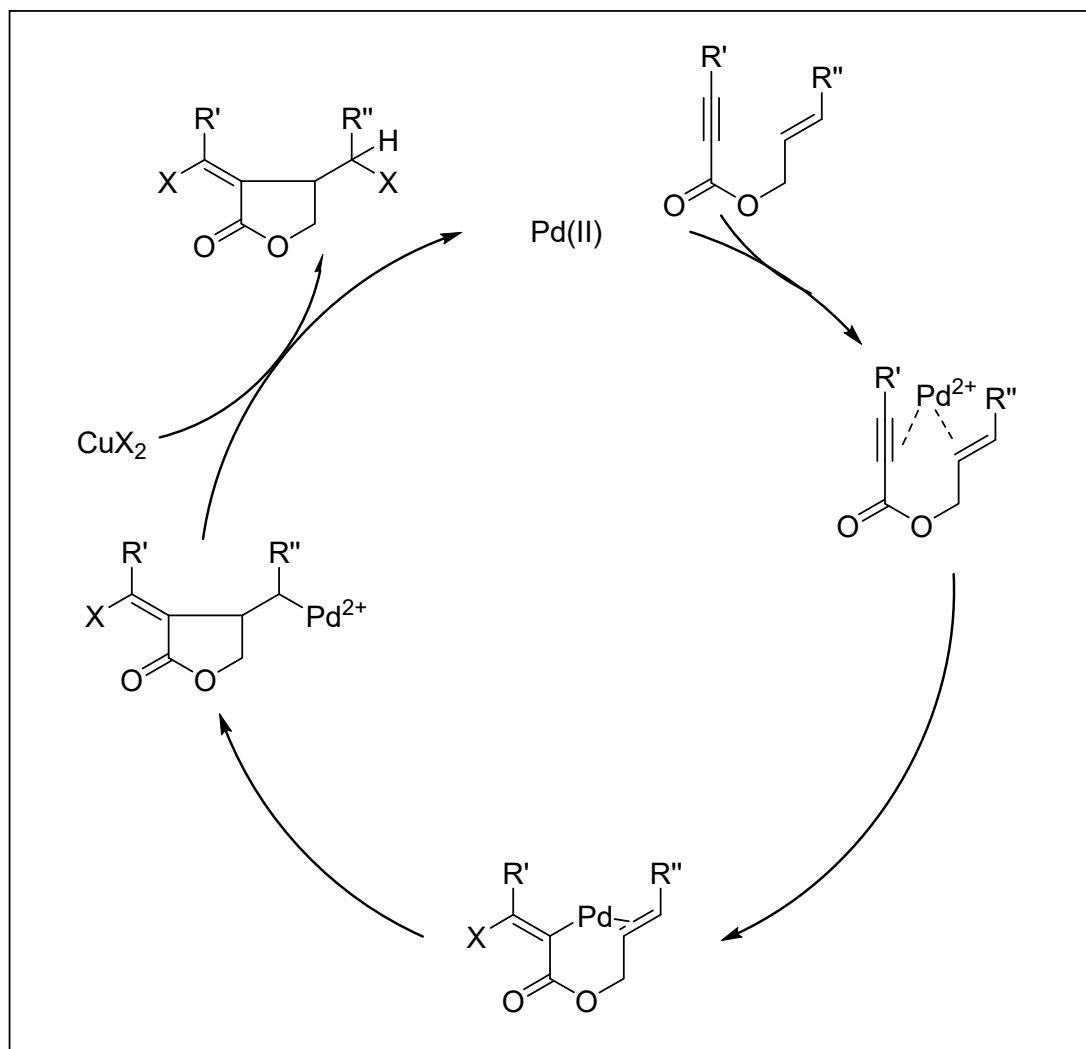
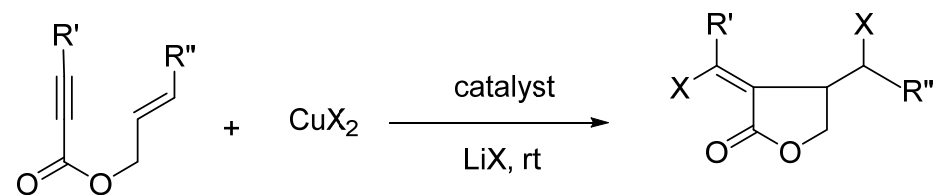
$R' \neq H$



