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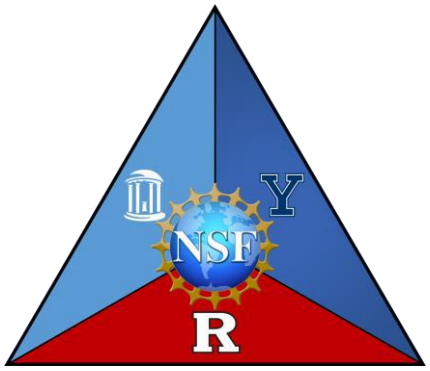

(PXP)Mo Pincer Complexes for Catalytic Dinitrogen Reduction: Synthesis, Characterization and Mechanistic Studies

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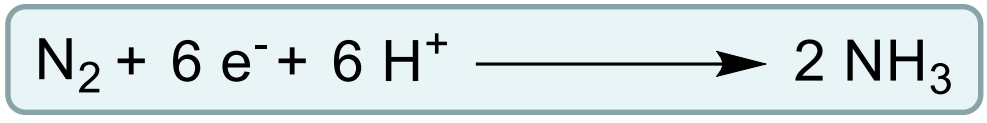
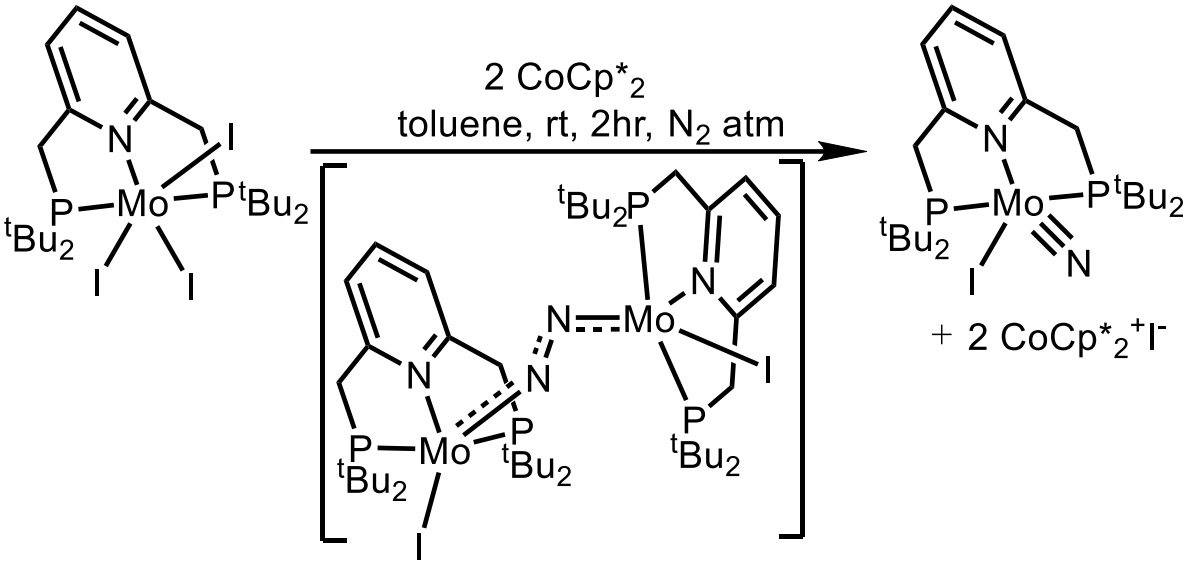
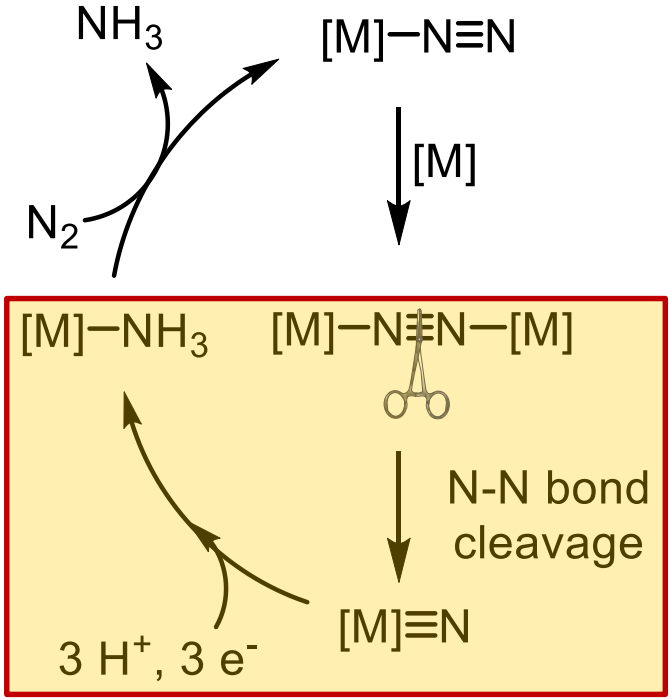
Nishibayashi: Reduction of N_2 catalyzed by (PNP)Mo complexes



