XU LAB
Innovation through Catalysis

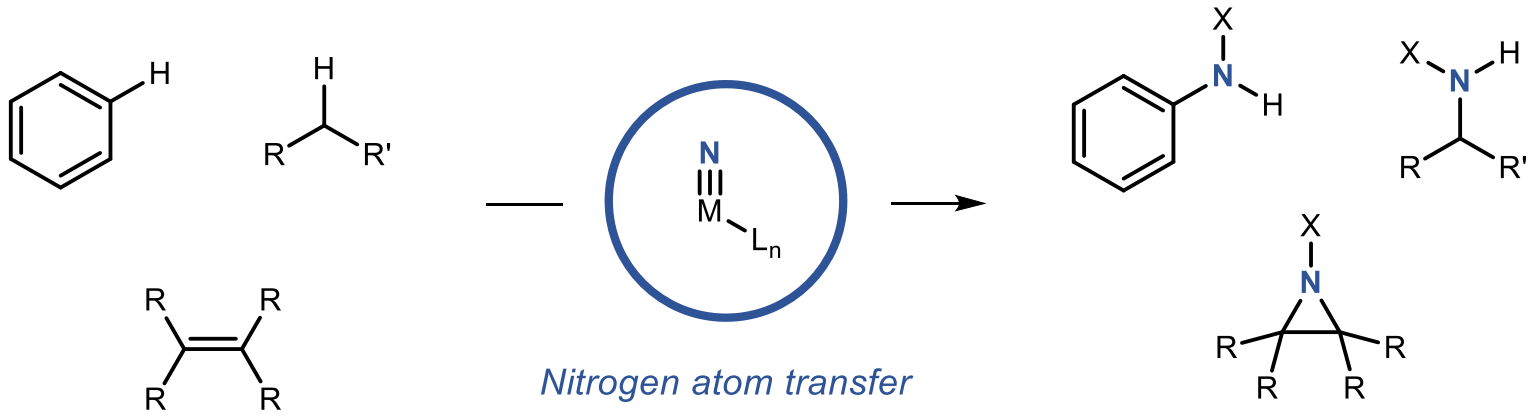
北京大学
PEKING UNIVERSITY

XU GROUP
Department of Chemistry, Peking University

Selected Weekly Literature Presentations

Disclaimer:
These slides contain personal interpretations and may include errors or subjective views.

Transition metal mediated nitrogen-atom transfer

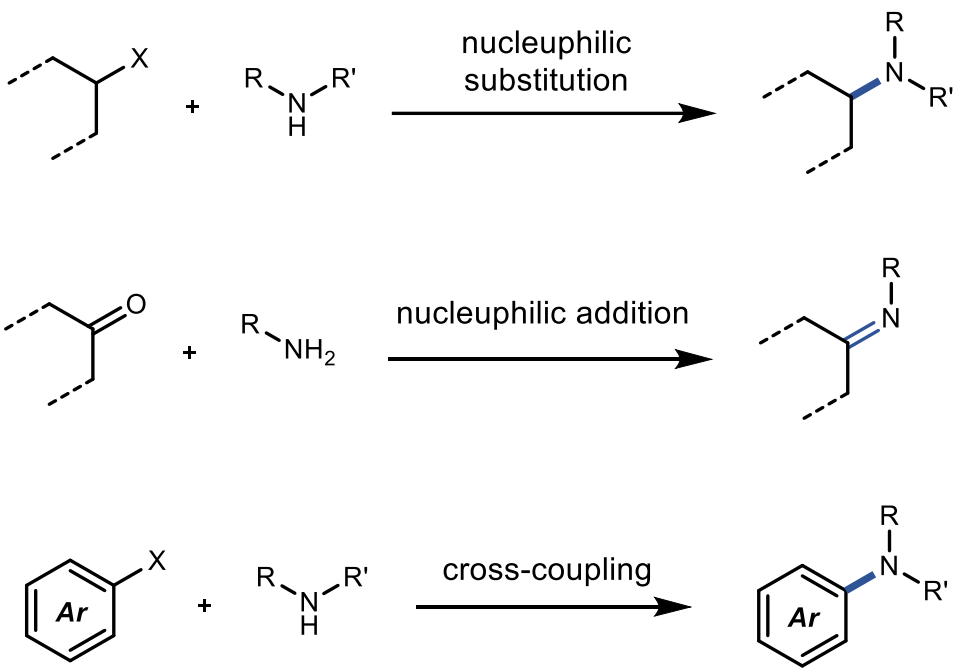


Ken Chen

Group meeting

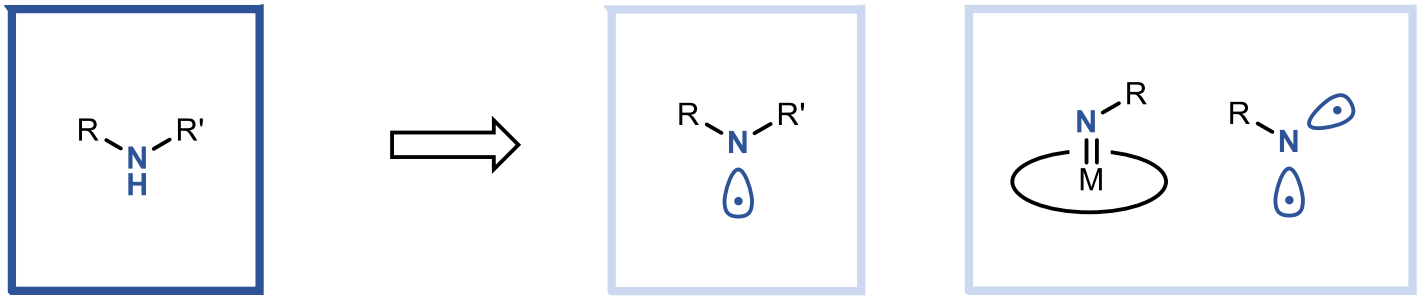
Oct. 28th, 2023

Synthesis of nitrogen containing compounds



- Inherent nucleophilicity
- Pre-oxidized substrates

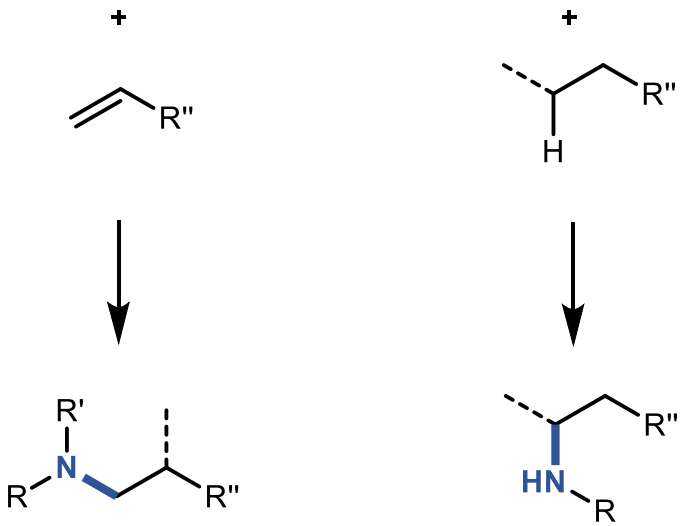
Inverting inherent nucleophilicity of nitrogen center



feedstock chemicals

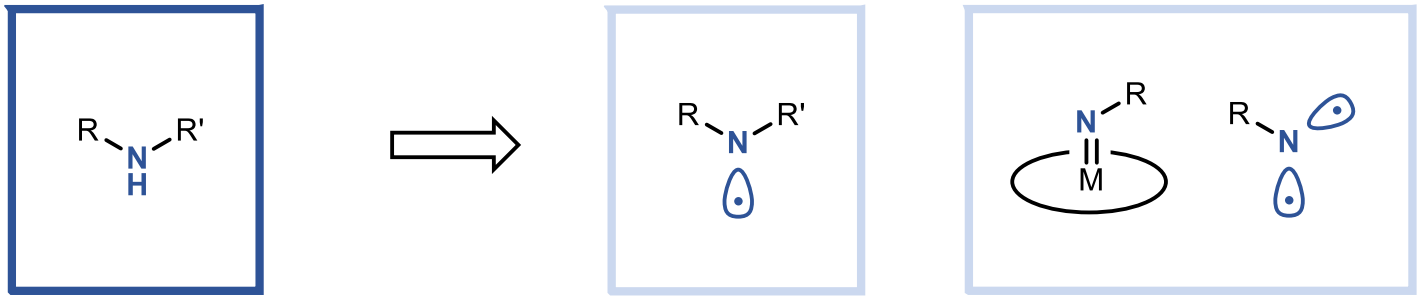
nitrogen-centered radicals

nitrene



- New chemical properties

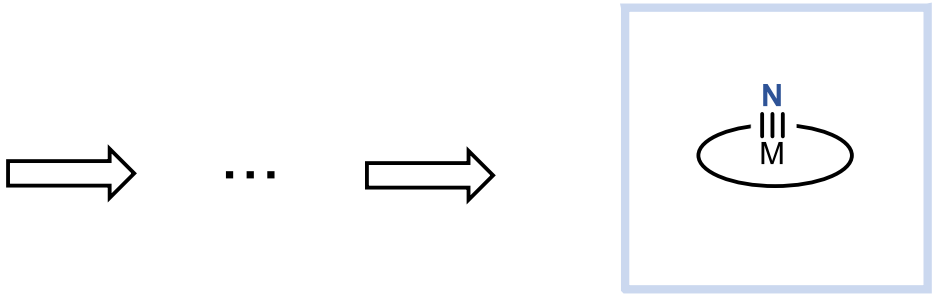
Inverting inherent nucleophilicity of nitrogen center



feedstock chemicals

nitrogen-centered radicals

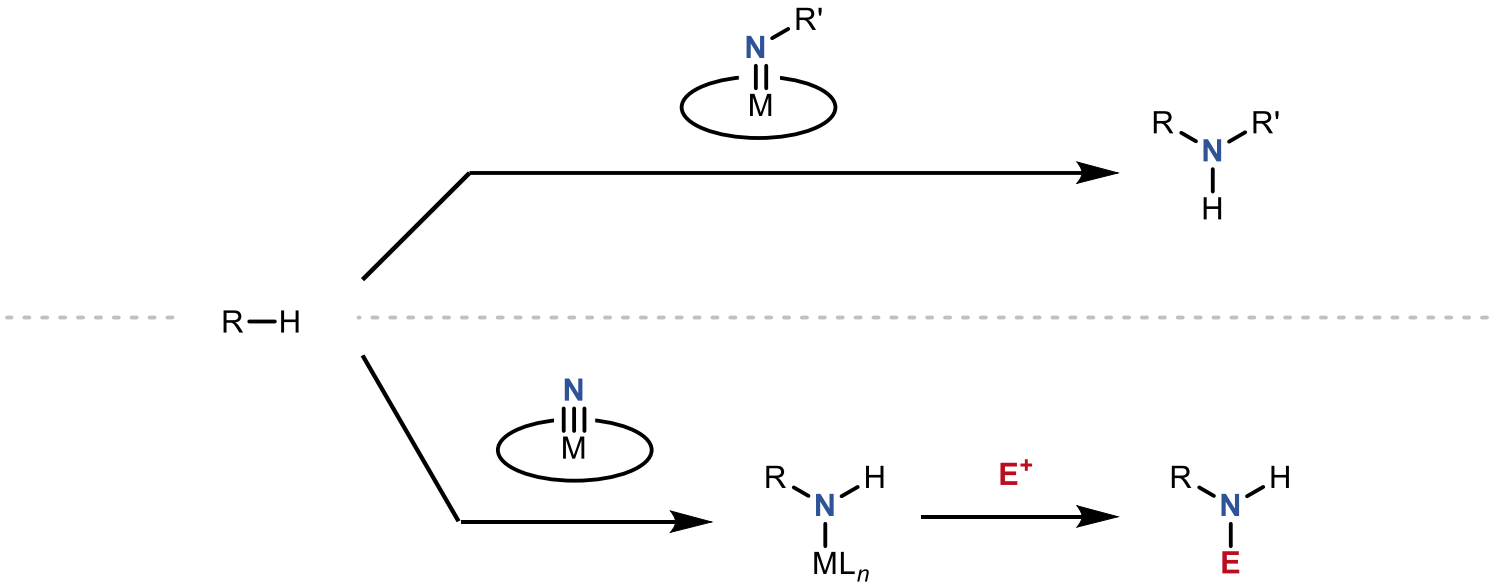
nitrene



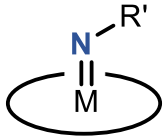
metal nitrides ?

Nitrogen group transfer VS nitrogen atom transfer

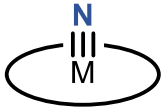
- Nitrogen **group** transfer (NGT)



- Nitrogen **atom** transfer (NAT)



- Limited N-substituents considering nitrene reactivity

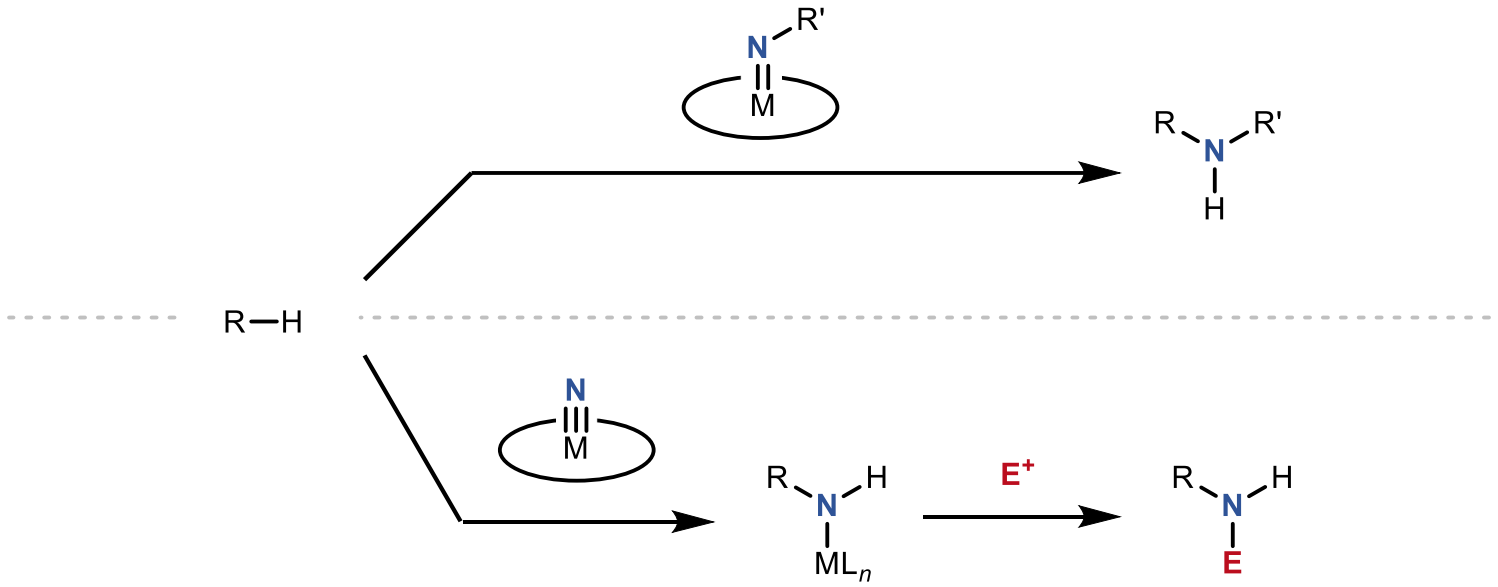


- More flexible N-atom building block

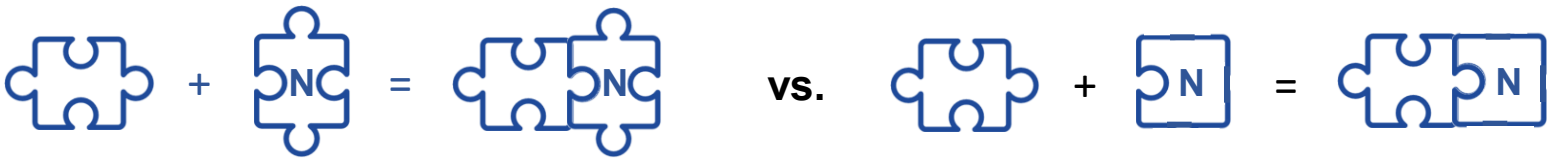
Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

Nitrogen group transfer VS nitrogen atom transfer

- Nitrogen **group** transfer (NGT)



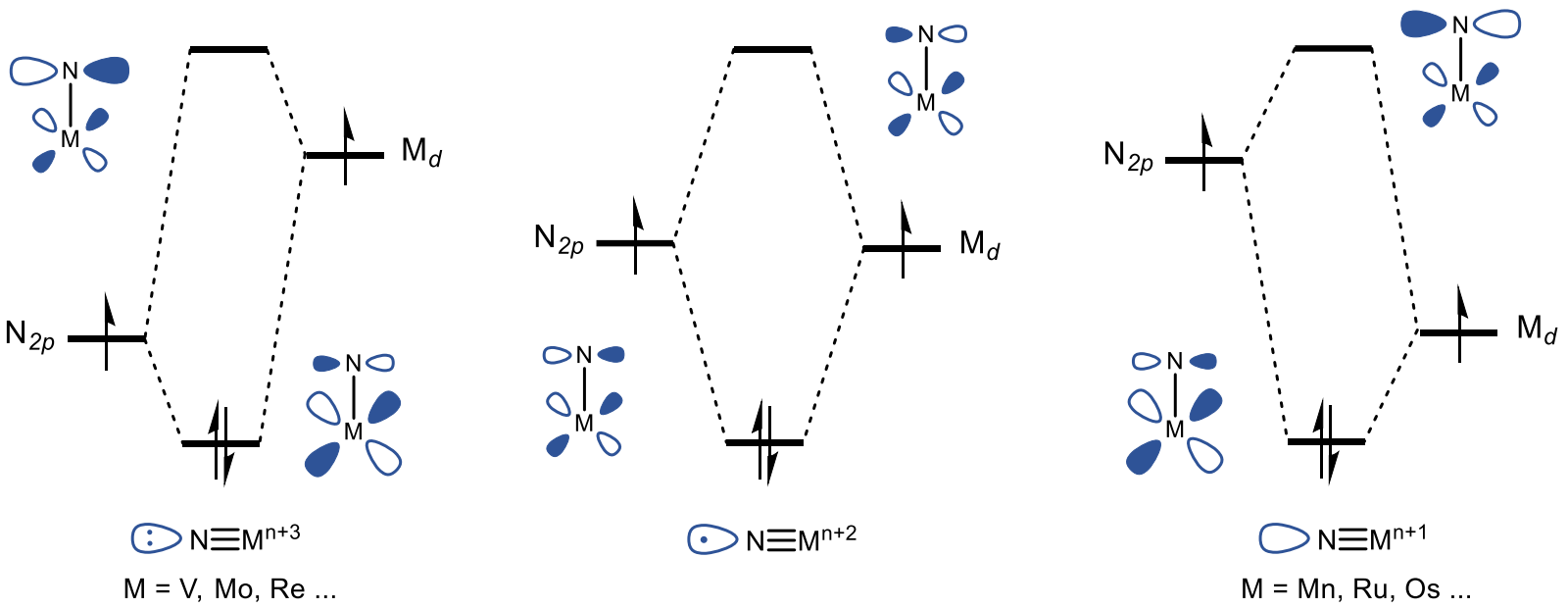
- Nitrogen **atom** transfer (NAT)