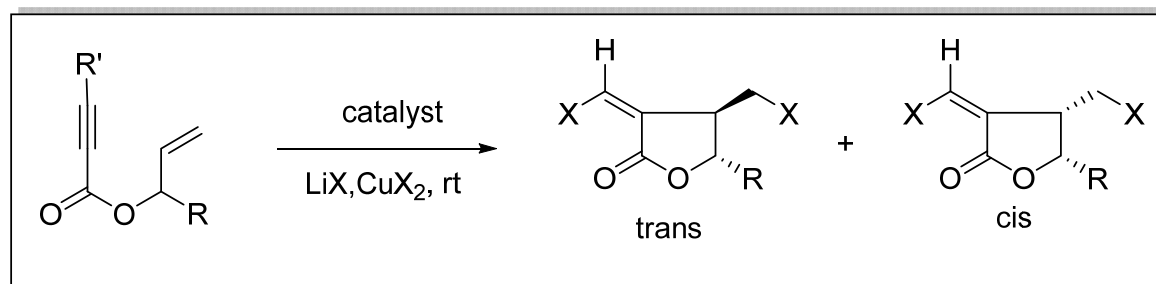
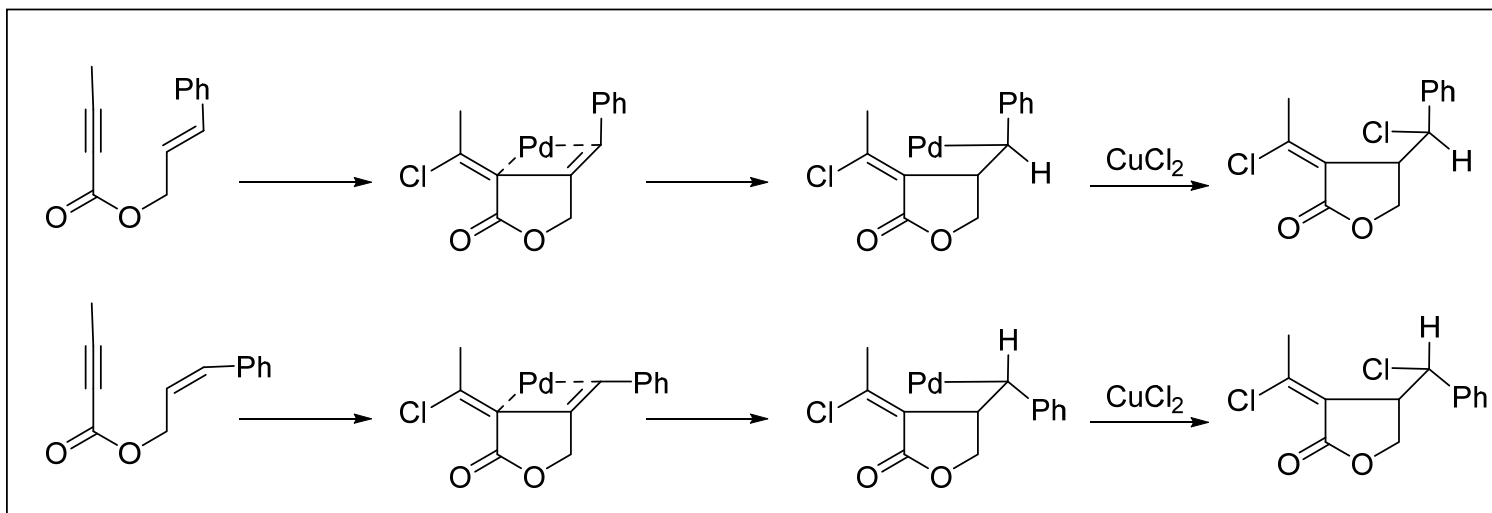
$Y = X, OH, OAc$



