

Transformations of Dinitrogen

Shi Group

**Zhai Dandan
2019-02-11**

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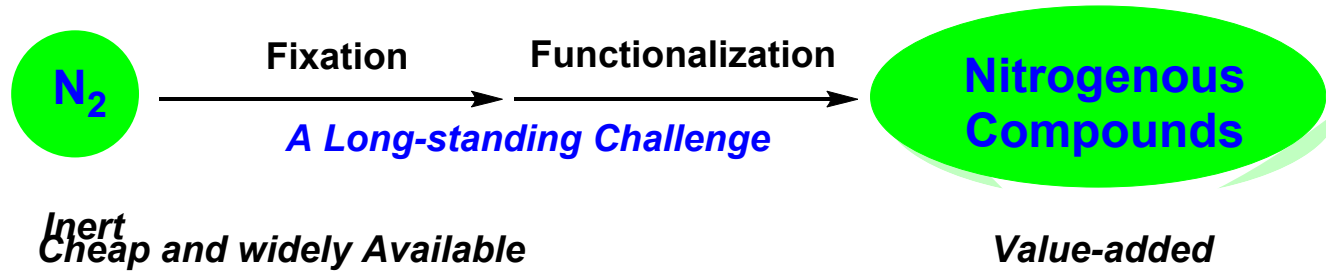
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III. Functionalization of Coordinated Dinitrogen

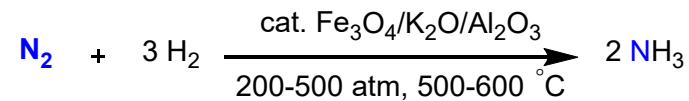
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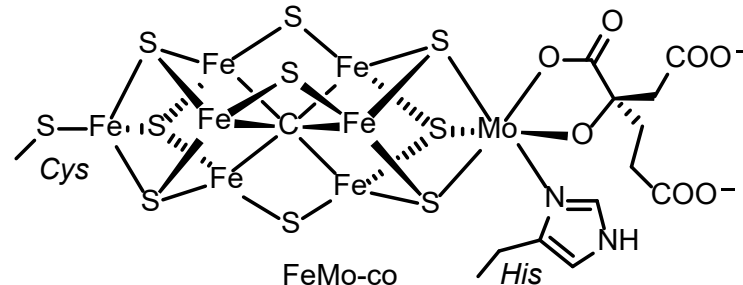
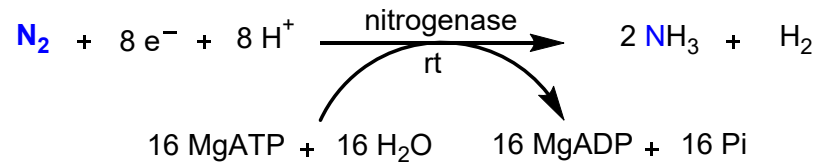


Industrial Haber-Bosch Process

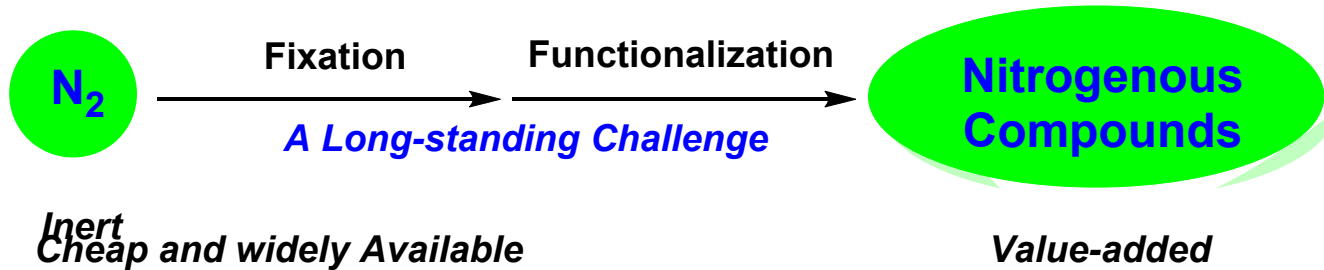


Liu, H. *Ammonia Synthesis Catalysts*; Chemical Industry Press & World Scientific: Singapore, 2013

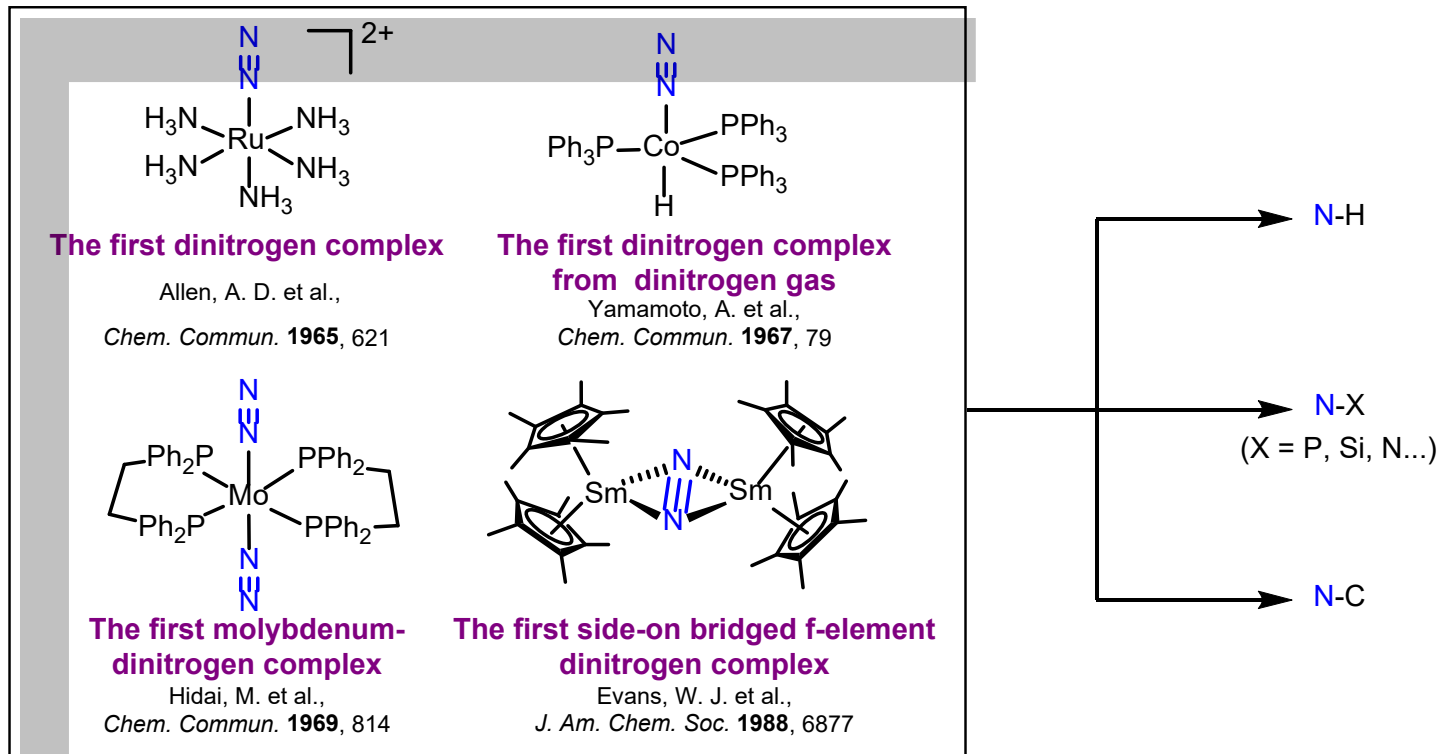
Biological Nitrogen Fixation and the Active Site of Nitrogenase



