Light-Driven Dinitrogen Activation with Transition Metal Complexes

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Introduction

'N' Element Presents in:

- Organic: R-NH_2, R-NO_2…
- Inorganic: NH_3, HNO_3…
- Life: Protein, Nucleic Acid…

N_2

Abundant in Air

Difficulties in N_2 Fiaxtion:

- Nonpolar Molecular
- Bond Dissociation Energy: 941 kJ/mol
- Ionization Potential: 15.6 eV
- HOMO-LUMO Gap: 10.82 eV

Most Organisms Lack the Ability to Metabolize N_2

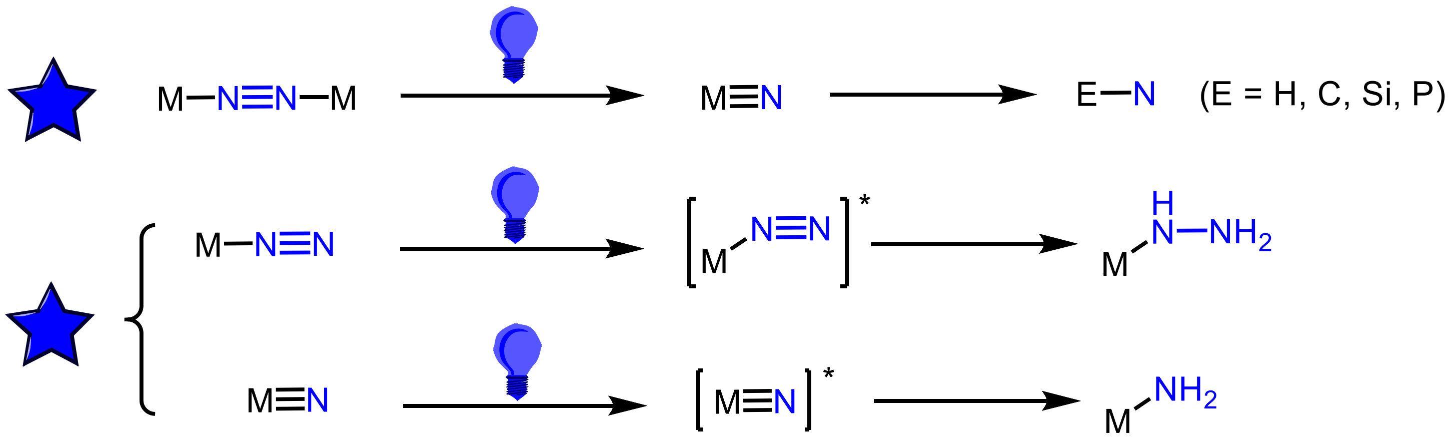
Haber-Bosch Process

The greatest invention of the 20th century

$$N_2 + 3\ H_2 \xrightarrow[\text{200-500 atm, 500-600 }^{o}\text{C}]{\text{cat. }Fe_3O_4/K_2O/Al_2O_3} 2\ NH_3$$

Stoichiometric

Catalytic

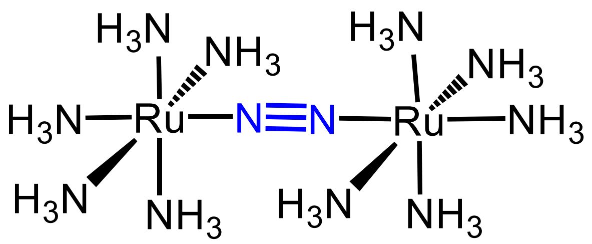


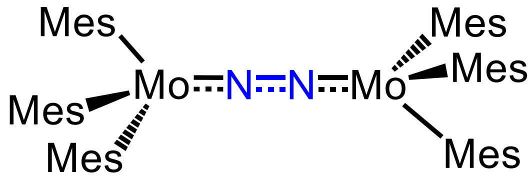
Light-driven N_2 activation avoided harsh conditions

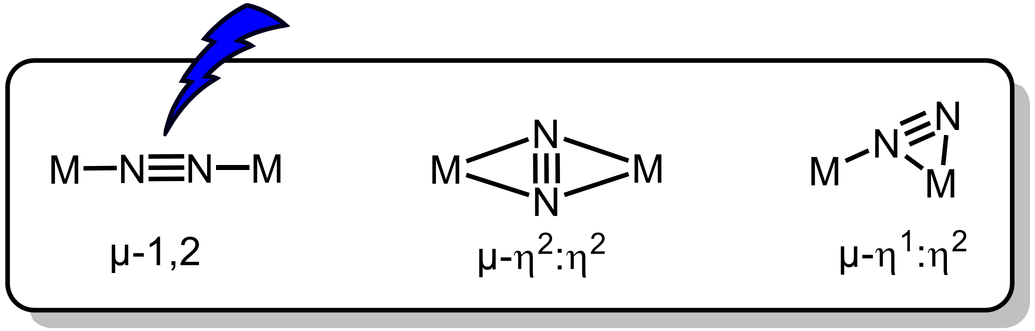
(1) von Laue, M., et al. *Naturwissenschaften*, **1934**, *22*, 97-108; (2) Boudart, M., et al. *Top. Catal.* **1994**, *1*, 405-413; (3) Xi, Z., et al. *Chin. J. Chem.* **2023**, *41*, 2400-2407.

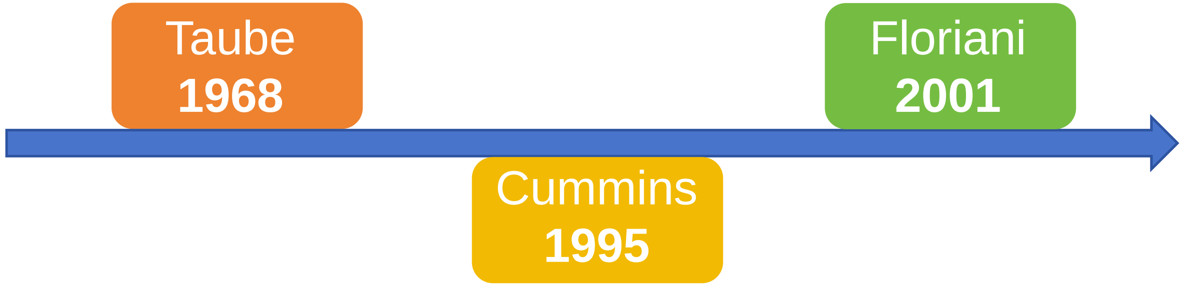
Introduction

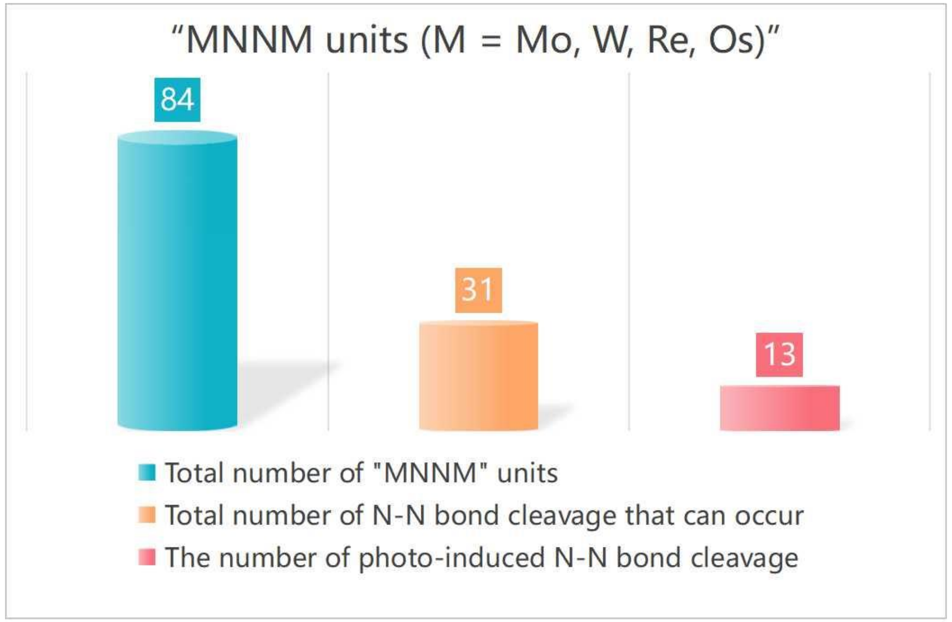
The first N-N bond cleavage under photochemical conditions

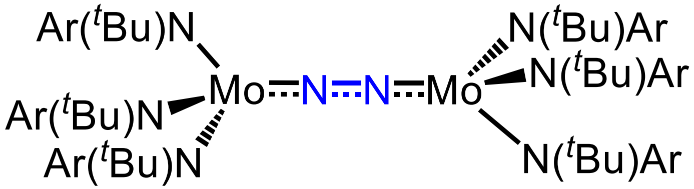








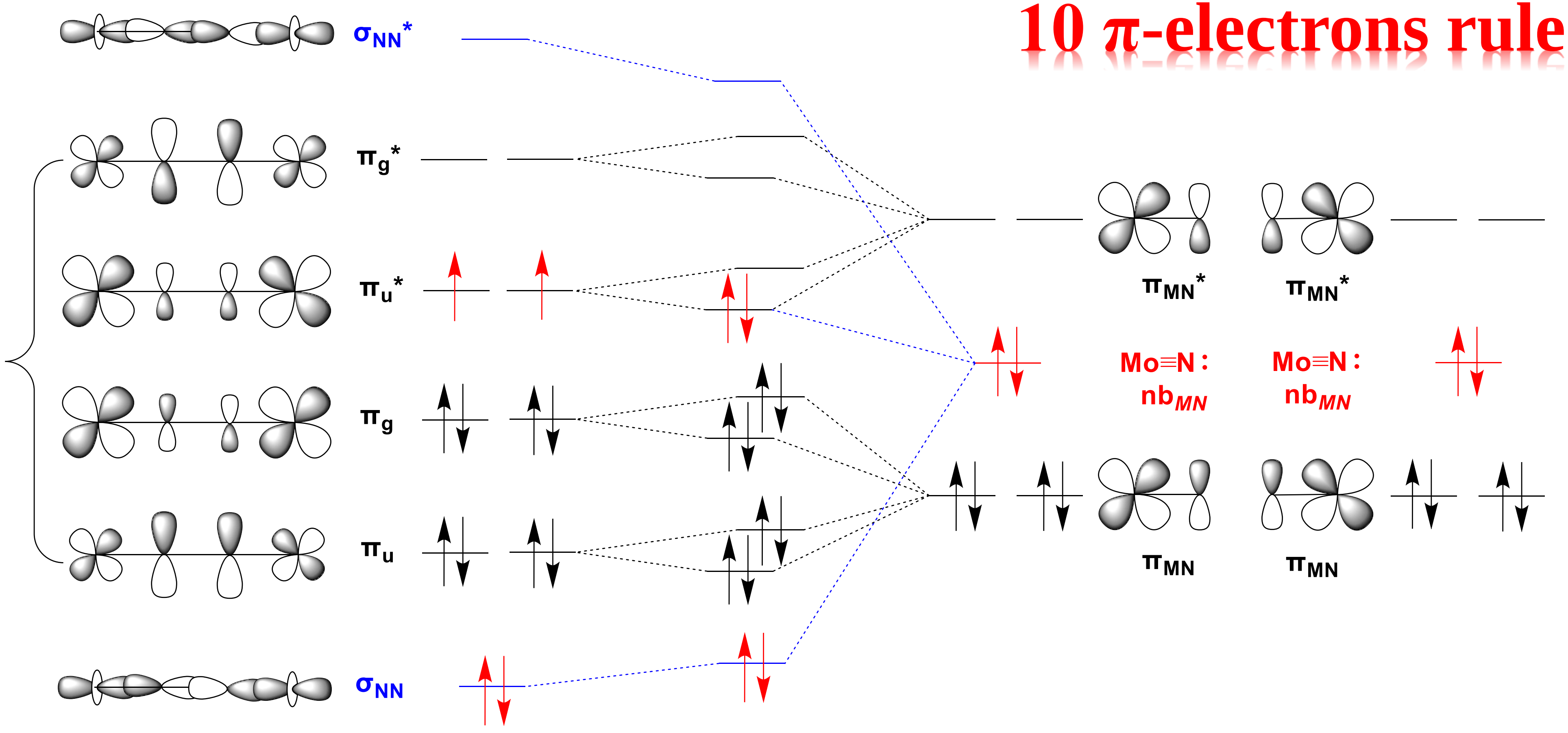


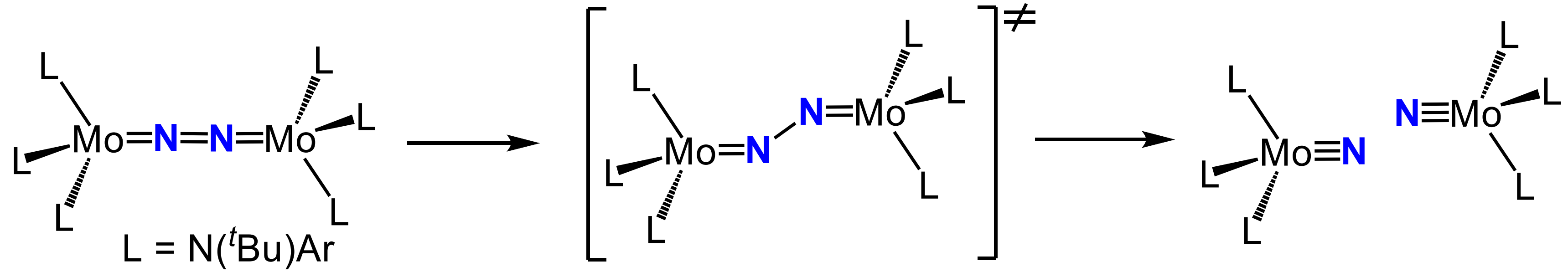


The first N-N bond cleavage under thermal conditions

(1) Taube, H., et al. *Science* **1968**, *159*, 320−322; (2) Cummins, C. C., et al. *Science* **1995**, *268*, 861−863; (3) Floriani, C., et al. *Angew. Chem., Int. Ed.* **2001**, *40*, 3907−3909.

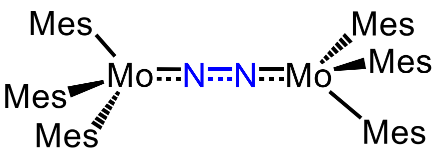
10 π-electrons rule



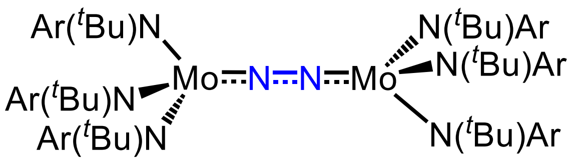


(1) Cummins, C. C., et al. *J. Am. Chem. Soc.* **1996**, *118*, 8623–8638; (2) Morokuma, K., et al. *J. Am. Chem. Soc.* **1995**, *117*, 12366–12367.