金属有机化学基元反应设计新的有机合成

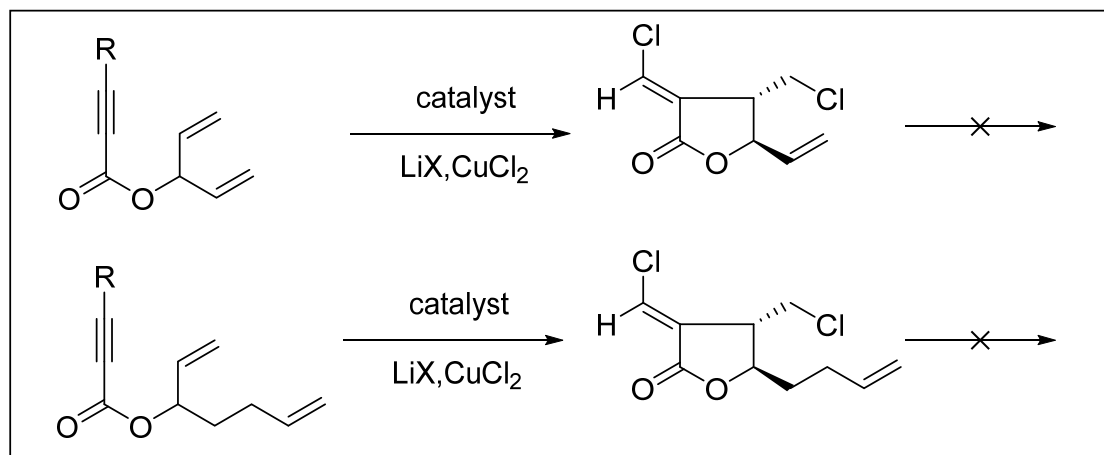
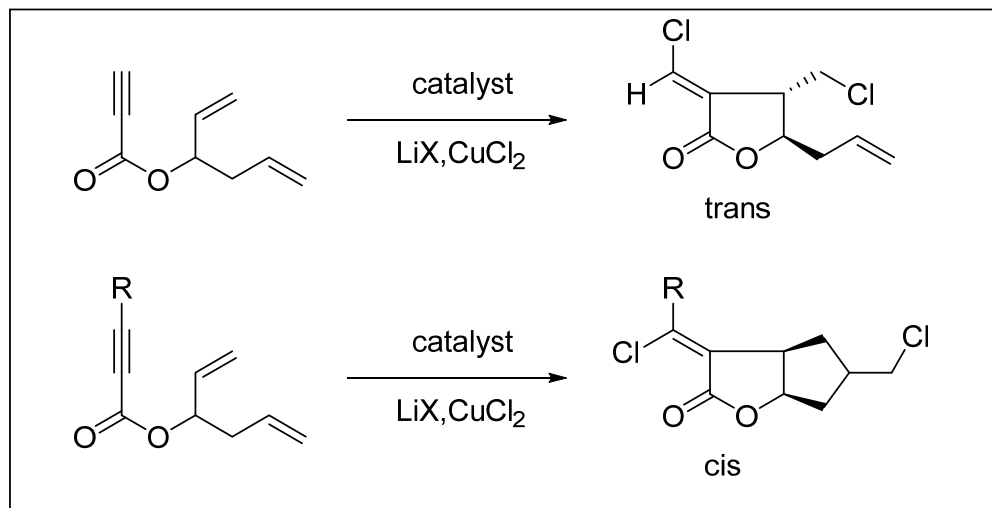