NAT **NGT**

Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

Reactivity modes of terminal M–N complexes



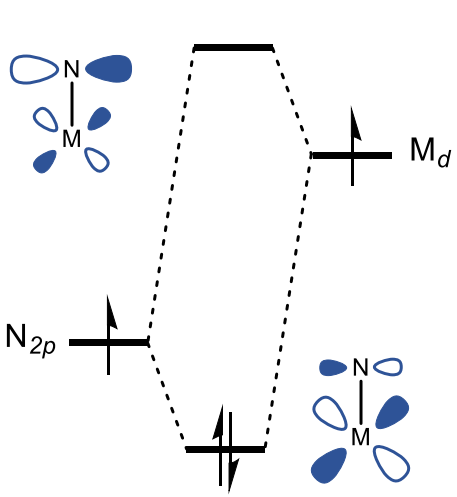
- Reactivity modes are decided by relative energy of M_d and N_{2p}

⇩

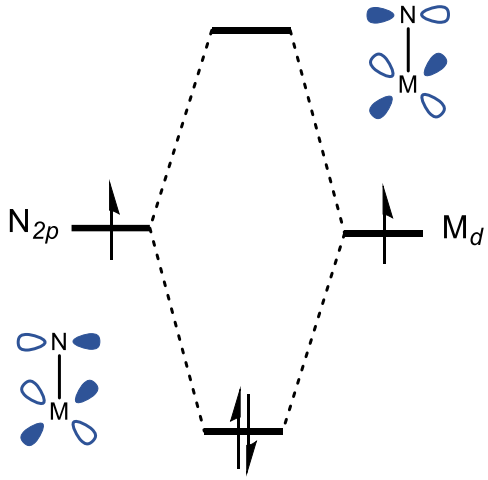
- Energy of M_d is affected by both metal center and ligands

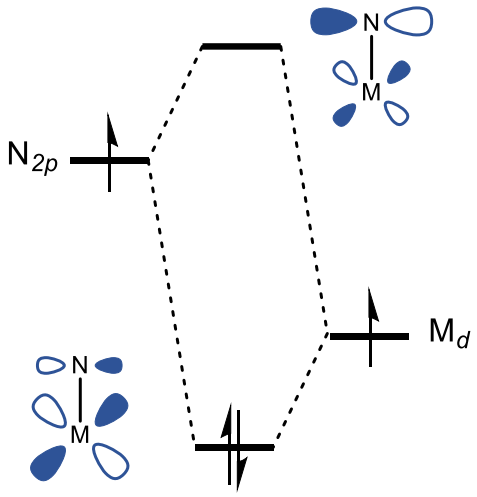
Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

Reactivity modes of terminal M–N complexes

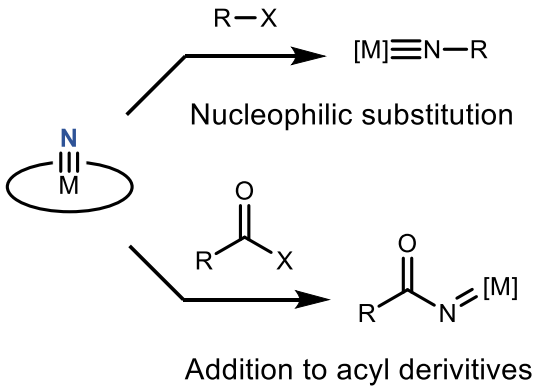


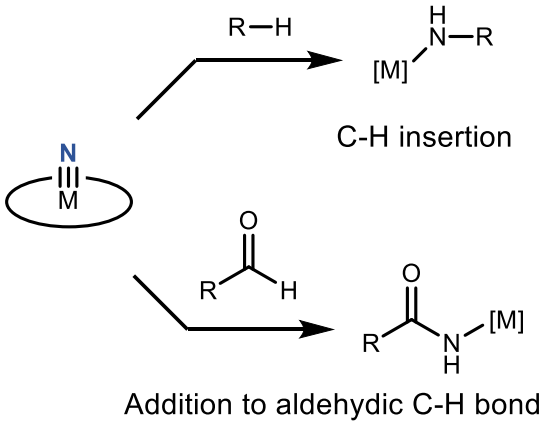
M = V, Mo, Re ...

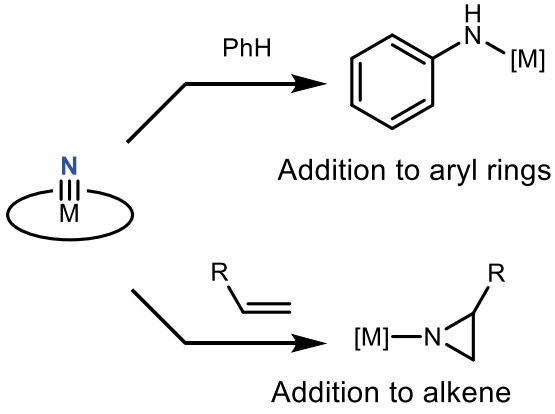




M = Mn, Ru, Os ...



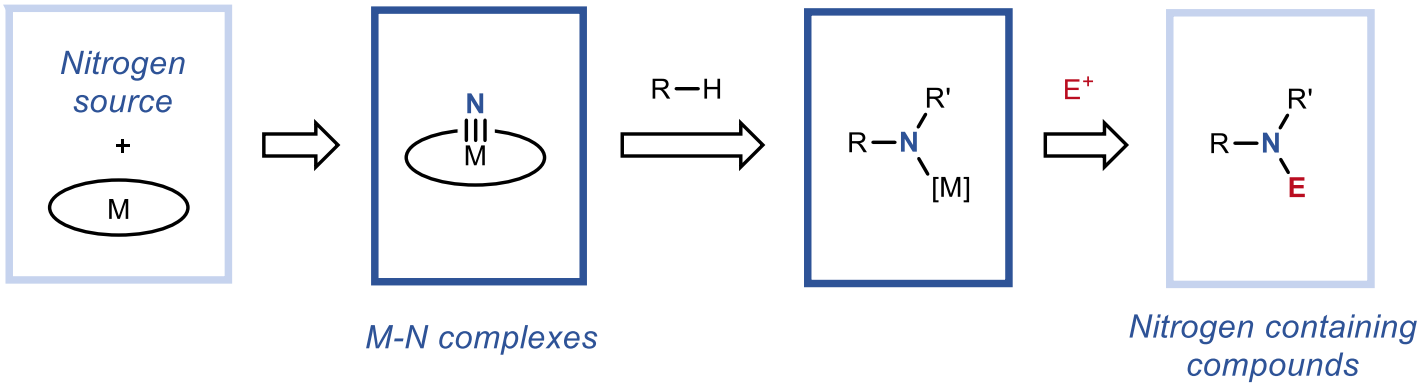




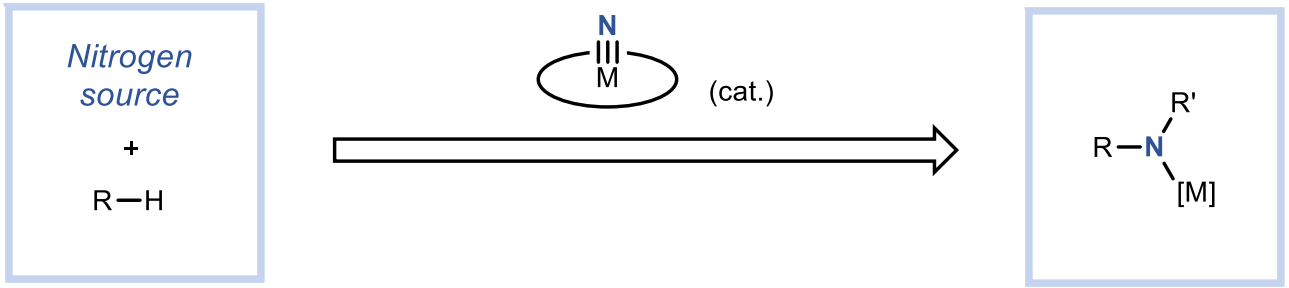
Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

Utilizing M-N complex in organic synthesis

- Stoichiometric nitrogen atom transfer (well-developed)

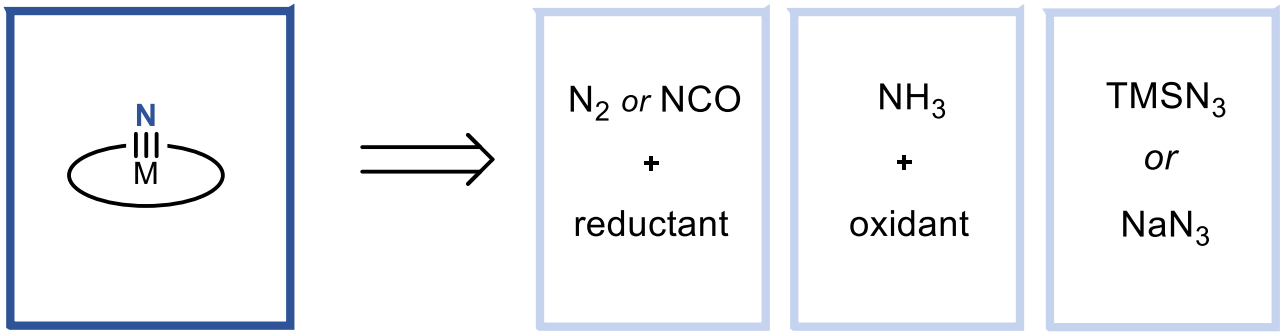


- Catalytic nitrogen atom transfer (elusive)



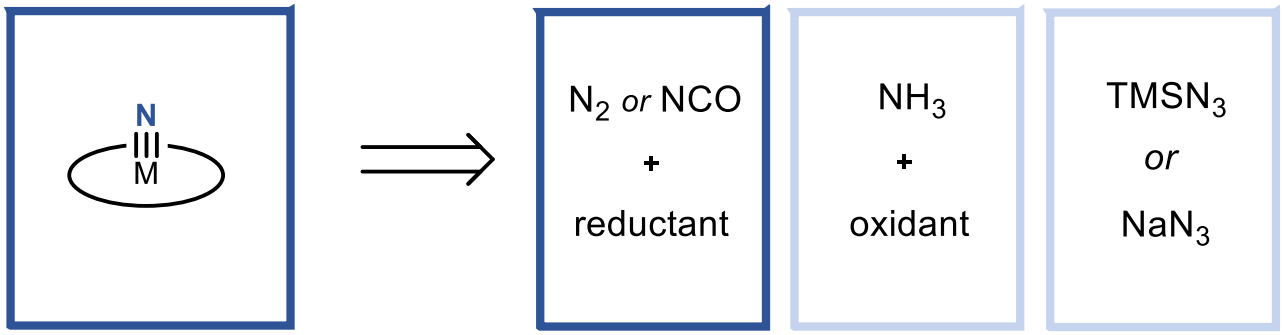
Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

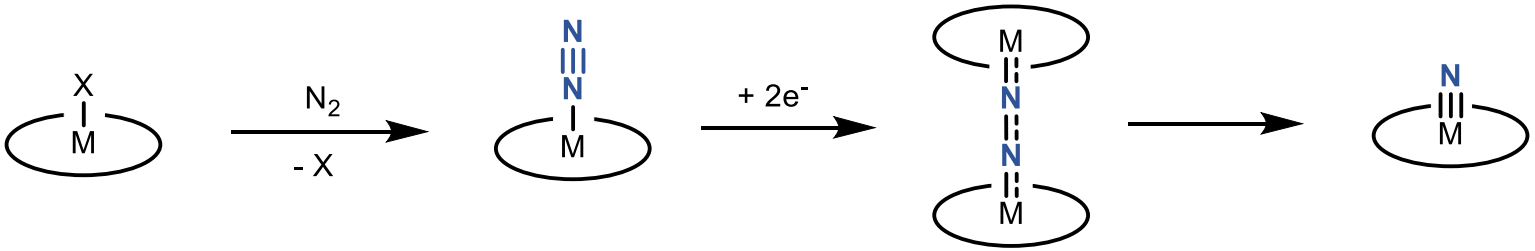
Nitrogen sources and limitations



Groves, J. T. *et al. Inorg. Chem.* **1983**, *22*, 884–887.

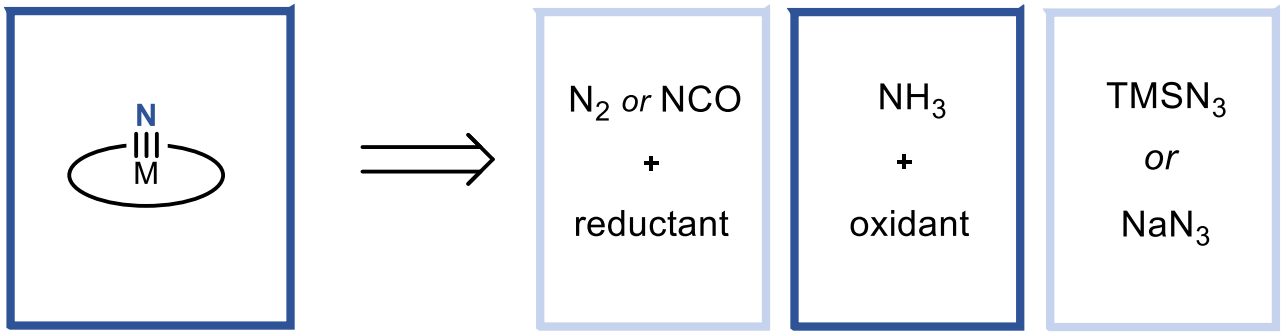
Nitrogen sources and limitations

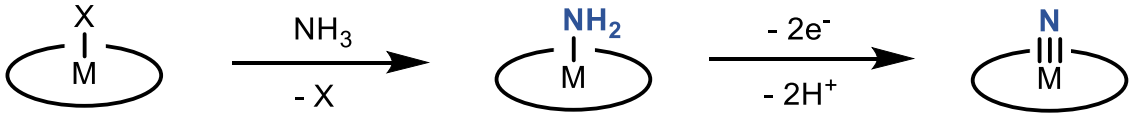




Christopher C. C. *et al*. ***Science* 1995**, *268*, 861–863.

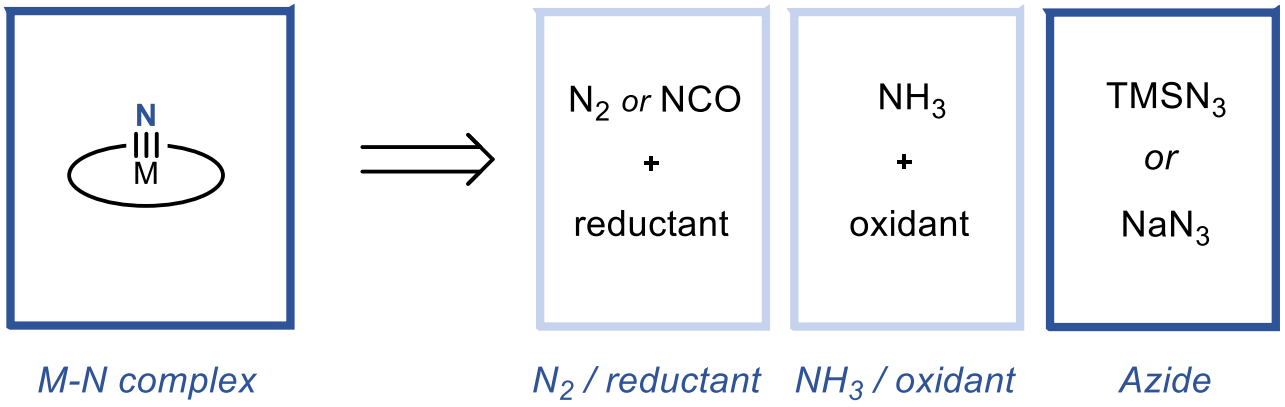
Nitrogen sources and limitations

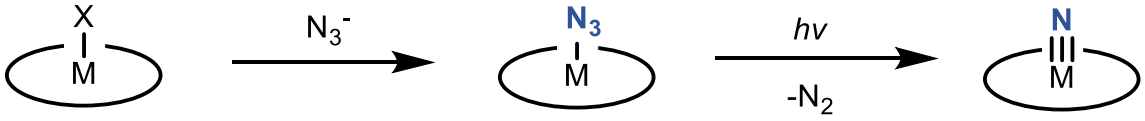




Hill. C. L. *et al. J. Am. Chem. Soc*. **1982**, *104*, 7318–7319.

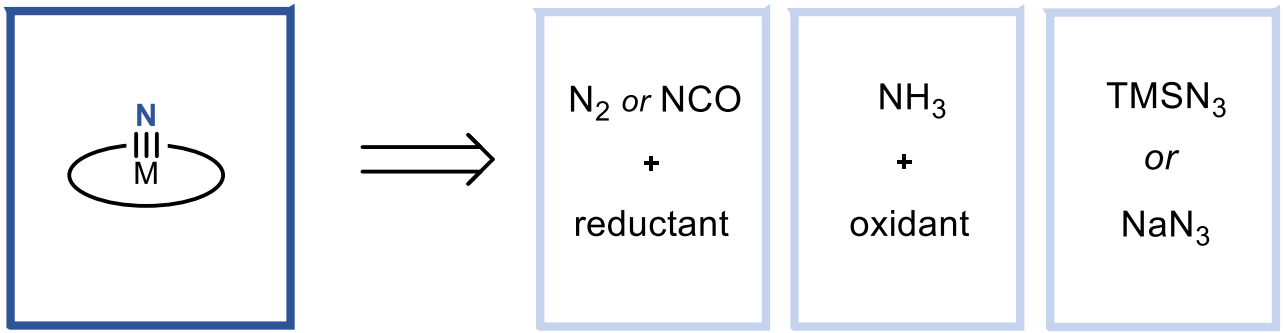
Nitrogen sources and limitations





Groves, J. T. *et al. Inorg. Chem.* **1983**, *22*, 884–887.

Nitrogen sources and limitations

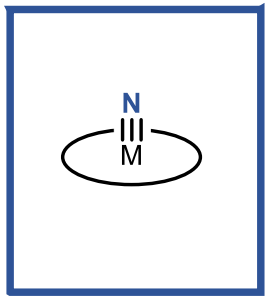


- Require harsh conditions to form M-N complex
- Stoichiometric M-N reagent needed and stepwise reaction
- Catalytic process could be developed

Carreira, E. M. *et al. Acc. Chem. Res.* **1997**, *30*, 364–372.

Nitrogen atom transfer reactions

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***



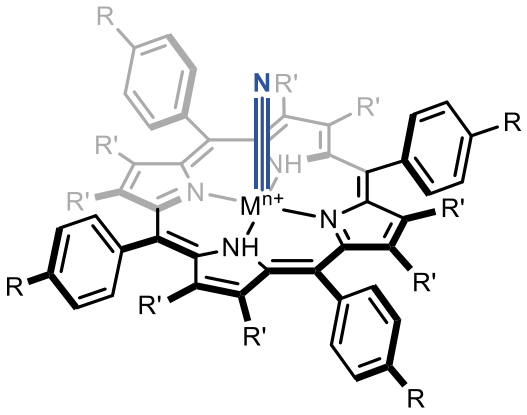
Groves, J. T. *et al. Inorg. Chem.* **1983**, *22*, 884–887.