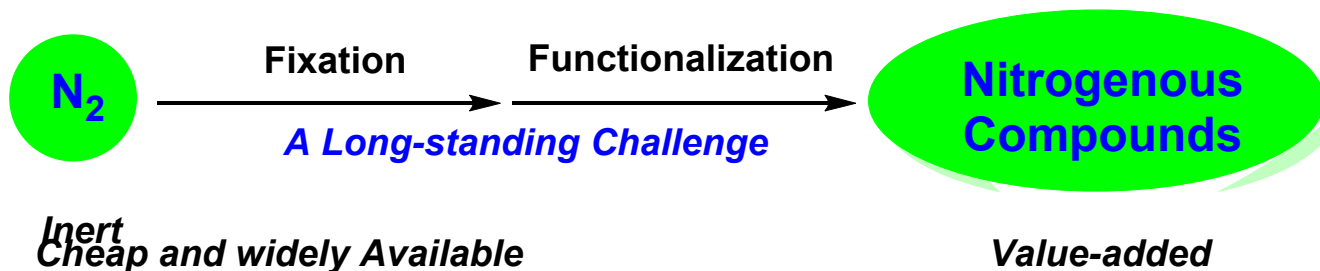
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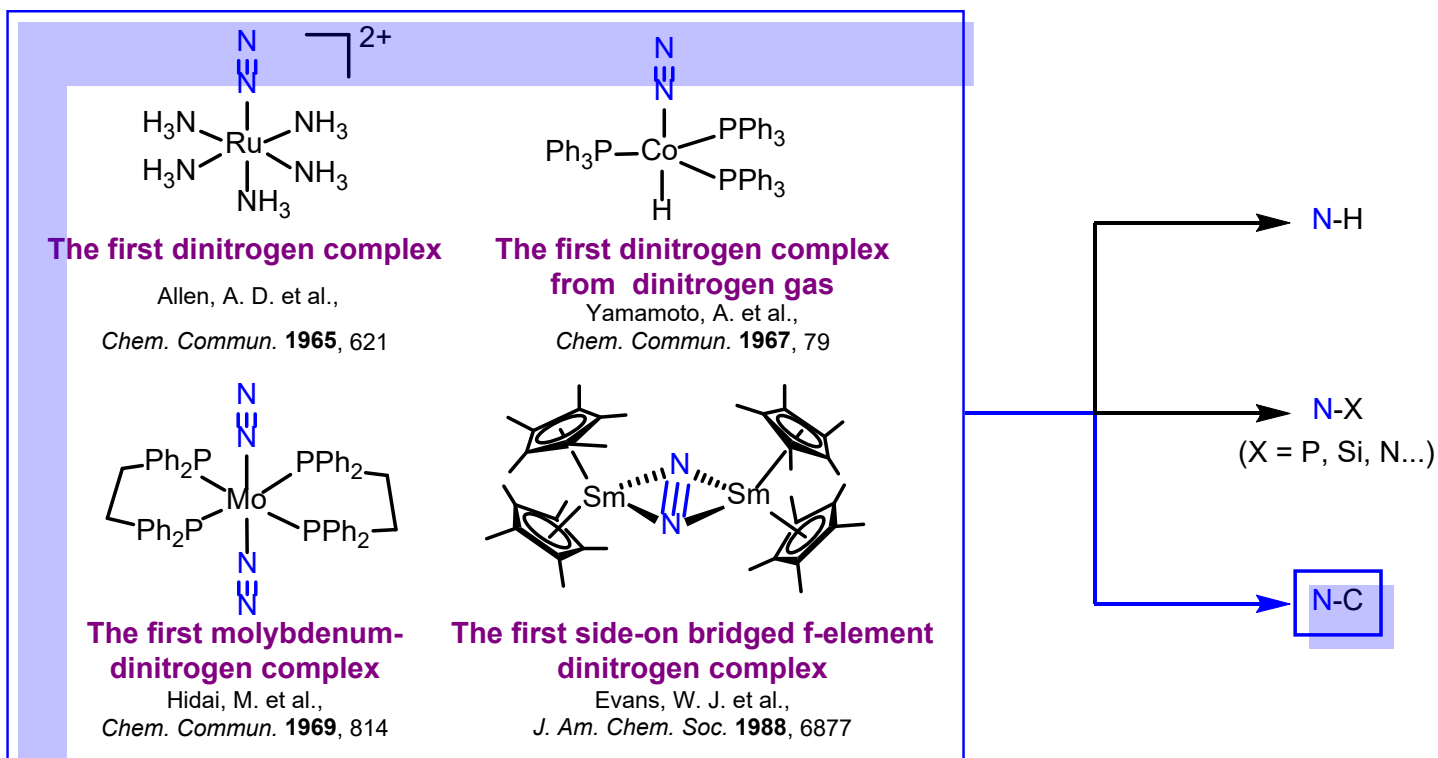
Transition-Metal-Dinitrogen Complexes and Their Transformations



Introduction



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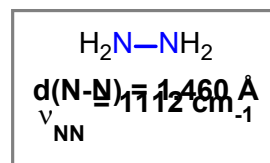
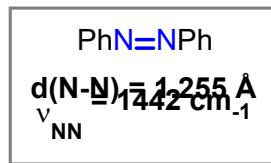
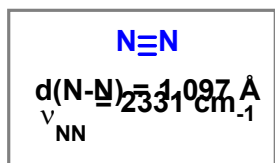
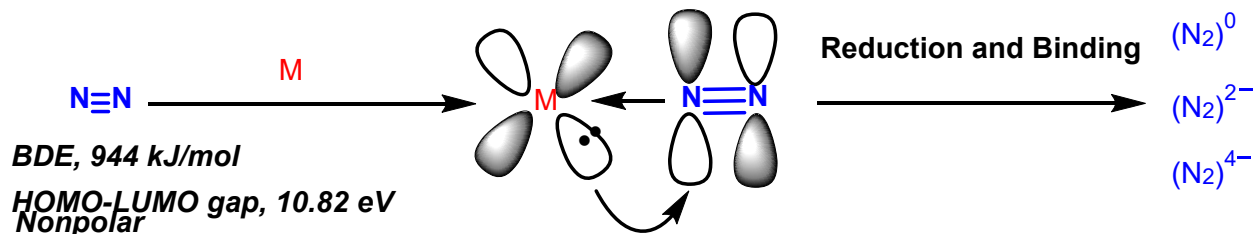
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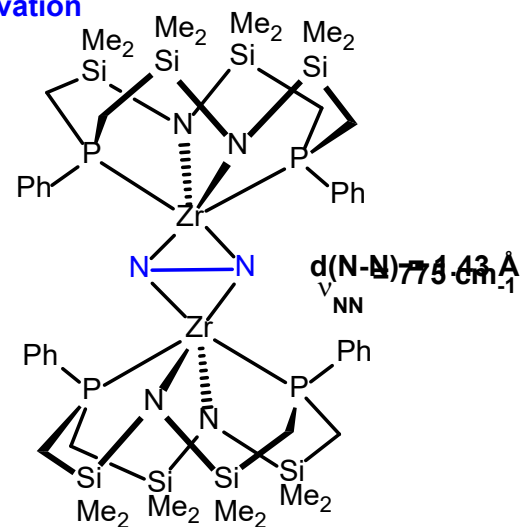
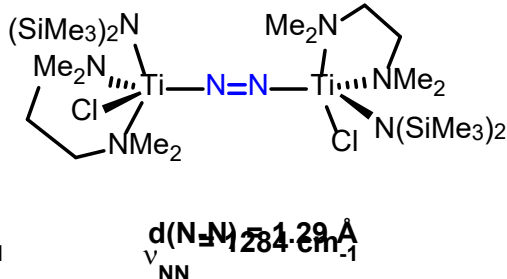
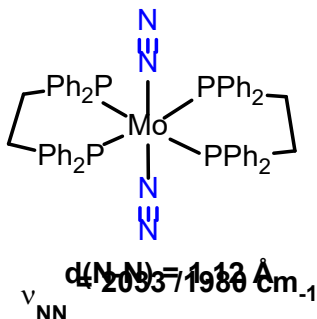
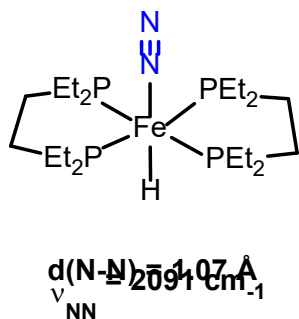
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Structures of Transition-Metal-Dinitrogen Complexes

Activation of Coordinated N_2 Ligand

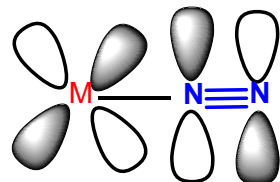


No activation Weak activation Moderate activation Strong activation High activation \rightarrow N-N bond cleavage