金属有机化学基元反应设计新的有机合成



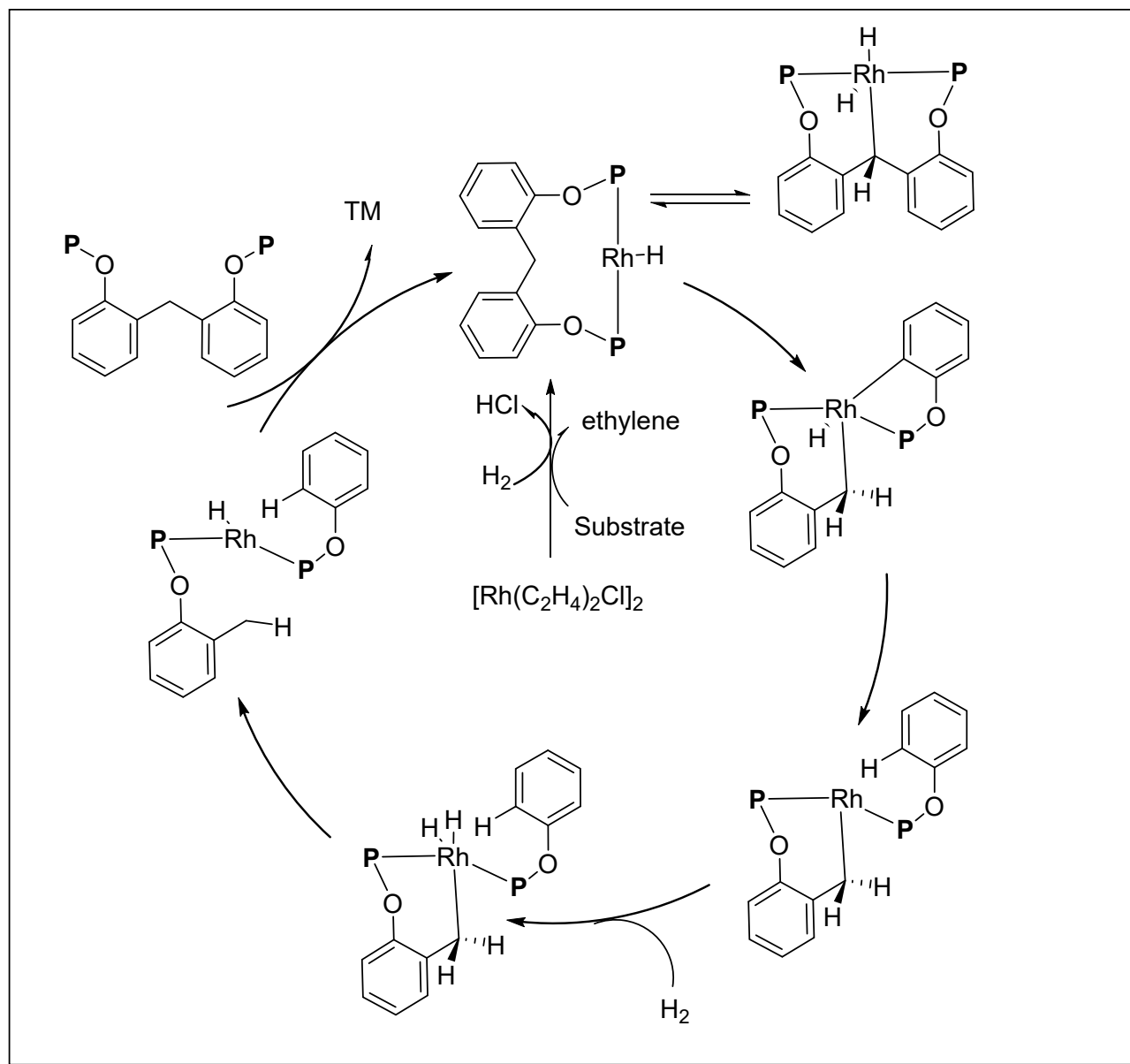
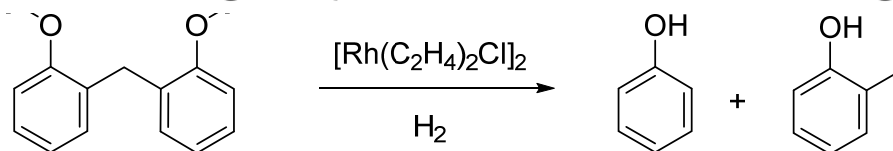
在这一反应中观察到了与上一个反应类似的诱导效应