Nitrogen atom transfer reactions

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***

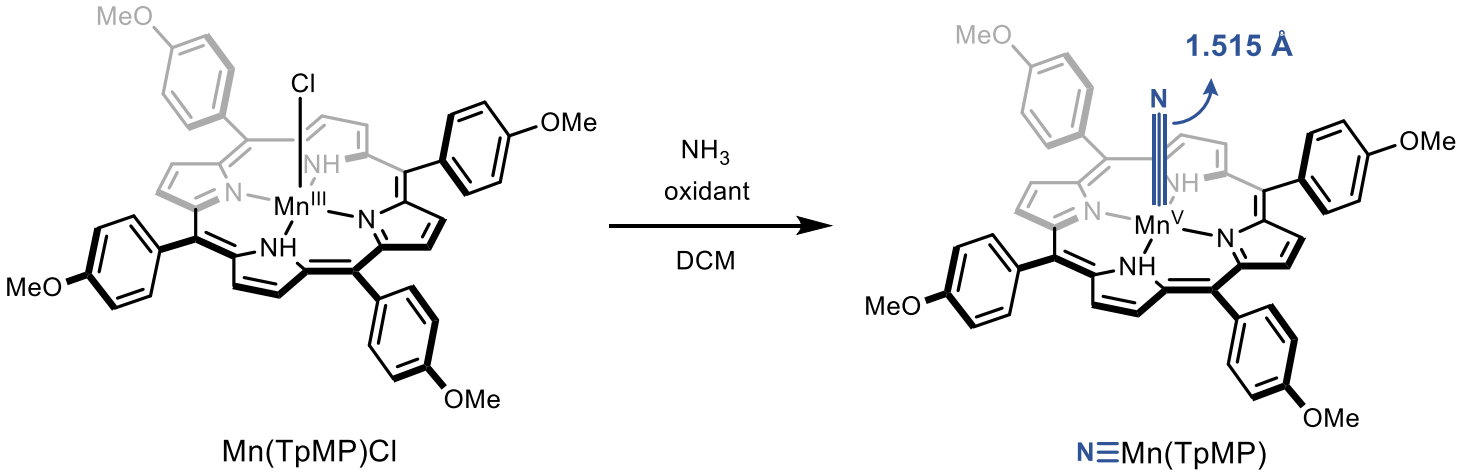
Groves, J. T. *et al. Inorg. Chem.* **1983**, *22*, 884–887.

Preparation of metal nitrides complex



Gouterman, 1979	M = Os, R = H, R' = Et
Hill, 1982	M = Mn, R = Me, Et, OMe *etc*., R' = H
Groves, 1983	M = Cr, R = Me, R' = H

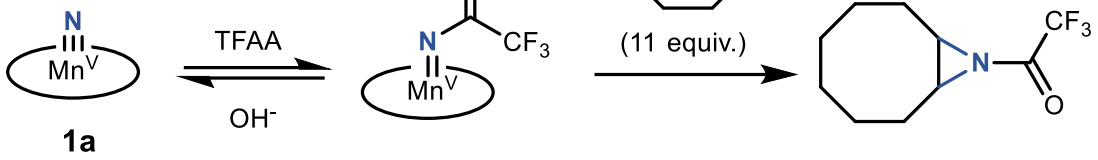
Hill 1982

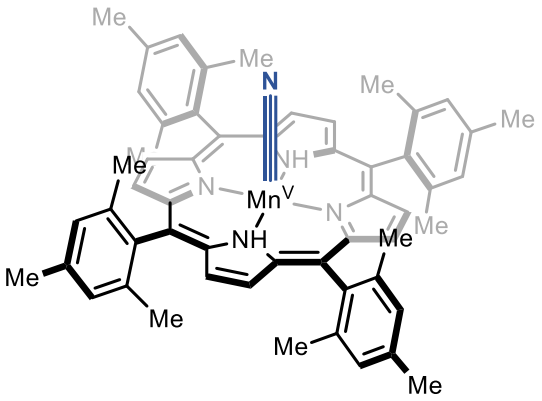


Mn(TpMP)Cl N≡Mn(TpMP)

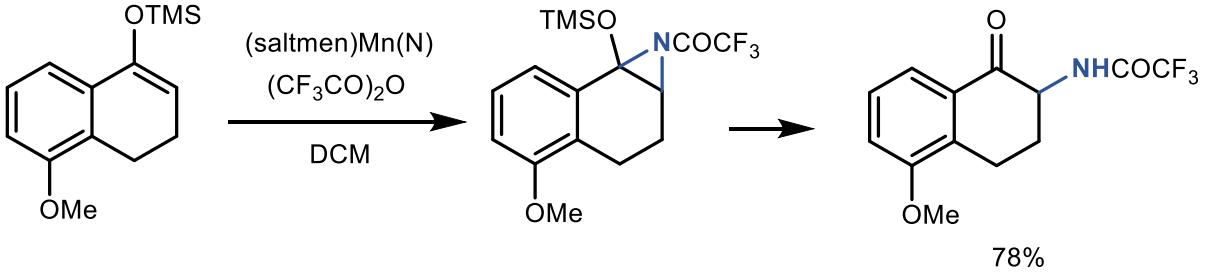
Gouterman, M. *et al. J. Am. Chem. Soc.* **1980**, *102*, 198–207.
Hill, C. L. *et al*. J. Am. Chem. Soc. **1982**, *104*, 7318-7319.
Groves, J. T. *et al. Inorg. Chem.* **1983**, *22*, 884–887.

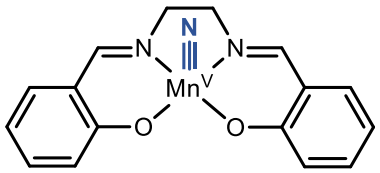
Aziridination activated by anhydride





1a, **N≡**Mn(TMP)

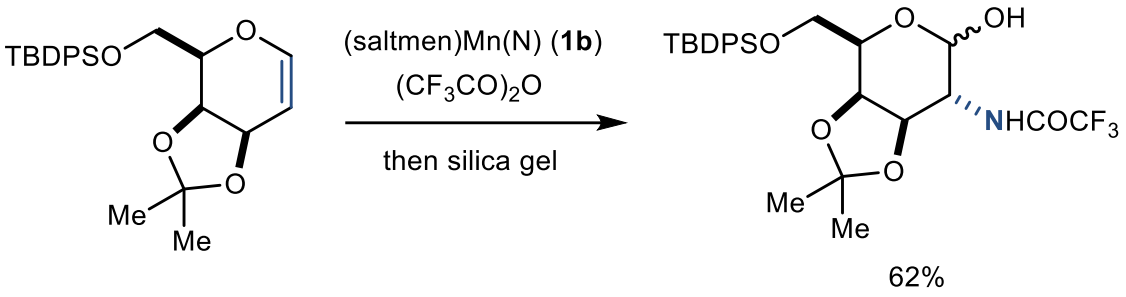




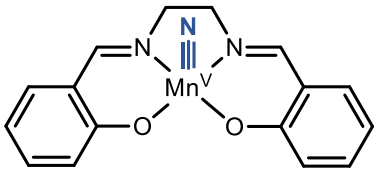
1b, **N≡**Mn(saltmen)

Groves, J. T. *et al. J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.
Carreira, E, M. *et al. J. Acc. Chem. Res.* **1997**, *30,* 364-372.

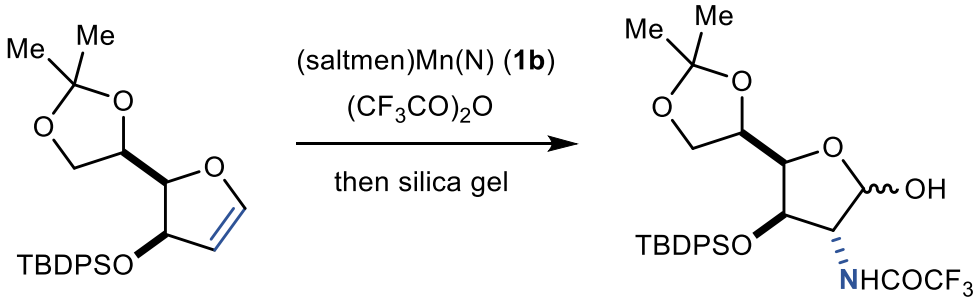
Aziridination activated by anhydride



62%



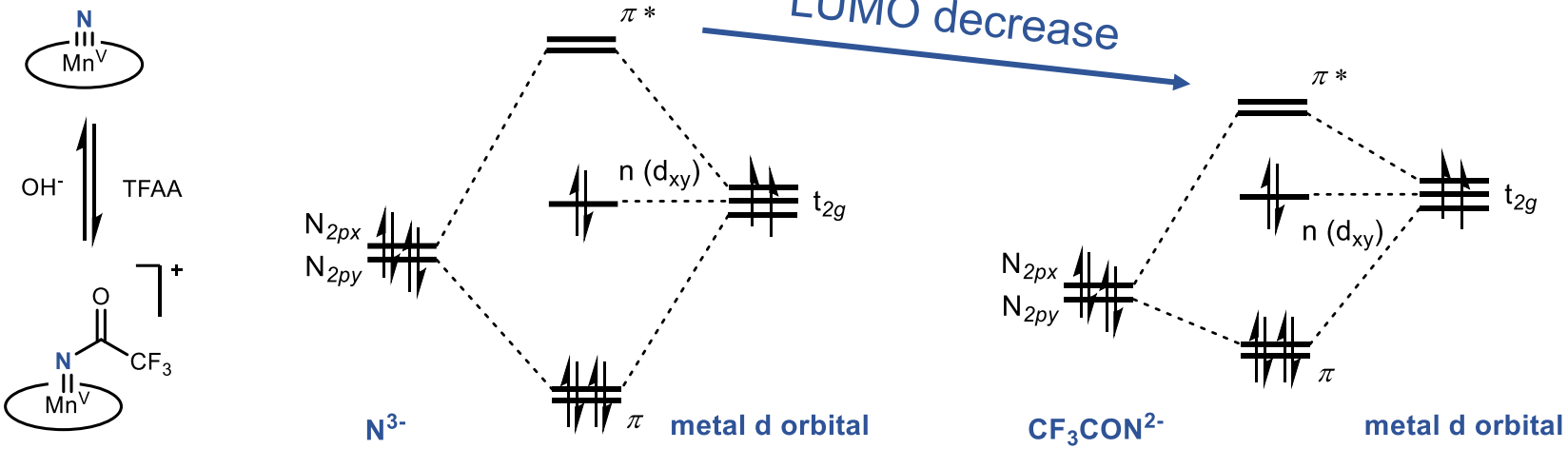
1b, N≡Mn(saltmen)



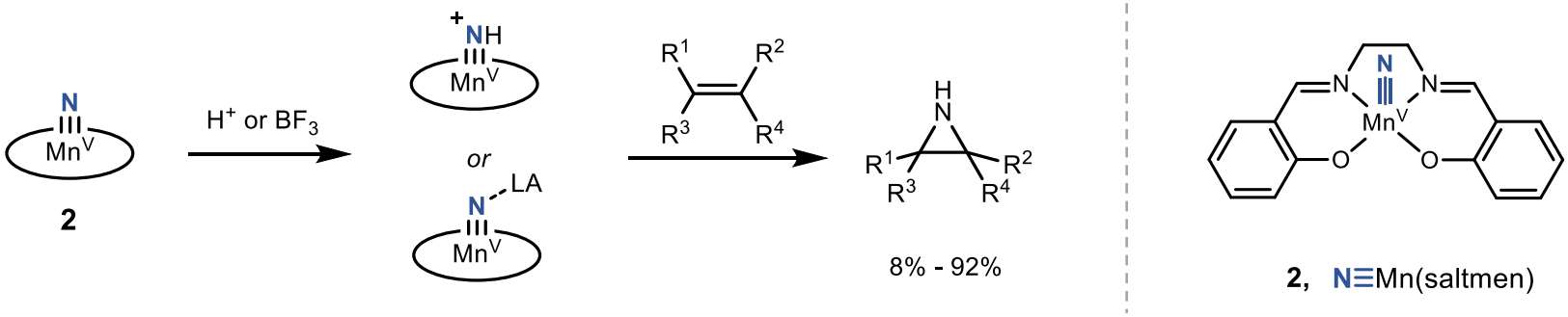
80%

Carreira, E, M. *et al. J. Acc. Chem. Res.* **1997**, *30,* 364-372.

Aziridination activated by anhydride

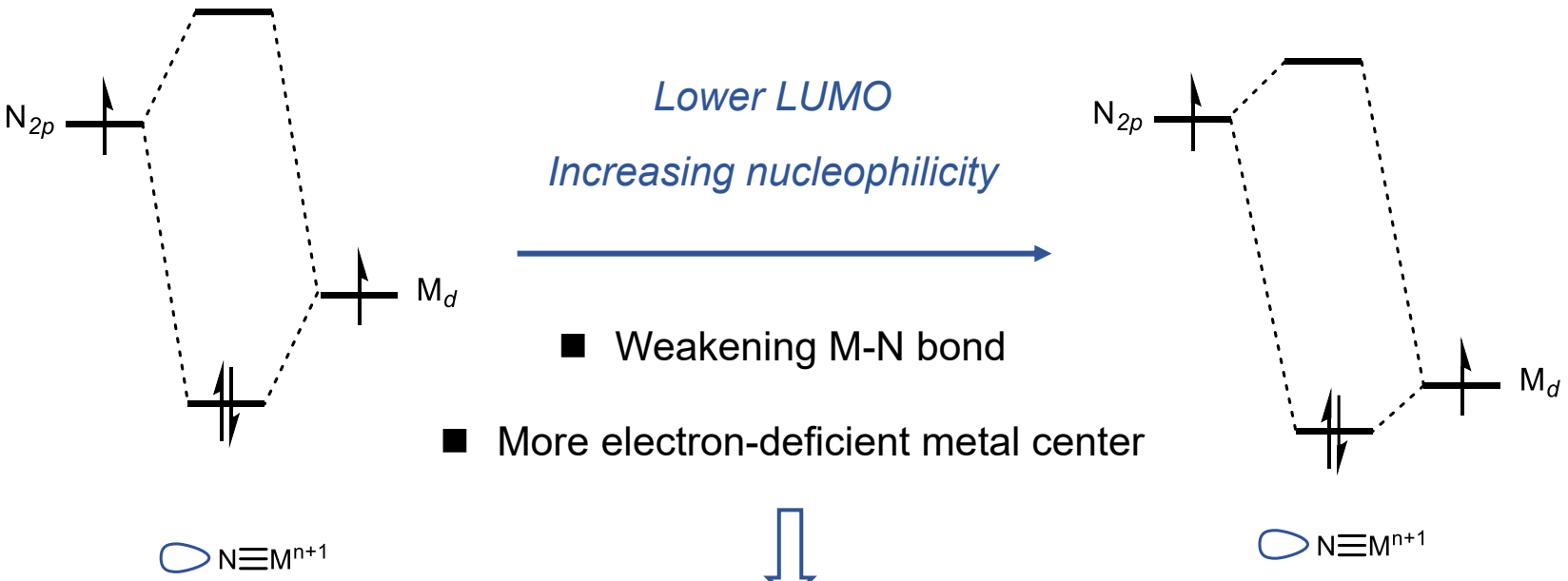


■ Weaker M-N bond ⟹ ■ Lower LUMO



Groves, J. T. *et al. J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.
Lau. T. *J. Chem. Soc. Dalton Trans.* **1999**, 2411–2414.

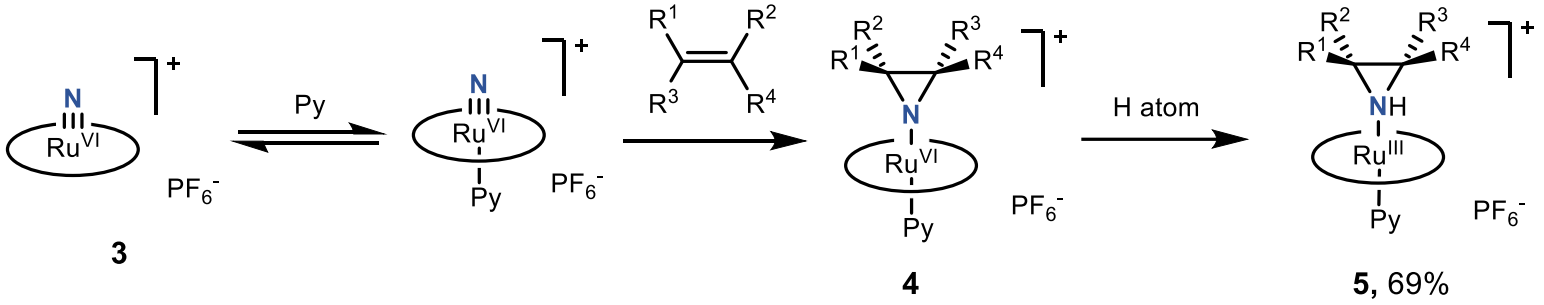
Direct nitrogen atom transfer



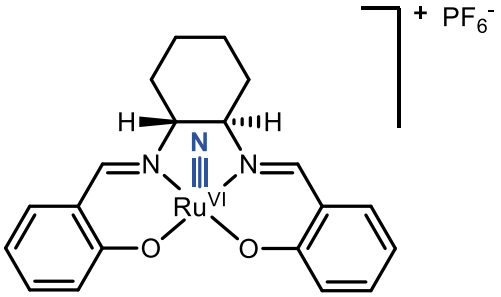
- Weakening M-N bond
- More electron-deficient metal center

Directed nitrogen atom transfer

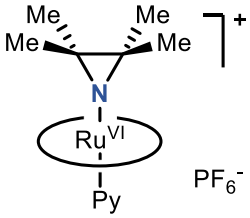
Direct aziridination by Ru complex cation



3 **4** **5**, 69%



3, N≡Ru(salchda)PF_6

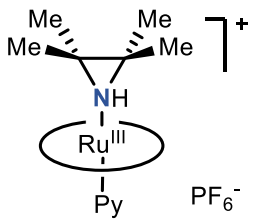


4

m/z = 599

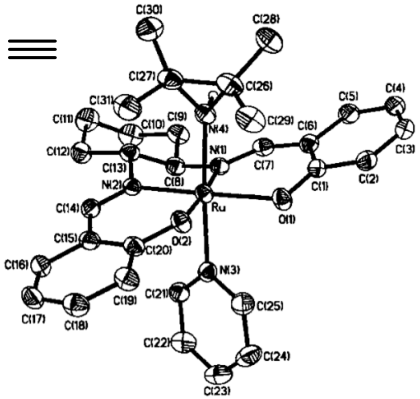
m/z = 520 (-Py)

diamagnetic



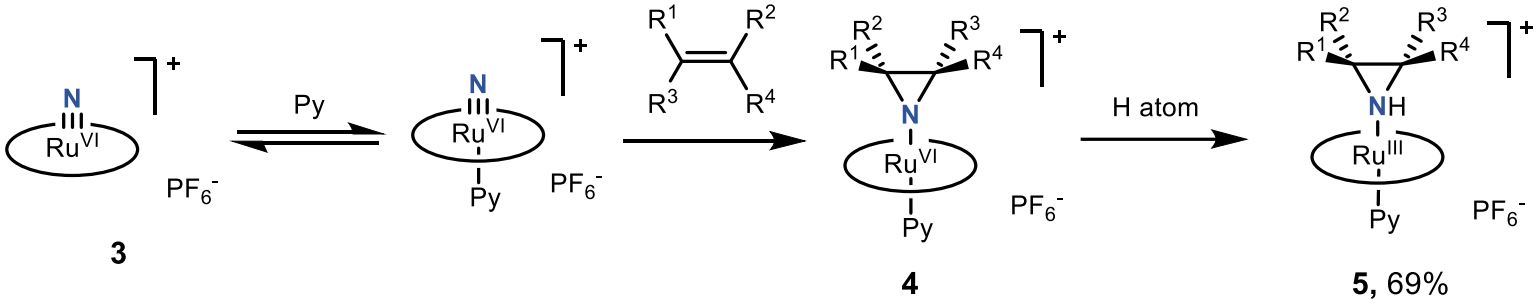
5

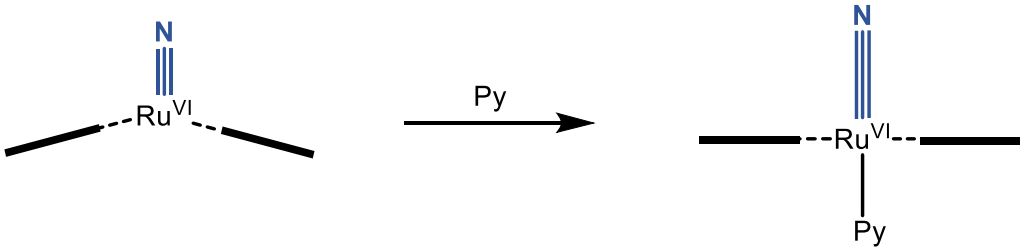
μ_{eff} = 1.99 μ_B



Lau. T. *et al. J. Am. Chem. Soc.* **2004**, *126*, 15336–15337.