Photo-induced Stoichiometric Dinitrogen Activation

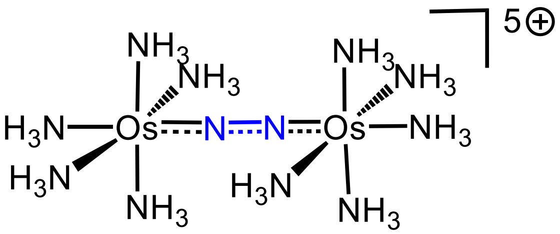


Floriani 2001

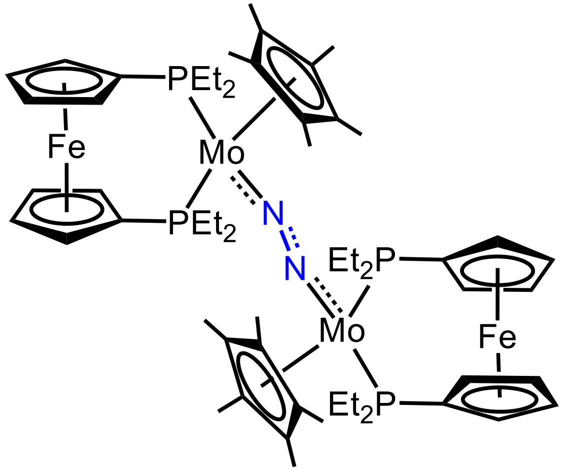


Ar = C_6H_3-3,5-Me_2

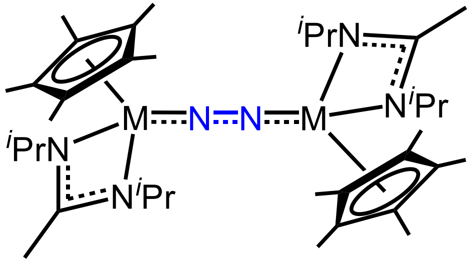
Cummins 2008



Vogler 2010

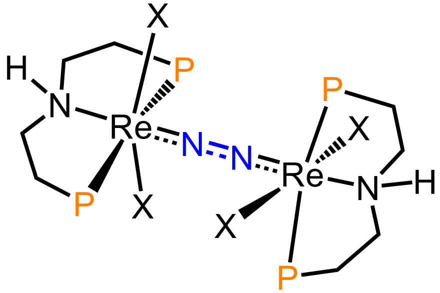


Nishibayashi 2014



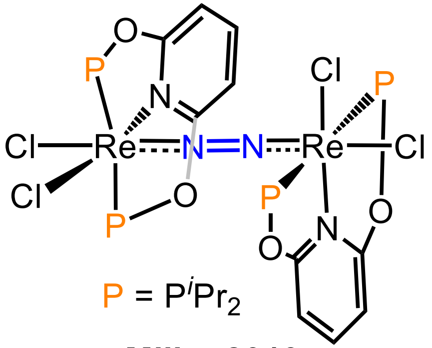
M = Mo, W

Sita 2015



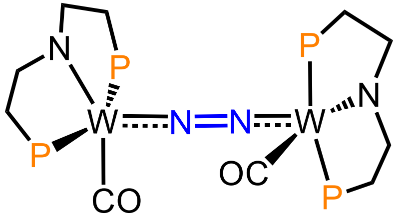
P = P^iPr_2, X =Cl, Br

Schneider 2018 and 2022



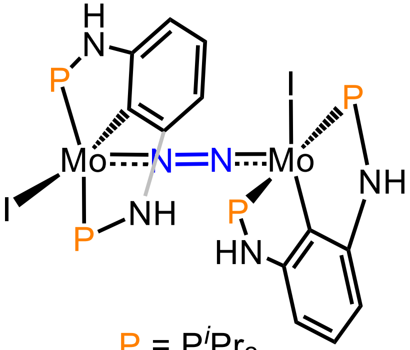
P = P^iPr_2

Miller 2019



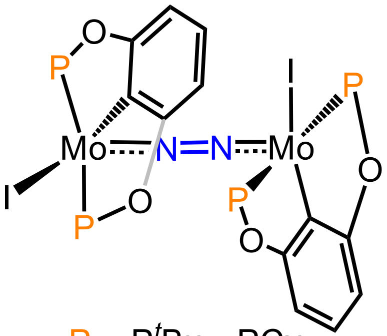
P = P^tBu_2

Schneider 2021



P = P^iPr_2

Liao 2022



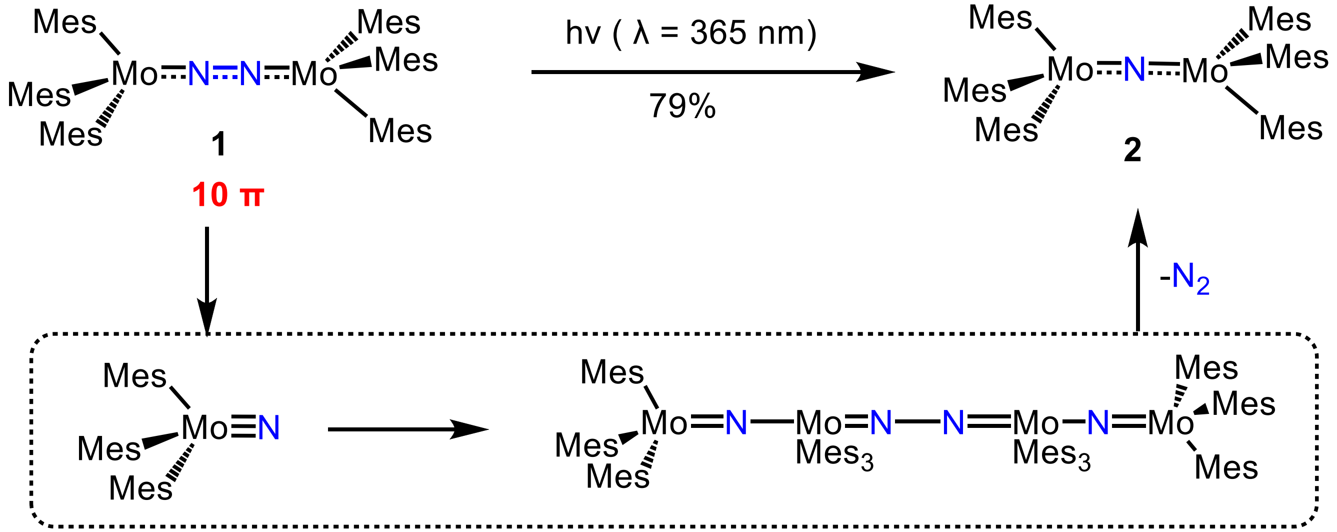
P = P^tBu_2, PCy_2

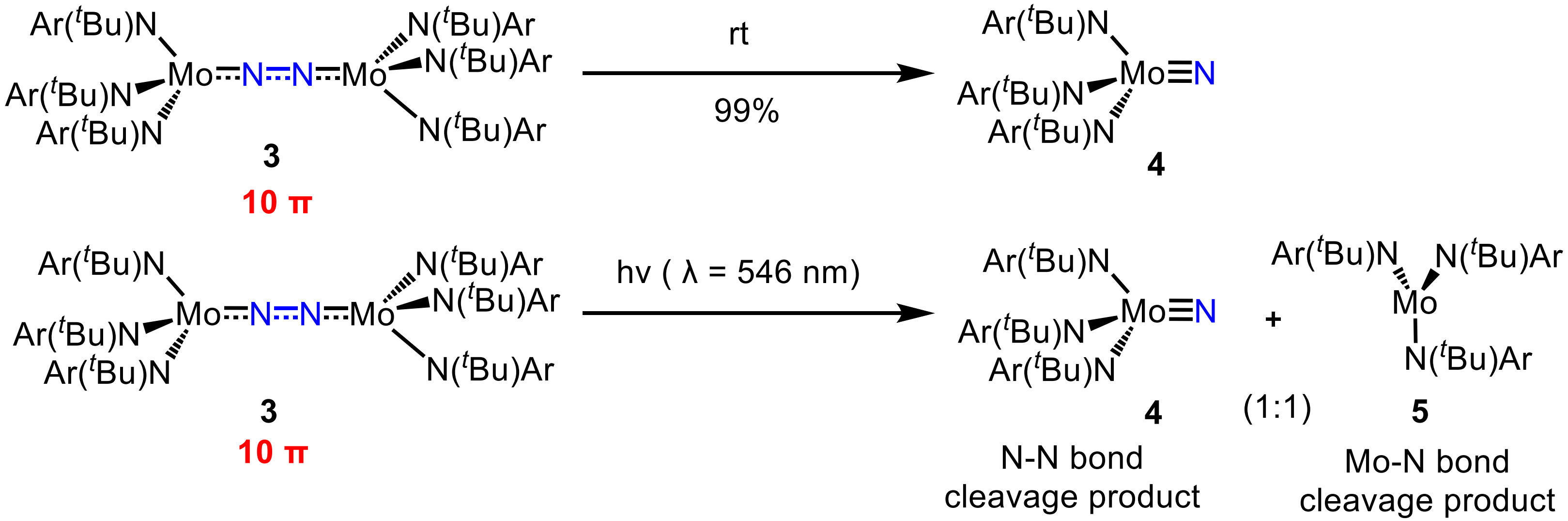
Liao 2025

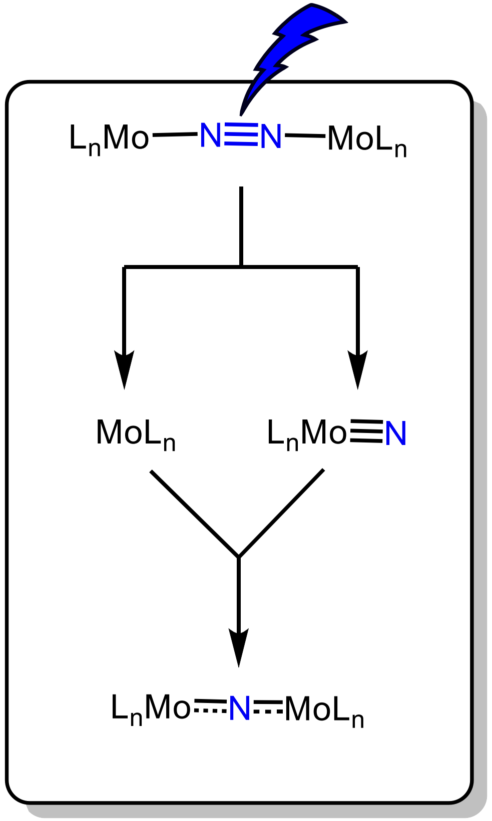
V	Cr	Mn	Fe	Co
Nb	Mo	Tc	Ru	Rh
Ta	W	Re	Os	Ir

Photo-induced Stoichiometric Dinitrogen Activation

Floriani & Cummins



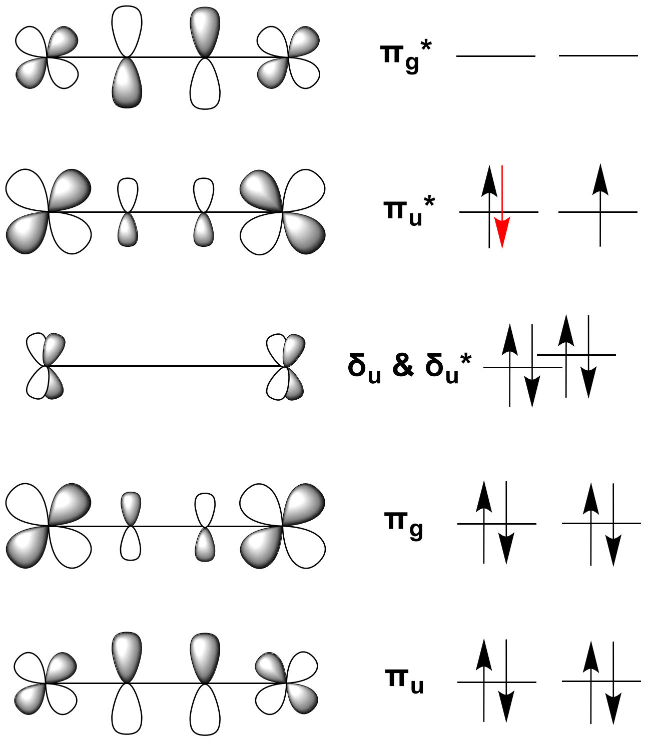


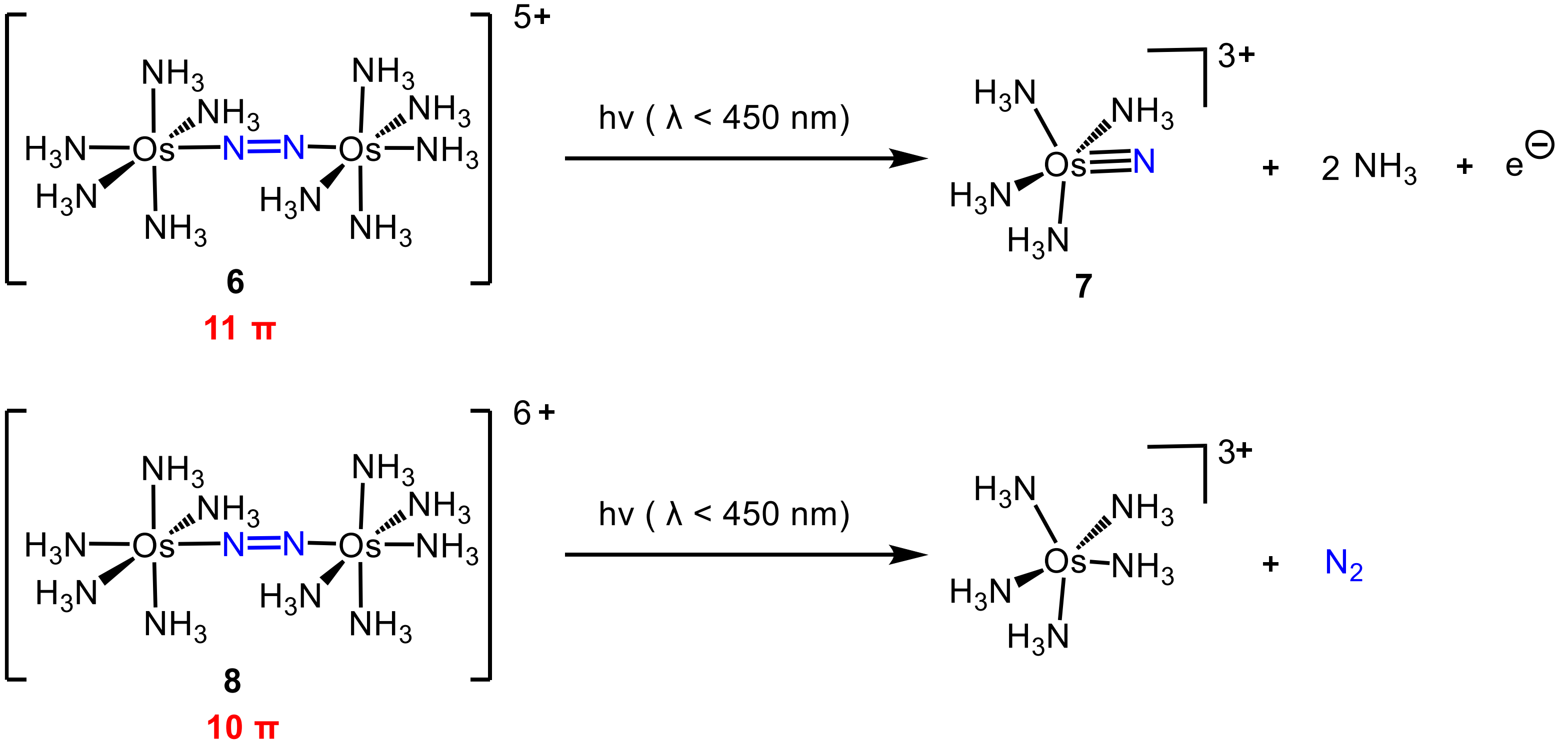


(1) Floriani, C., et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 3907-3909; (2) Cummins, C. C., et al. *J. Am. Chem. Soc.* **2008**, *130*, 9394-9405.