金属有机化学基元反应设计新的有机合成



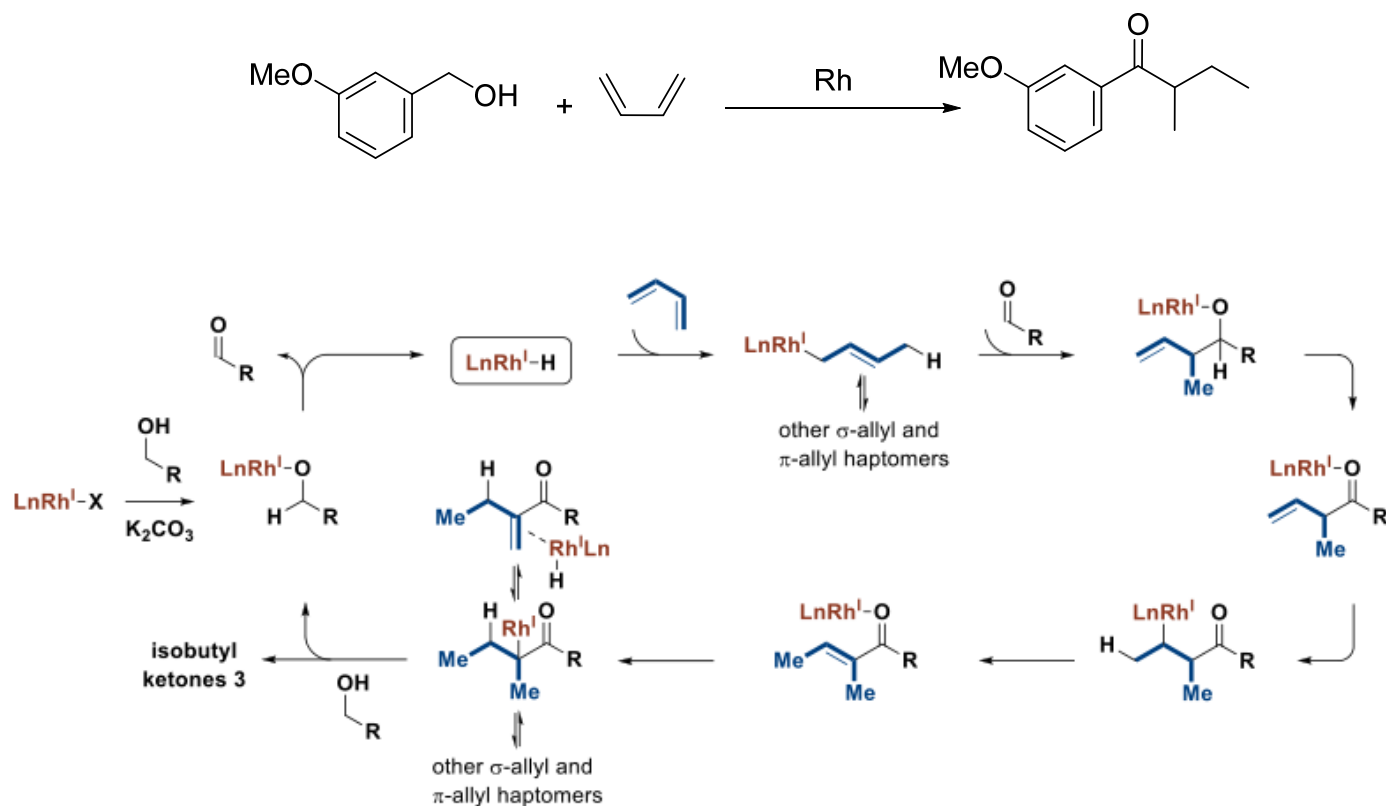
Catalytic Activation of Unstrained C(Aryl)–C(Alkyl) Bonds in 2,2'-Methylenediphenols

Jun Zhu,[†] Yibin Xue,[†] Rui Zhang, Benjamin L. Ratchford, and Guangbin Dong*



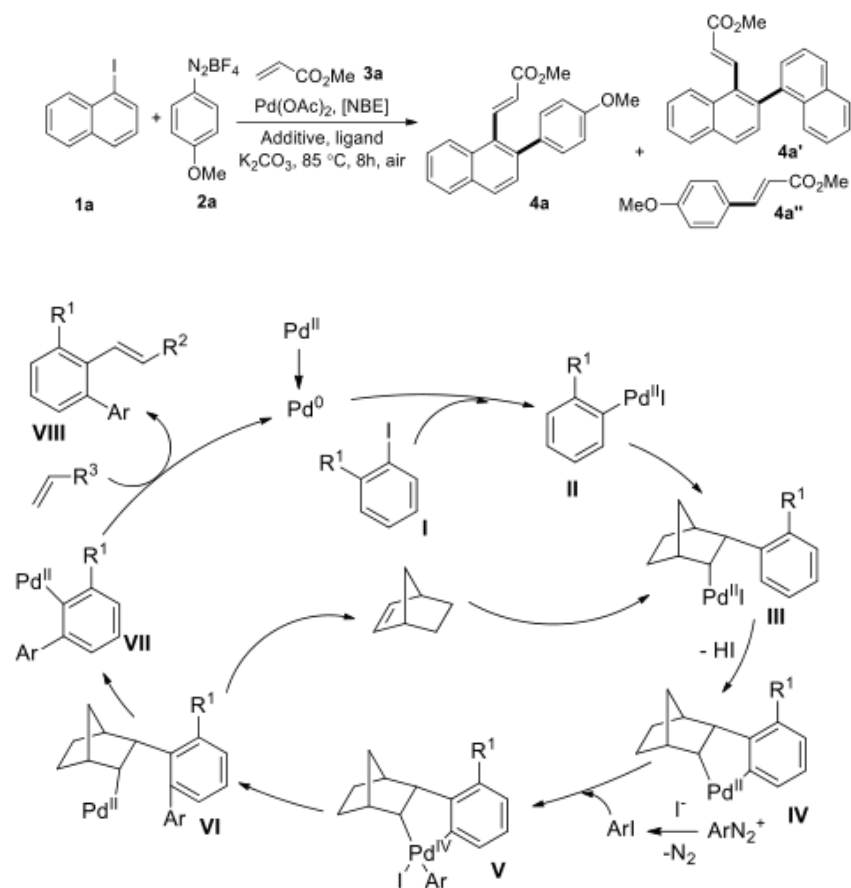
Conversion of Primary Alcohols and Butadiene to Branched Ketones via Merged Transfer Hydrogenative Carbonyl Addition–Redox Isomerization Catalyzed by Rhodium