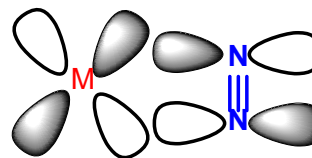


Structures of Transition-Metal-Dinitrogen Complexes

Dinitrogen Coordination Modes in Transition Metal Complexes



End-on π -interactions



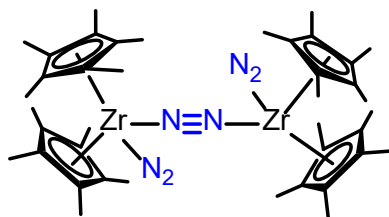
Side-on π -interactions

Weak activation	Strong activation	Coordination modes
$M-N\equiv N$	$M=N=N$	A: monomeric, end-on; $M(\eta^1-N_2)$
$M \begin{array}{c} \diagup N \\ \diagdown N \end{array}$		B: monomeric, side-on; $M(\eta^2-N_2)$
$M-N\equiv N-M$	$M=N-N=M$	C: dimeric, end-on; $M_2(\mu-\eta^1: \eta^1-N_2)$
$M \begin{array}{c} \diagup N \\ \diagdown N \end{array} M$	$M \begin{array}{c} \diagup N \\ \diagdown N \end{array} M$ $M \begin{array}{c} \diagup N \\ \diagdown N \end{array} M$ $M \begin{array}{c} \diagup N \\ \diagdown N \end{array} M$	D: dimeric, side-on; $M_2(\mu-\eta^2: \eta^2-N_2)$
	$M \begin{array}{c} \diagup N \\ \diagdown N \\ \diagup N \\ \diagdown N \end{array} M$	E: trimetric, end-on, side-on, end-on (ESE); $M_3(\mu-\eta^1: \eta^2: \eta^1-N_2)$
	$M \begin{array}{c} \diagup N \\ \diagdown N \\ \diagup N \\ \diagdown N \end{array} M$	F: trimetric, end-on, side-on, side-on (SES); $M_3(\mu-\eta^1: \eta^2: \eta^2-N_2)$
	$M \begin{array}{c} \diagup N \\ \diagdown N \\ \diagup N \\ \diagdown N \end{array} M$	G: (hexametallic), end-on; $M_3(\mu-\eta^3: \eta^3-N_2)$

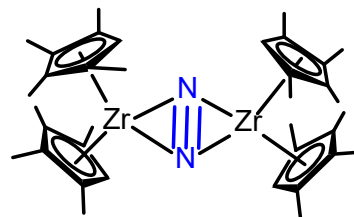
Structures of Transition-Metal-Dinitrogen Complexes

Factors Affecting N₂-activation

Ligand environment



$d(\text{N-N}) = 1.18 \text{ \AA}$
Bercaw, J. E. et al.,
J. Am. Chem. Soc. **1974**, 6229



$d(\text{N-N}) = 1.46 \text{ \AA}$
Chirik, P. J. et al.,
Nature **2004**, 527

Metal atoms

IIIB	IVB	VB	VIB	VIIB	VIII		IB	IIB	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac									

- binds and activates N₂ toward reactions
- binds N₂ with weakening
- binds N₂ without weakening

Higher-energy d orbitals;
In a lower oxidation state

→ Stronger π -backbonding

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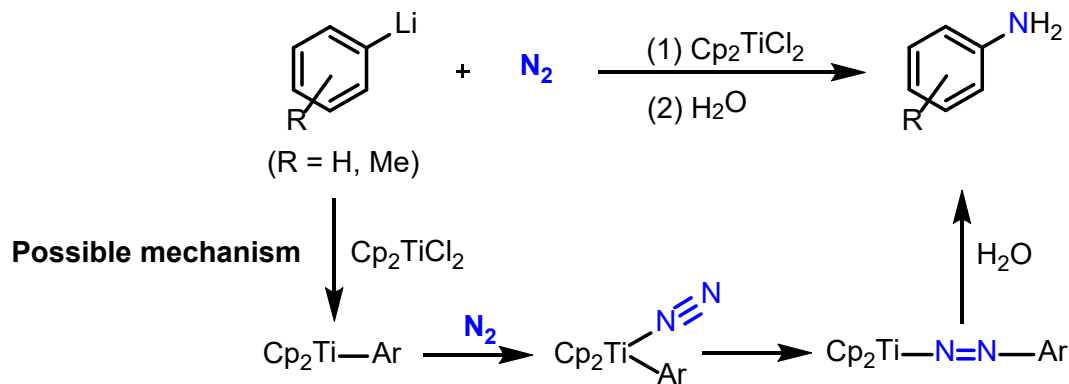
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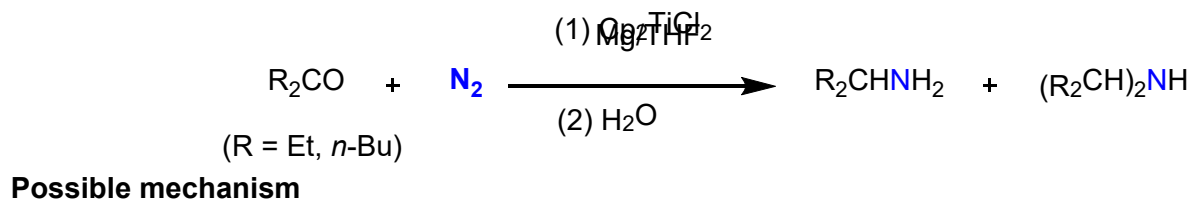
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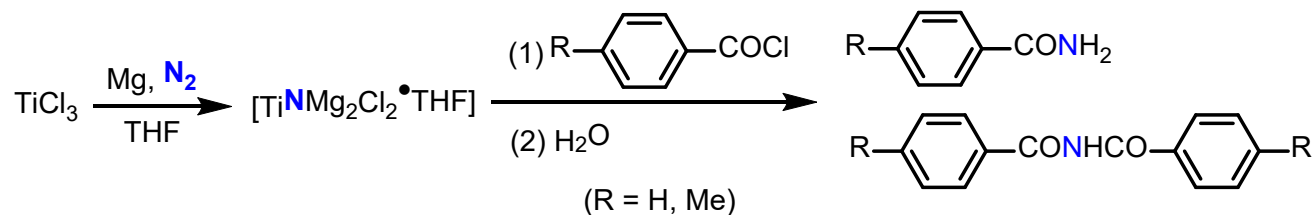
One-pot Synthesis of Organonitrogen Compounds From Molecular Nitrogen



Volpin, M. E. et al., *Chem. Commun.* **1968**, 1038



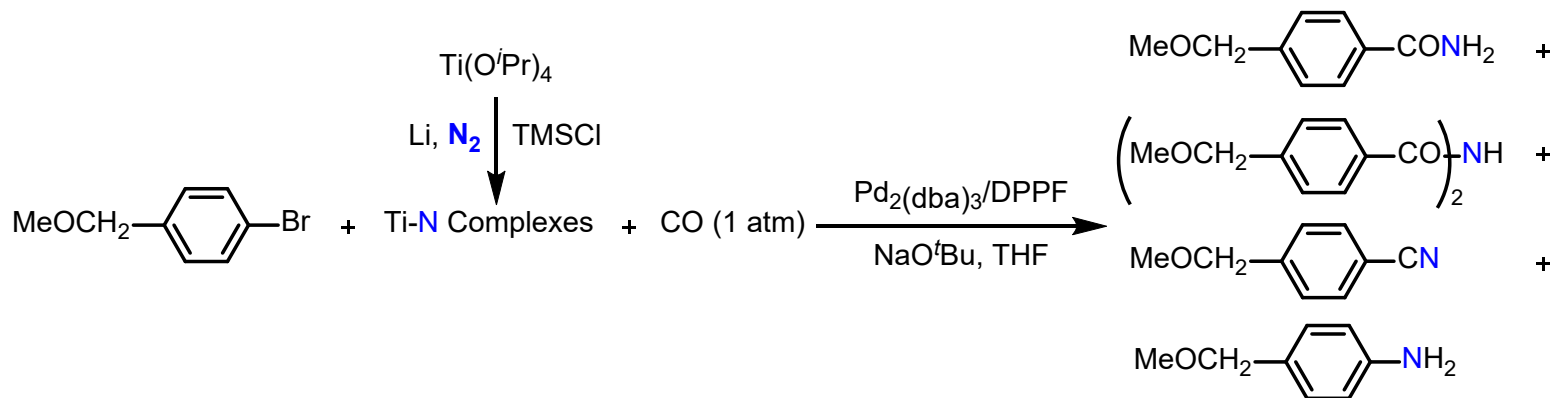
van Tamelen, E. E. et al., *J. Am. Chem. Soc.* **1970**, 92, 5253