Photo-induced Stoichiometric Dinitrogen Activation

Vogler

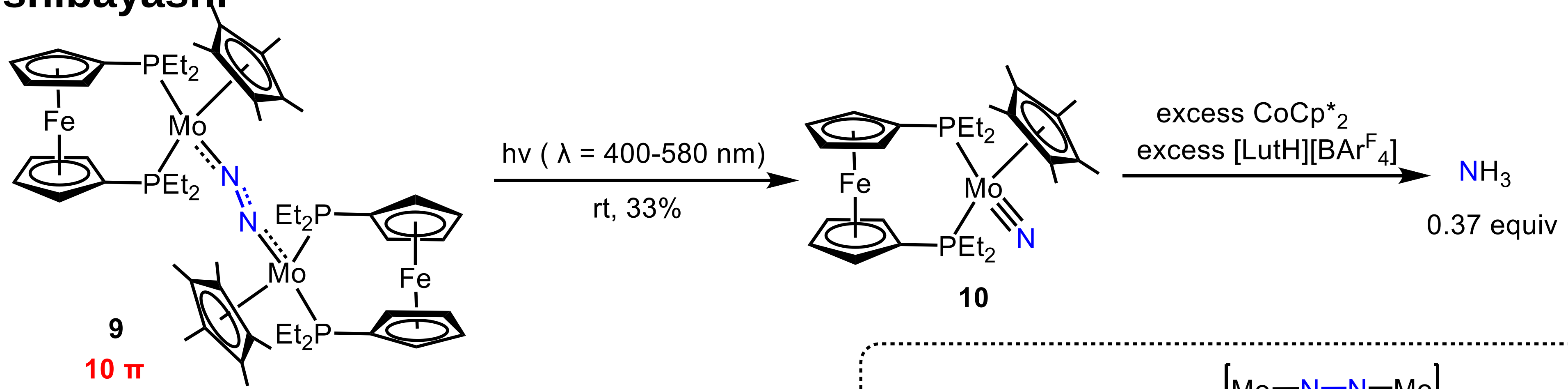


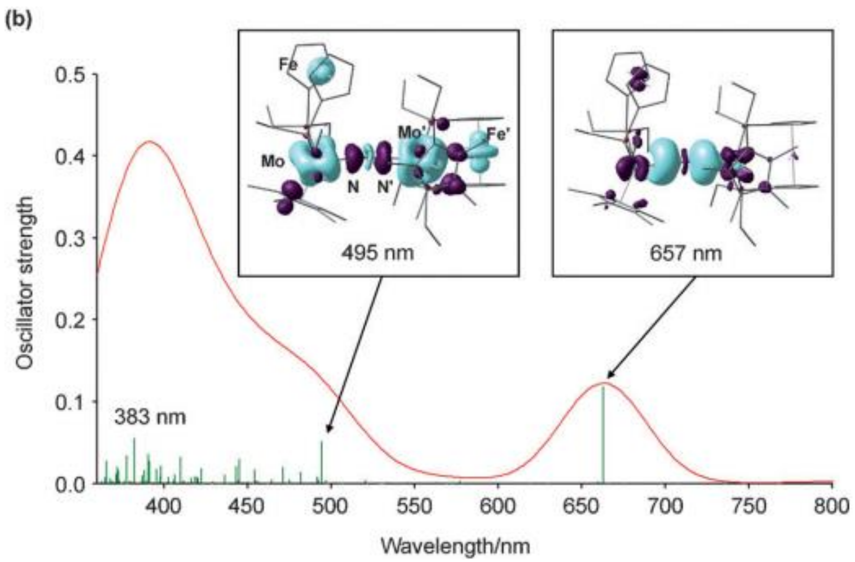


(1) Vogler, A., et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 1591–1593.

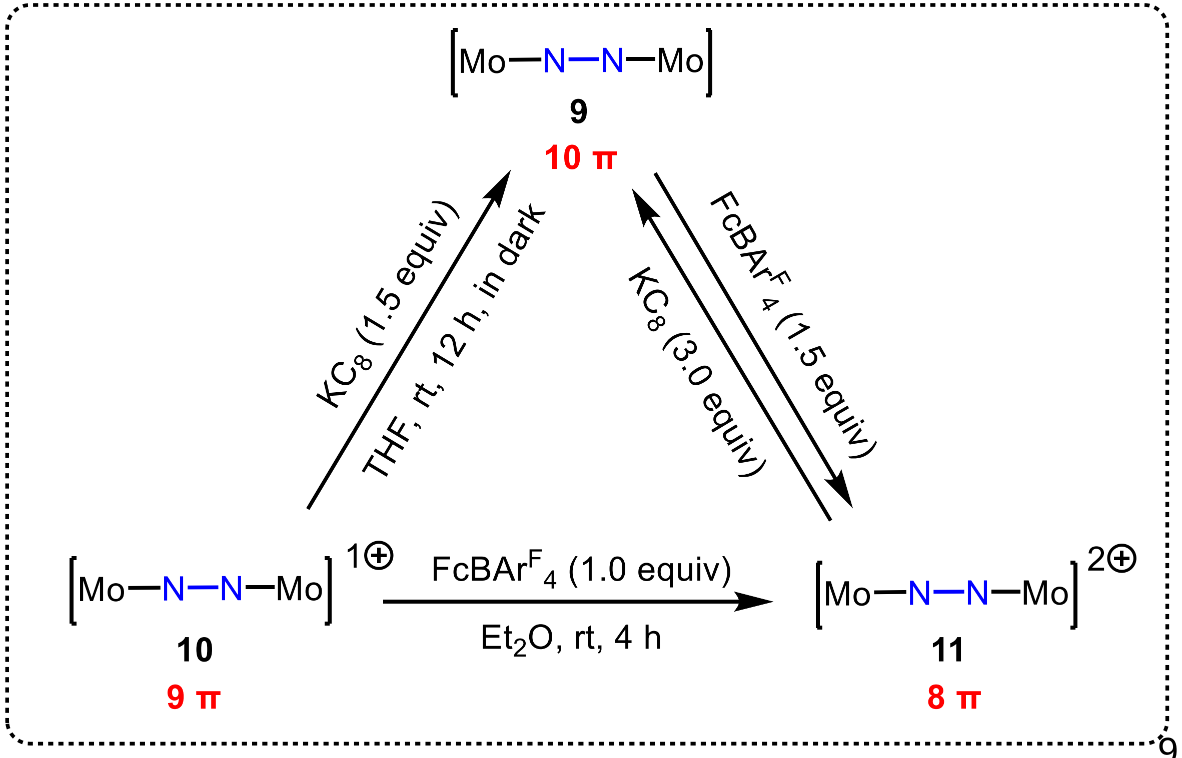
Photo-induced Stoichiometric Dinitrogen Activation

Nishibayashi





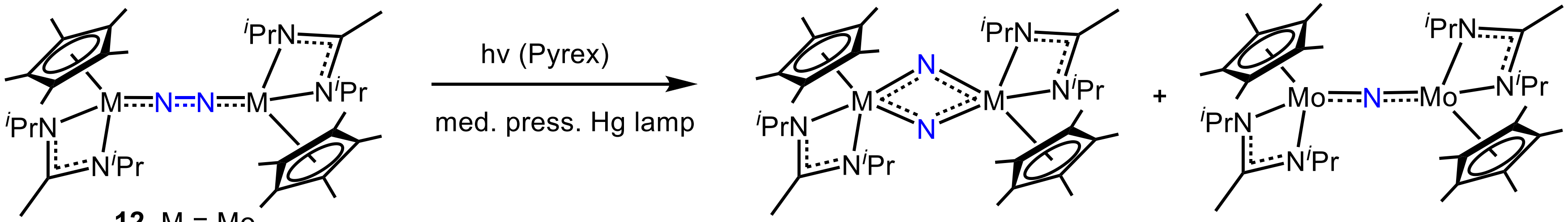
electron density difference maps (EDDMs)



Nishibayashi, Y., et al. *Angew. Chem. Int. Ed.* **2014**, *53*, 11488 –11492.

Photo-induced Stoichiometric Dinitrogen Activation

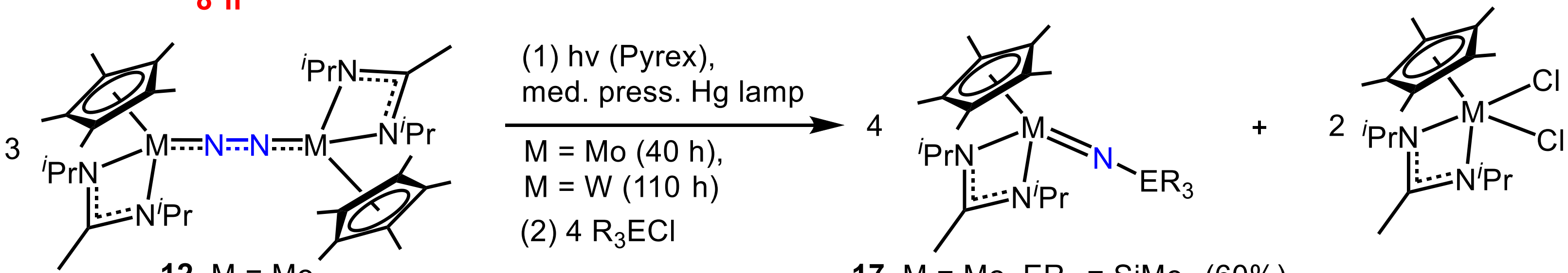
Sita



12, M = Mo
13, M = W
8 π

14, M = Mo, 47%
15, M = W, 65%

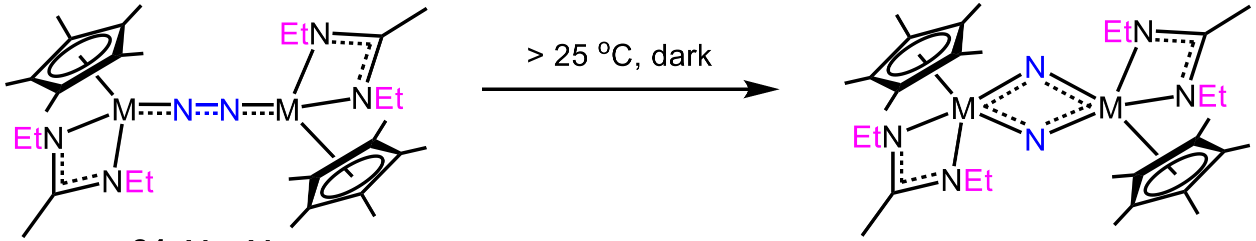
16, 12%



12, M = Mo
13, M = W
8 π

17, M = Mo, ER_3 = $SiMe_3$ (60%)
18, M = W, ER_3 = $SiMe_3$ (63%)
19, M = Mo, ER_3 = $SiPh_3$ (62%)
20, M = Mo, ER_3 = $GeMe_3$ (66%)
21, M = Mo, ER_3 = CMe_3 (36%)

22, M = Mo (paramegnetic)
23, M = W (33%)



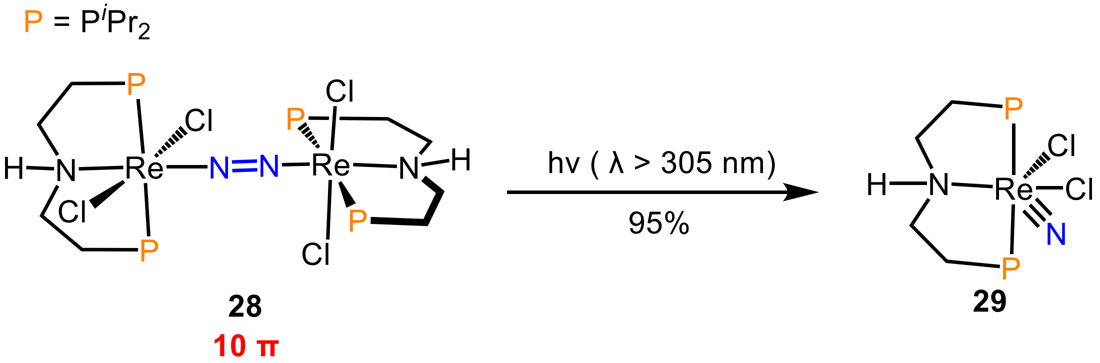
24, M = Mo
25, M = W
8 π

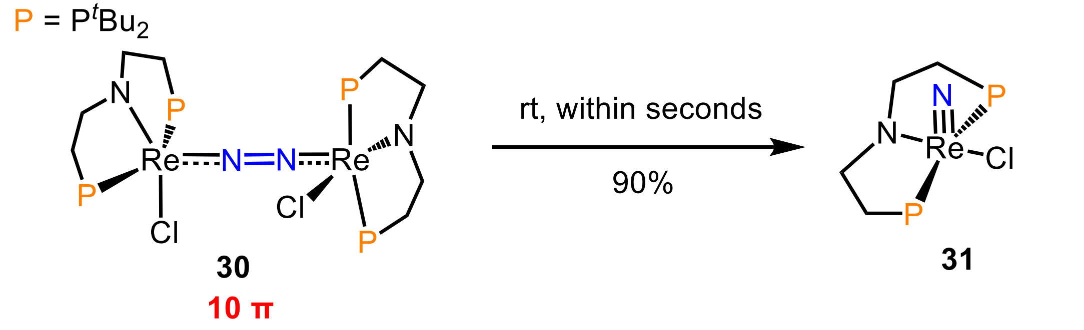
26, M = Mo (80%)
27, M = W (77%)

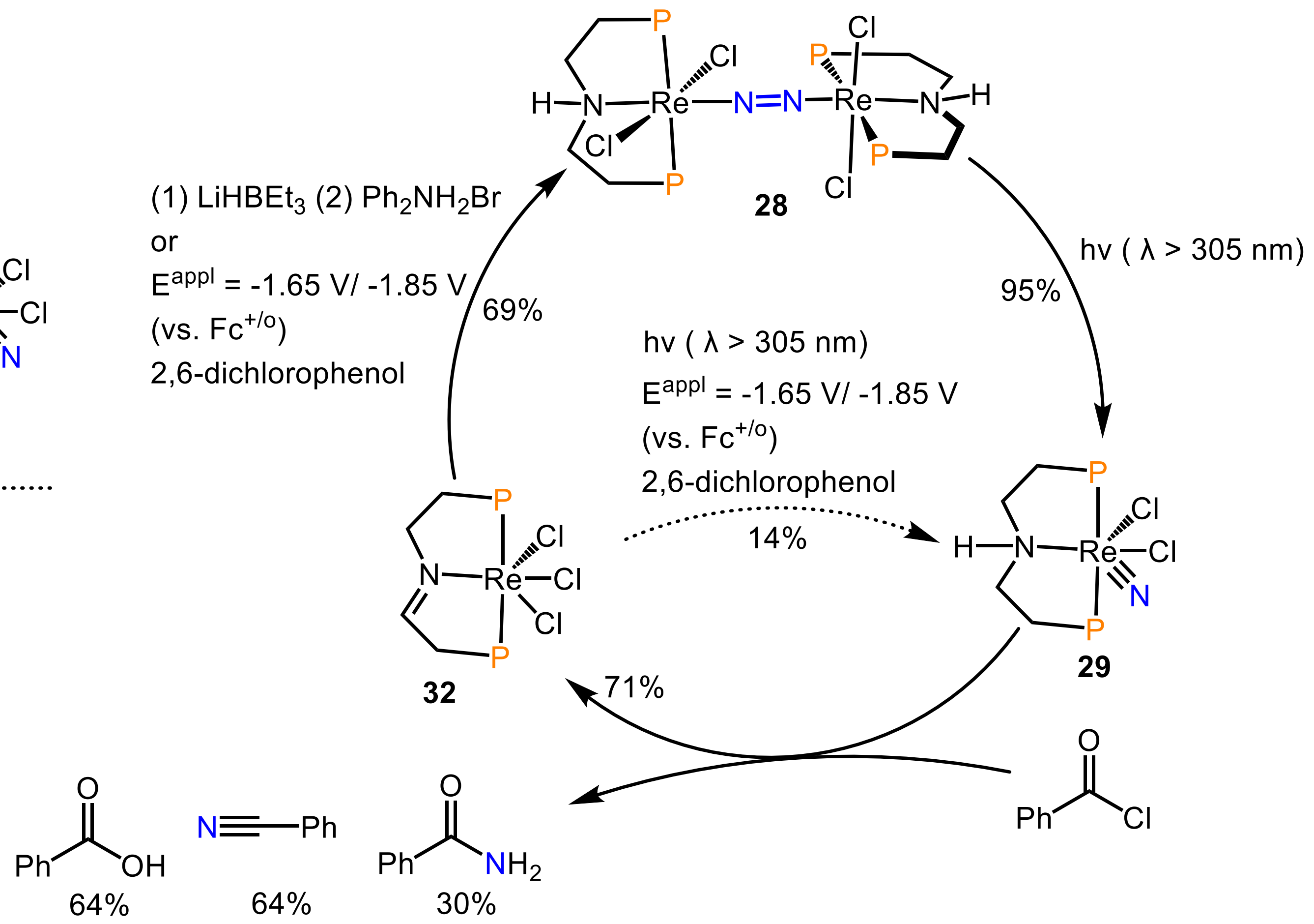
(1) Sita, L. R., et al. *Angew. Chem. Int. Ed.* **2015**, *54*, 10220–10224; (2) Sita, L. R., et al. *J. Am. Chem. Soc.* **2016**, *138*, 14856–14859.