Brian J. Spinello, Jessica Wu, Yoon Cho, and Michael J. Krische*



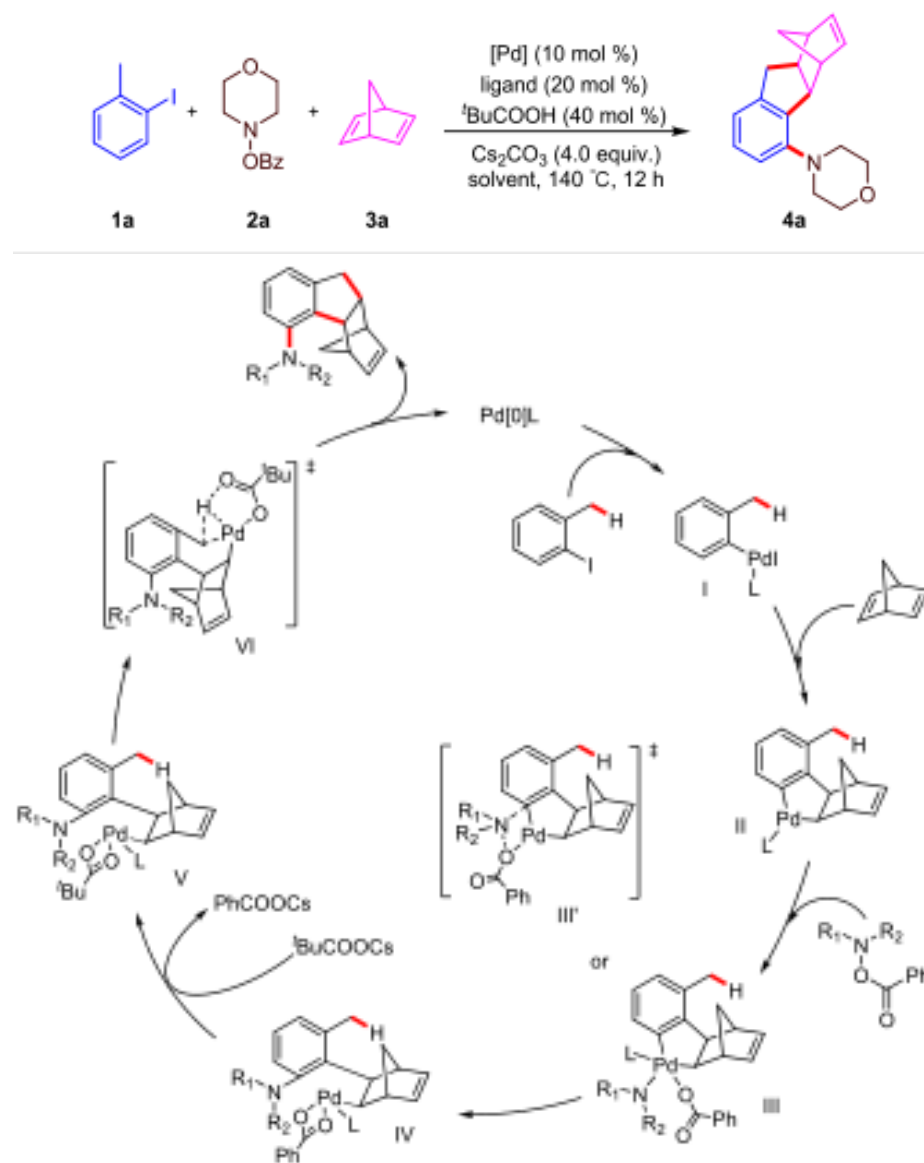
Aryl Diazonium Salts: Powerful Arylating Agents for Catellani-Type *ortho*-Arylation