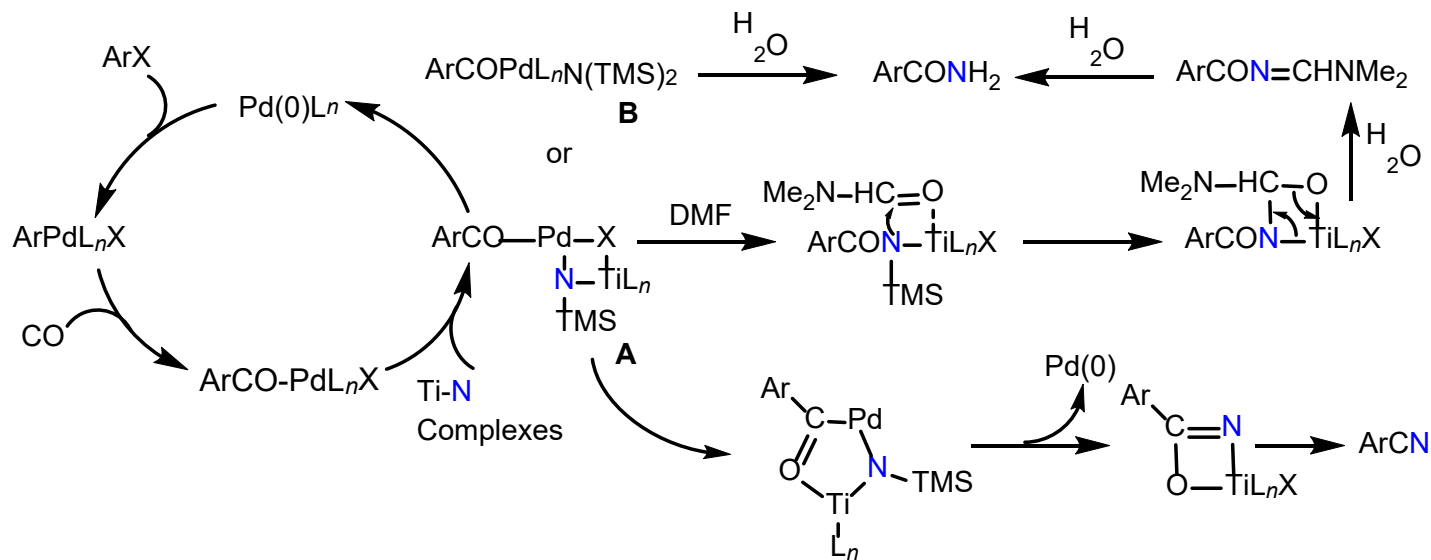
Mori, M. et al., *Tetrahedron Lett.* **1987**, 28, 6187

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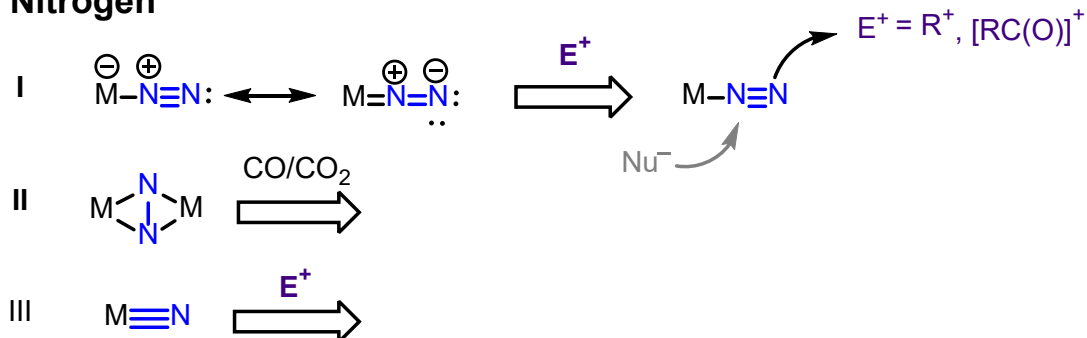


Possible mechanism

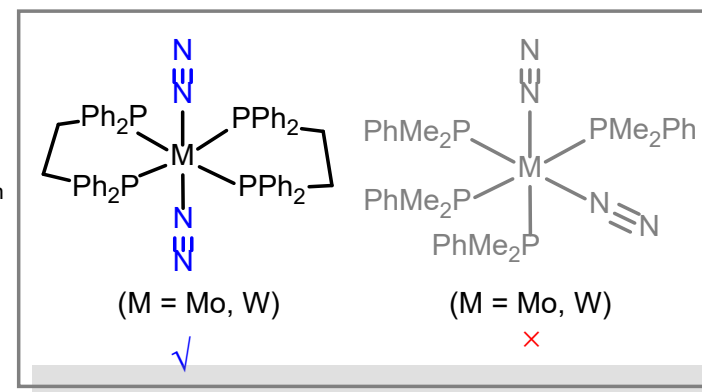
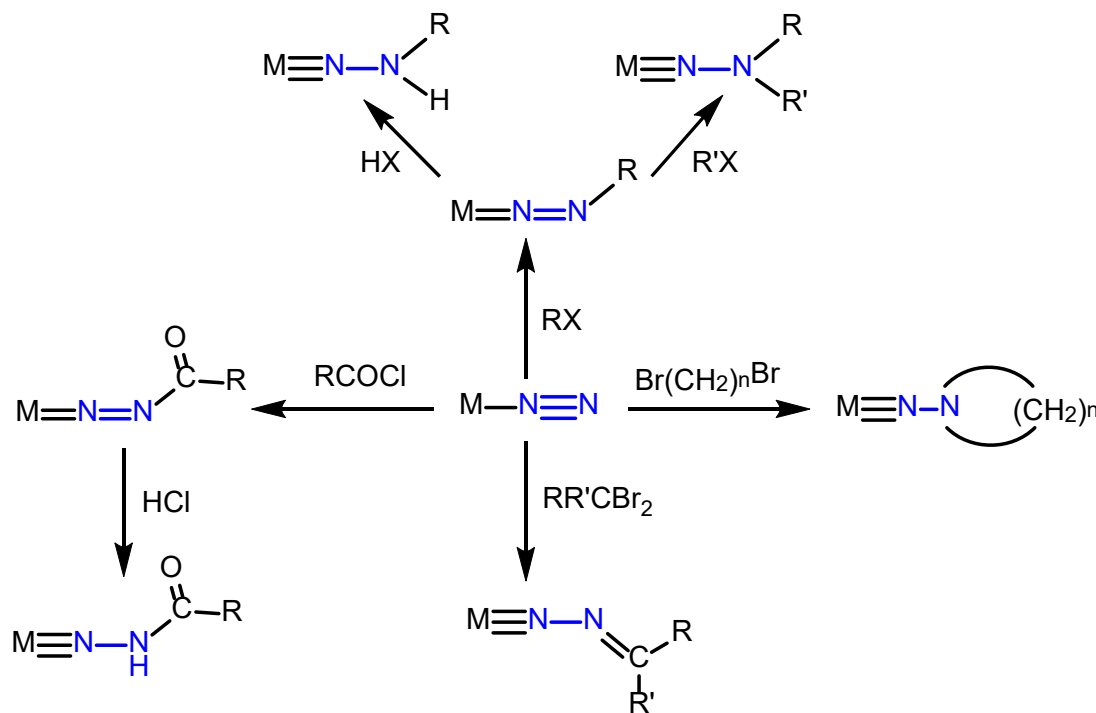