Photo-induced Stoichiometric Dinitrogen Activation

Schneider



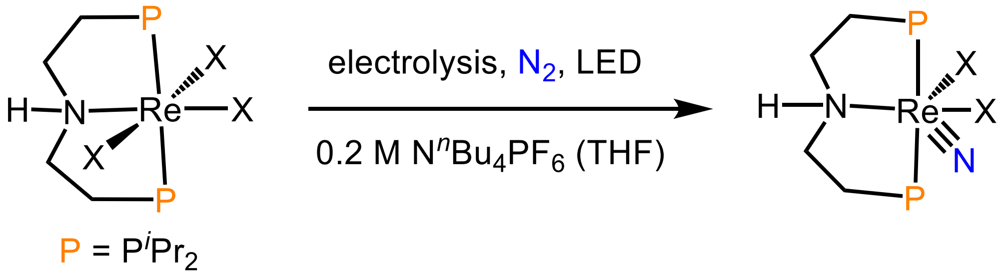




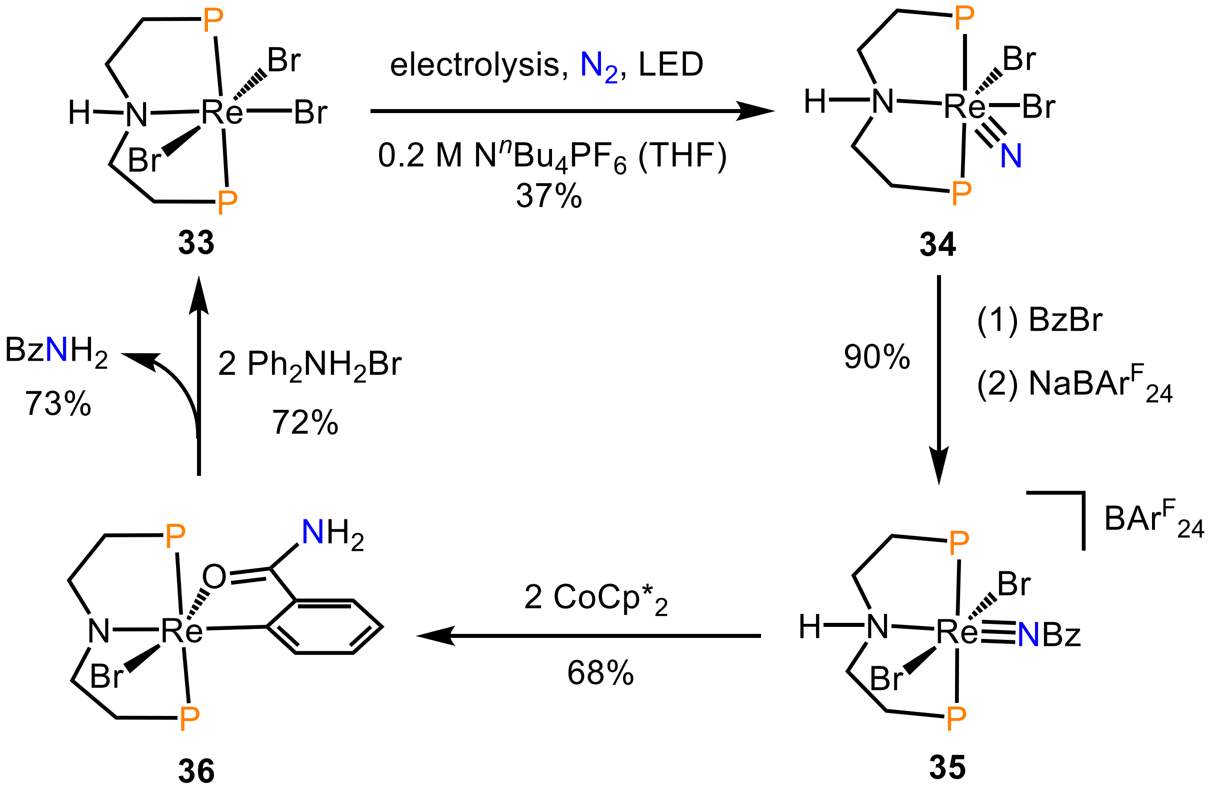
(1) Schneider, S., et al. *J. Am. Chem. Soc.* **2014**, *136*, 6881−6883; (2) Schneider, S., et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 830–834.

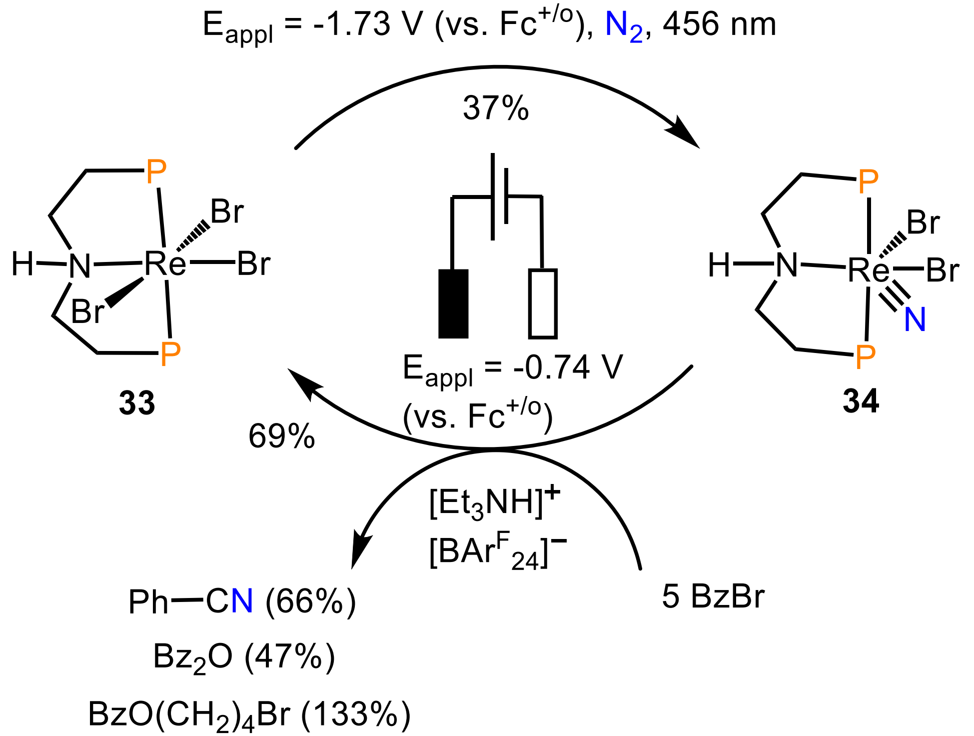
Photo-induced Stoichiometric Dinitrogen Activation

Schneider



Complex	X	E_{appl}	Wavelength	yield(FE)
28	Cl	-1.90V	390 nm	20% (18%)
33	Br	-1.73V	456 nm	37% (22%)
34	I	-1.53V	456 nm	53% (53%)

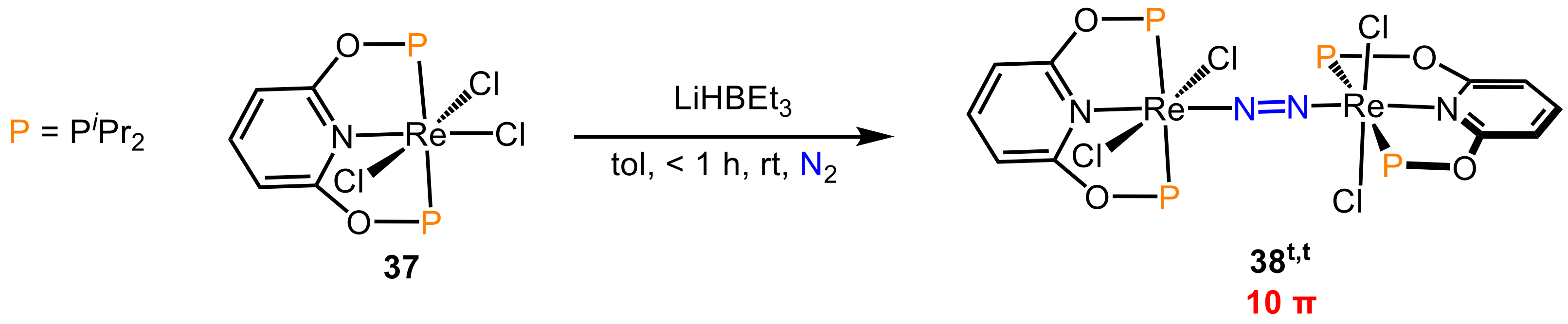


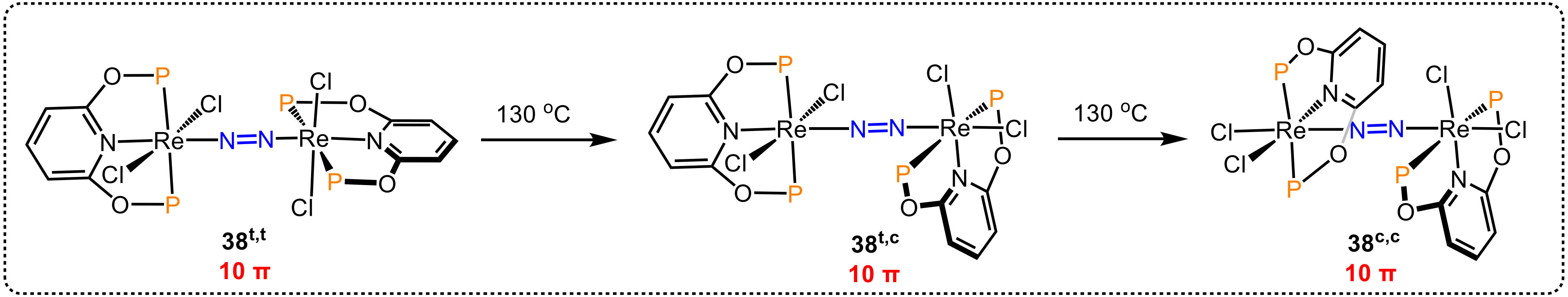


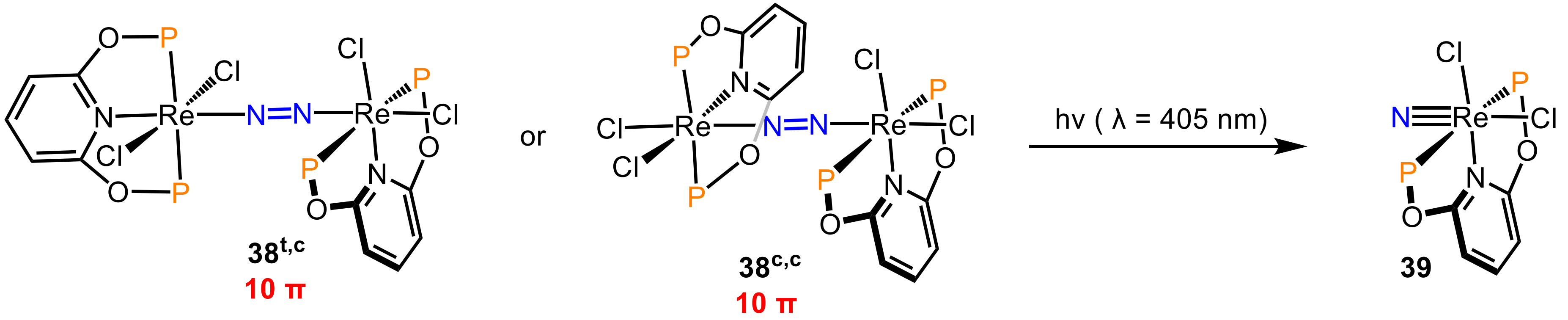
Schneider, S., et al. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205922.

Photo-induced Stoichiometric Dinitrogen Activation

Miller





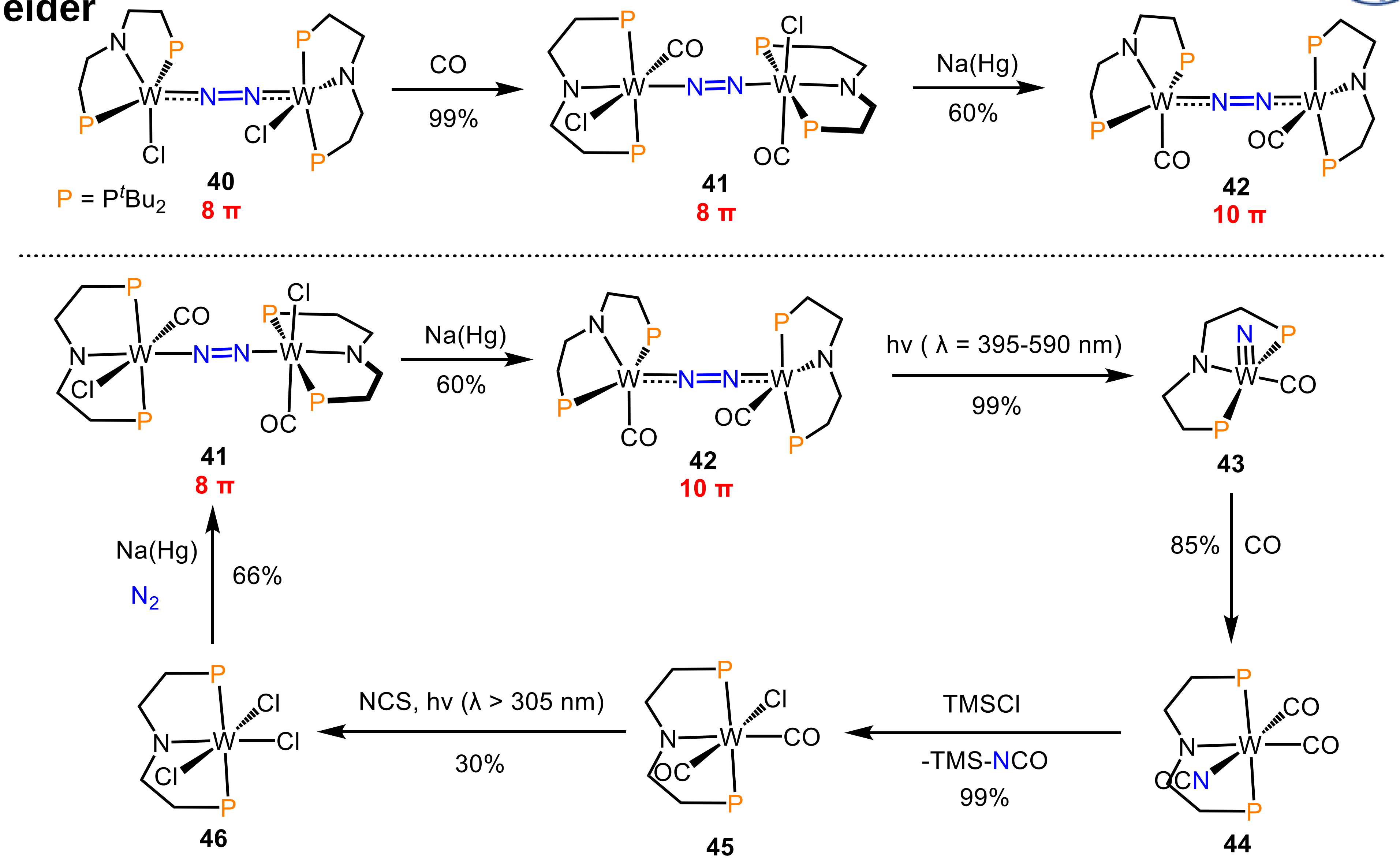


24% for **38^{t,c}**
47% for **38^{c,c}**

Miller, A. J. M., et al. *J. Am. Chem. Soc.* **2019**, *141*, 20198−20208.