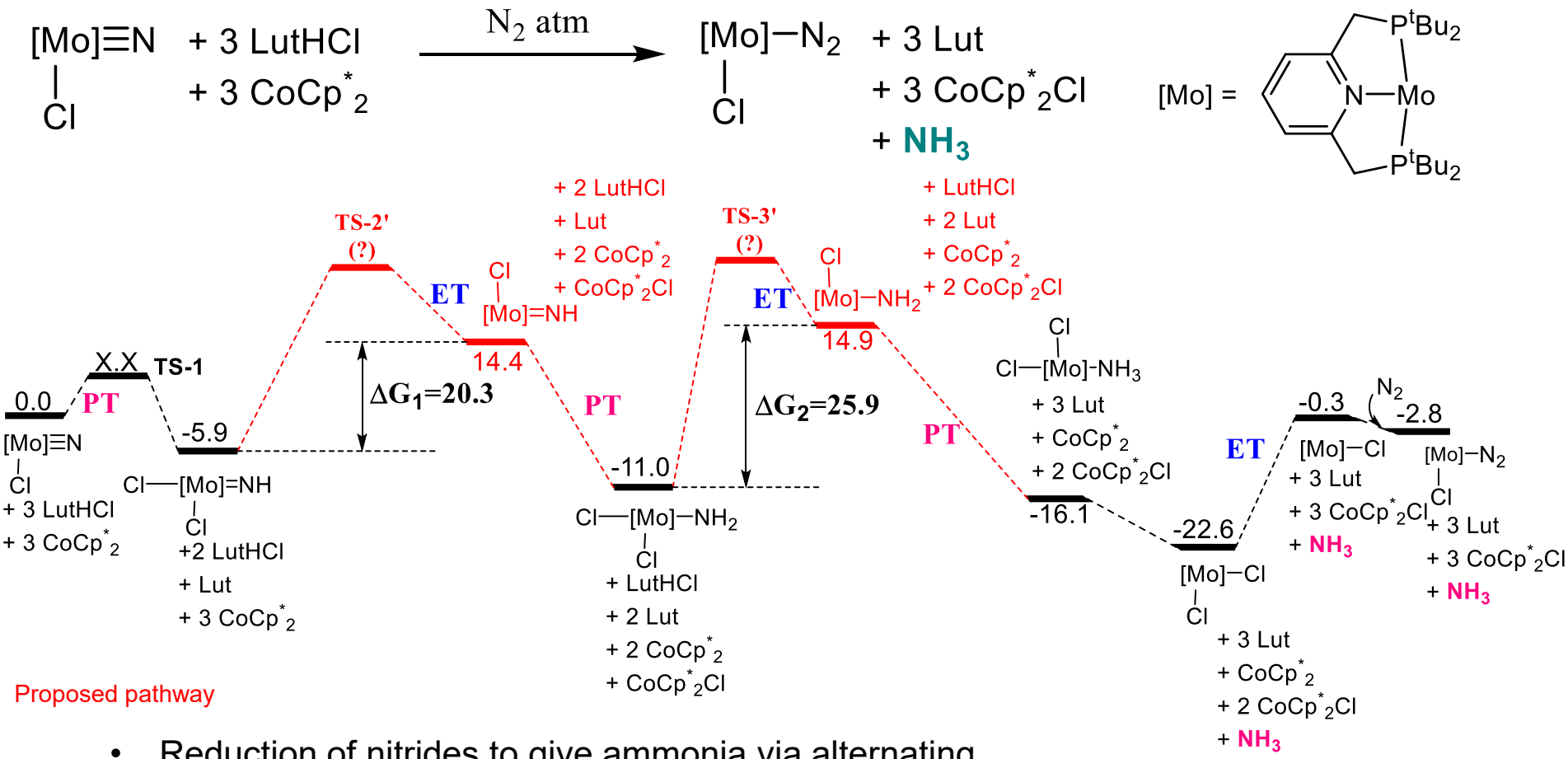




- Nishibayashi's $(PNP)MoI_3$ reported to catalyze reduction of N_2 to NH_3 by Cp^*_2Co and Lutidine•H^+OTf^- or Collidine•H^+OTf^-
- **Mechanistic insight into each of these steps required to design better catalysts**

Nishibayashi and co-workers *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1111.
Nishibayashi and co-workers *Nature* **2019**, *568*, 536.

“Conventional” Pathway for Reduction of Mo nitride intermediate



Proposed pathway

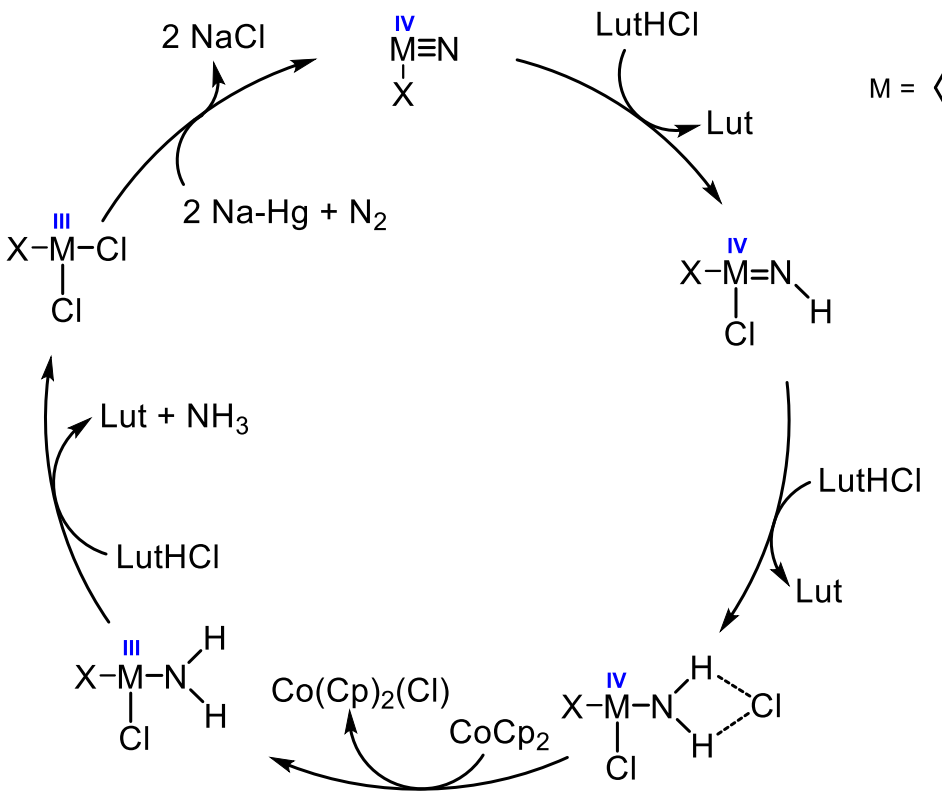
- Reduction of nitrides to give ammonia via alternating protonations and one-electron reductions

➔ **Electron transfers/halide loss are calculated to be thermodynamically very unfavorable**

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Gibbs free energies in kcal/mol

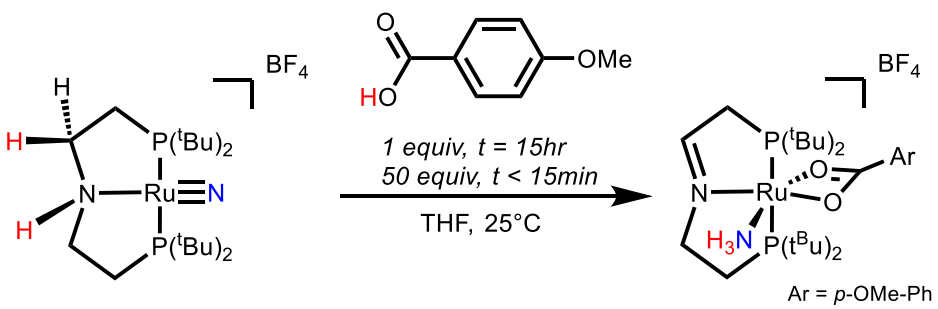
Calculated pathway for nitride protonation to give NH_3



We calculate a pathway in which 2 H^+ are added to the nitride and X^- is added to Mo, before the first reduction