Functionalization of Coordinated Dinitrogen

Reactivity of Coordinated Nitrogen



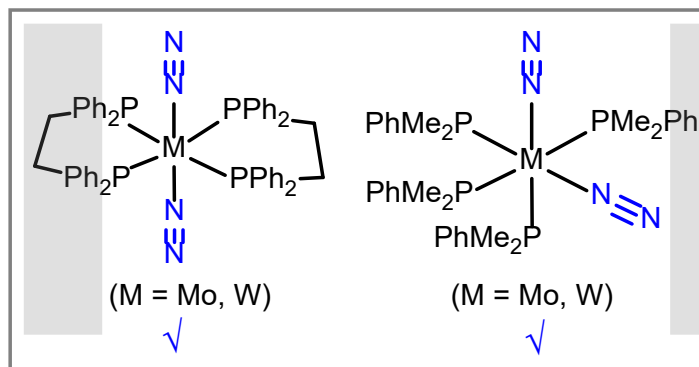
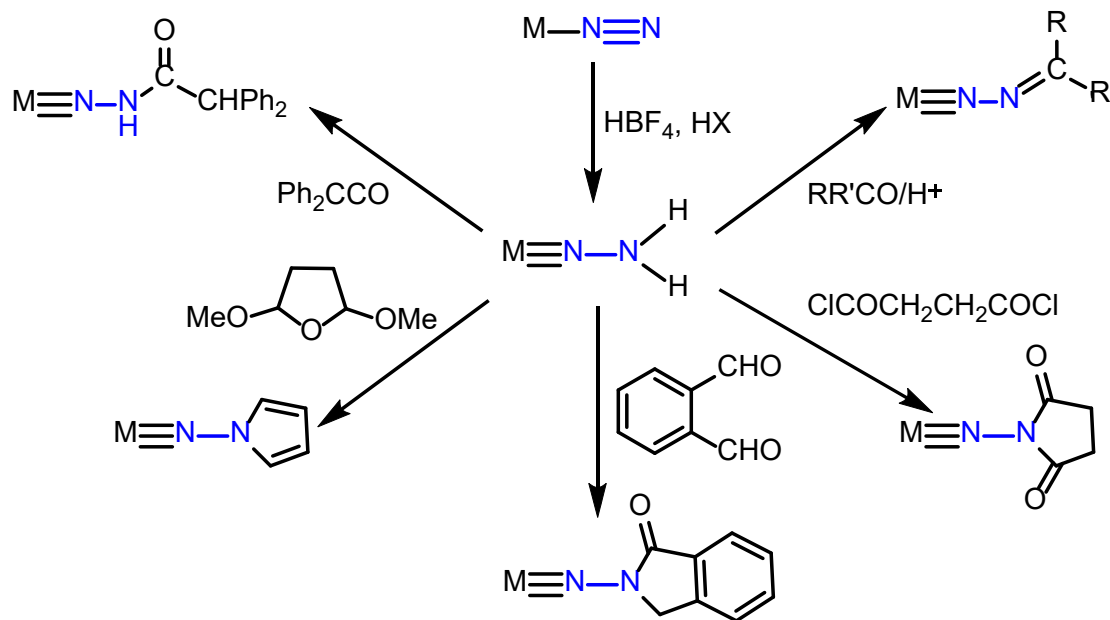
C-N Bond Formation at Coordinated N_2 ^{νν} Reaction with Organic Halides



Chatt, J. et al., *J. Chem. Soc., Chem. Commun.* **1972**, 444
Hidai, M. et al., *J. Organomet. Chem.* **1978**, 152, 239

Functionalization of Coordinated Dinitrogen

C-N Bond Formation at Coordinated N_2 ^{viii}
Hydrazido(2-) or Diazenido Complexes



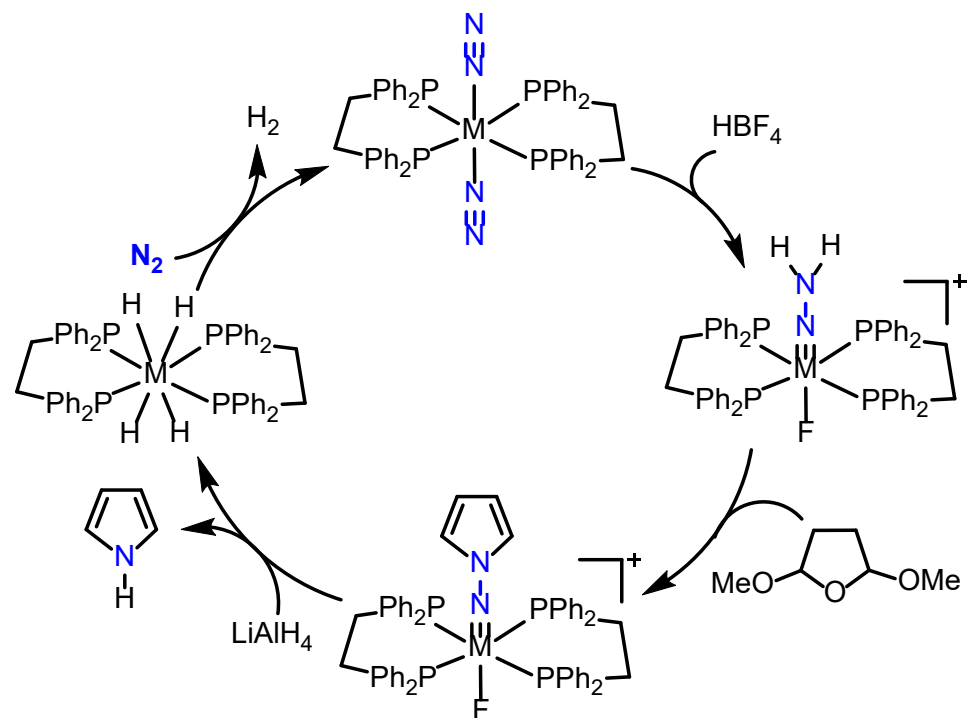
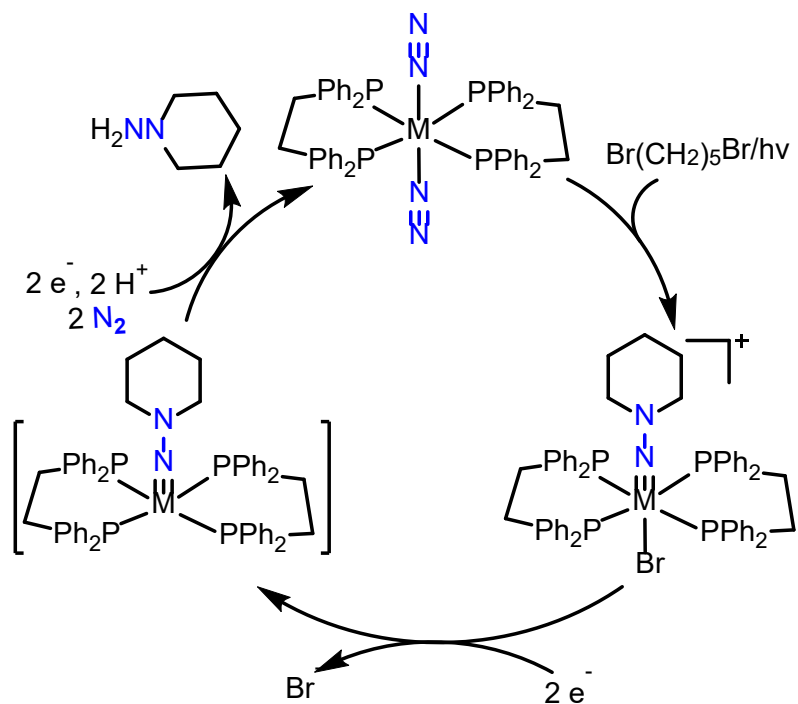
Hidai, M. et al., *Bull. Chem. Soc. Jpn.* **1981**, 54, 1773