Photo-induced Stoichiometric Dinitrogen Activation

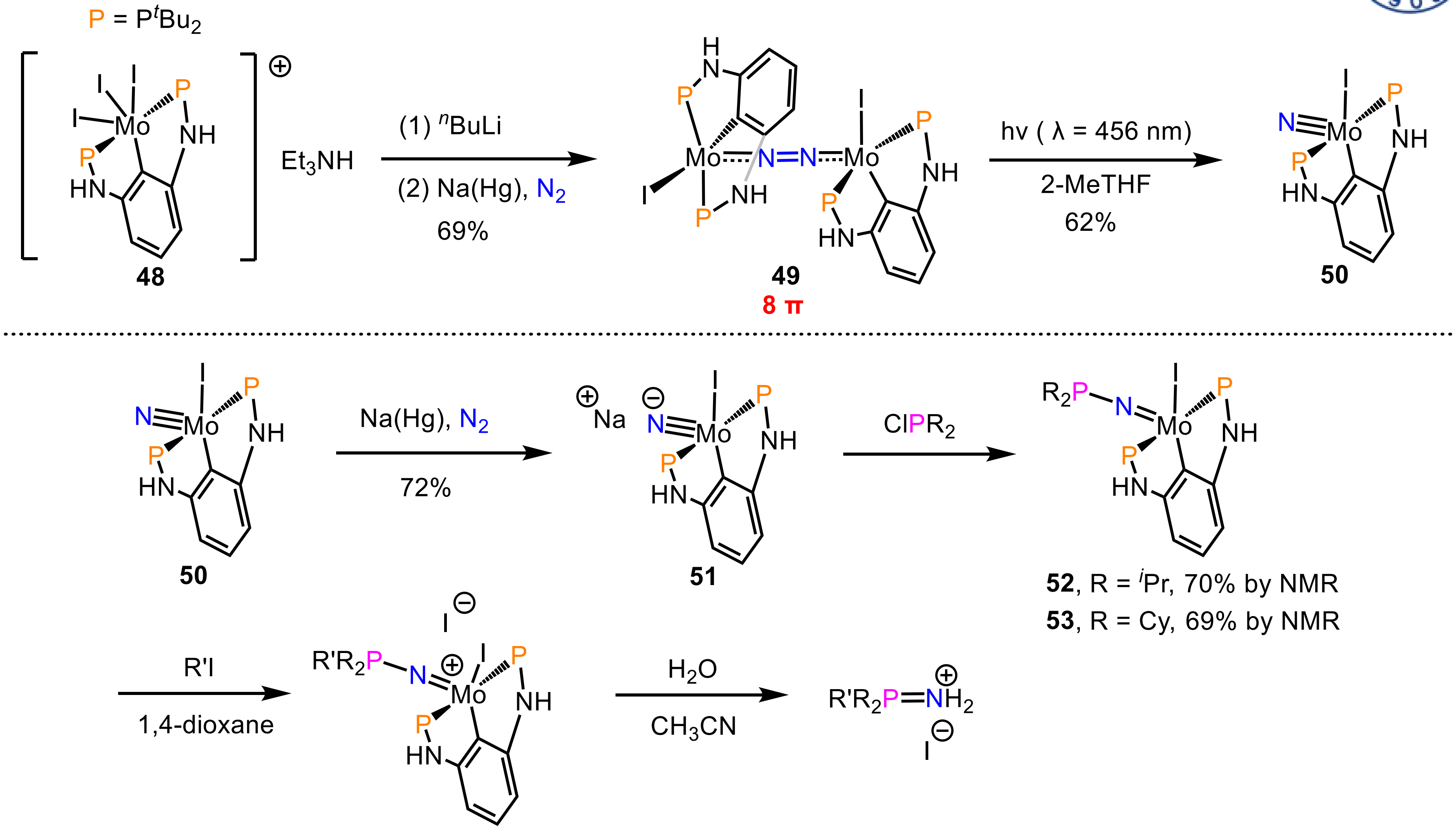
Schneider



(1) Schneider, S., et al. *Chem. Sci.*, **2019**,*10*, 10275-10282; (2) Schneider, S., et al. *JACS Au* **2021**, *1*, 879−894.

Photo-induced Stoichiometric Dinitrogen Activation

Liao



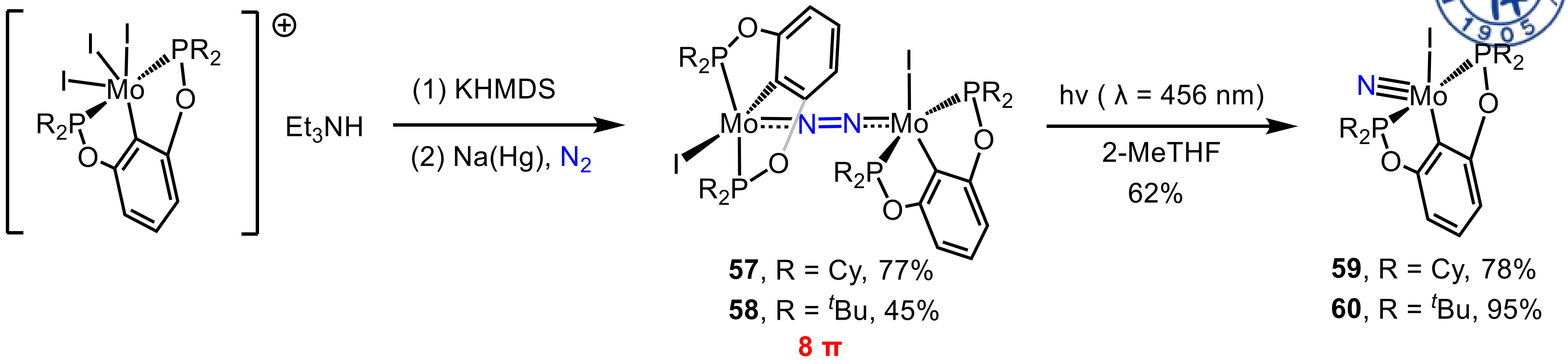
54, R = ^{i}Pr, R' = Me, 52%
55, R = Cy, R' = Me, 65%
56, R = ^{i}Pr, R' = Et, 43%

R = ^{i}Pr, R' = Me, 62%
R = Cy, R' = Me, 54%
R = ^{i}Pr, R' = Et, 65%

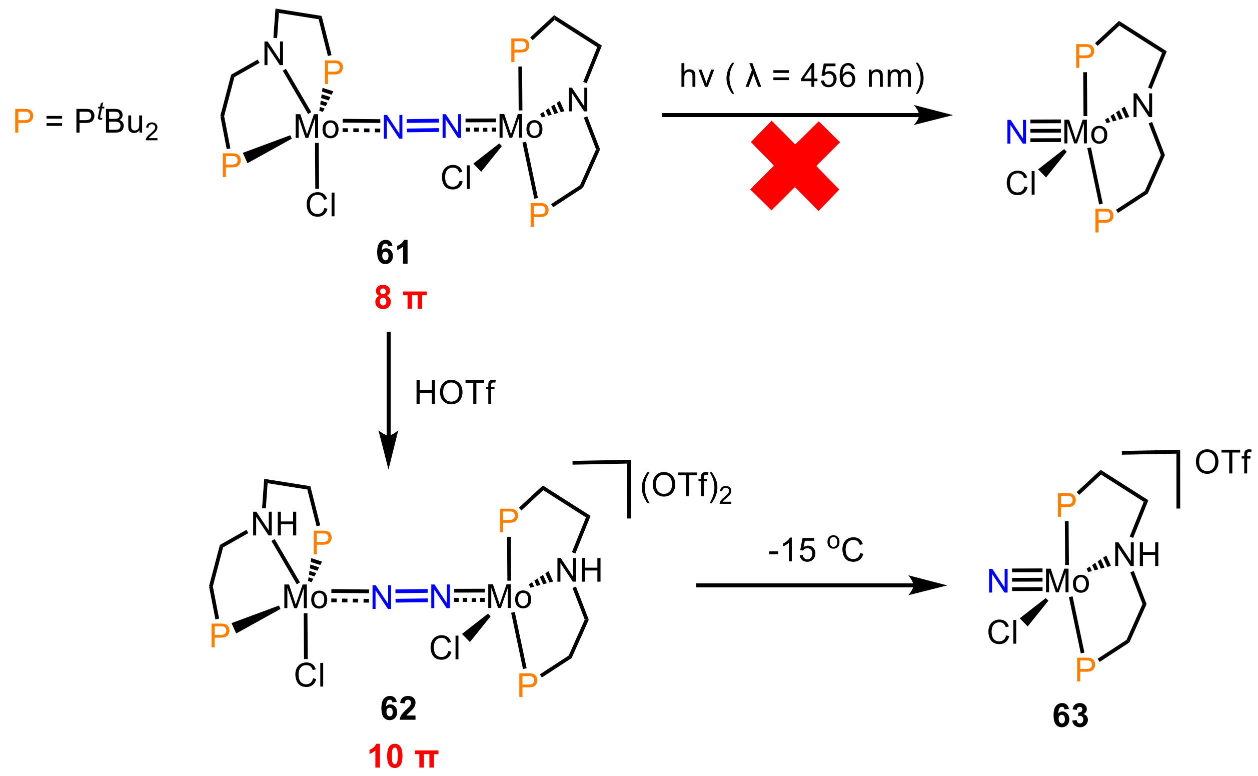
Liao, Q., et al. *J. Am. Chem. Soc.* **2022**, *144*, 2444−2449.

Photo-induced Stoichiometric Dinitrogen Activation

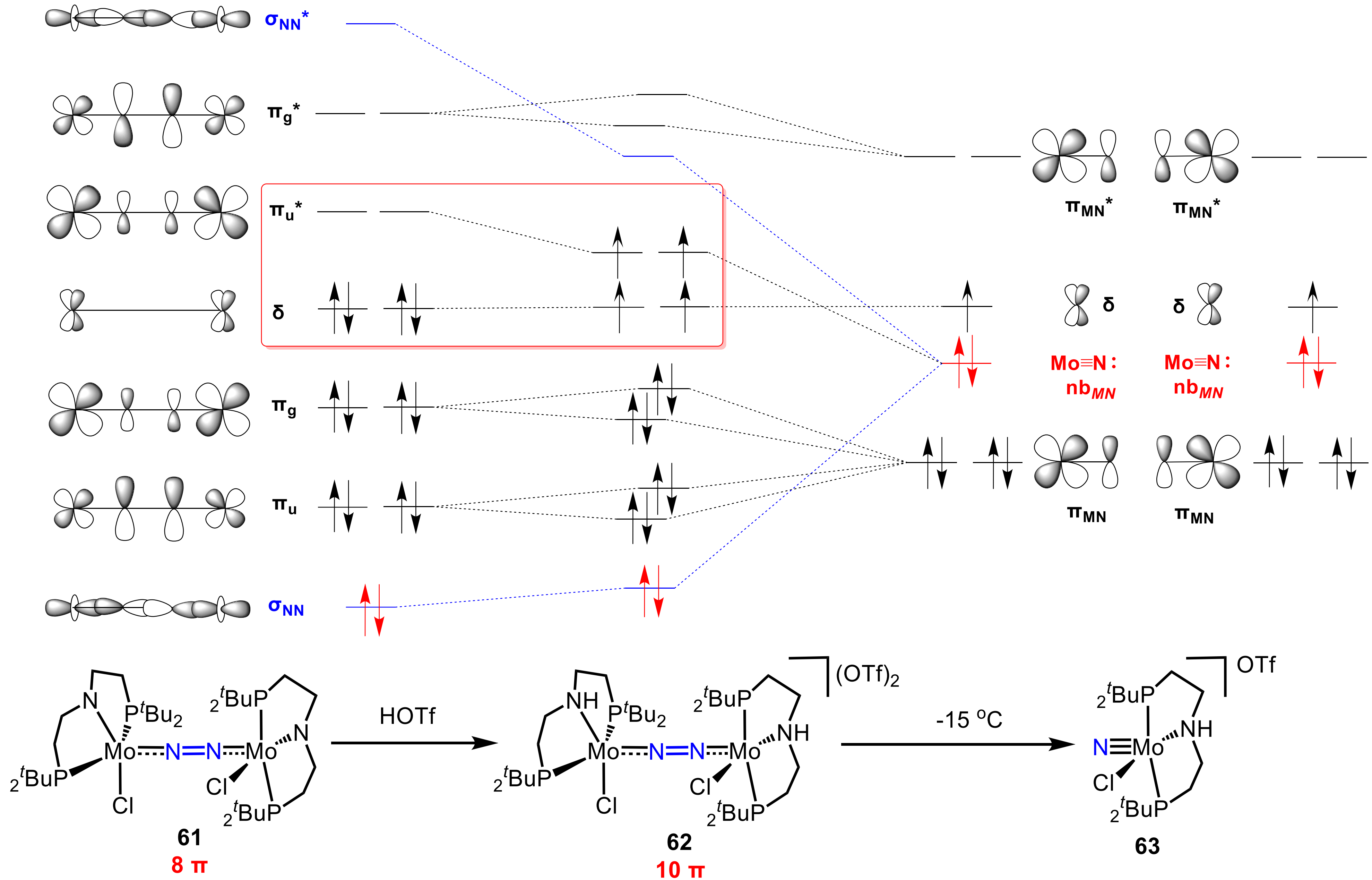
Liao



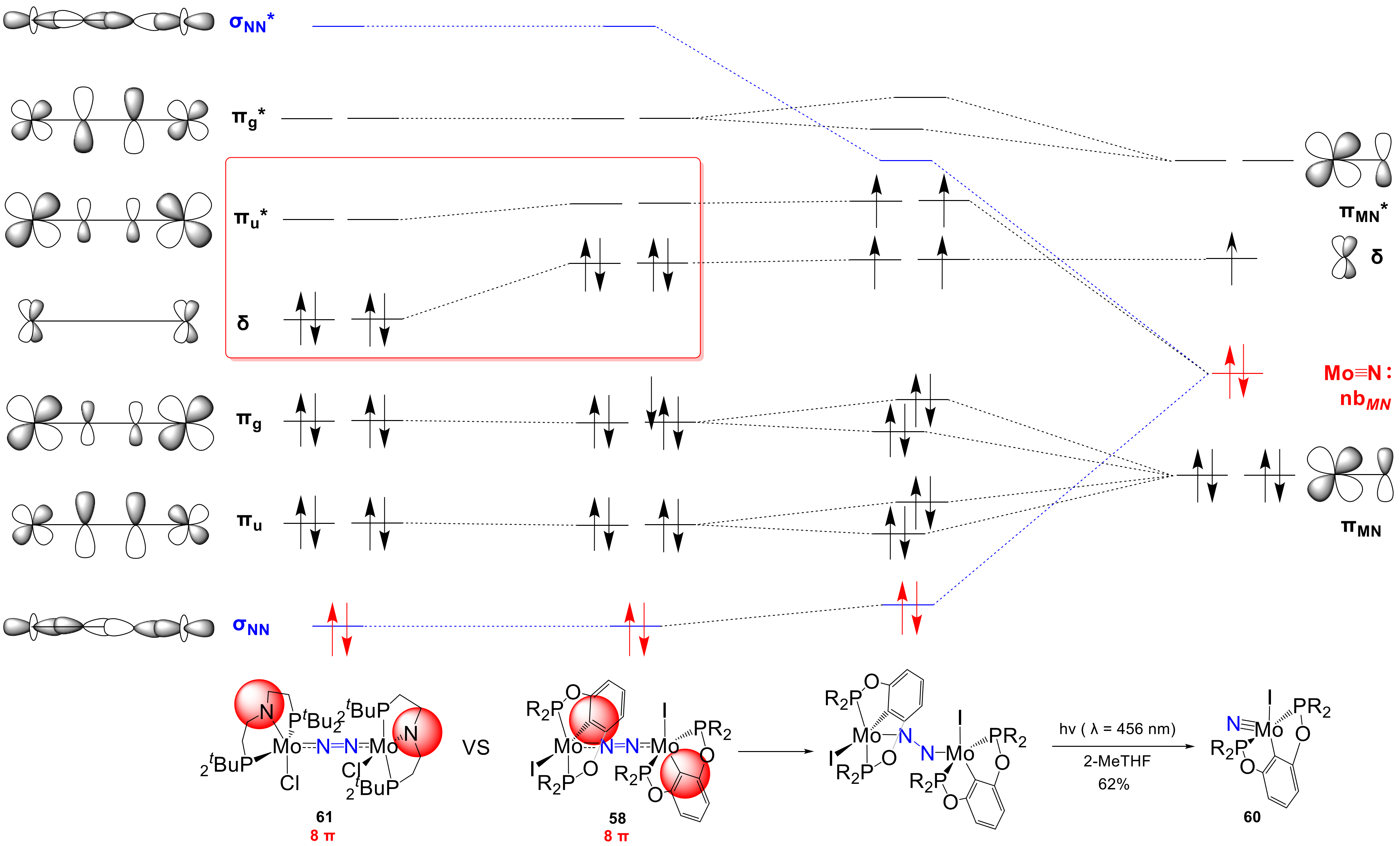
Schneider



(1) Liao, Q., et al. *J. Am. Chem. Soc.* **2025**, *147*, 3747–3757; (2) Schneider, S., et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 5872-5877.