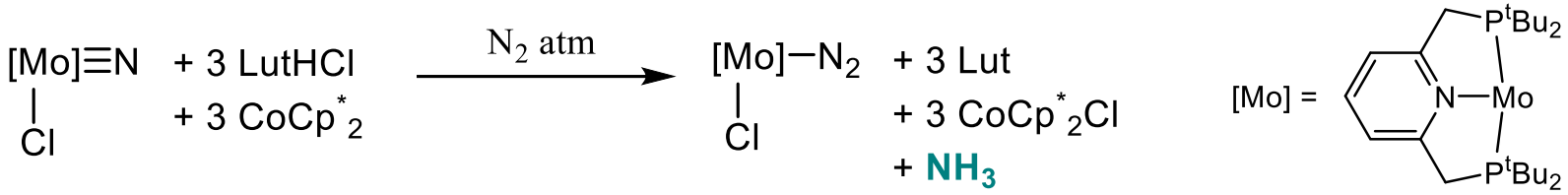
Exact sequence:

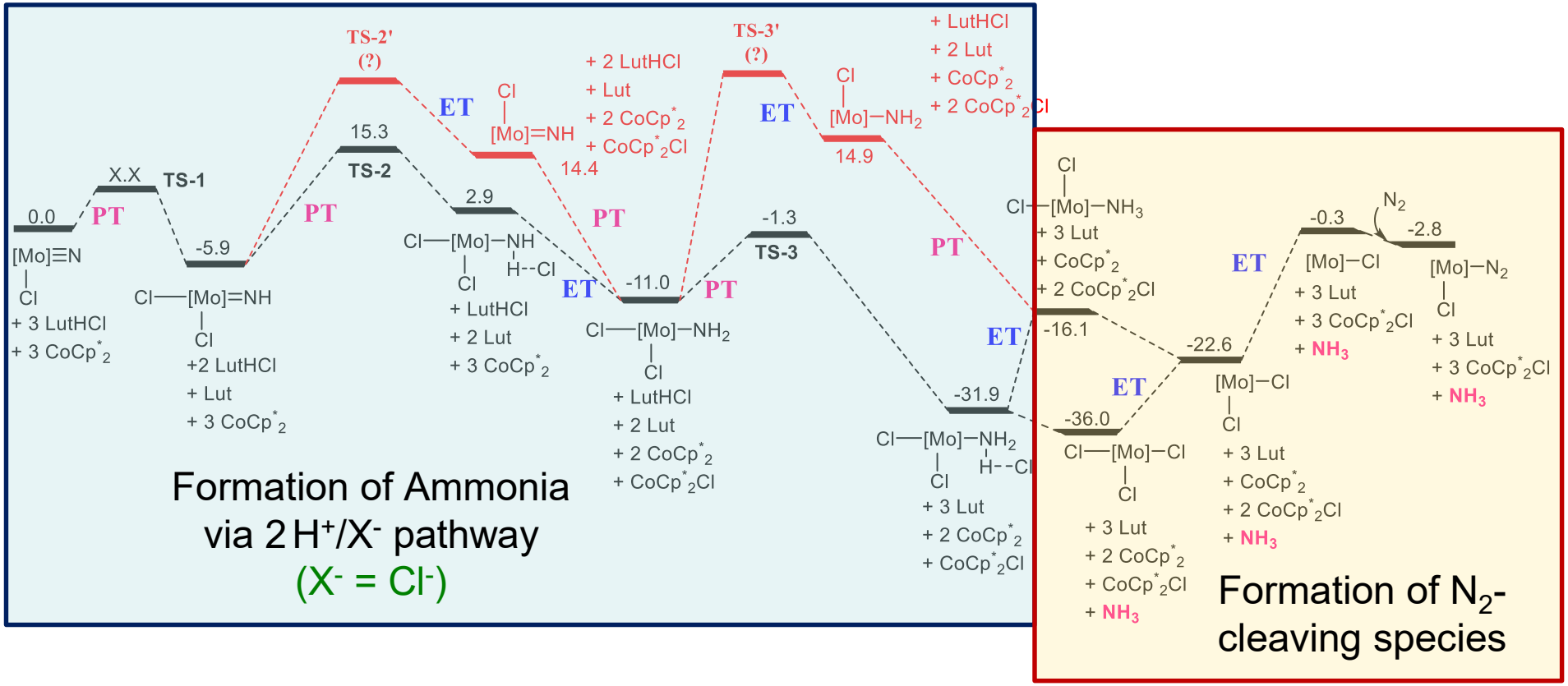
2 H^+ and 1 Cl^- followed by 1 e^- reduction and then another H^+ generate ammonia and the trihalide complex



Lindley, B. M.; Bruch, Q. J.; White, P. S.; Hasanayn, F.; Miller, A. J. M. *J. Am. Chem. Soc.* **2017**, *139*, 5305.