Hidai, M. et al., *J. Organomet. Chem.* **1992**, 423, 39

Hidai, M. et al., *J. Am. Chem. Soc.* **1995**, 117, 12181

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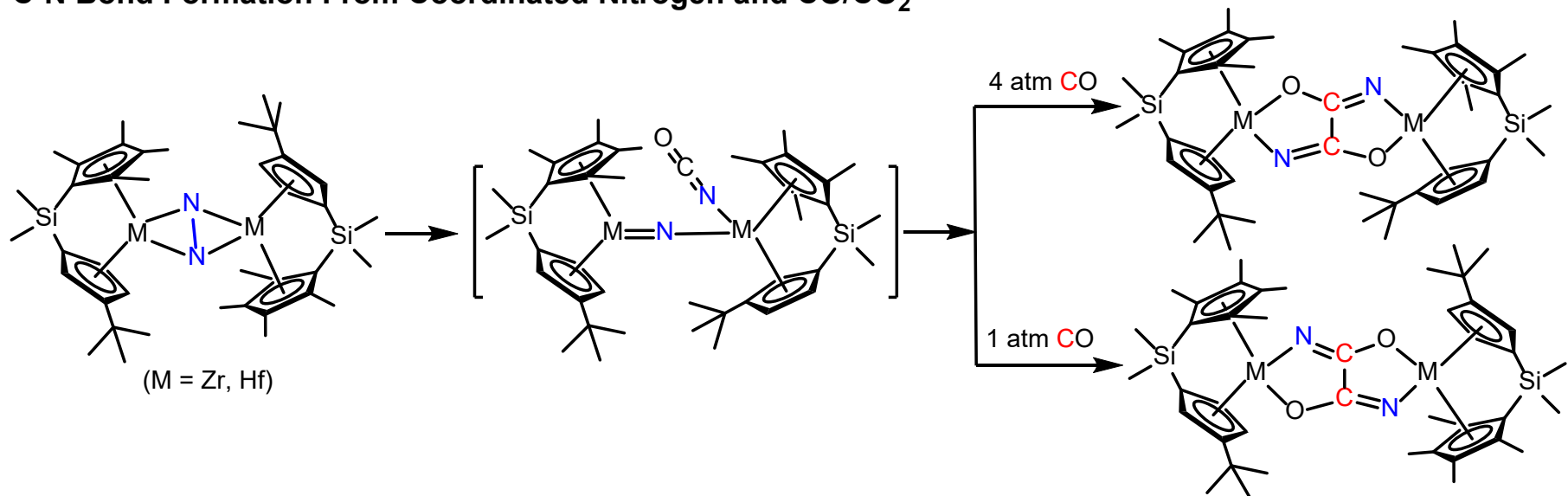
Leigh, G. J. et al., *J. Chem. Soc., Chem. Commun.* **1981**, 1033

Leigh, G. J. et al., *J. Chem. Soc., Chem. Commun.* **1982**, 747

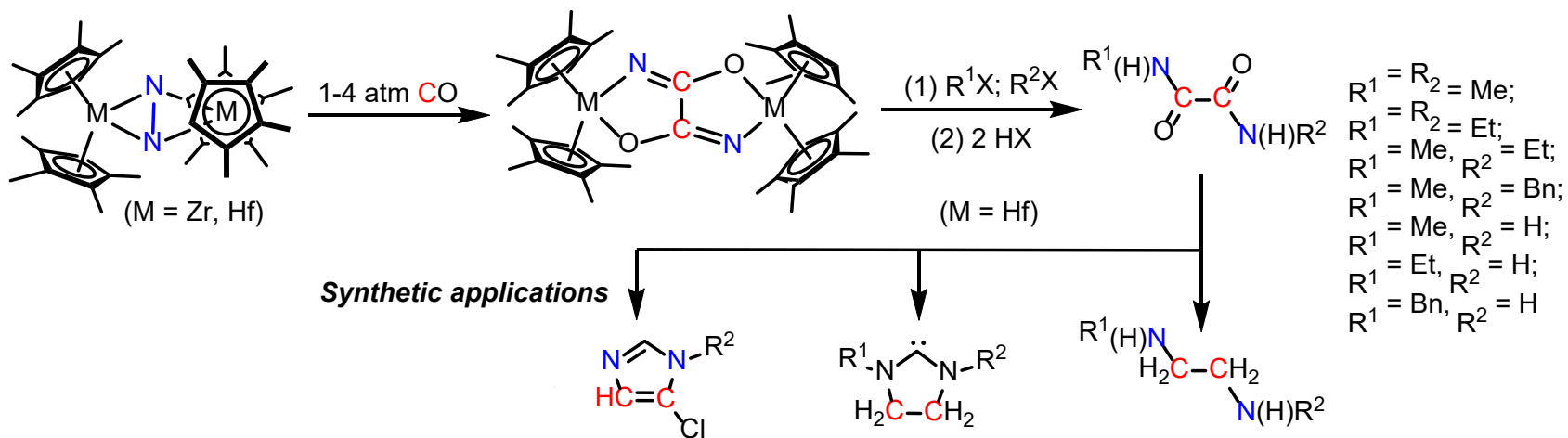
Hidai, M. et al., *J. Am. Chem. Soc.* **1995**, 117, 12181

Functionalization of Coordinated Dinitrogen

C-N Bond Formation From Coordinated Nitrogen and CO/CO₂



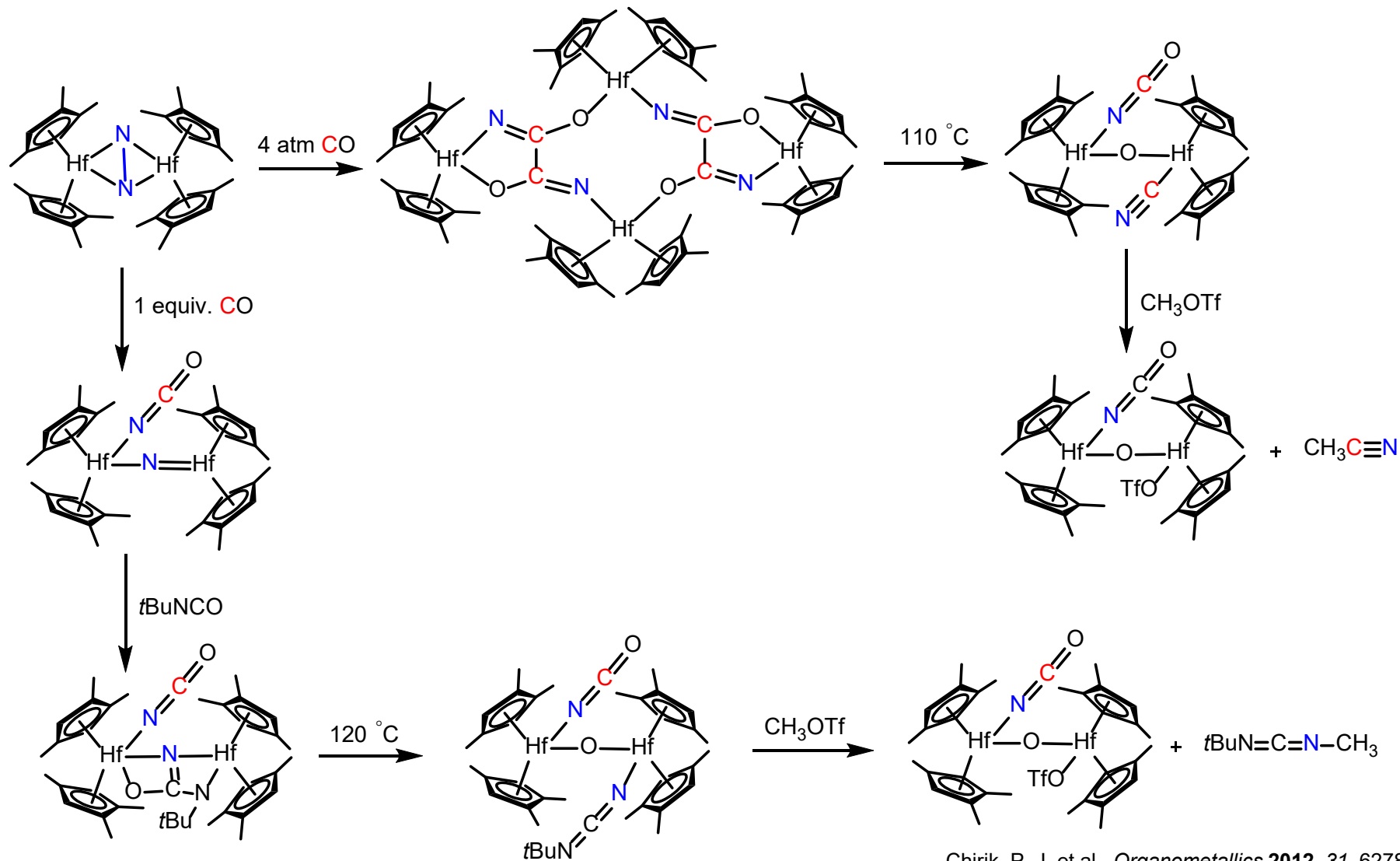
Chirik, P. J. et al., *Nat. Chem.* **2010**, 2, 30