Direct aziridination by Ru complex cation



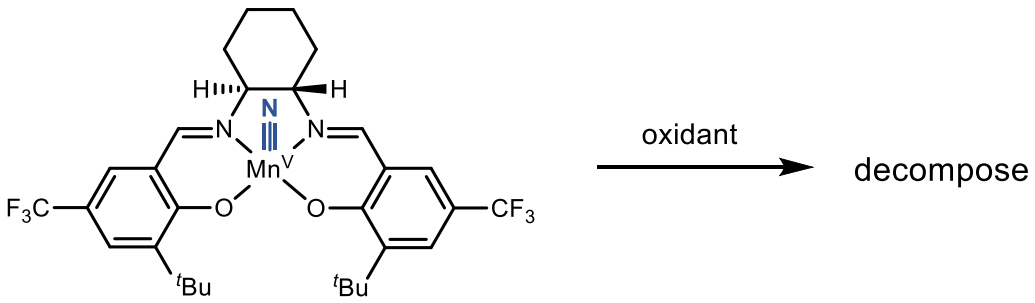


- More electron deficient metal center
- Introduce *trans* ligand

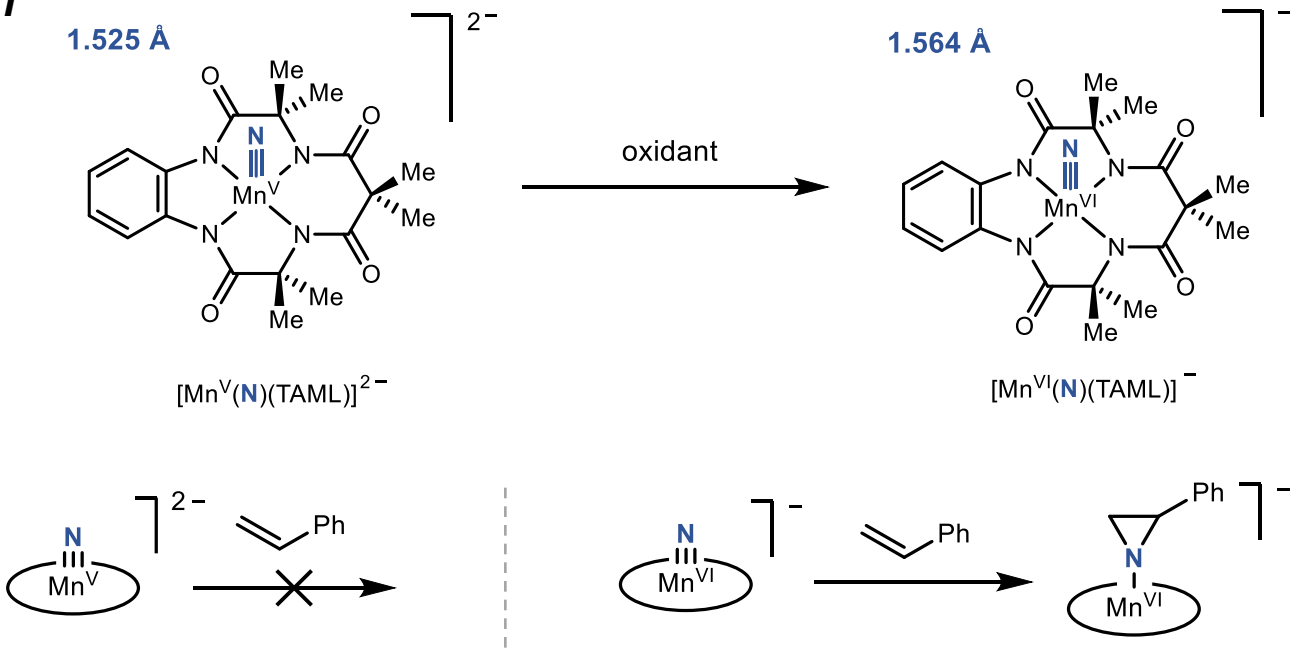
Lau. T. *et al. J. Am. Chem. Soc.* **2004**, *126*, 15336–15337.

Direct aziridination by Mn(VI) complex

Storr 2016

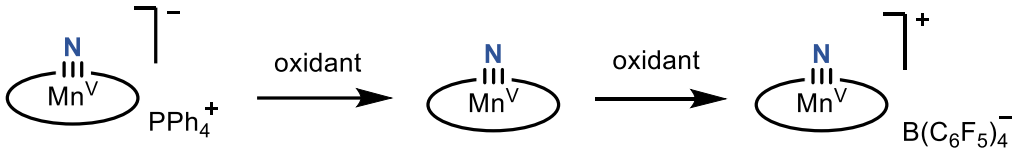


Lau 2021

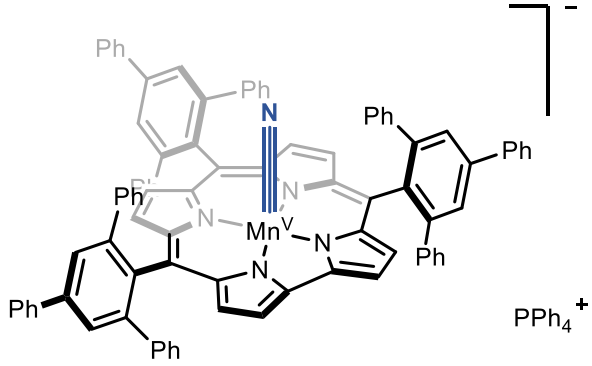


Storr. T. *et al. J. Am. Chem. Soc.* **2016**, *138*, 15299−15302.
Lau. T. *et al. J. Am. Chem. Soc.* **2021**, *143*, 15863–15872.

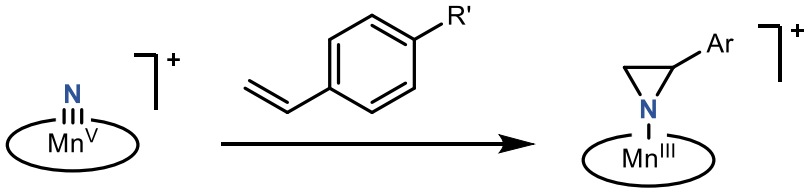
Increasing electrophilicity by adjusting ligands (with redox active ligands)



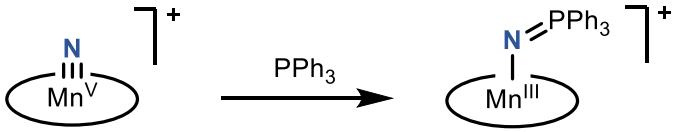
6 **7** **8**



6, N≡Mn(TTPPC)PPh_4

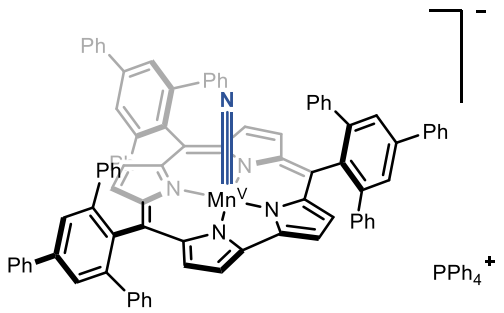


R' = H, Me, Cl, OMe, CF_3

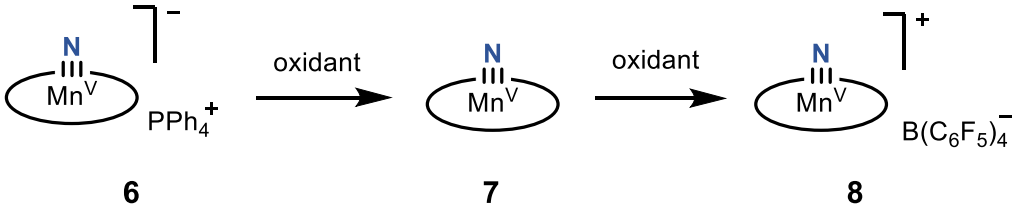


Lau. T. *et al. J. Am. Chem. Soc.* **2022**, *144*, 7588–7593.

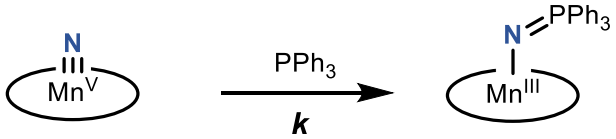
Increasing electrophilicity by adjusting ligands (with redox active ligands)



6 N≡Mn(TTPPC)PPh_4

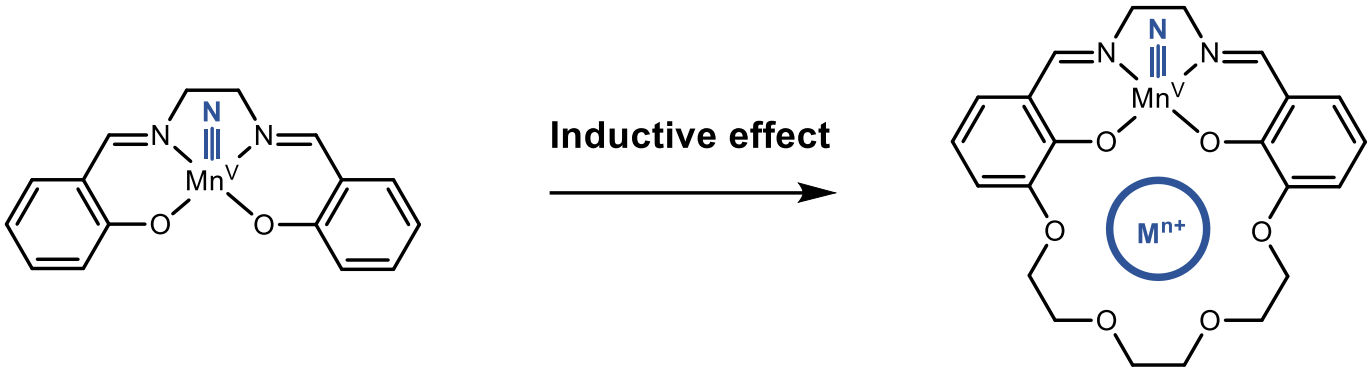


Mn-N bond length / Å	1.527	1.514	1.546
$E^{1/2}$ (vs $Cp_2Fe^{+/0}$) / V	-0.569	0.231	0.70
k / $M^{-1}\times s^{-1}$	No reaction	3.4×10^{-3}	2.1×10^{5}



Lau. T. *et al. J. Am. Chem. Soc.* **2022**, *144*, 7588–7593.

Increasing electrophilicity by adjusting ligands (with non-redox active cation)



M^{n+} =	non	K^+	Ba^{2+}	Sr^{2+}
$E^{1/2}$ (vs $Cp_2Fe^{+/0}$) / V	0.454	0.616	0.805	0.880

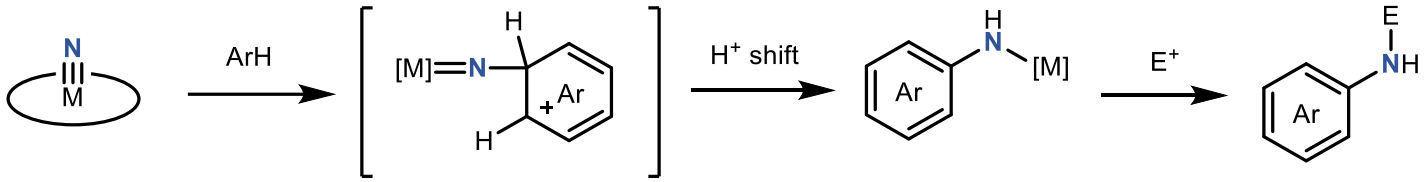
M^{n+} =	K^+	Sr^{2+}	Eu^{3+}
$E^{1/2}$ (vs $Cp_2Fe^{+/0}$) / V	0.616	0.880	1.16

Increasing $E_{1/2}$ and reactivity

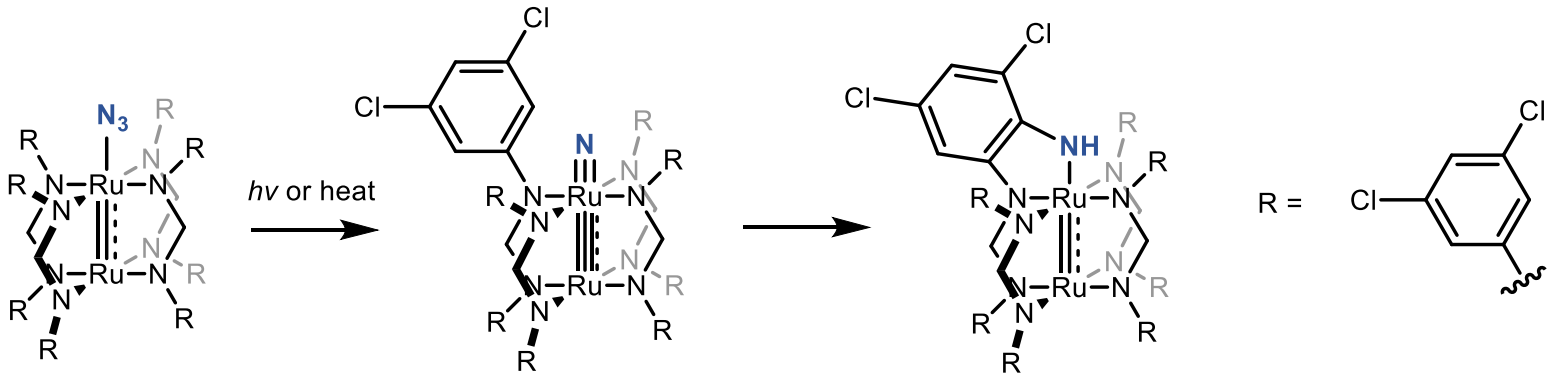
Yang, J. Y. *et al. Angew. Chem. Int. Ed.* **2018**, *57,* 14037–14042.

Reactions with aryl compounds

- Intramolecular addition



First work:

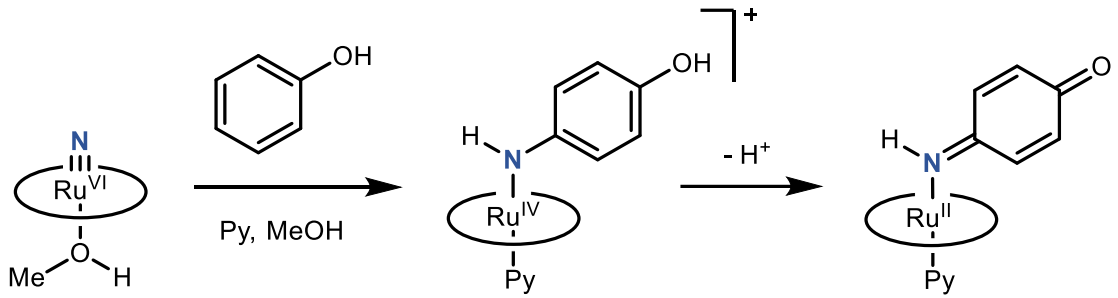


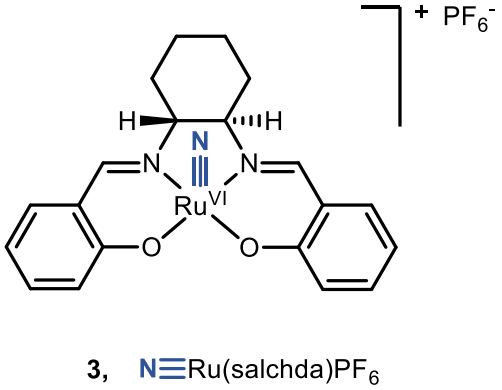
- Ru-N bond weakening by Ru-Ru bond
- Bulky substituents prevent decomposition

Berry, J. F. *et al.* Angew. Chem. Int. Ed. **2008**, *47*, 10102–10105.
Berry, J. F. *et al. J. Am. Chem. Soc.* **2010**, *132*, 12228–12230.

Reactions with aryl compounds

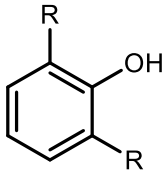
- Electrophilic addition





3, N≡Ru(salchda)PF_6

with



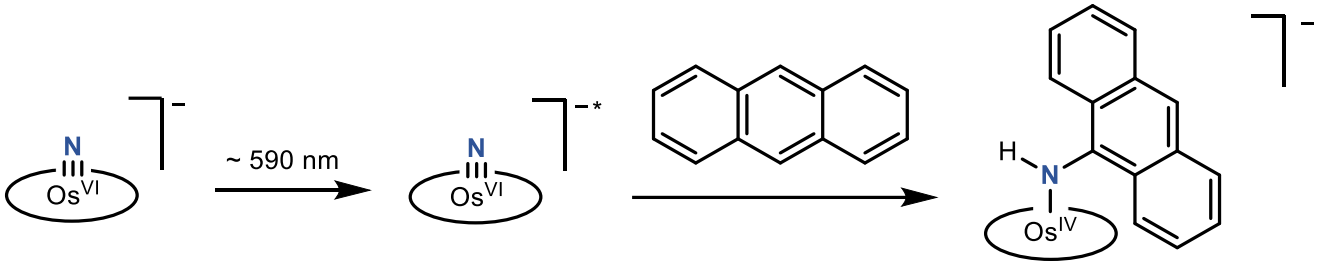
R =	MeO	^{t}Bu	Me	H	Cl
k / M^{-1} s^{-1}	8.08	2.38	1.06	0.18	0.039

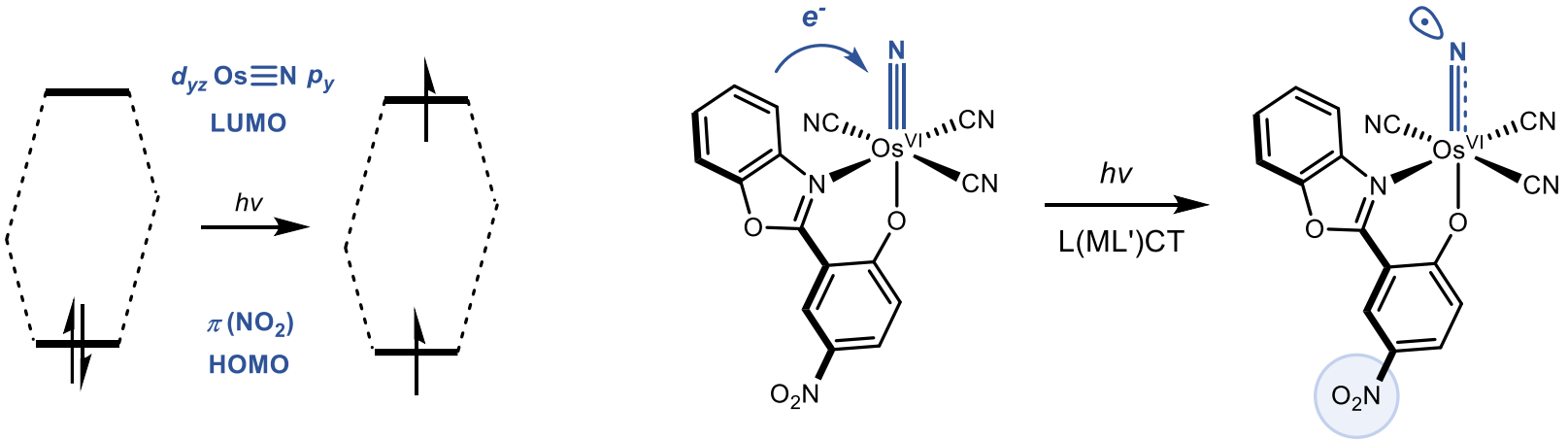
- Electrophilic addition

Lau. T. *et al. J. Am. Chem. Soc.* **2016**, *138,* 5817–5820.