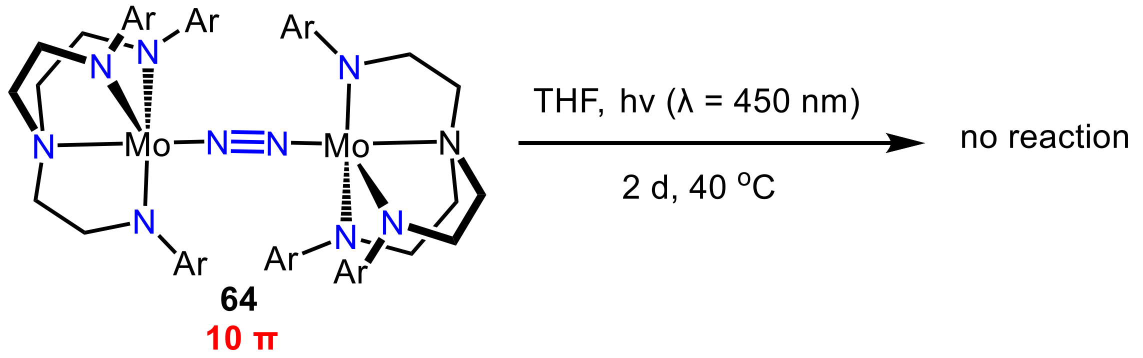
Schneider, S., et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 5872-5877

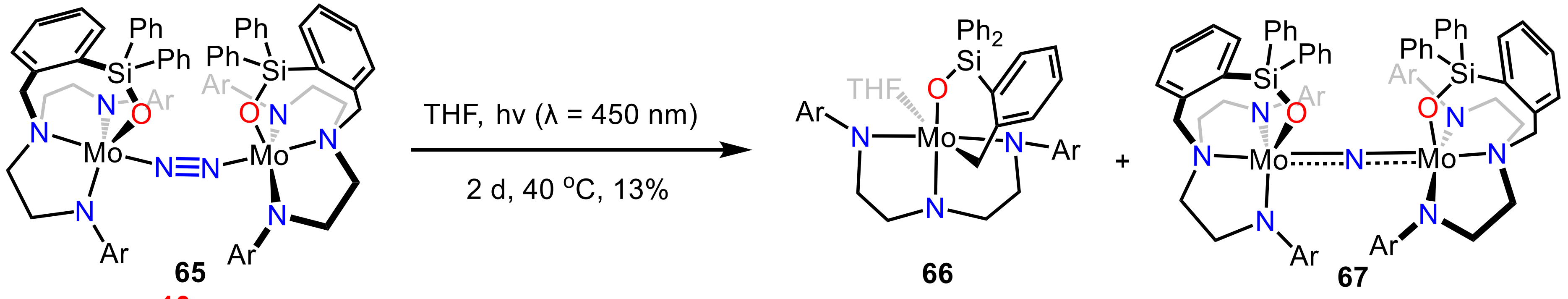


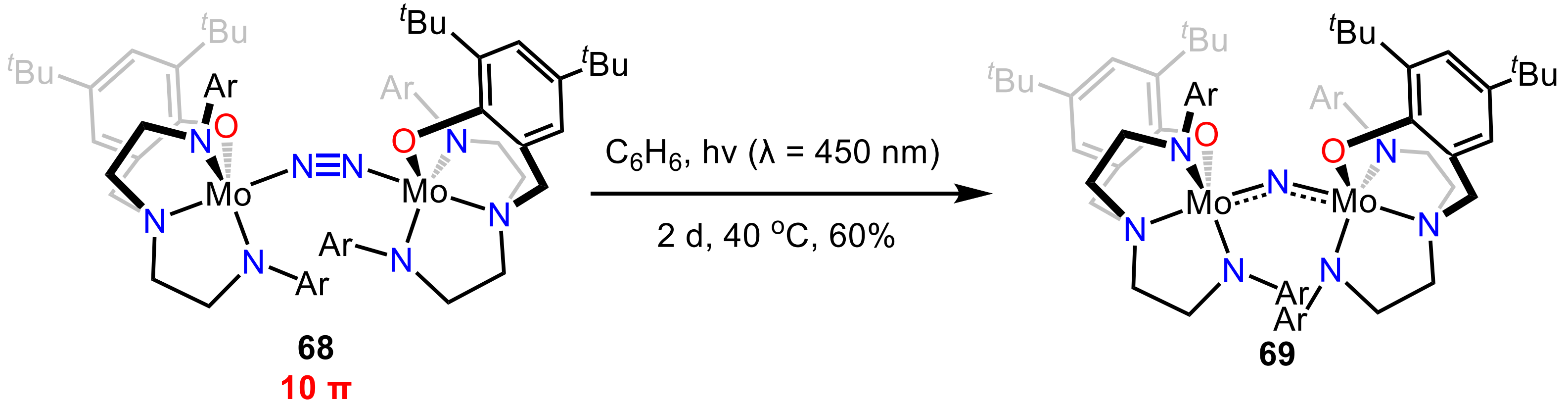
(1) Liao, Q., et al. *J. Am. Chem. Soc.* **2025**, *147*, 3747–3757; (2) Schneider, S., et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 5872-5877.

Photo-induced Stoichiometric Dinitrogen Activation

Shi





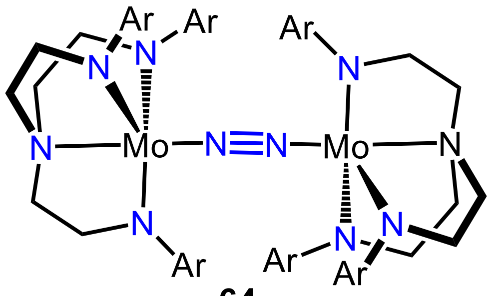


Ar = 3,5-$Me_2C_6H_3$

Shi, Z-J., et al. manuscript in preparation

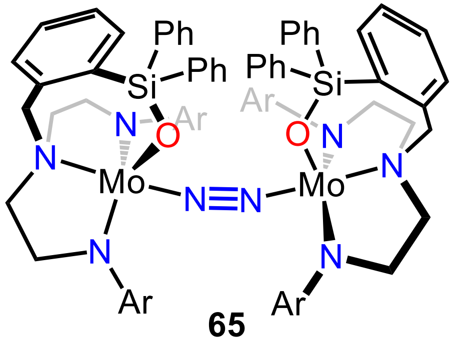
Photo-induced Stoichiometric Dinitrogen Activation

Shi



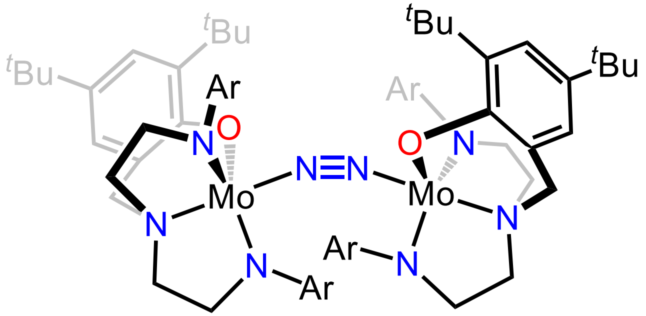
64

10 π



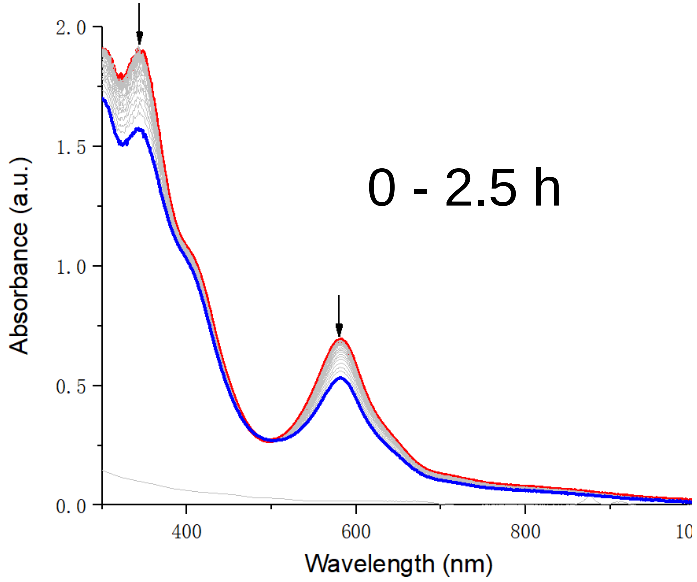
65

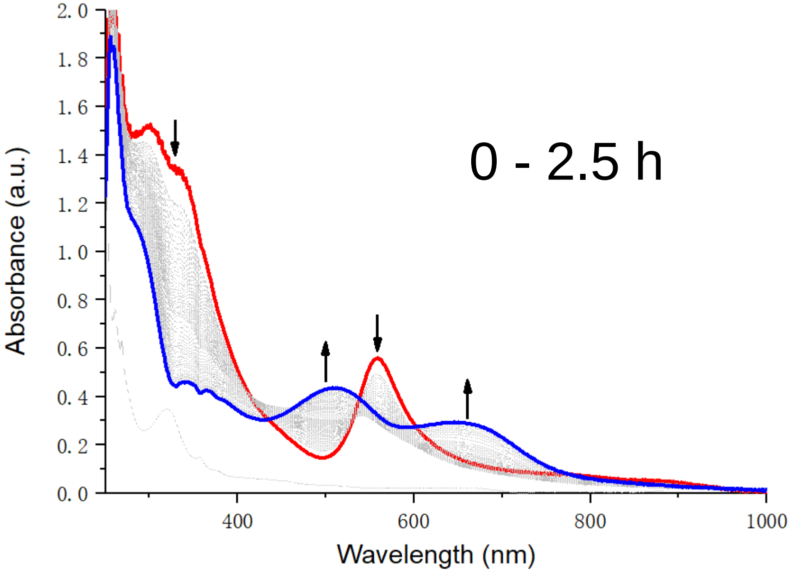
10 π

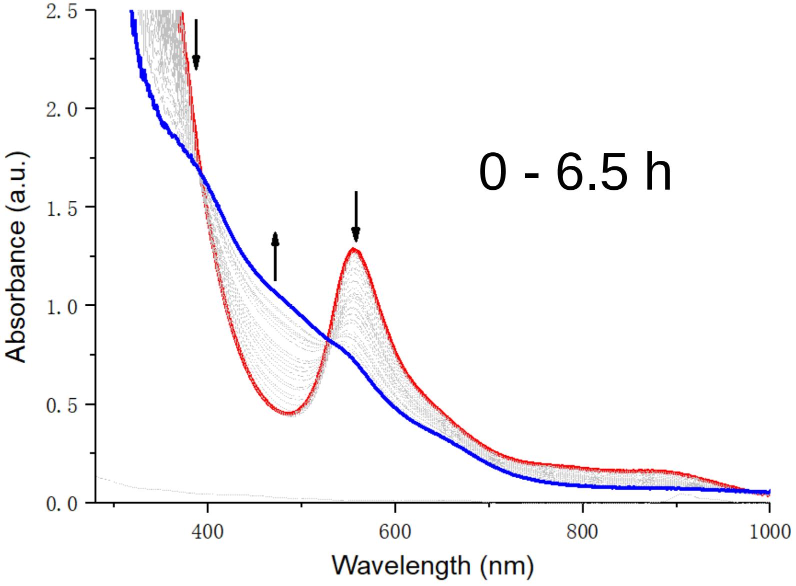


68

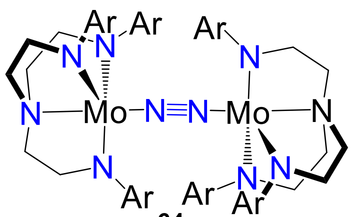
10 π



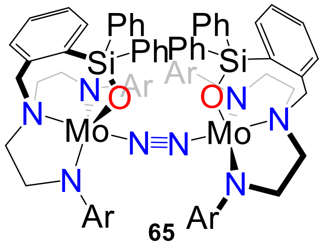




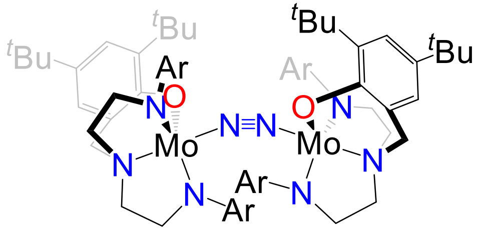
Shi, Z-J., et al. manuscript in preparation