Calculated pathway for nitride protonation to give NH_3: X^- = Cl^-



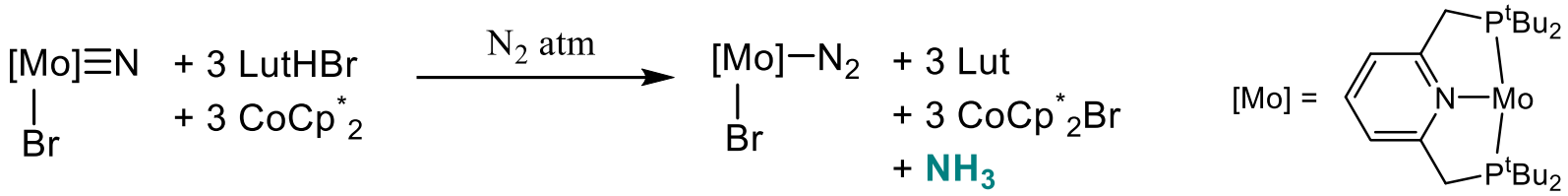


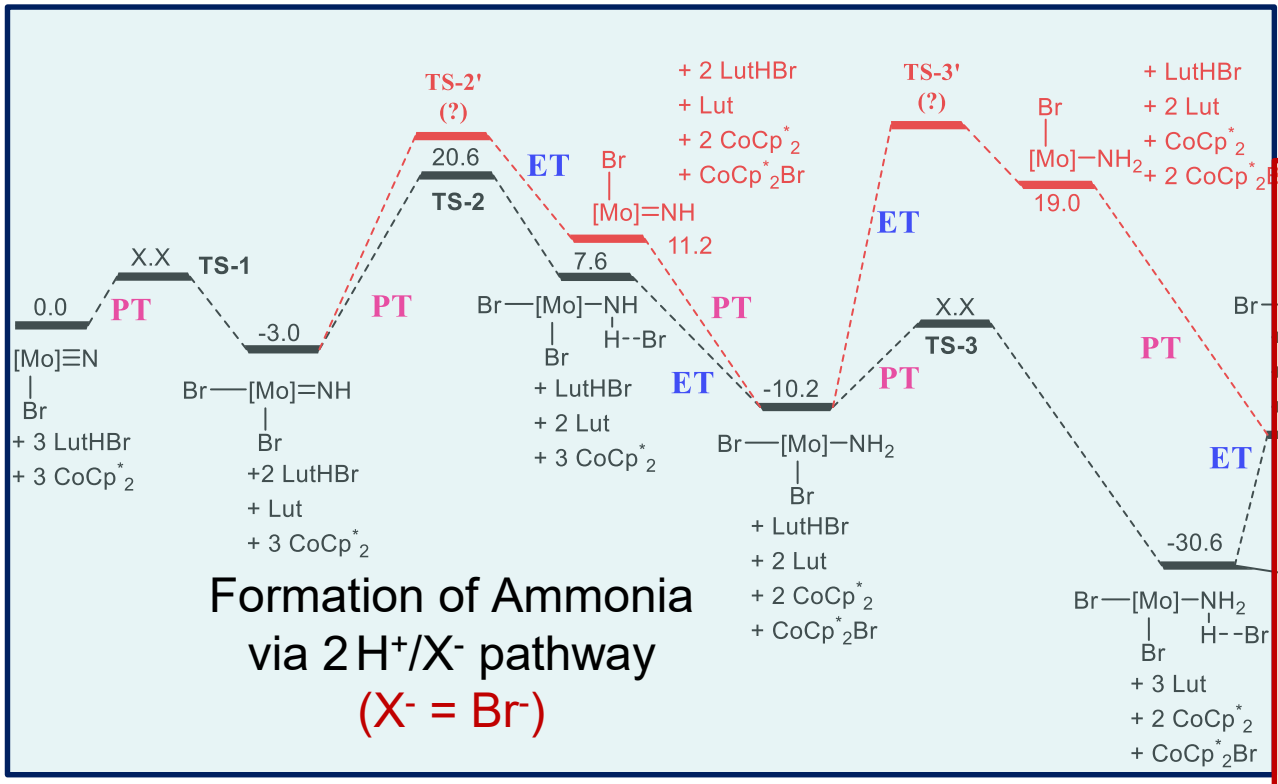
Proposed pathway
Minimum energy pathway

Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Calculated pathway for nitride protonation to give NH_3: X^- = Br^-