Chirik, P. J. et al., *J. Am. Chem. Soc.* **2010**, 132, 15340

Functionalization of Coordinated Dinitrogen

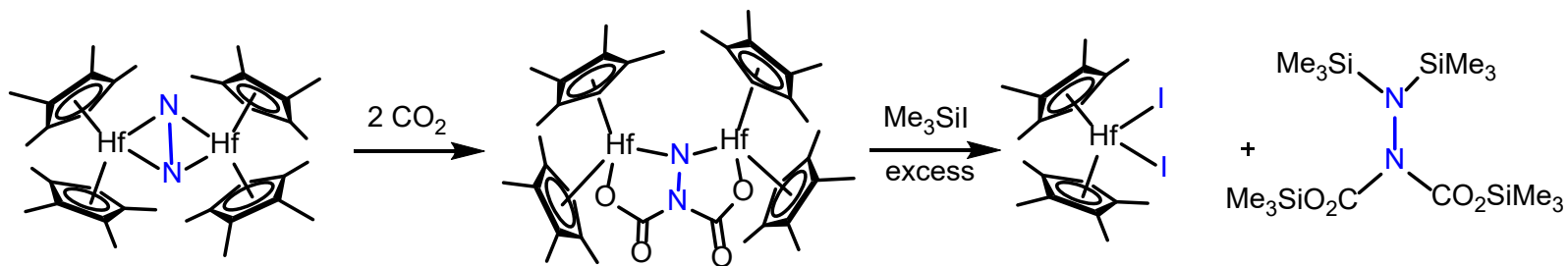
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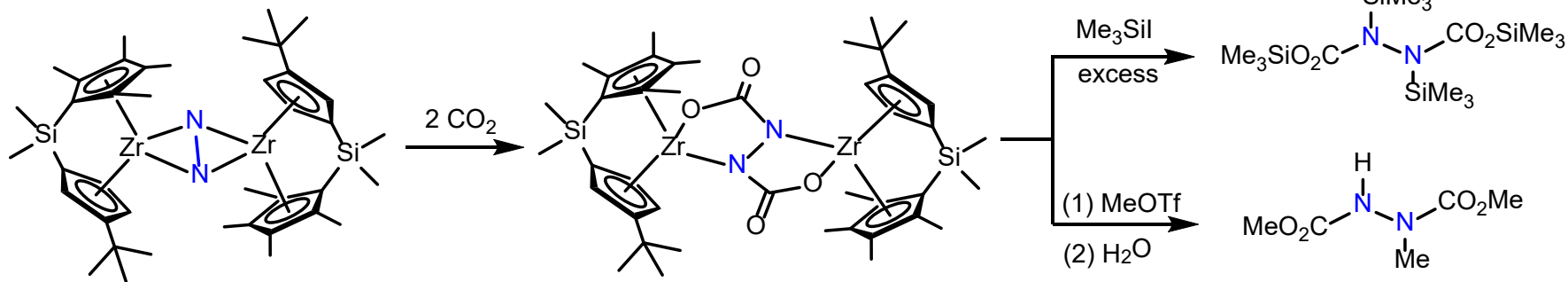
Chirik, P. J. et al., *Organometallics* **2012**, 31, 6278
Chirik, P. J. et al., *J. Am. Chem. Soc.* **2013**, 135, 11373

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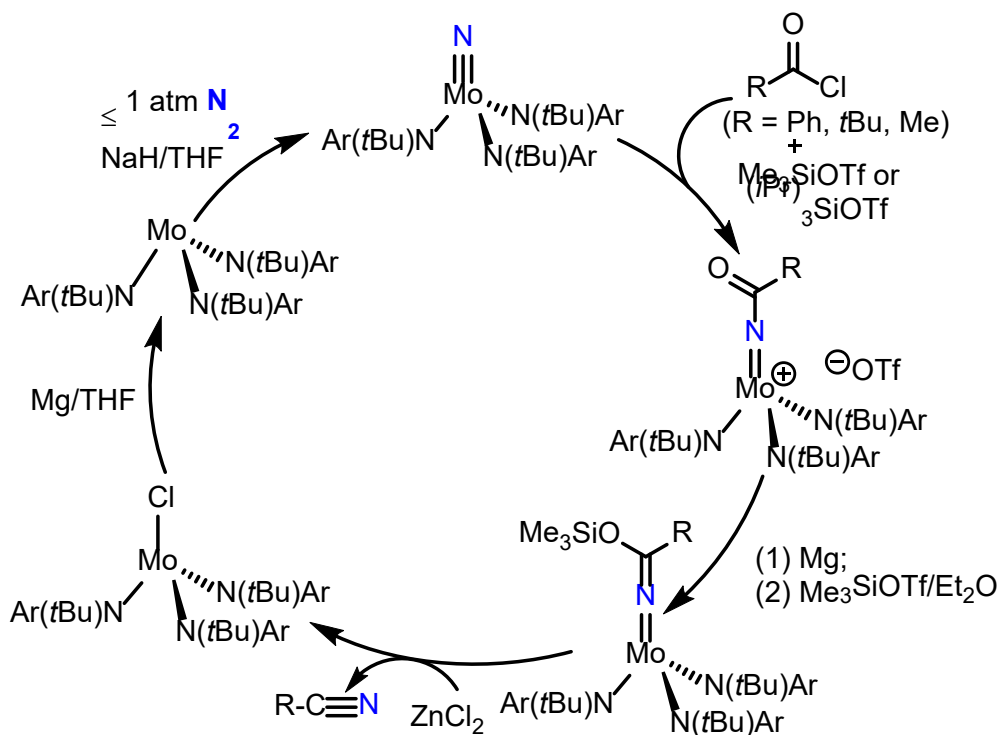
Chirik, P. J. et al., *Angew. Chem., Int. Ed.* **2007**, *46*, 2858



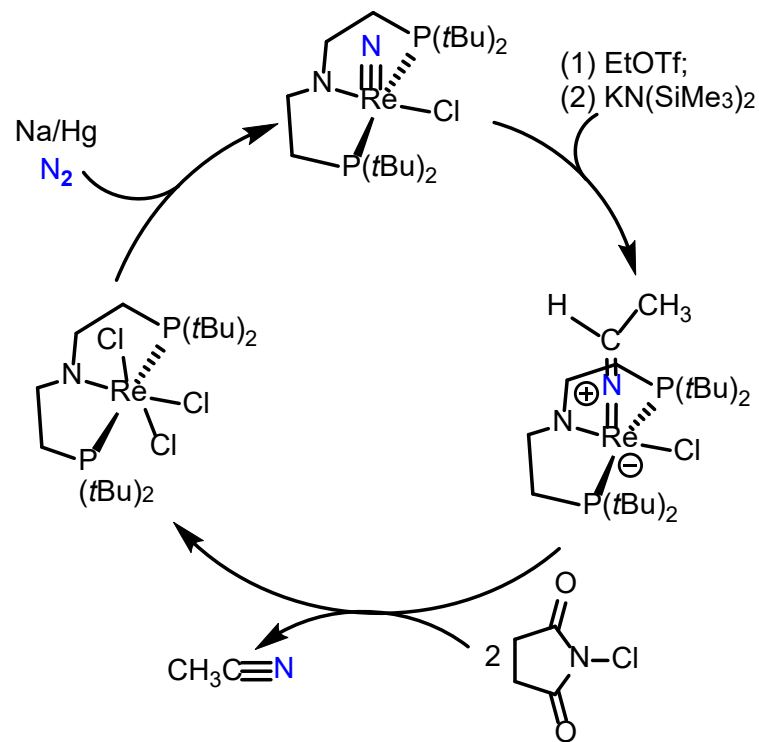
Chirik, P. J. et al., *J. Am. Chem. Soc.* **2008**, *130*, 4248