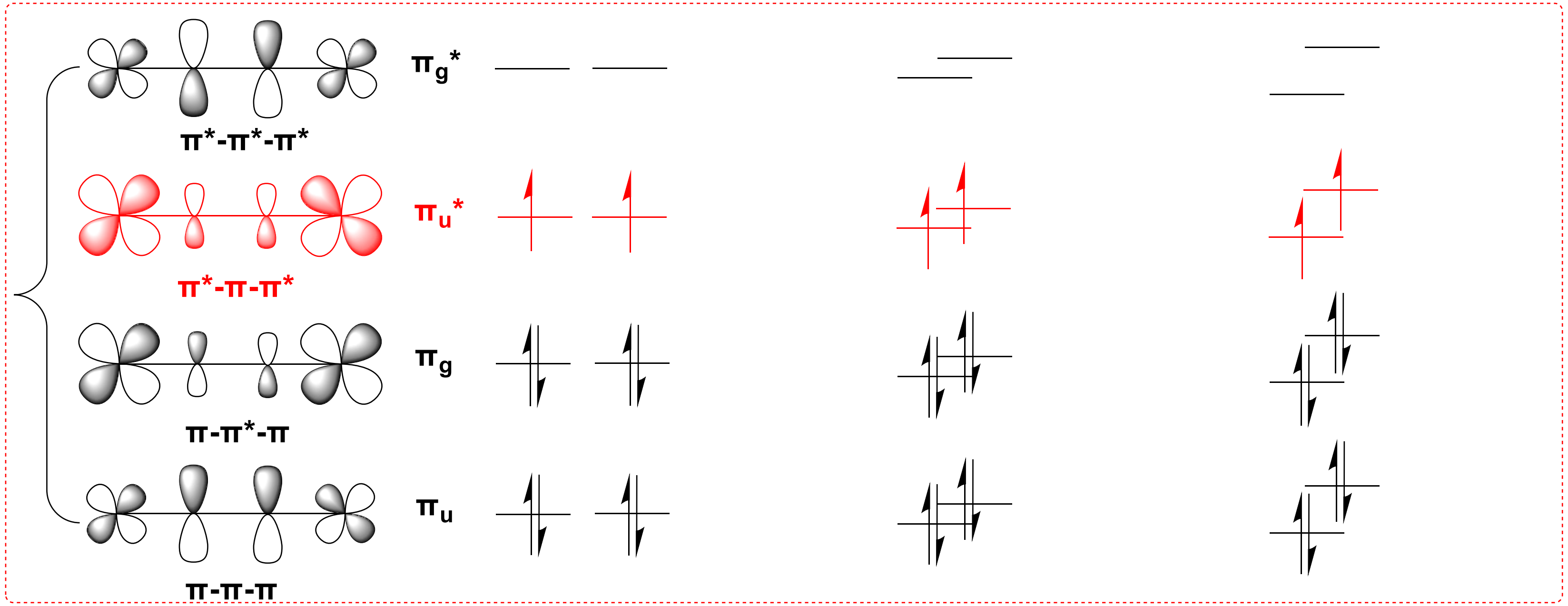
64
10 π

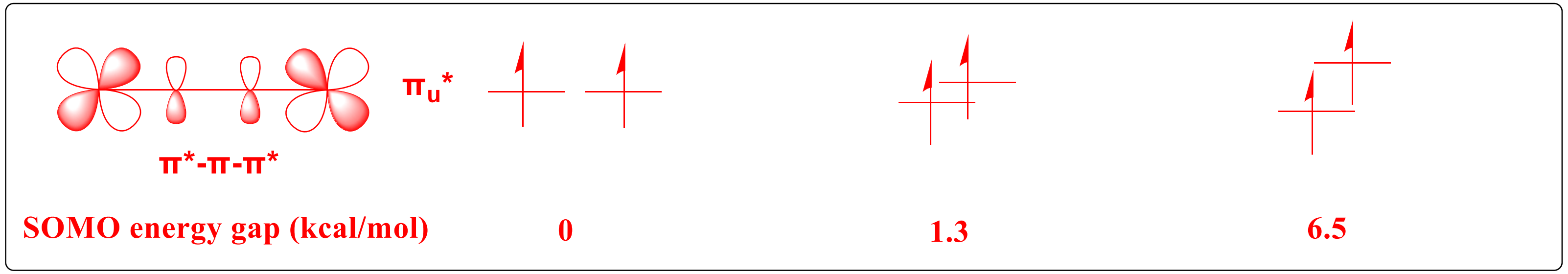


65
10 π



68
10 π

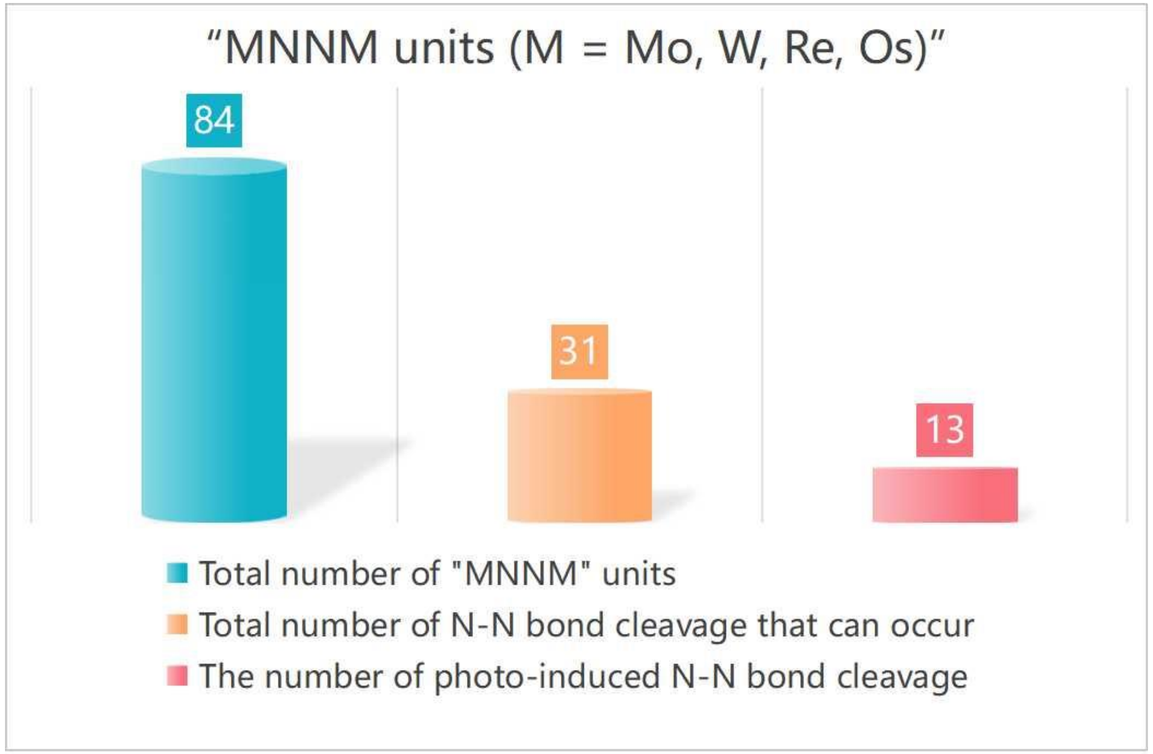


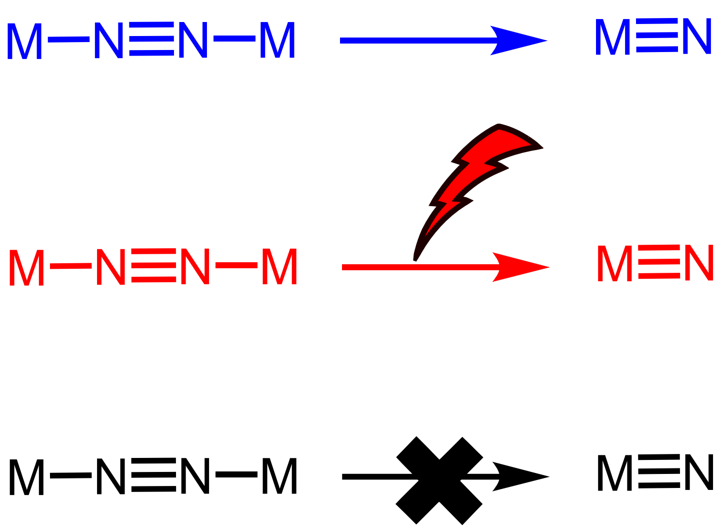


Shi, Z-J., et al. manuscript in preparation

Summary and Outlook

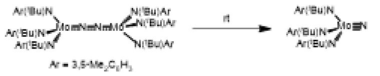
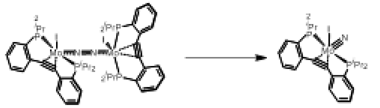
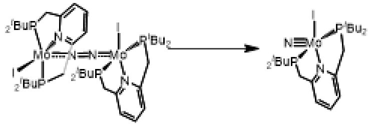
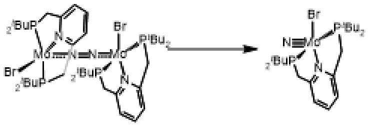
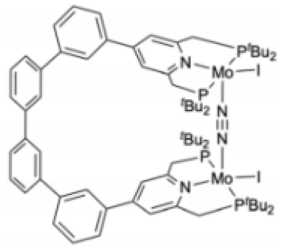
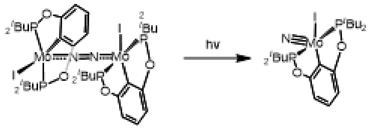
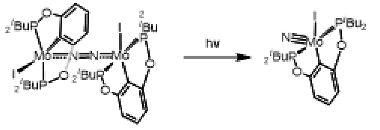
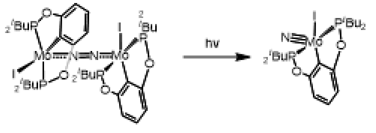
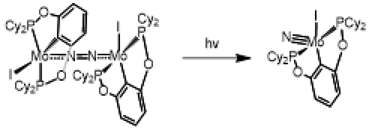
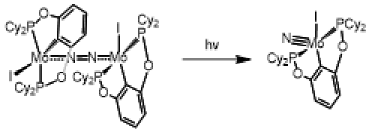
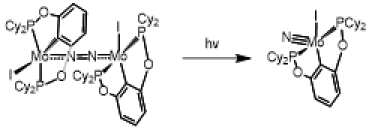
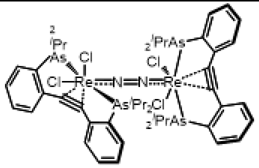
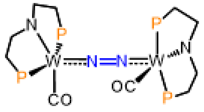
What exactly is the role of light in this reaction?

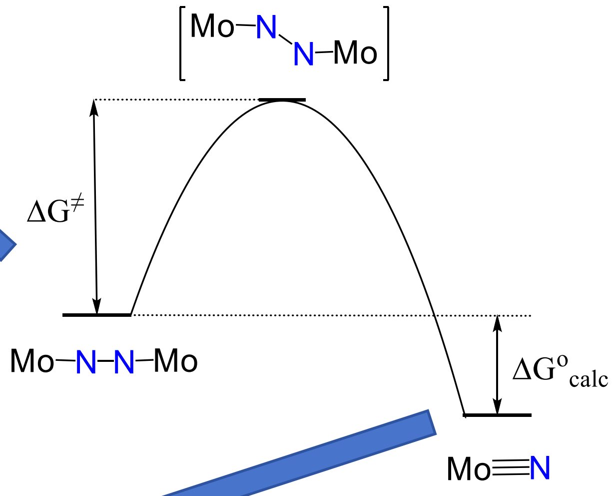




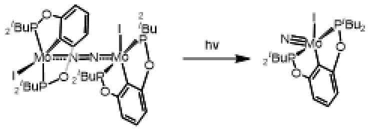
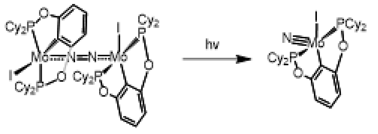
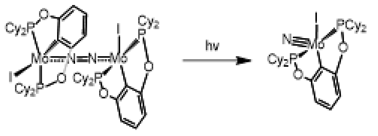
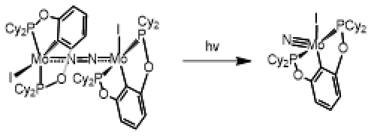
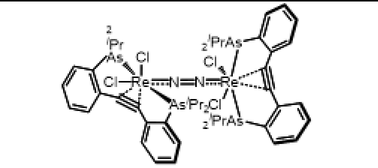
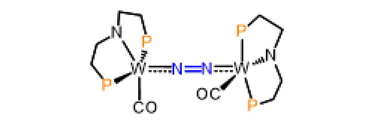
(1) Taube, H., et al. *Science* **1968**, *159*, 320−322; (2) Cummins, C. C., et al. *Science* **1995**, *268*, 861−863; (3) Floriani, C., et al. *Angew. Chem., Int. Ed.* **2001**, *40*, 3907−3909.

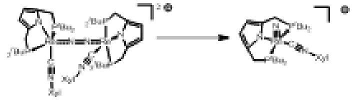
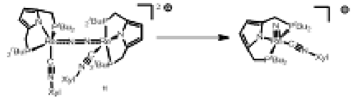
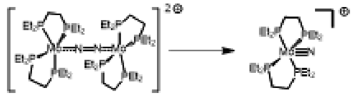
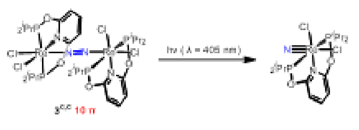
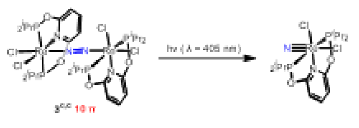
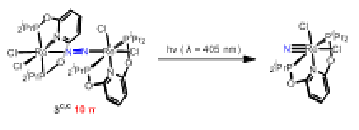
Summary and Outlook

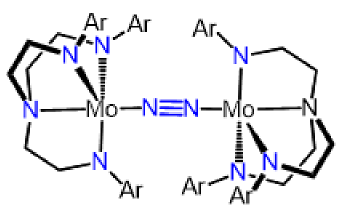
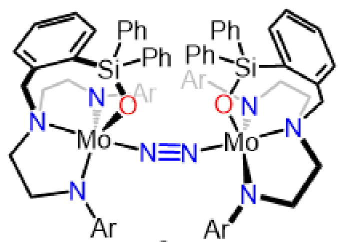
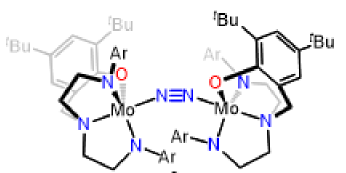
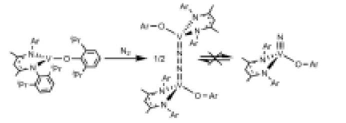
Entry	Reaction	n	$\Delta G^{\neq}$ [kcal mol^{-1}]	ΔG^{o}_{calc} [kcal mol^{-1}]	Ref
1		10	22.5±1.5(exp)	-46.0	1,2
2		10	26	-19.8	3
3		10	21.8(in tol) 21.8(in THF)	-27.6(in tol) -32.8(in THF)	4
4		10	19	-24	5
5		10	21.2(in THF)	-35.7(in THF)	6
6		8	26.8	-7.2	7
7	 -1	9	18.7	-14.5	7
8	 -2	10	13.9	-34.3	7
9		8	26.2	-8.6	7
10	 -1	9	20.4	-14.[illegible]	7
11	 -2	10	13.0	-35.6	7
12 未		10	56±8	12±7	8
13		10	26.9 25.5(holland) 19.9(exp)	-40.3 -40.8(h)	9
14	 P = P^{t}Bu$_2$	10	29.4 34.2(DFT)	3.6 -0.7(DFT)	10
15		10	12.2	-48.8	11