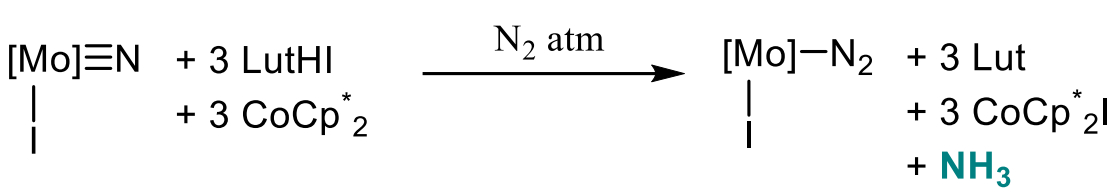
Proposed pathway

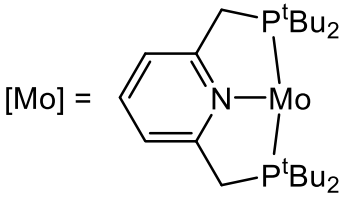
Minimum energy pathway

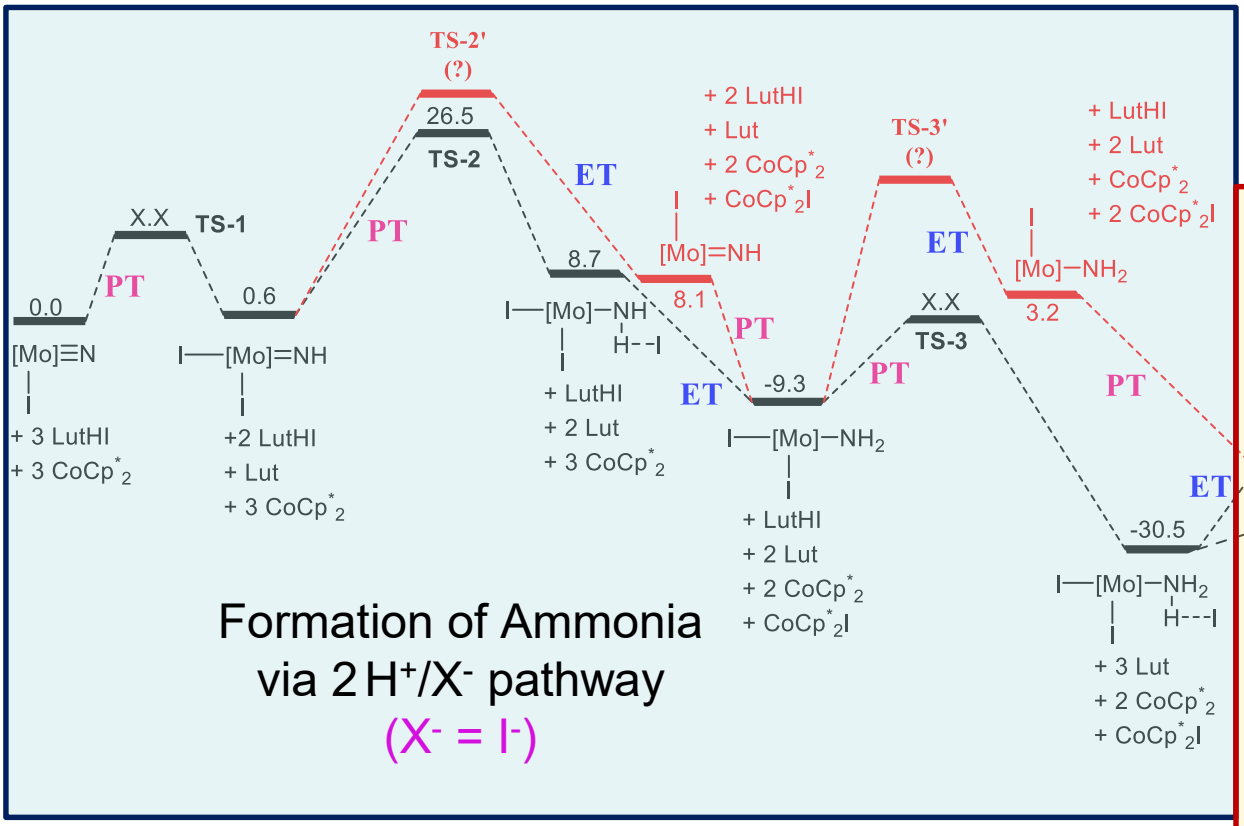
Gibbs free energies in kcal/mol

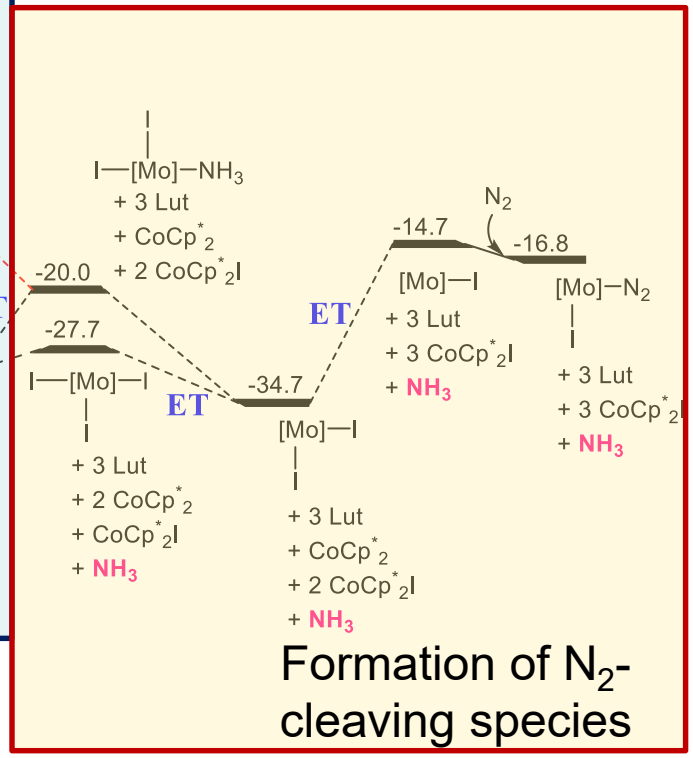
Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Calculated pathway for nitride protonation to give NH_3: X^- = I^-









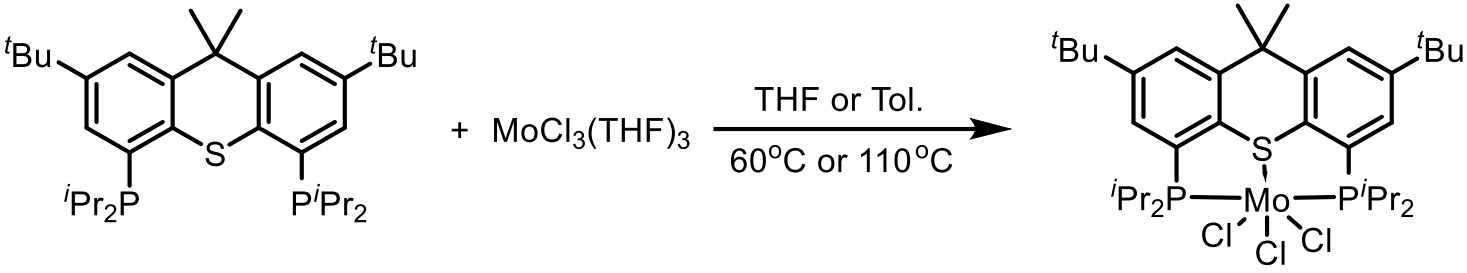
Proposed pathway

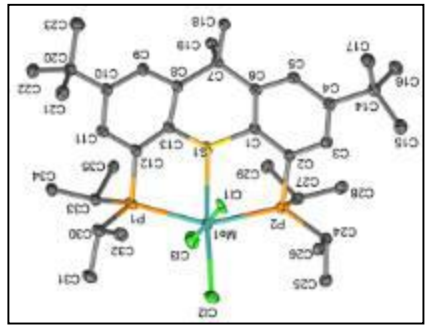
Minimum energy pathway

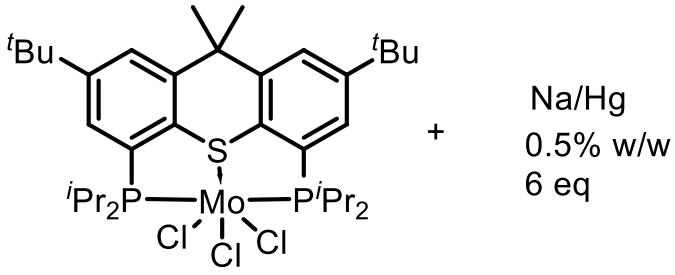
Gibbs free energies in kcal/mol

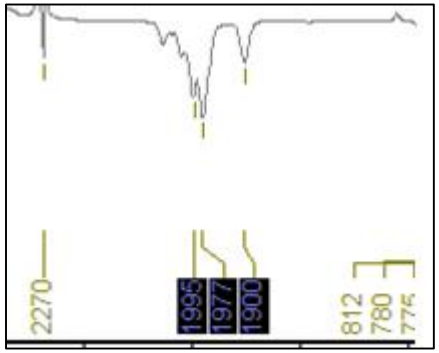
Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

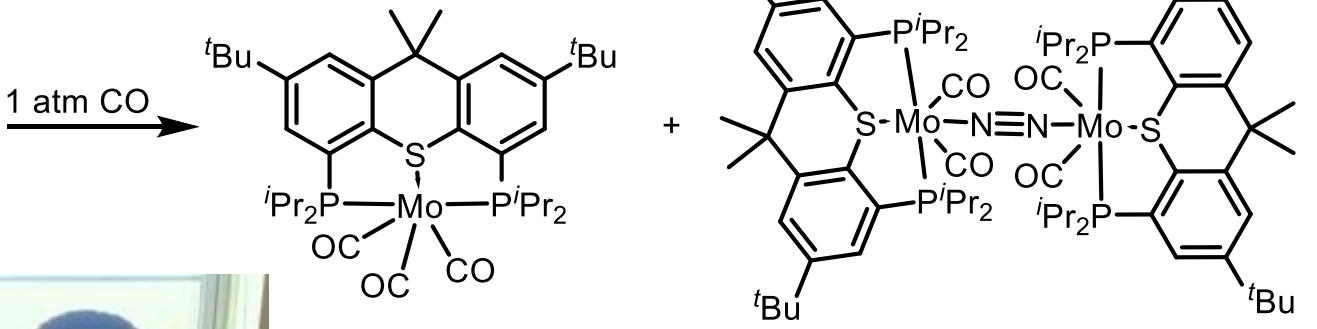
New pincer-Mo catalyst for N_2 Reduction: (PSP)Mo