Functionalization of Coordinated Dinitrogen

C-N Bond Formation via Reactive Transition Metal Nitride Complexes



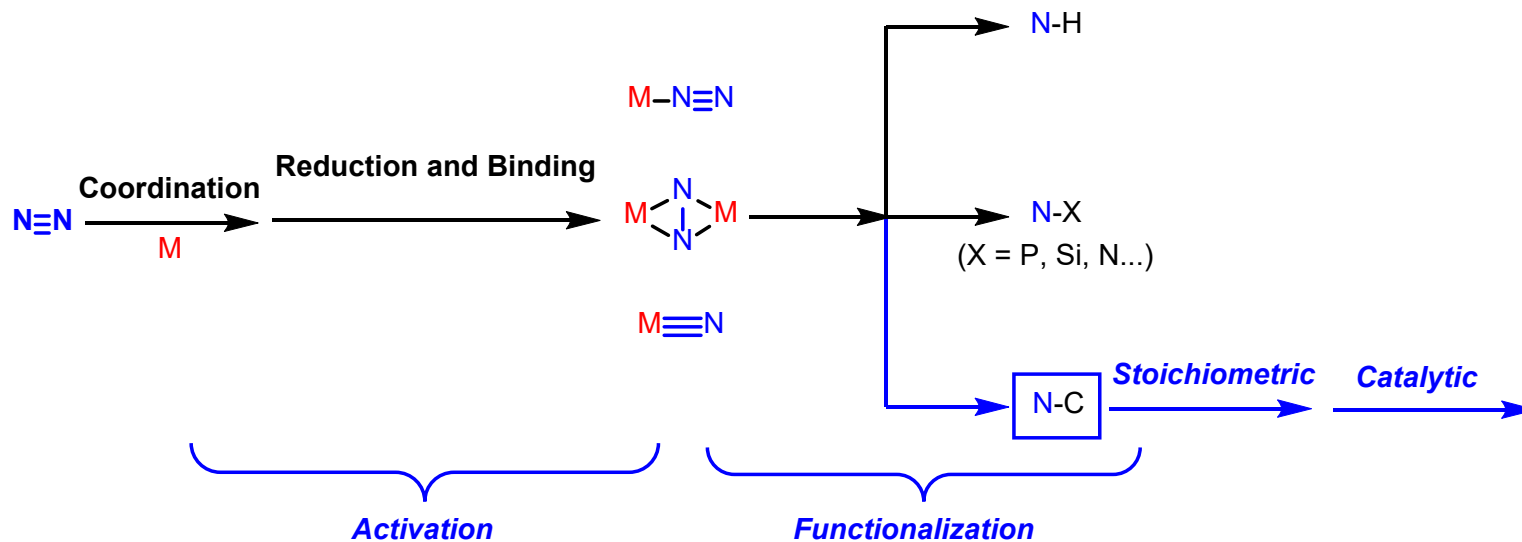
Cummins, C. C. et al., *J. Am. Chem. Soc.* **2006**, 128, 14036



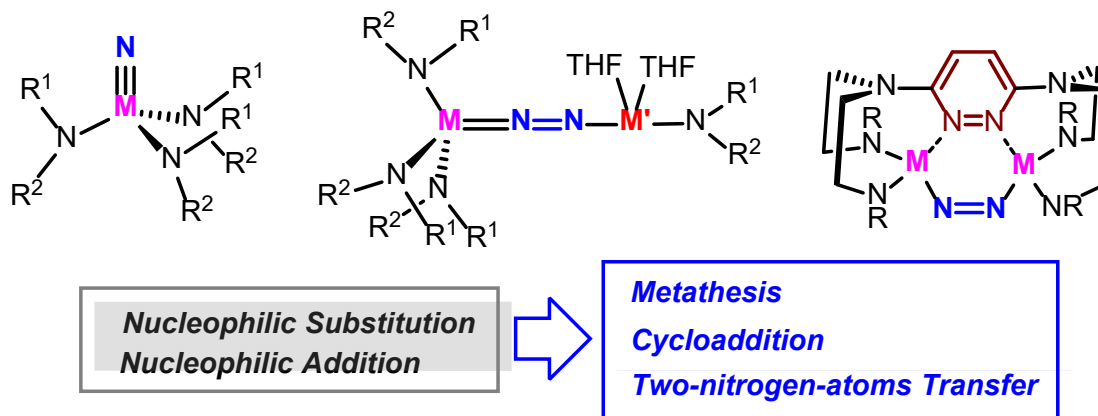
Schneider, S. et al., *Angew. Chem., Int. Ed.* **2016**, 55, 4786

Conclusio

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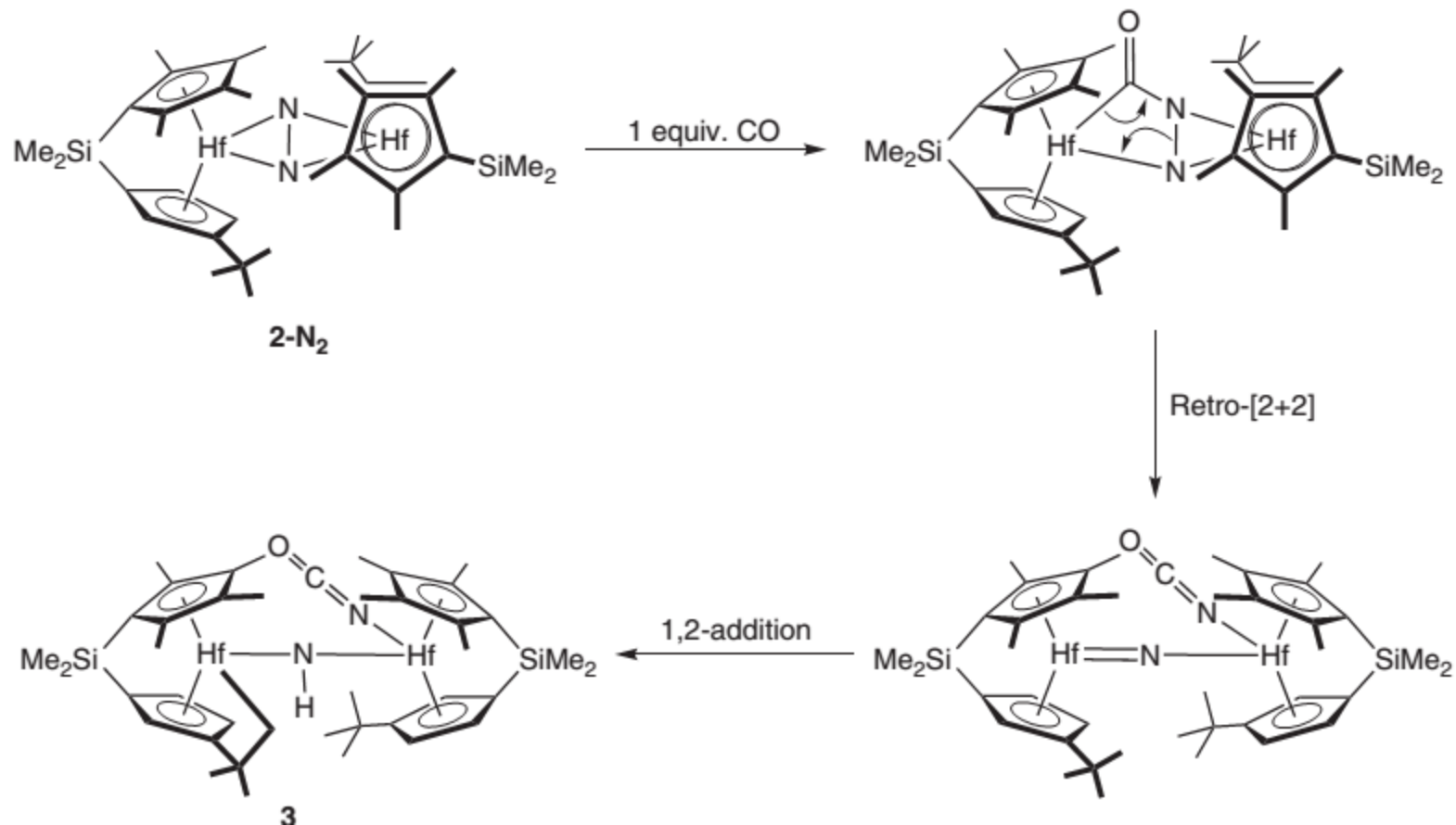


Where Do We Go From Here?



Thanks for Your Attention

Dinitrogen Activation and Functionalization



Dinitrogen Activation and Functionalization