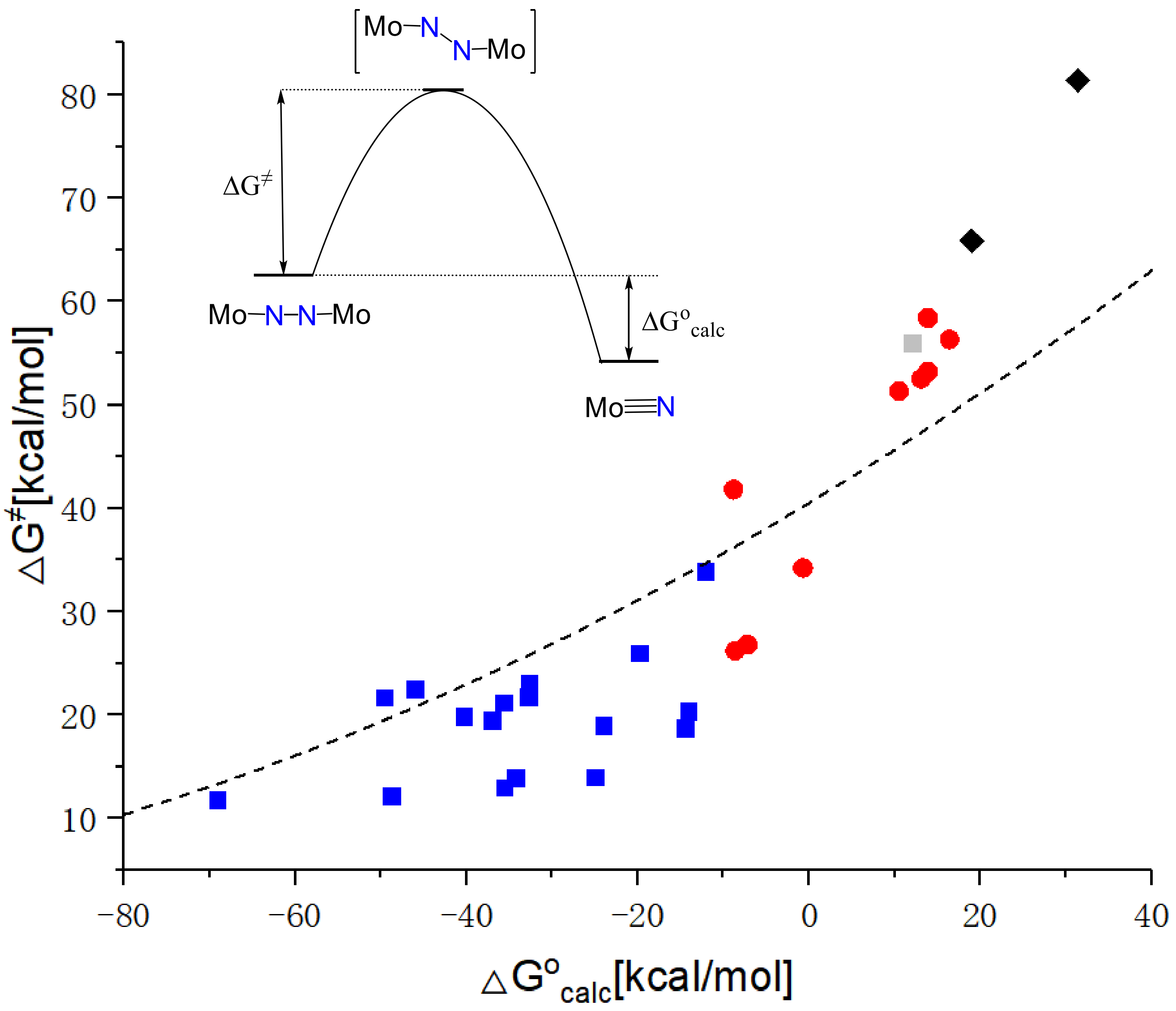
Summary and Outlook

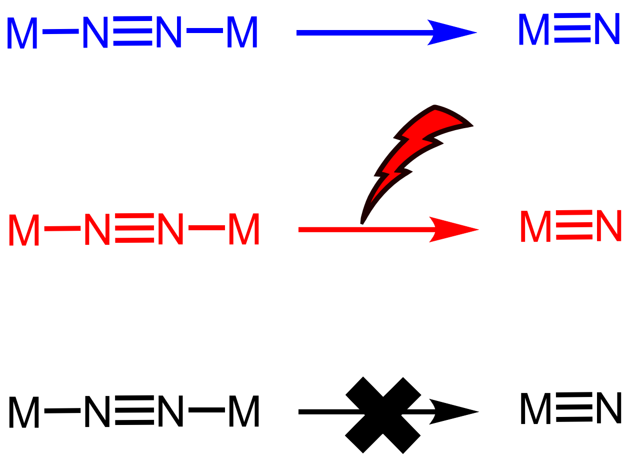
8	 -2	10	13.9	-34.3	7
9		8	26.2	-8.6	7
10	 -1	9	20.4	-14.1	7
11	 -2	10	13.0	-35.6	7
12 未		10	56±8	12±7	8
13		10	26.9 25.5(holland) 19.9(exp)	-40.3 -40.8(h)	9
14	 P = P^{t}Bu$_2$	10	29.4 34.2(DFT)	3.6 -0.7(DFT)	10
15		10	12.2	-48.8	11

16		10	14 32(从基态算)	-25 -7(从基态算)	12
17	 TT	10	52	-7	12
18	 tBu=H	10	33.9	-12.1	13
19		10	19.5(exp) 21(cal)	-37	14
20		10	21.7	-49.6	15
21		10	11.8	-69.1	16
22 未	 TT	10	53.2	13.9	17
23 未	 CT	10	52.5	13.1	17
24	 CC	10	51.3	10.5	17
25		10	41.8	-8.8	18

25		10	41.8	-8.8	18
26 未	 1	10	65.9 46(以三为准)	19	
27	 2	10	58.4	13.9	
28	 3	10	56.3	16.4	
29		11	23.1	-32.7	19
30 未		8	81.4	31.4	20

Summary and Outlook





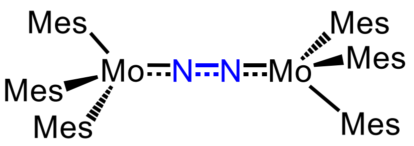
Marcus model

$\Delta G^{\ddagger} = (\lambda + \Delta G^{\circ})$^2/4λ

for λ = 154 kcal mol^{-1}

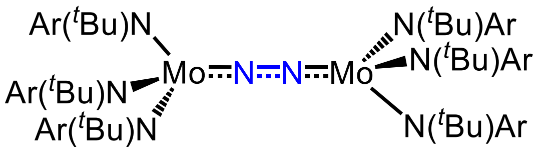
R^2= 0.8096

Summary and Outlook



Floriani 2001

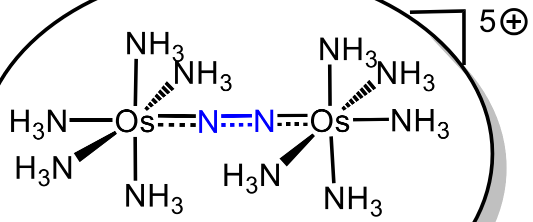
10 π



Ar = C_6H_3-3,5-Me_2

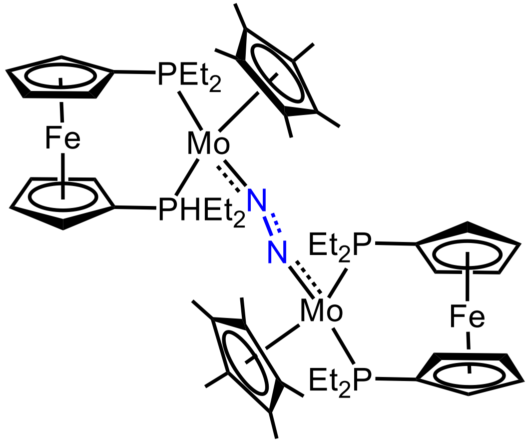
Cummins 2008

10 π



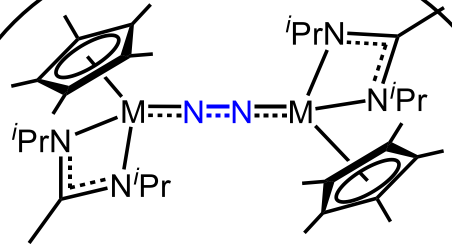
Vogler 2010

11 π



Nishibayashi 2014

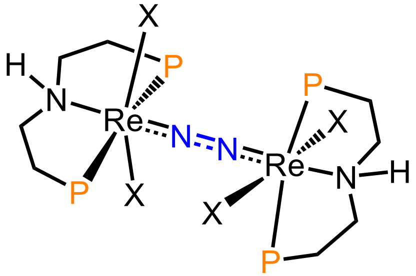
10 π



M = Mo, W

Sita 2015

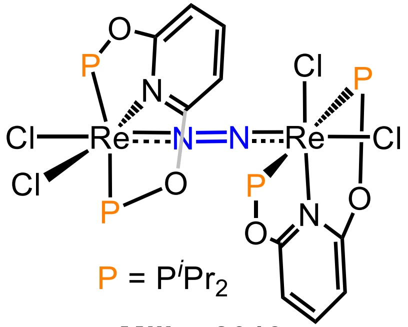
8 π



P = P^{i}Pr$_2$, X =Cl, Br

Schneider 2018 and 2022

10π

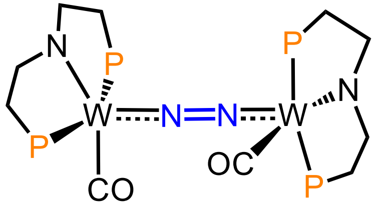


P = P^{i}Pr$_2$

Miller 2019

10π

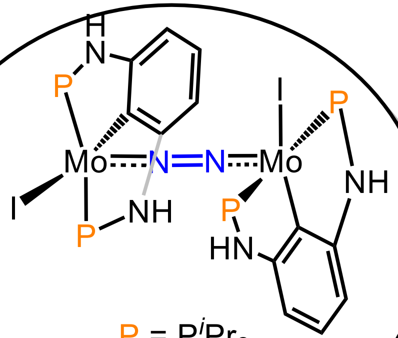
Photochemical cleavage of the N-N bond disrupts the conventional 10-π electrons rule observed under thermal conditions.



P = P^{t}Bu$_2$

Schneider 2021

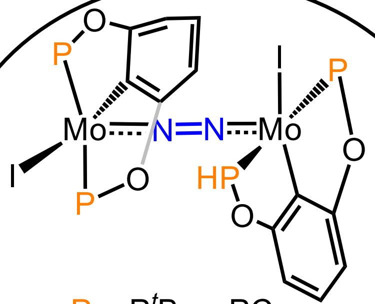
10π



P = P^{i}Pr$_2$

Liao 2022

8 π



P = P^{t}Bu$_2$, PCy$_2$

Liao 2025

8 π

Summary and Outlook

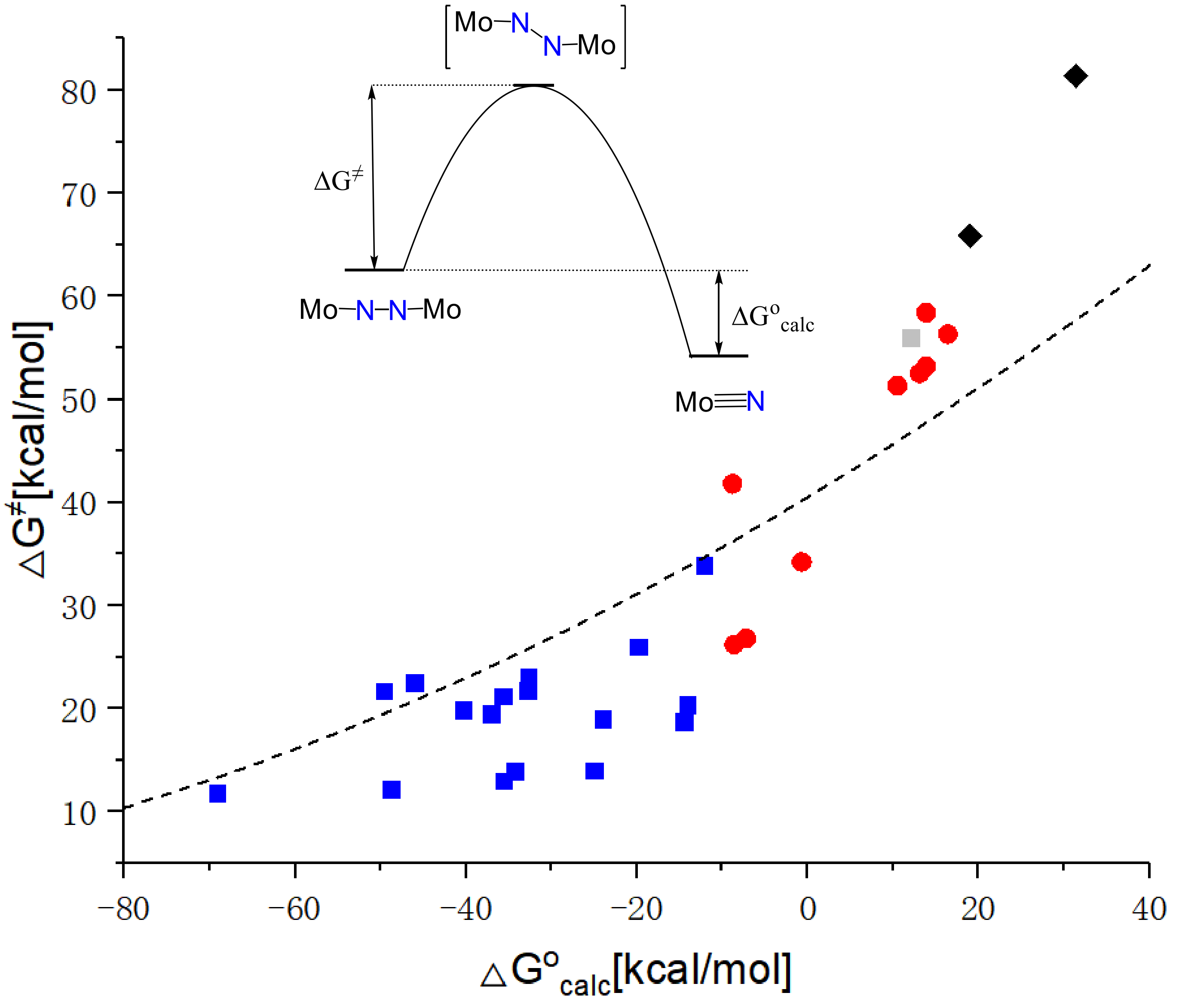
What exactly is the role of light in this reaction?

First, it provides additional energy, enabling certain M-N-N-M complexes to overcome higher transition state energy barriers, potentially leading to products that are even less stable than the reactants.

Second, light excitation promotes the transition of metal center δ-electrons into π* antibonding orbitals, allowing some complexes that do not conform to the "10-π electrons rule" to undergo N≡N bond cleavage under photochemical conditions.

(1) Taube, H., et al. *Science* **1968**, *159*, 320−322; (2) Cummins, C. C., et al. *Science* **1995**, *268*, 861−863; (3) Floriani, C., et al. *Angew. Chem., Int. Ed.* **2001**, *40*, 3907−3909.

Summary and Outlook

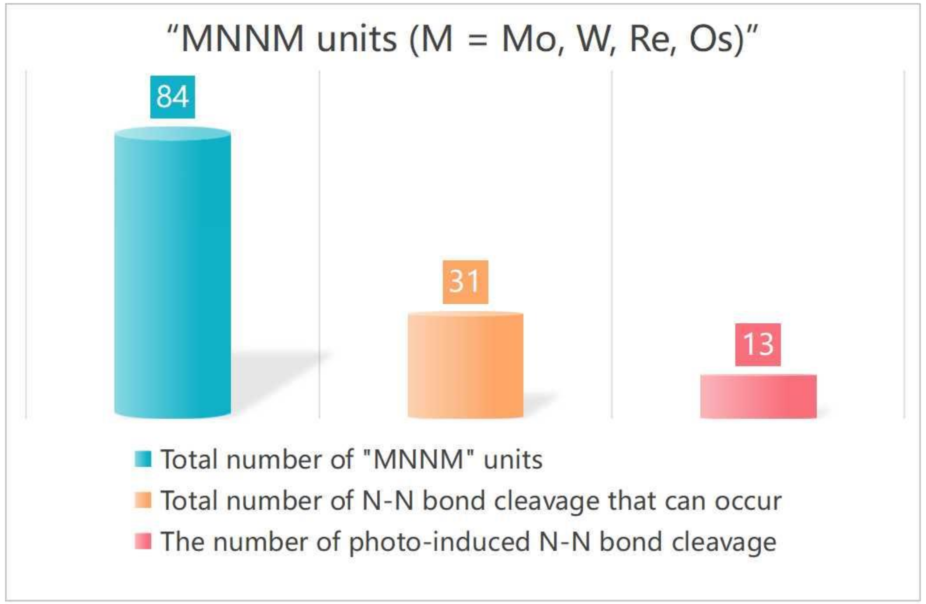


Marcus model

$\Delta G^{\ddagger} = (\lambda + \Delta G^{\circ})^2/4\lambda$

for λ = 154 kcal mol^{-1}

$R^2 = 0.8096$



Thanks