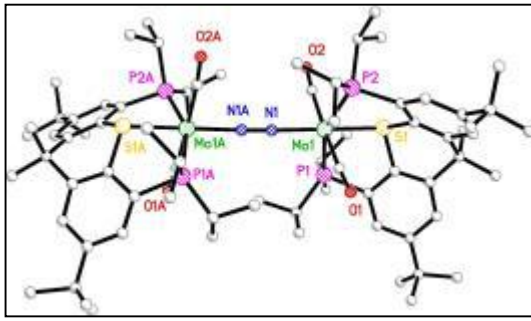






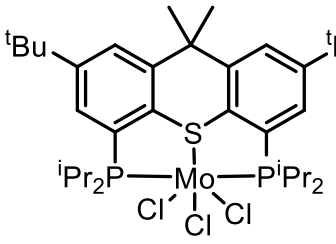






Experiments done by Xiaoguang Zhou

Investigations of N_2 Reduction by (PSP)Mo: Key Intermediates



+ NaI 2 eq + Na/Hg 2 eq

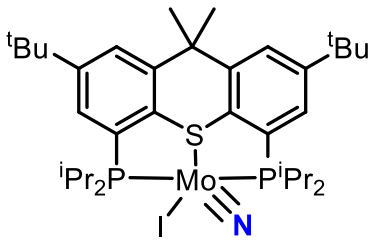
N_2

rt, THF

-NaCl

-NaI

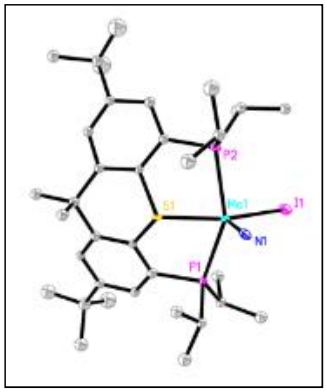
-Hg^0

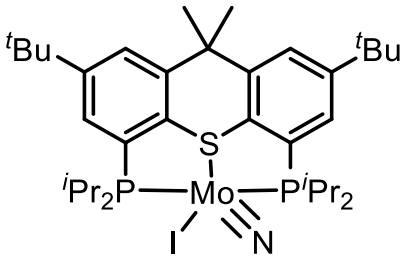


^{15}N NMR: s, 446 ppm

(CH_3NO_2 as standard)

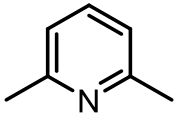
^{31}P NMR: s, 80.4 ppm





^{31}P NMR: 80.4 ppm

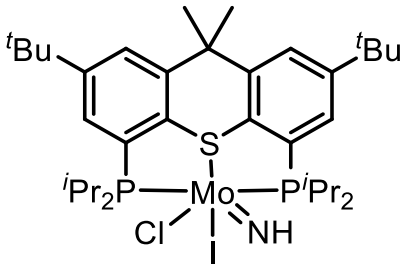
+

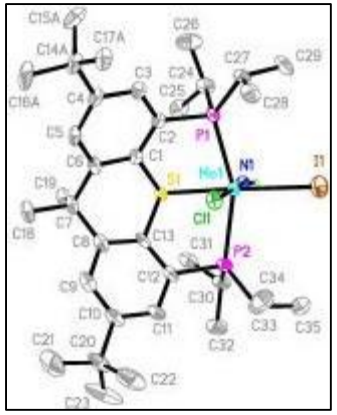


3eq or 5 eq

C_6D_6

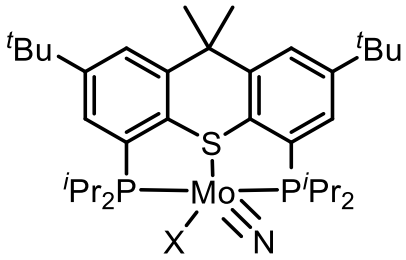
rt





3 eq or 5 eq

Cp_2Co



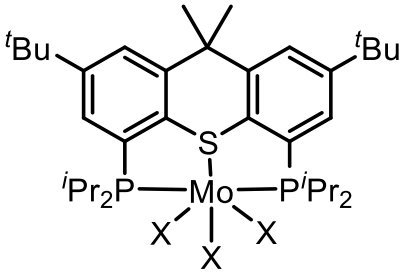
^{31}P NMR: 80.6 ppm

+ Cp_2Co

Excess ^{t}BuONa

-^{t}BuOH

-NaX



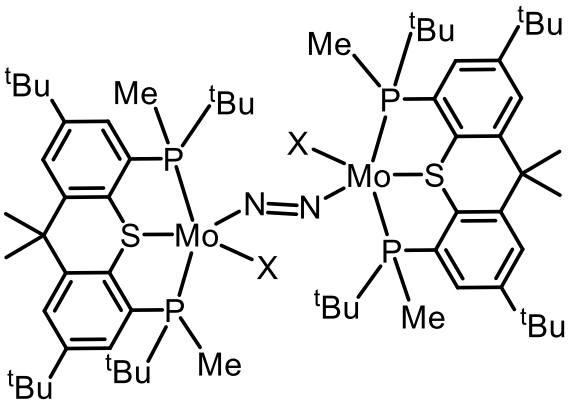
+ $Cp_2Co^+X^-$

+ NH_3

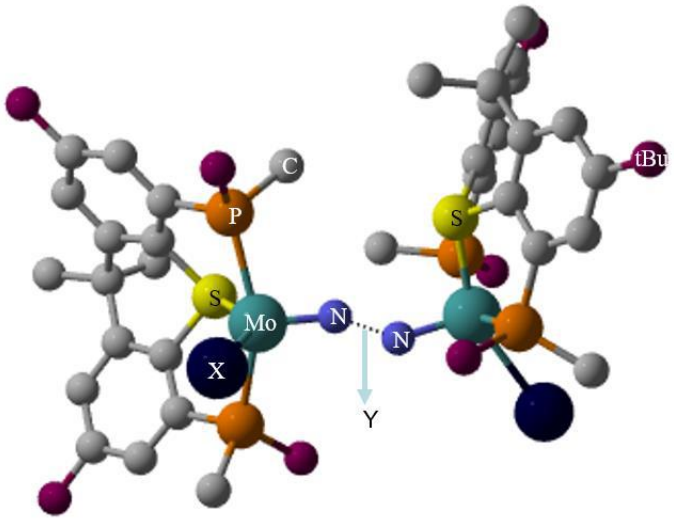
Experiments done by Xiaoguang Zhou

Nitrogen Splitting by (PSP)Mo: Effect of Anion

Level of theory: M06/SDD/6-31G(d,p)