Reactions with aryl compounds

- Addition to inactivated arene

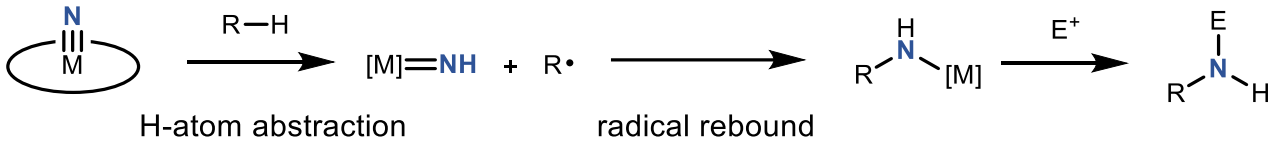


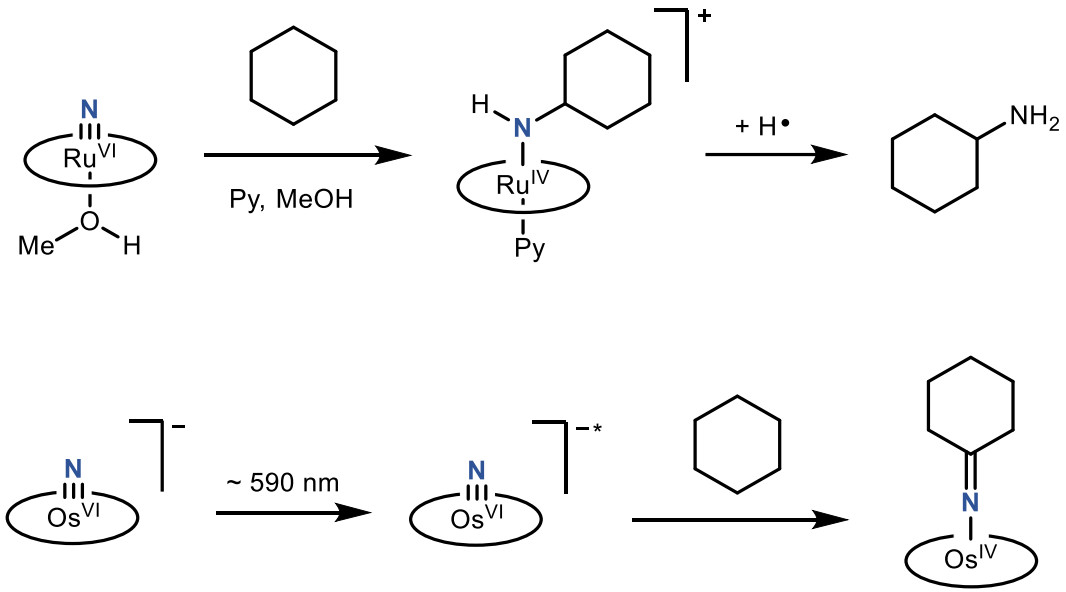


- More electron deficient
- Weaker M-N bond

Lau. T. *et al. Commun. Chem.* **2019**, *2*, 40.

C-H insertion

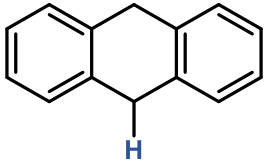
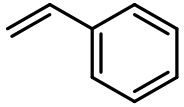
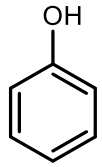
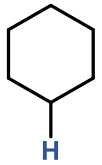


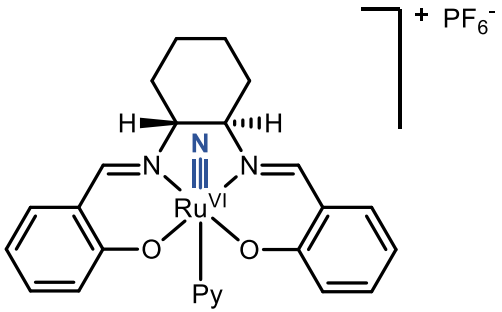


Lau. T. *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 9101–9104.
Lau. T. *et al. Commun. Chem.* **2019**, *2*, 40.

Chemo selectivity?

Decrease in reactivity →

Substrates	PPh_3				
	addition with PPh_3	C-H insertion of DHA	Aziridination	Electrophilic addition	C-H insertion cyclohexane
k / M^{-1} s^{-1}	> 10^3	10^1 – 10^0	~10^{-2}	10^0 – 10^{-2}	~10^{-3}

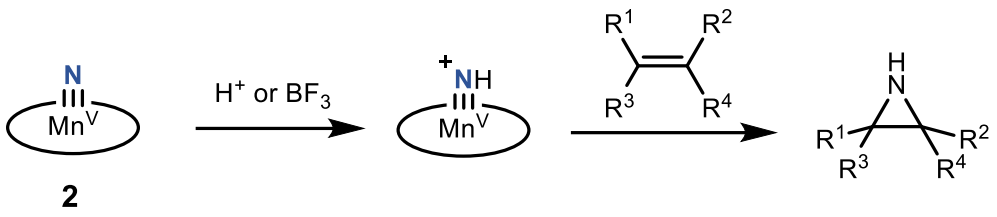


- Close rate constant for different reactions
- Hard to control chemical selectivity

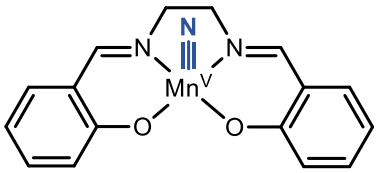
Lau. T. *et al. J. Am. Chem. Soc.* **2016**, *138,* 5817–5820.
Lau. T. *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 9101–9104.
Lau. T. *et al. J. Am. Chem. Soc.* **2021**, *143*, 15863–15872.
Lau. T. *et al. J. Am. Chem. Soc.* **2022**, *144*, 7588–7593.

Enantioselective aziridination

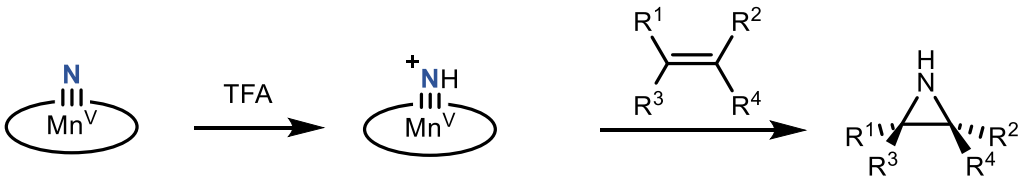
Recall:



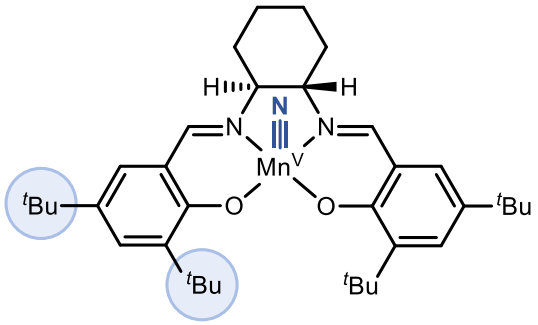
2



2, N≡Mn(saltmen)



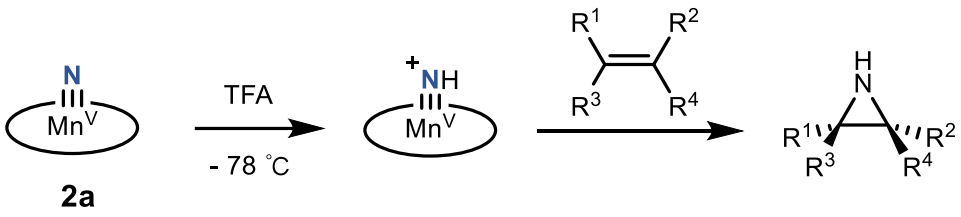
2a



2a

Lau. T. *et al. J. Chem. Soc. Dalton Trans.* **1999**, 2411–2414.

Enantioselective aziridination



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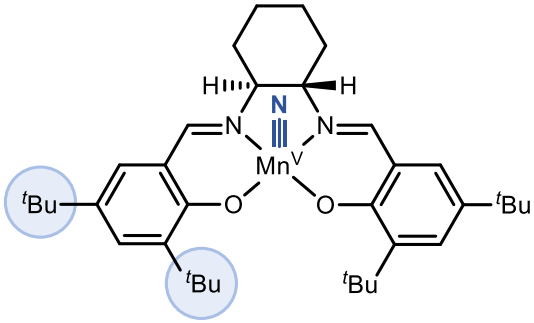

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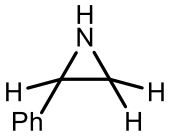
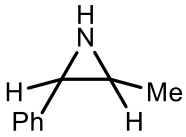
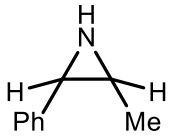


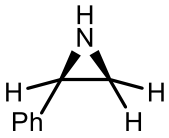
72%



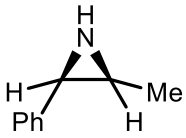
92%



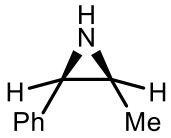
53%



36%, 81% ee



20%, 91% ee

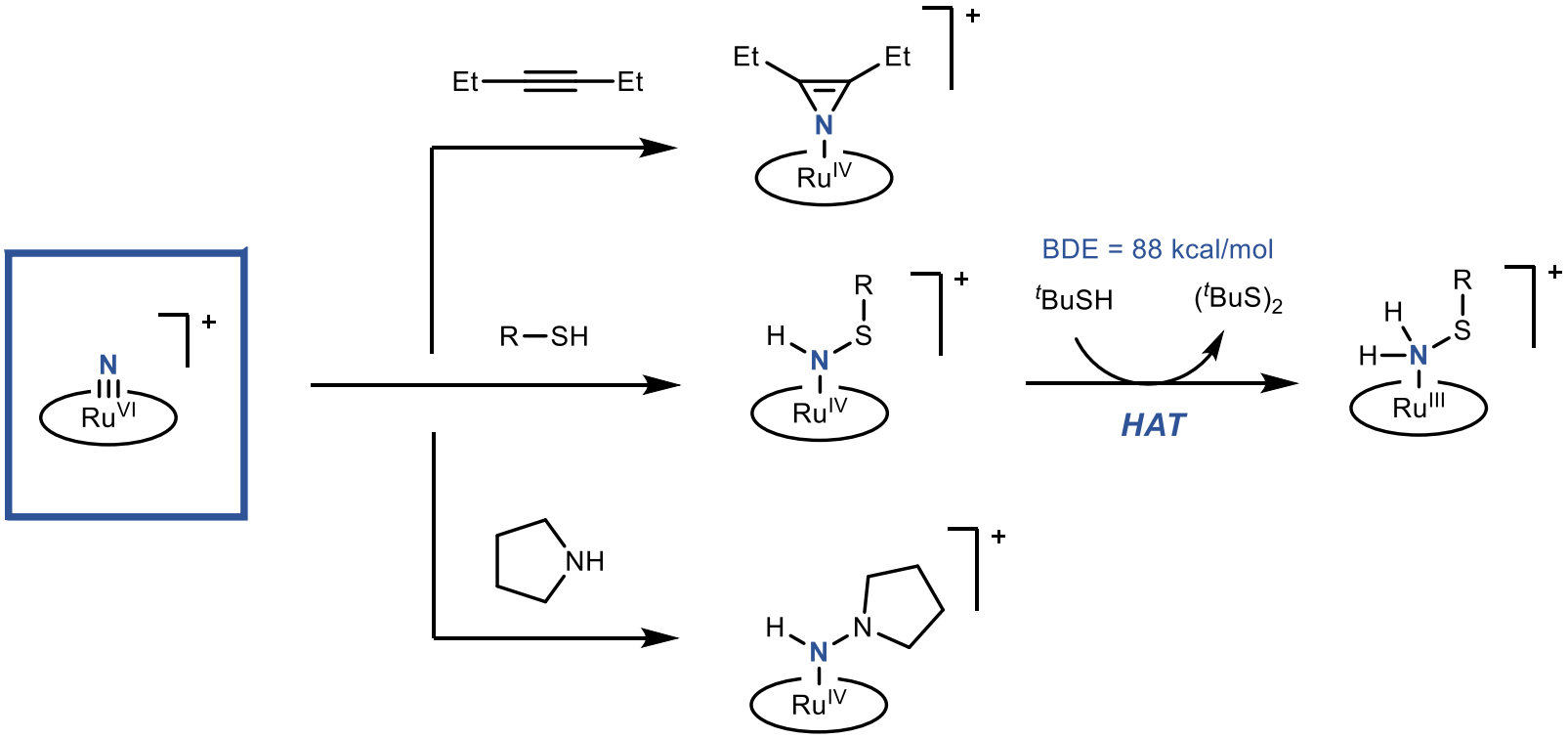


7%, 25% ee

- Increased ee
- Decreased yield

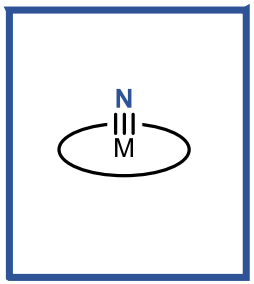
Lau. T. *et al*. *J. Chem. Soc. Dalton Trans.* **1999**, 2411–2414.

Reactions with other nucleophiles



Lau. T. *et al. Acc. Chem. Res.* **2014**, *47*, 427–439.

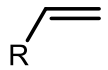
Summary

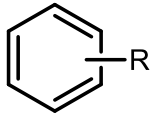


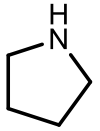
M-N complex

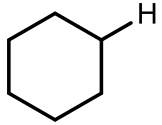
- Weaken the M-N bond
- Lower LUMO
  - Introduce *trans* ligand
  - Oxidize the metal center
  - Oxidize the ligand

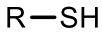
- Nitrogen atom transfer with nucleophiles











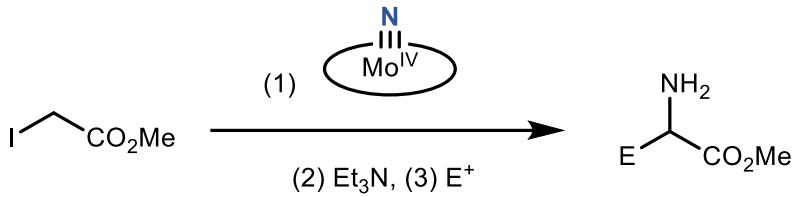
Lau. T. *et al. Acc. Chem. Res.* **2014**, *47*, 427–439.

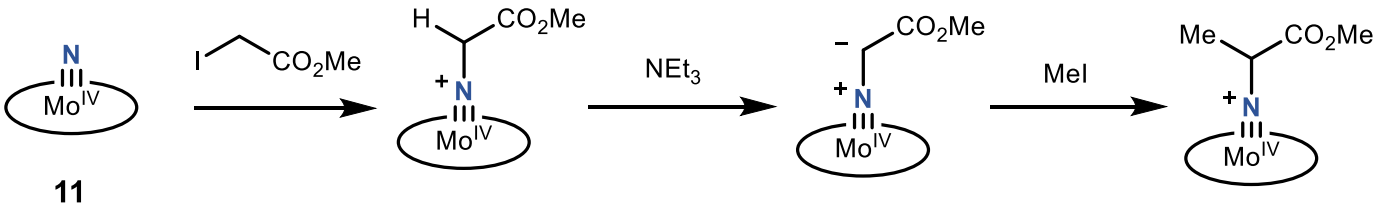
Nitrogen atom transfer reactions

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***

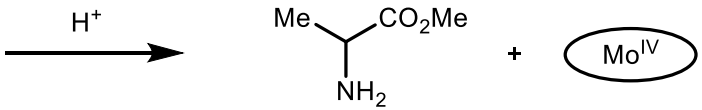
Synthesis of amino acid ester from nucleophilic nitrides

Pickett 1992





11



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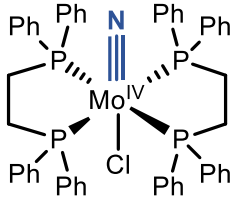
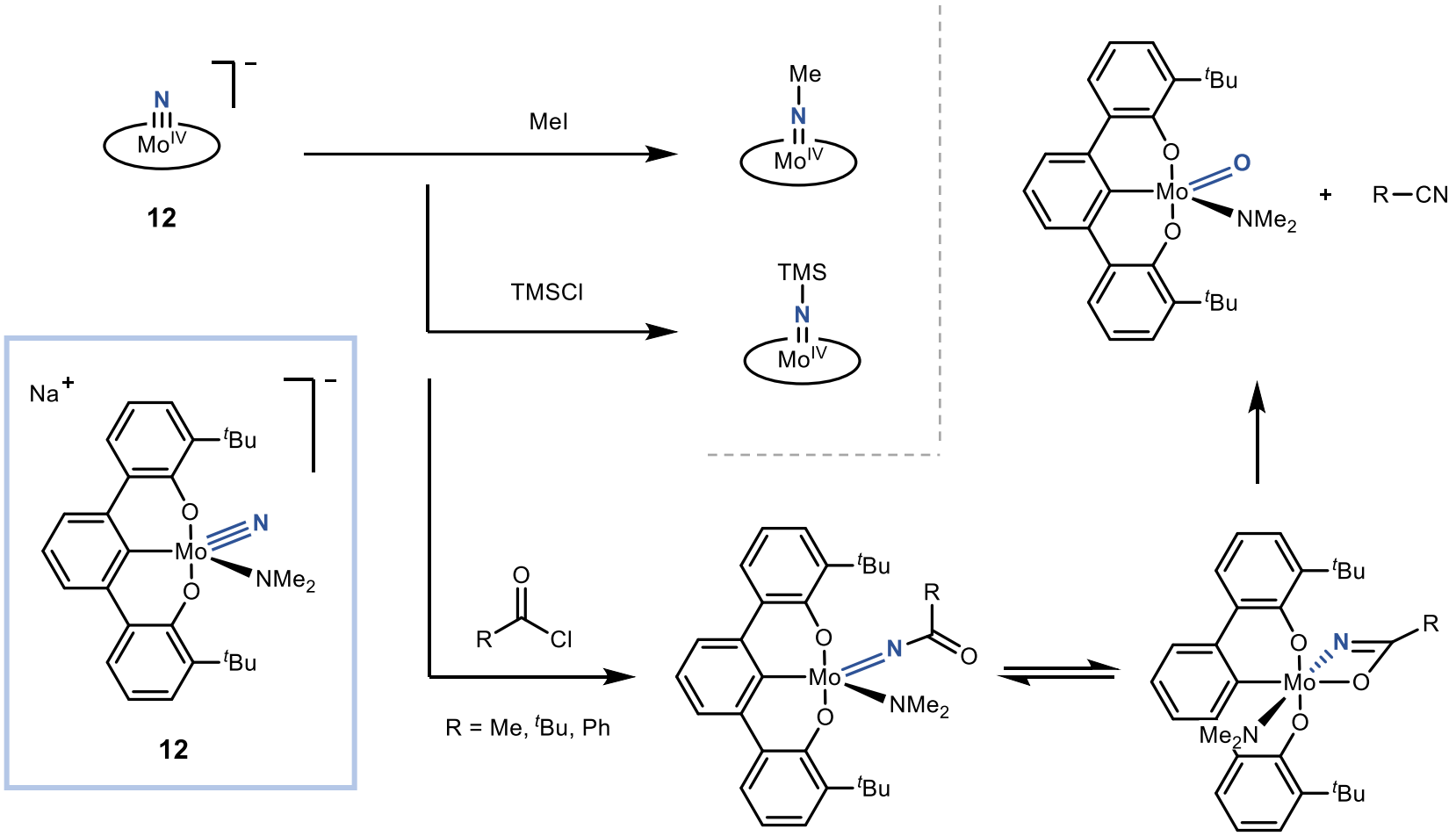


11

Pickett, C. J. *et al. J. Chem. Soc., Chem. Commun.,* **1992**, 1762-1763.