Ying Fu,^{*} Yu-Xia Zhang, and Liang-Liang Guo



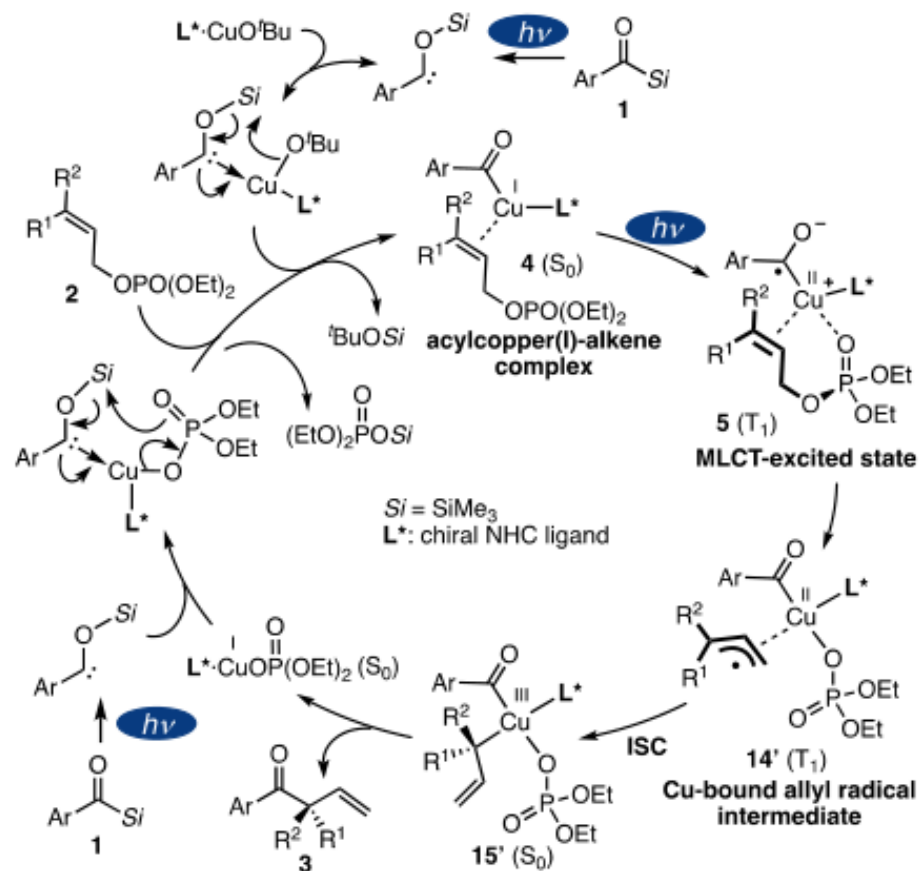
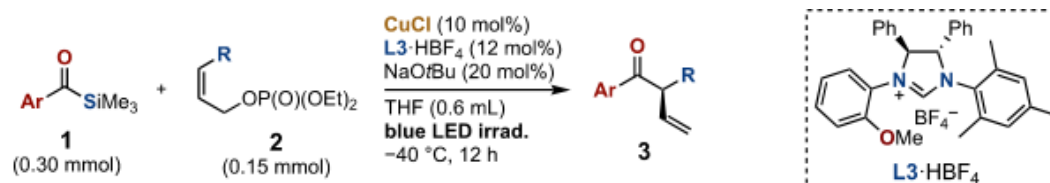
Palladium-Catalyzed C–H Amination/[2 + 3] or [2 + 4] Cyclization via C(sp³ or sp²)–H Activation

Yang An,[#] Yuke Li,[#] Xiao-Yan Zhang, Zhe Zhang, Xue-Ya Gou, Ya-Nan Ding, Qiao Li, and Yong-Min Liang*



Photoinduced Copper-Catalyzed Asymmetric Acylation of Allylic Phosphates with Acylsilanes

Yusuke Ueda, Yusuke Masuda, Tomohiro Iwai, Keisuke Imaeda, Hiroki Takeuchi, Kosei Ueno, Min Gao, Jun-ya Hasegawa,* and Masaya Sawamura*



Thanks!