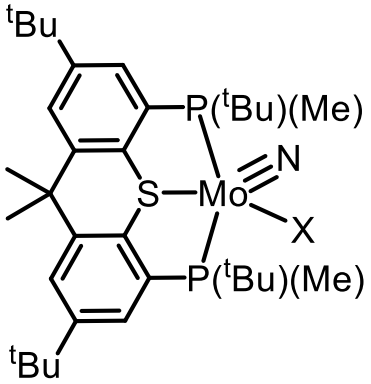


Dimer



TS

2



Nitride

X	Free Energies (*in* kcal/mol)
Cl^-	Dimer (0.0)
	TS (14.1)
	Nitride (-43.0)
Br^-	Dimer (0.0)
	TS (12.3)
	Nitride (-45.8)
I^-	Dimer (0.0)
	TS (10.0)
	Nitride (-44.9)

X	Y (*in* Å)
Cl^-	1.56
Br^-	1.55
I^-	1.54

Actual complex is (^{iPr4}PSP)Mo. (^{tBu2Me2}PSP)Mo used as model.[1]

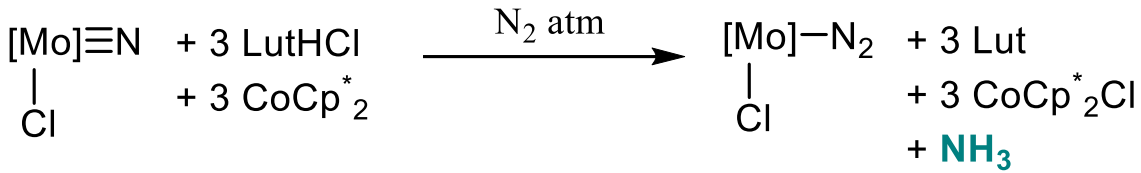
1. (a) Bezier, D.; Guan, C.; Krogh-Jespersen, K.; Goldman, A. S.; Brookhart, M. *Chem. Sci.* **2016**, *7*, 2579. (b) Kundu, S.; Choliy, Y.; Zhuo, G.; Ahuja, R.; Emge, T. J.; Warmuth, R.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *Organometallics* **2009**, *28*, 5432

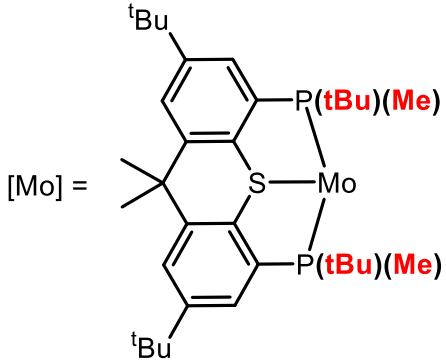
Barrier to nitrogen splitting : I^- < Br^- < Cl^-