Reactions of nucleophilic nitrides

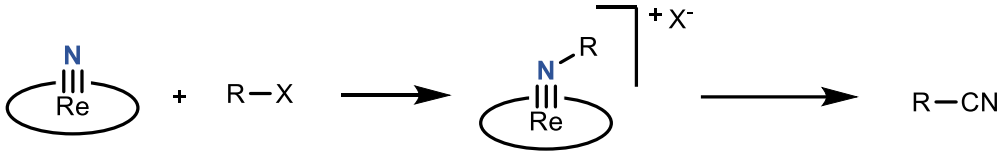
Veige 2008



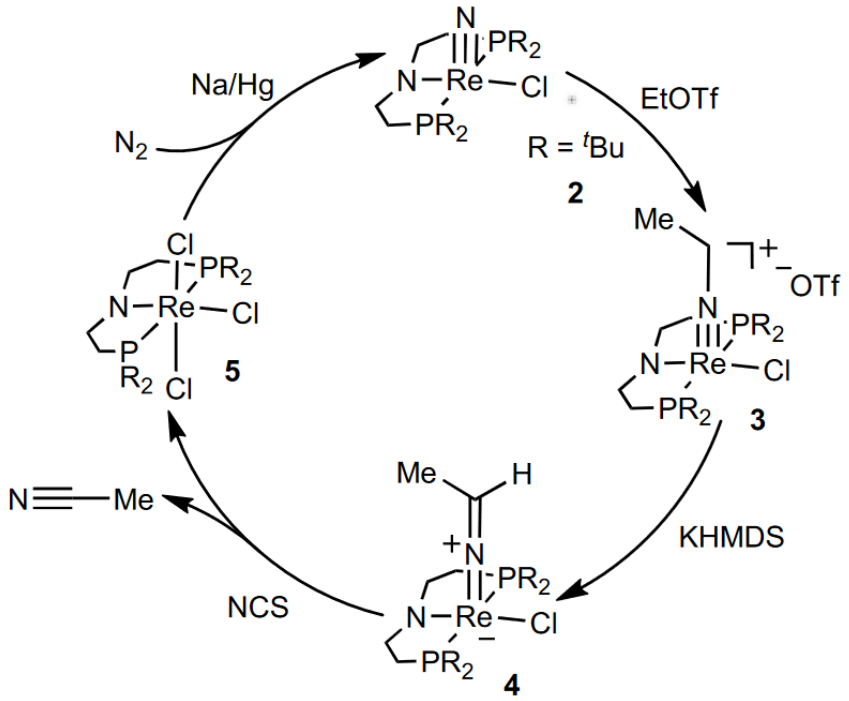
Veige, S. A. *et al. J. Am. Chem. Soc.* **2008**, *130,* 16128–16129.

Nucleophilic nitrides starting from N_2

Schneider 2016



R–X = EtOTf or BnBr



- N_2 activation

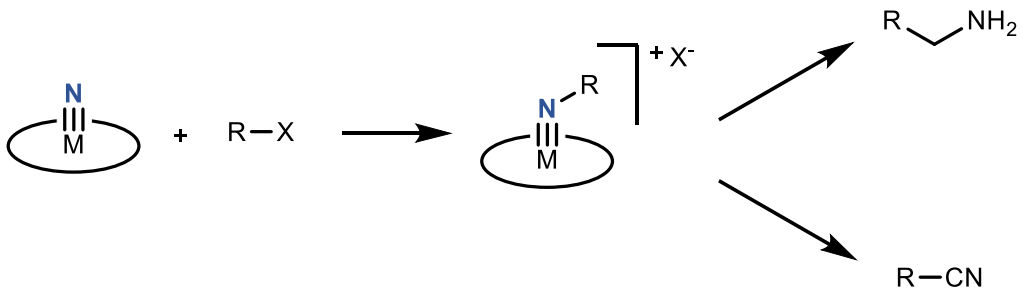
Schneider, S. *et al. Angew. Chem. Int. Ed.* **2016**, *55,* 4786–4789.

Summary

Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Nucleophilic nitrides *Electrophilic nitrides*

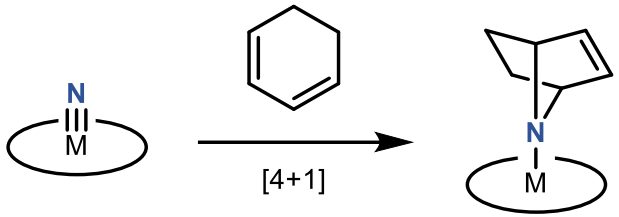
Strong σ-donor as ligand

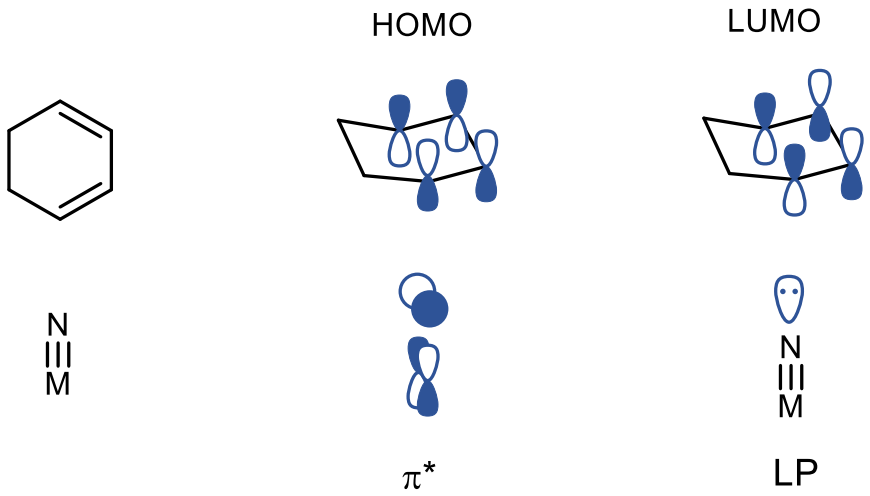


Nitrogen atom transfer reactions

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***

[4+1] Cycloaddition with metal nitride complex

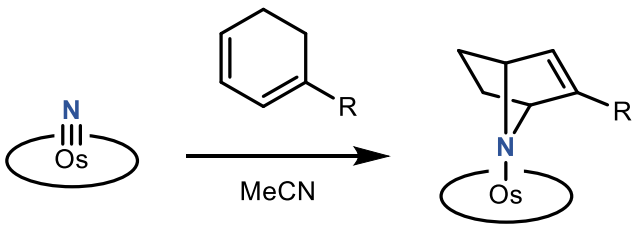


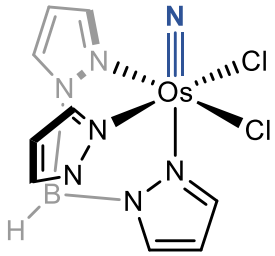


- The orbital energy of M-N complex could be adjusted to a proper level to undergo cycloaddition

Brown, S. N. *et al. J. Am. Chem. Soc.* **2001**, *123,* 7459–7460.

[4+1] Cycloaddition with metal nitride complex

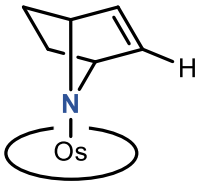




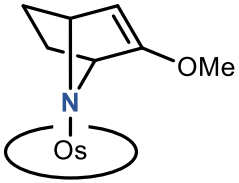
$N{\equiv}OsTpCl_2$

Neutral complex

with $TpOsNCl_2$



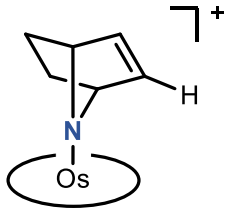
4 d, 80%



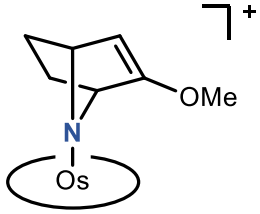
6 h, ~100%

Cationic complex

with cis-[(terpy)-$OsNCl_2$]PF_6



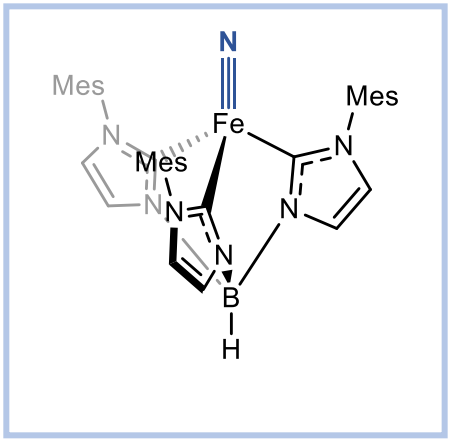
9 h, 25%



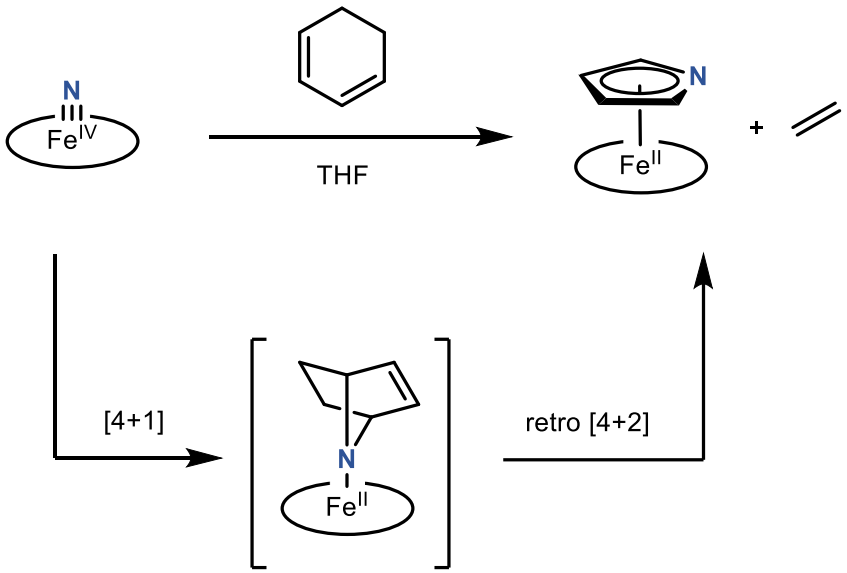
15 min, 93%

Brown, S. N. *et al. J. Am. Chem. Soc.* **2001**, *123,* 7459–7460.

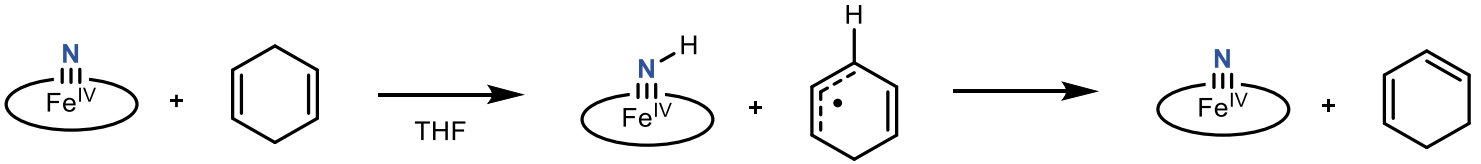
[4+1] Cycloaddition with metal nitride complex



■ Coordinatively and electronically unsaturated

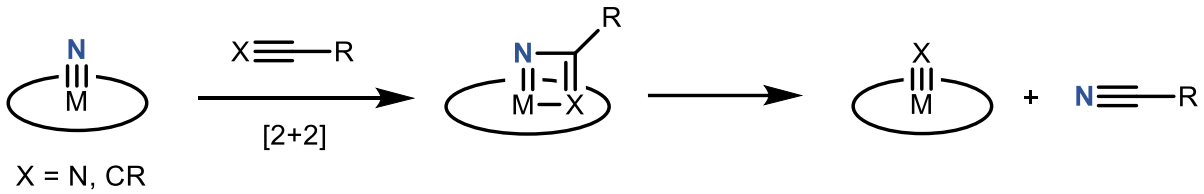


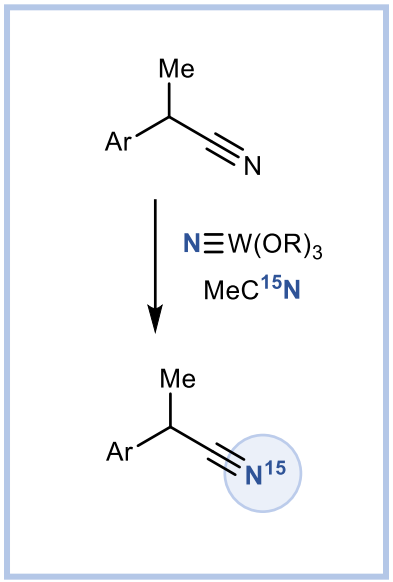
Isomerization



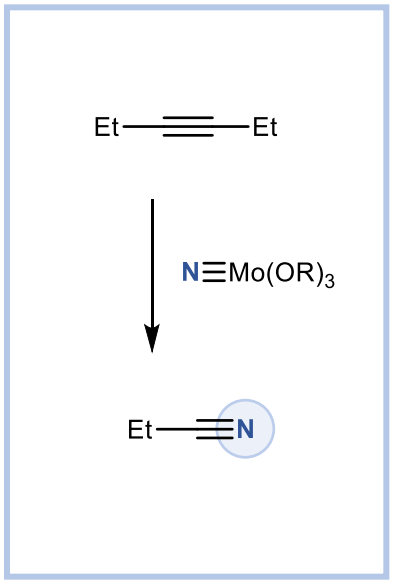
Smith, J. M. *et al. Inorg. Chem.* **2014**, *53,* 8425–8430.

[2+2] Cycloaddition with metal nitride complex

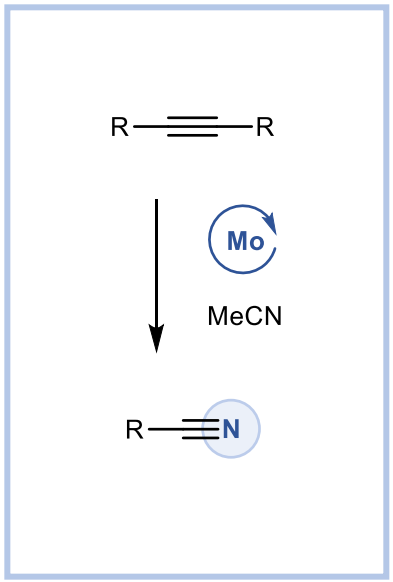




Labeling



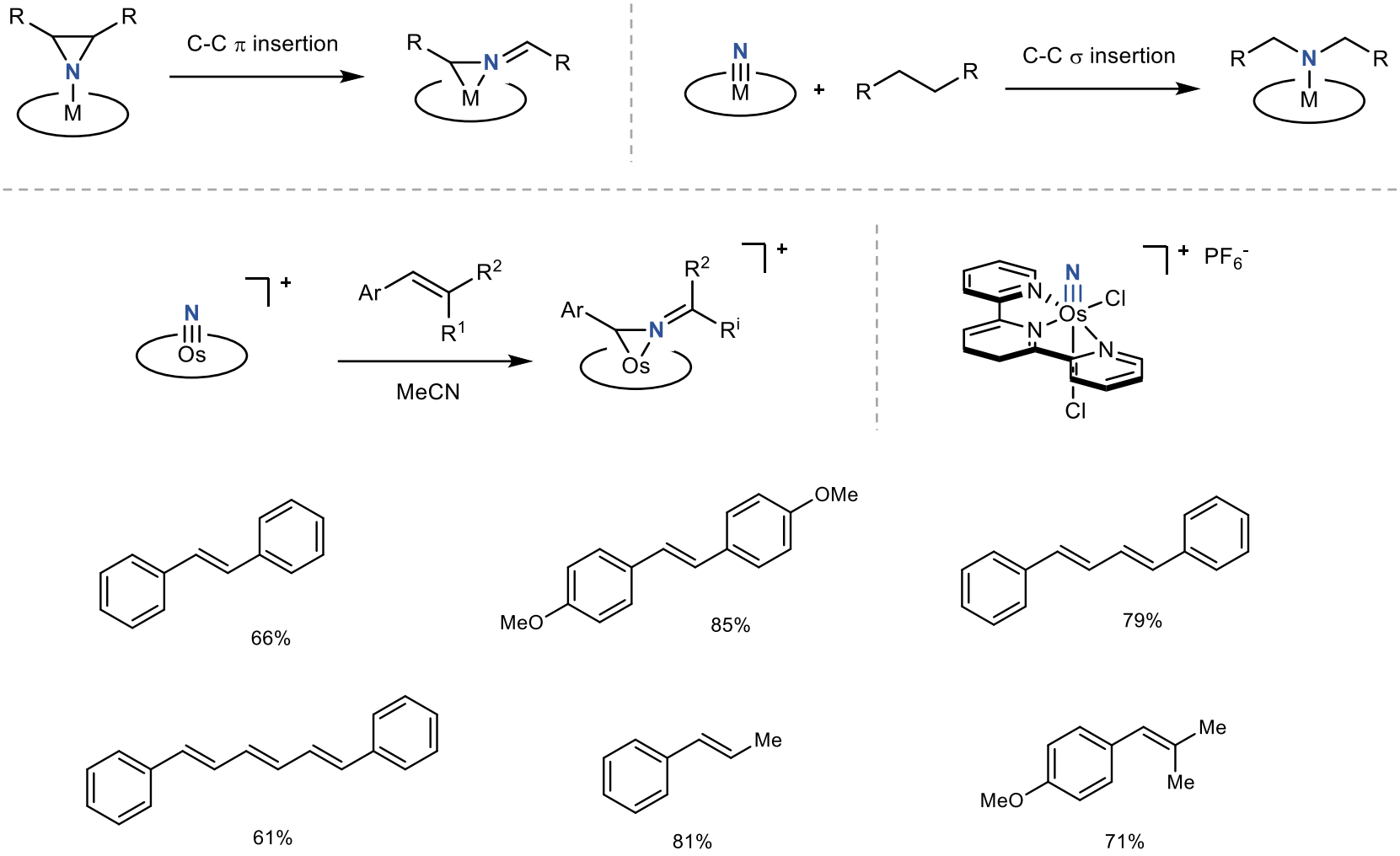
Nitrile-alkyne metathesis



Catalytic nitrile-alkyne metathesis

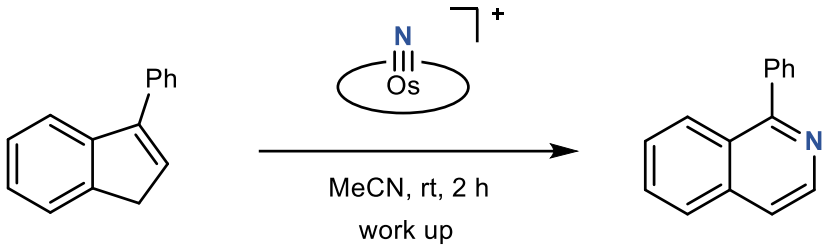
Johnson, M. J. A. *et al. J. Am. Chem. Soc.* **2006**, *128,* 9614–9615.
Johnson, M. J. A. *et al. J. Am. Chem. Soc.* **2007**, *129*, 3800–3801.
Quinlan, K. B. *et al. Chem. Comm.* **2003**, *1*, 126–127.

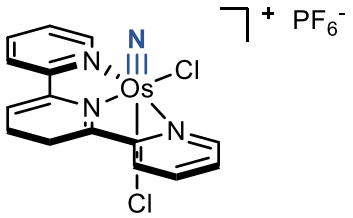
Rearrangement: Oxidative cleavage by metal nitrides

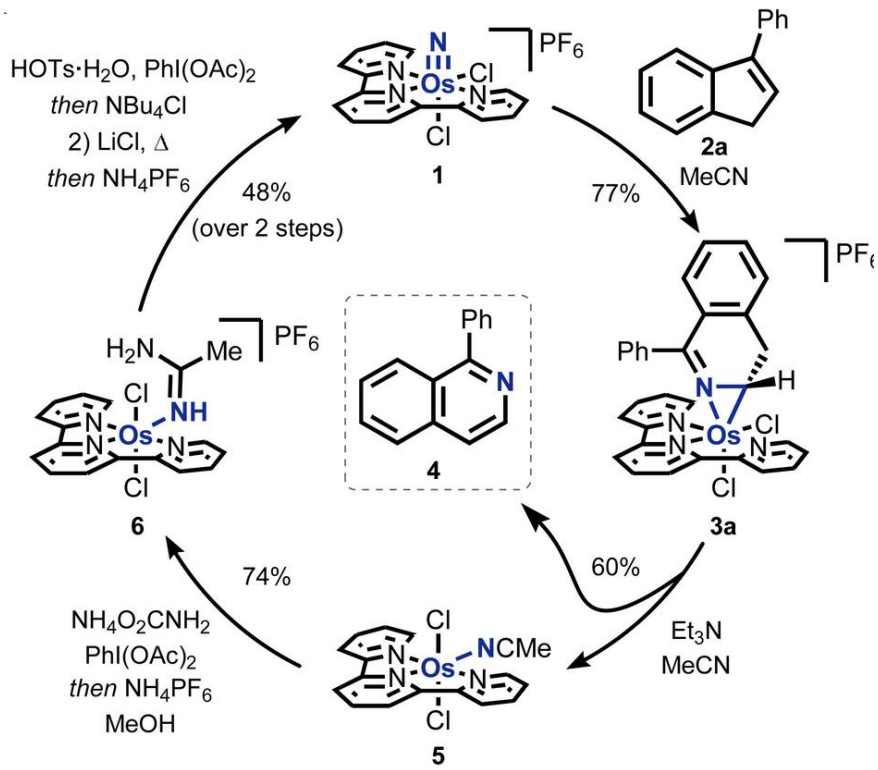


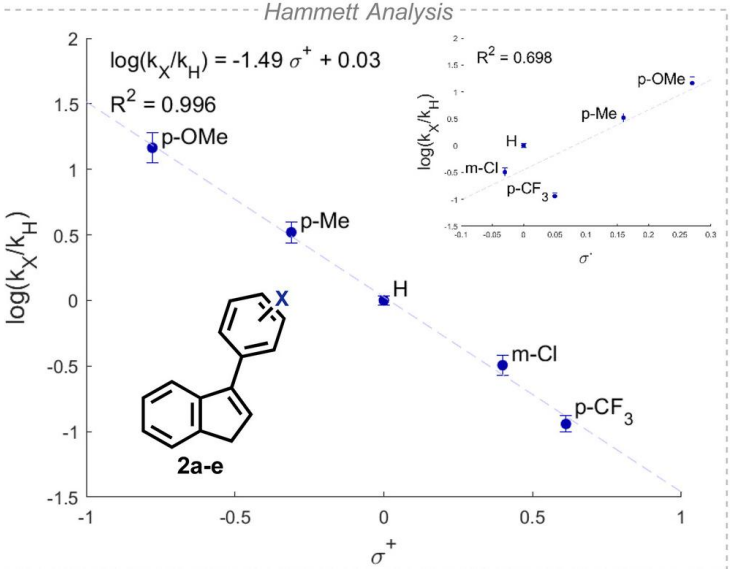
Brown, S. N. *J. Am. Chem. Soc.* **1999**, *121*, 9752–9753.

Molecular editing by oxidative cleavage by metal nitrides





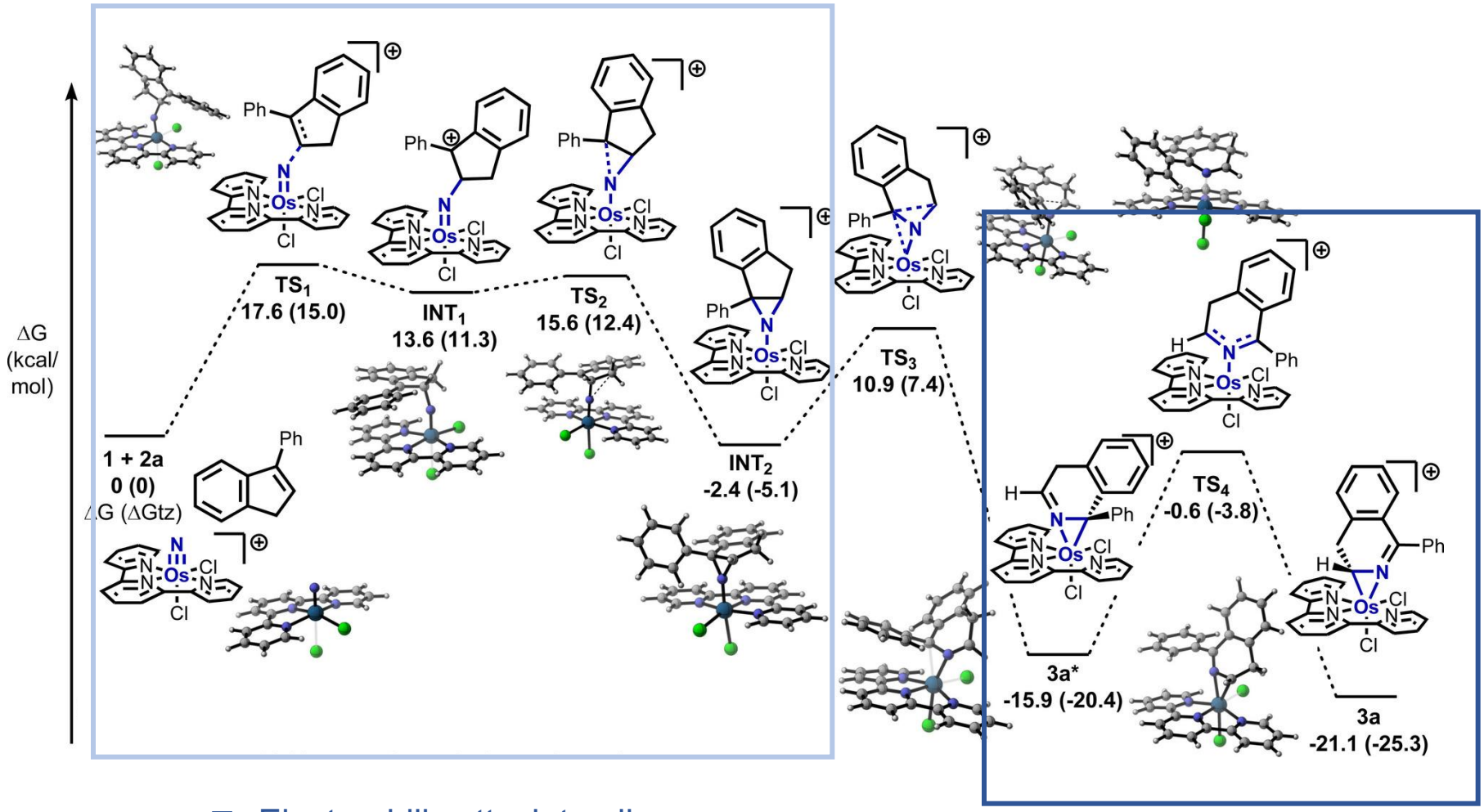




- Electrophilic attack to alkene

Levin, M. D. *et al. Angew. Chem. Int. Ed.* **2022**, *61,* e202213041.

Molecular editing by oxidative cleavage by metal nitrides

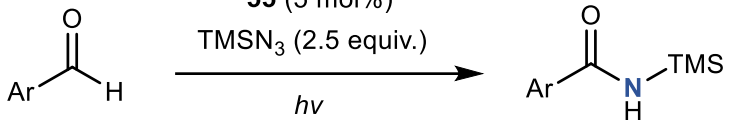


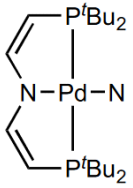
- Electrophilic attack to alkene
- Site selectivity deciding step

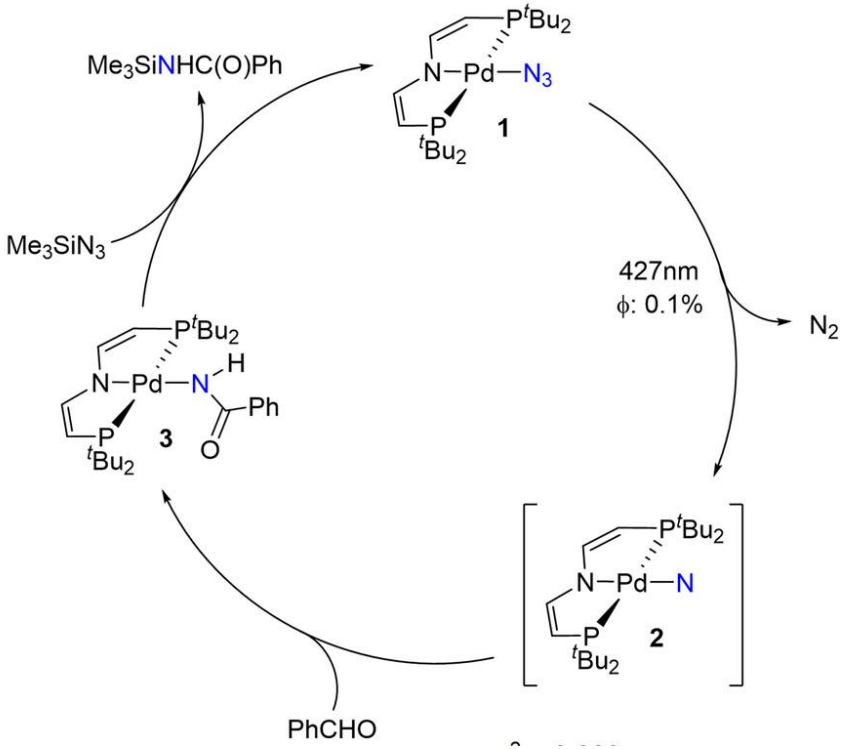
Levin, M. D. *et al. Angew. Chem. Int. Ed.* **2022**, *61*, e202213041.

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***

Catalytic C-H bond insertion



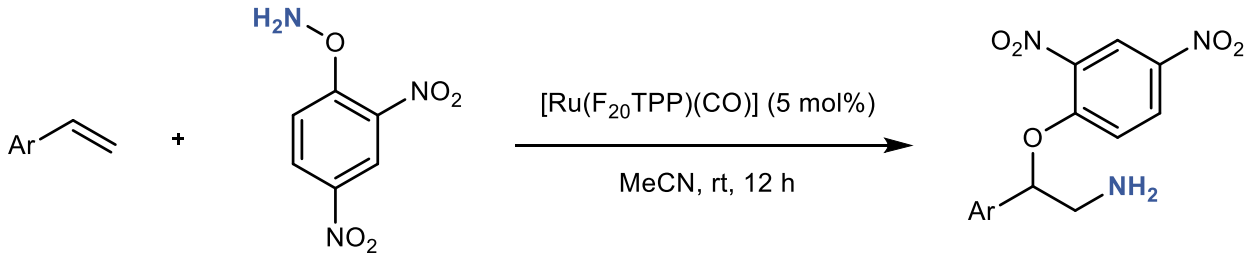


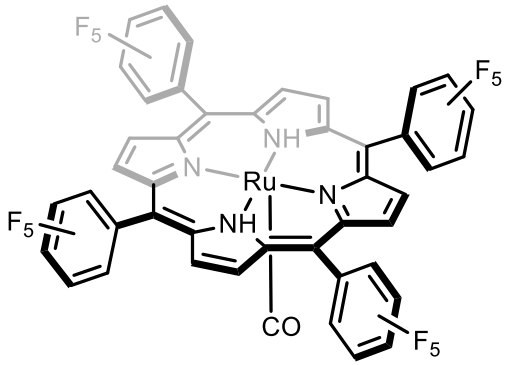


Ar	Yield (%)
Ph	89
2-MePh	91
3-MePh	76
4-MePh	76
4-FPh	82
4-BpinPh	56
4-CF_3Ph	59
4-NHAcPh	63
2-Py	91

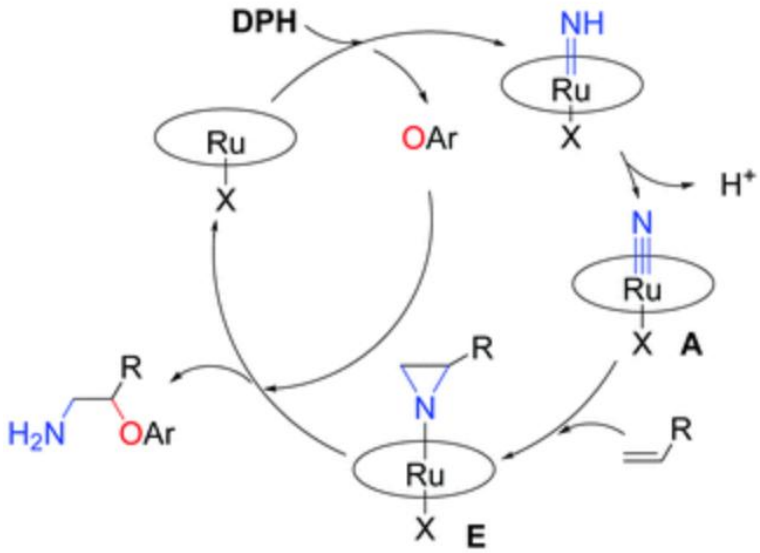
Schmidt-Räntsch, T. *et al. et al. Angew. Chem. Int. Ed.* **2022**, *61,* e202115626.

Catalytic alkene addition





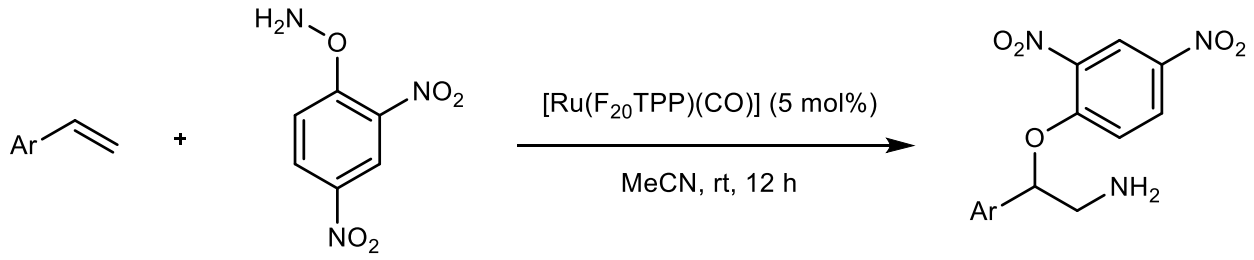
[Ru(F_{20}TPP)(CO)]

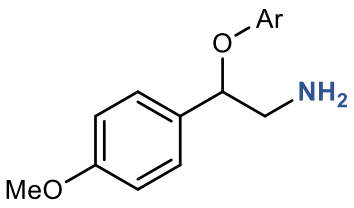


X = MeCN or vacant, OAr = 2,4-dinitrophenolate

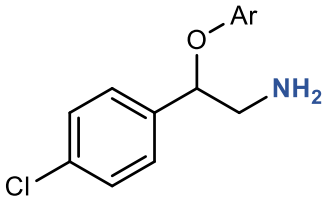
Che, C. T. *et al. Chem. Comm.* **2020**, *56,* 137–140.

Catalytic alkene addition

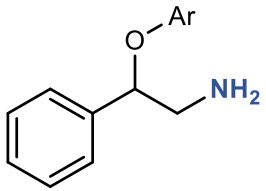




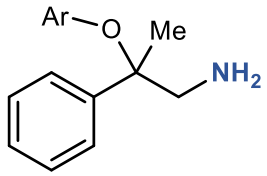
80%



26%



74%



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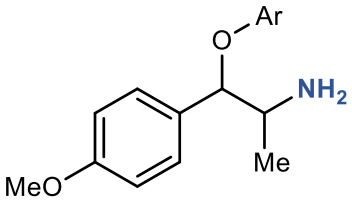
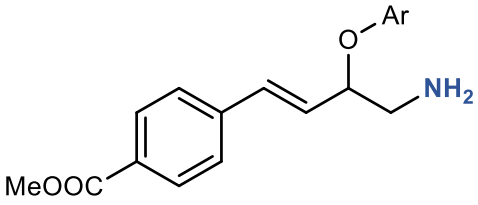


59%



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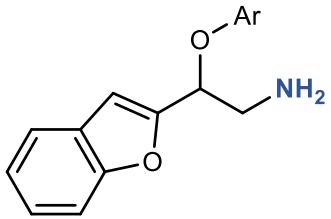
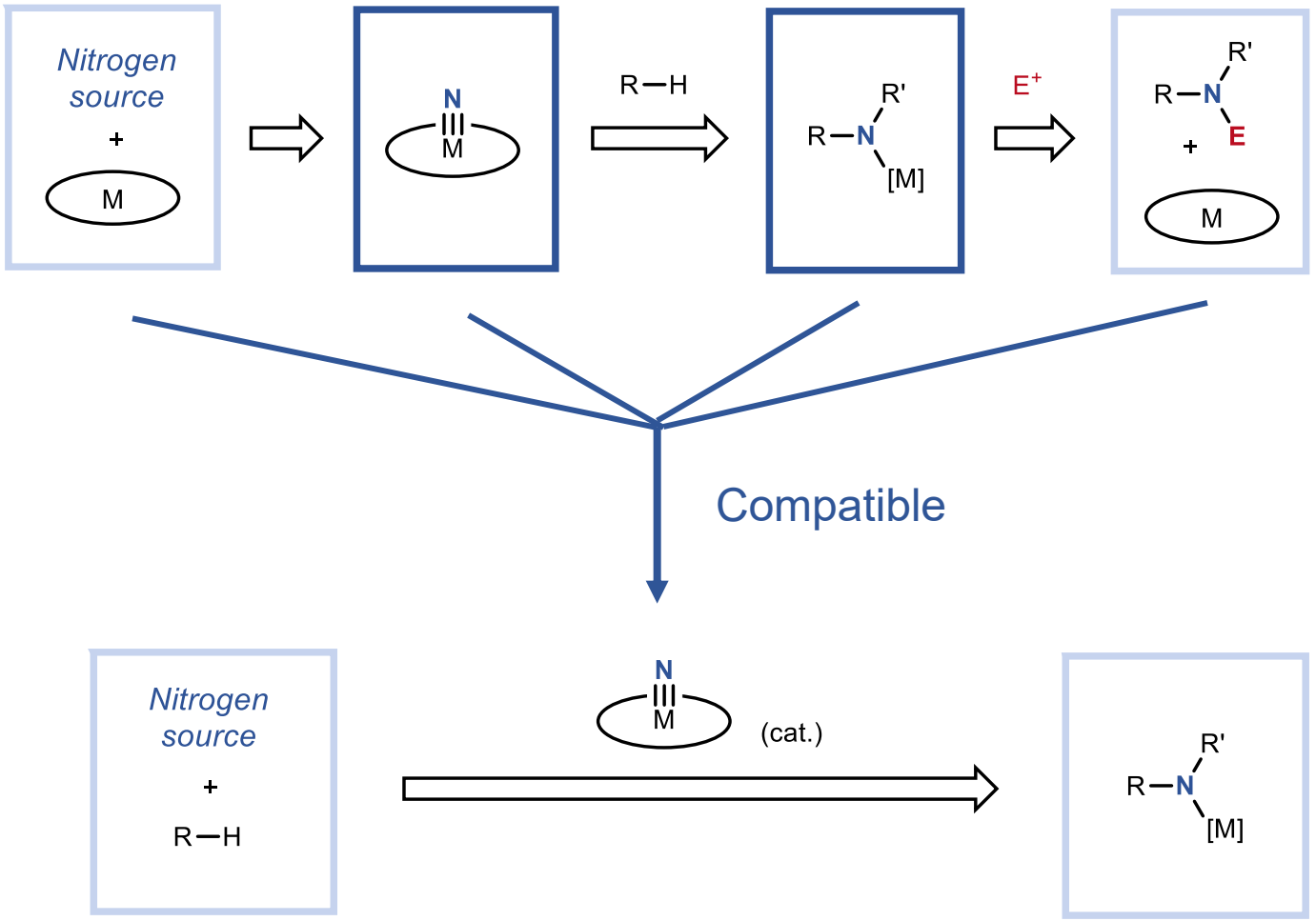


73%

Che, C. T. *et al. Chem. Comm.* **2020**, *56,* 137–140.

Summary

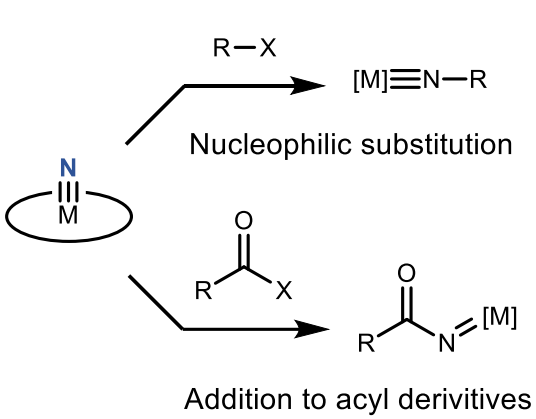


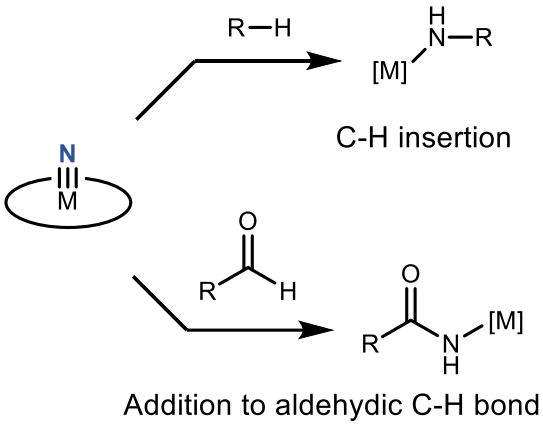
Che, C. T. *et al. Chem. Comm.* **2020**, *56,* 137–140.

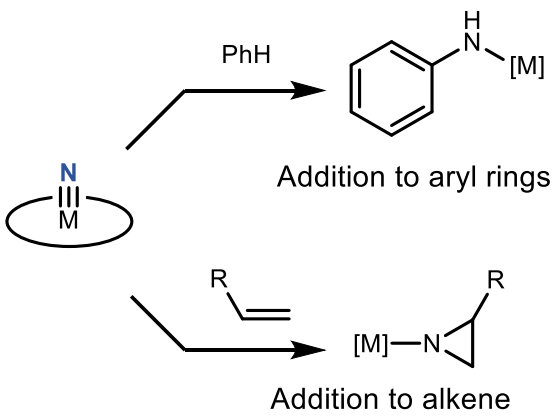
Nitrogen atom transfer reactions

- ***Stoichiometric nitrogen atom transfer***
  - Electrophilic nitrides
  - Nucleophilic nitrides
  - Cycloaddition and rearrangement
- ***Catalytic nitrogen atom transfer***
- ***Summary and perspective***

Summary







- Weaken the M-N bond
- Proper HOMO or LUMO
- Catalytic NAT

Reviews and books:

Powers, D. C. *et al. Nat. Rev. Chem.* **2023**, *7*, 424–438.

Carreira, E, M. *et al. J. Acc. Chem. Res.* **1997**, *30,* 364-372.

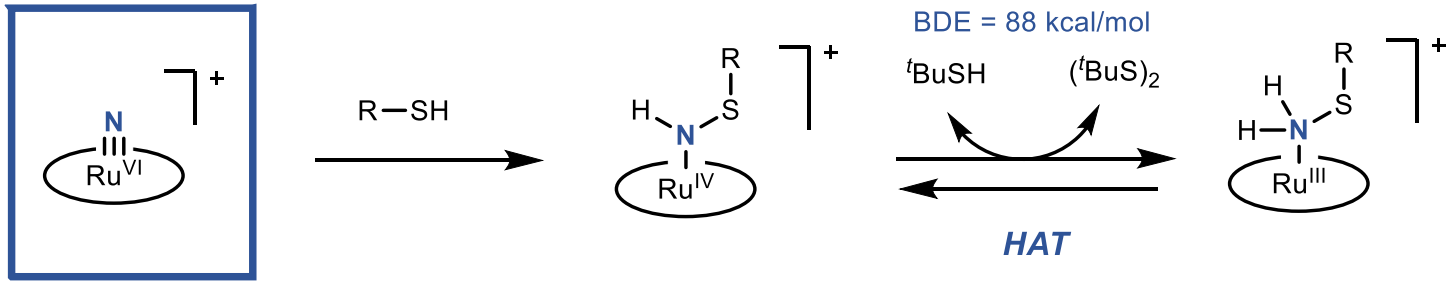
Lau. T. *et al. Acc. Chem. Res.* **2014**, *47,* 427–439.

Alexander D. R. *et al. Chem. Rev*. **2017**, *117,* 9140−9162.

Reactive Transition Metal Nitride Complexes. https://doi.org/10.1002/9781118792797.ch06

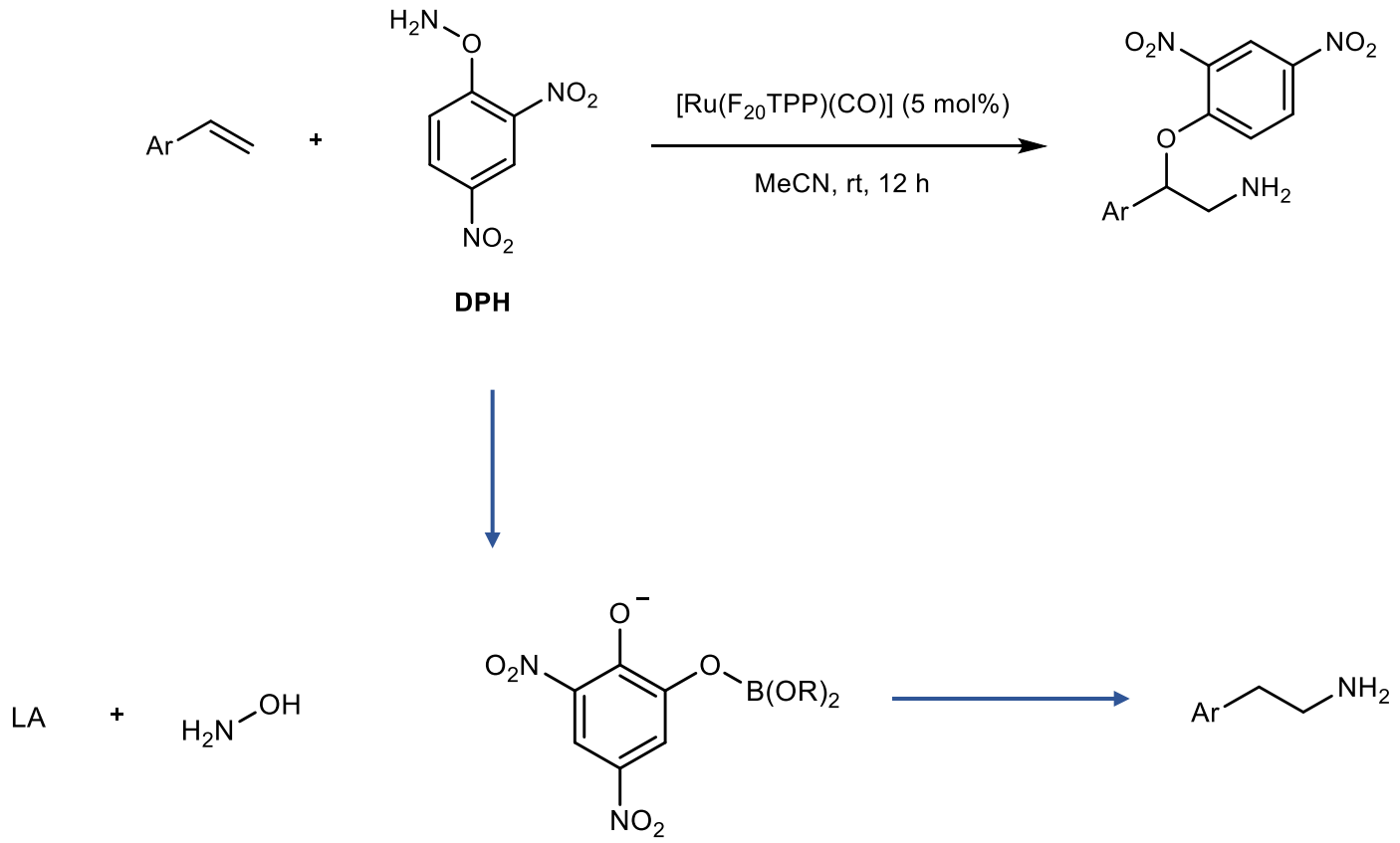
Perspective

- HAT reagent



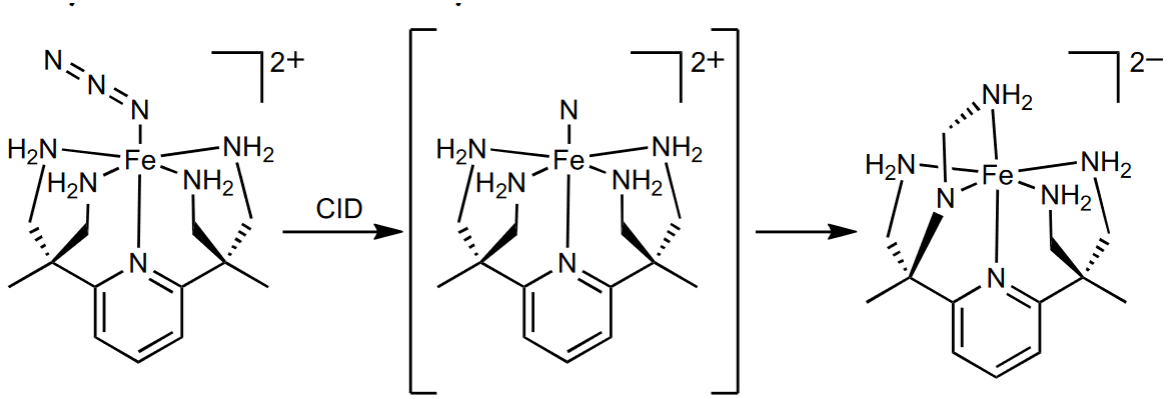
Perspective

- Catalytic NAT

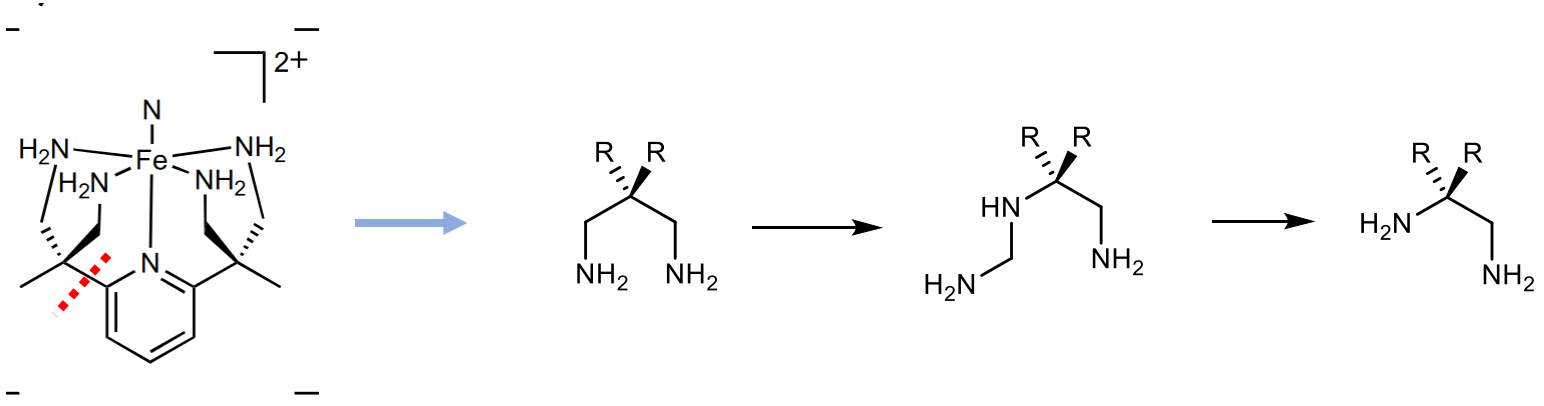


Perspective

- Rearrangement and molecular editing



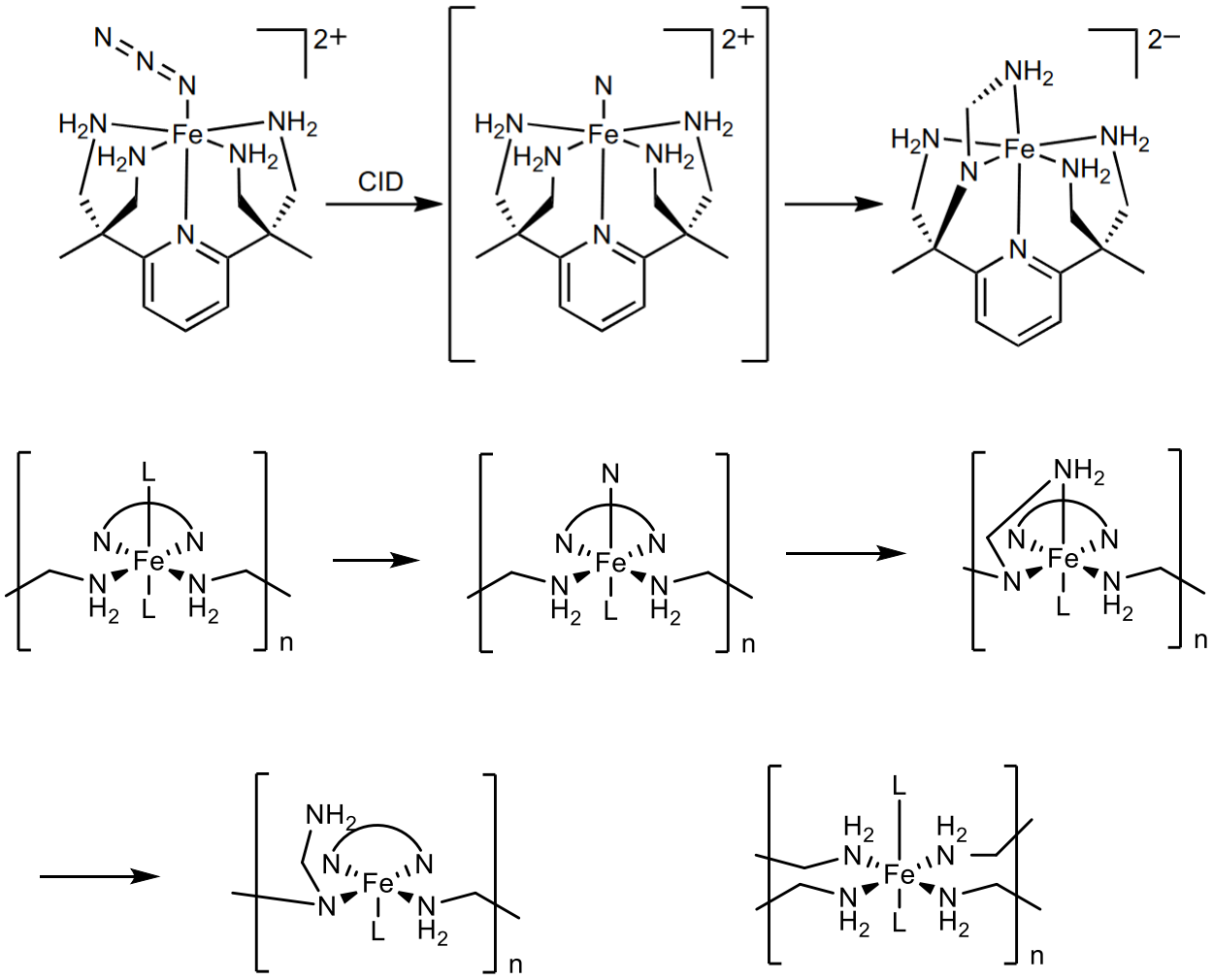
J. Am. Chem. Soc. 130, 4285–4294 (2008).



Perspective

- Macromolecular transformation

J. Am. Chem. Soc. 130, 4285–4294 (2008).



Perspective

- Macromolecular recycle