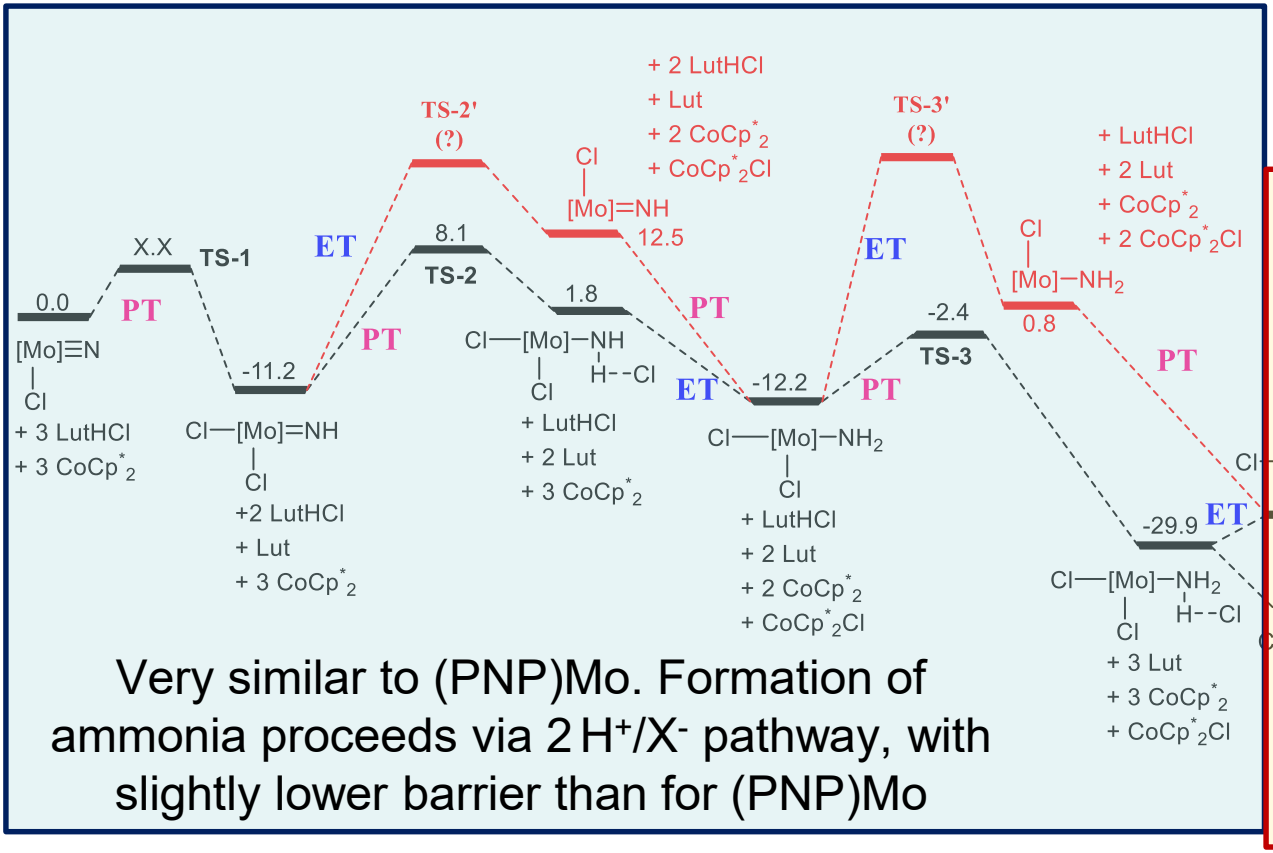
Gibbs free energies in kcal/mol

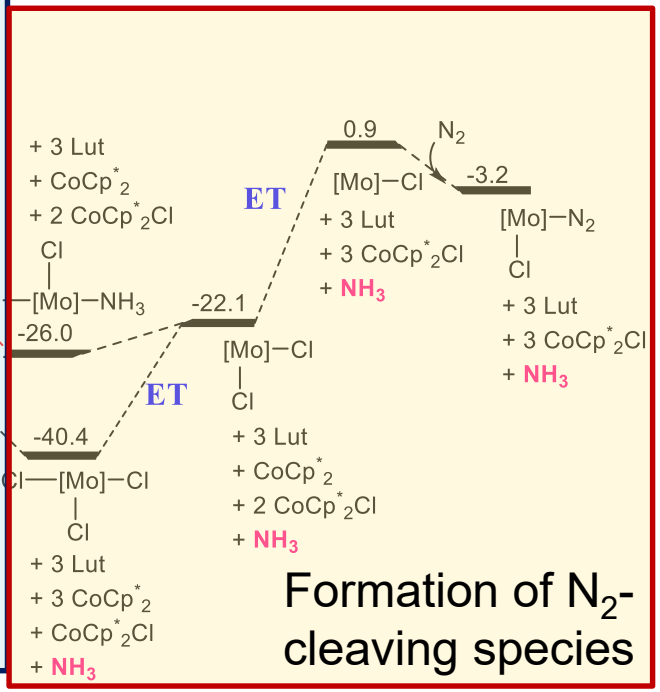
Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Nitride protonation to give NH_3 with (PSP)Mo. ($X^- = Cl^-$)





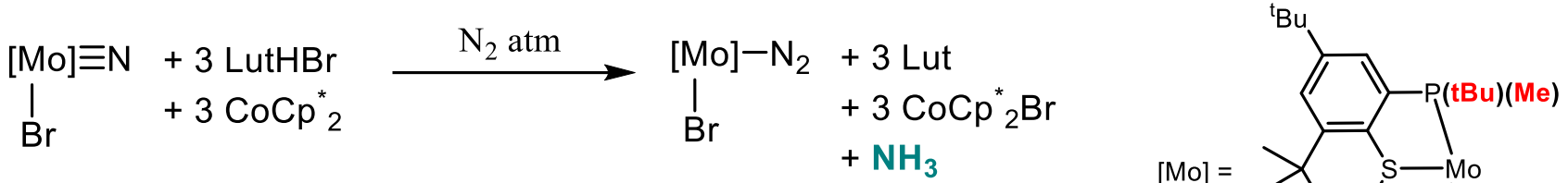


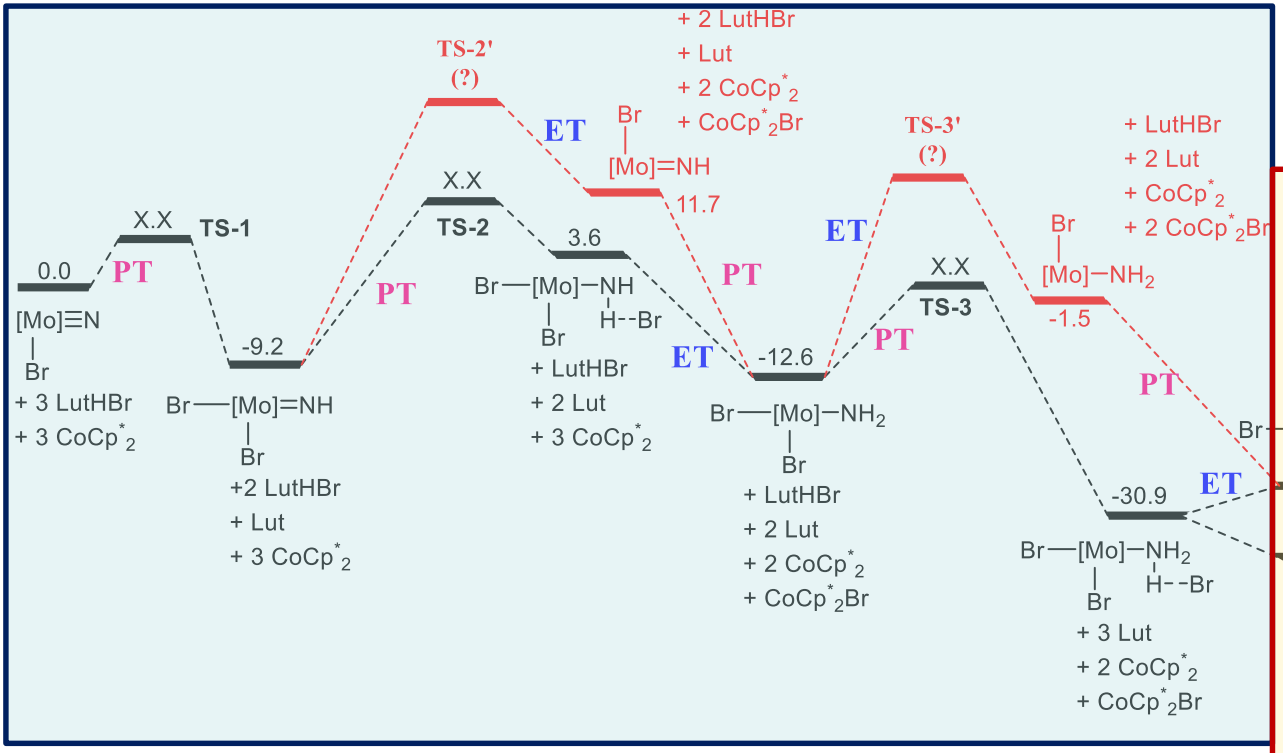


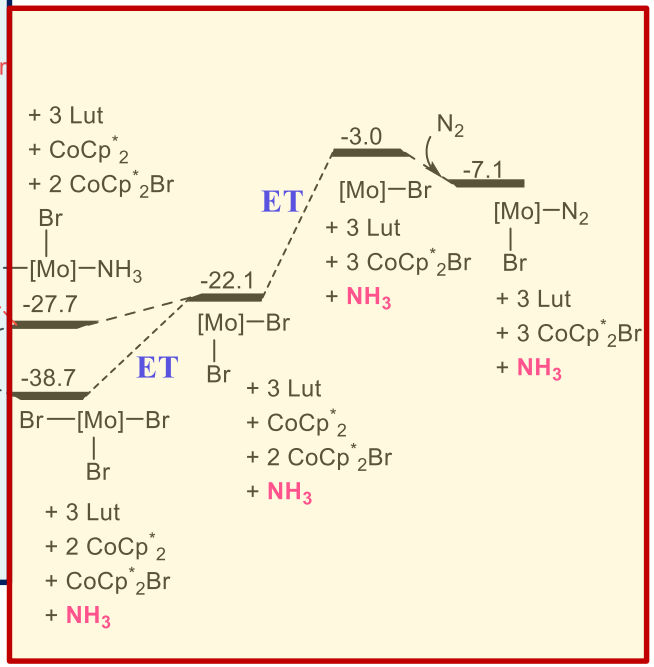
Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Nitride protonation to give NH_3 with (PSP)Mo. ($X^- = Br^-$)





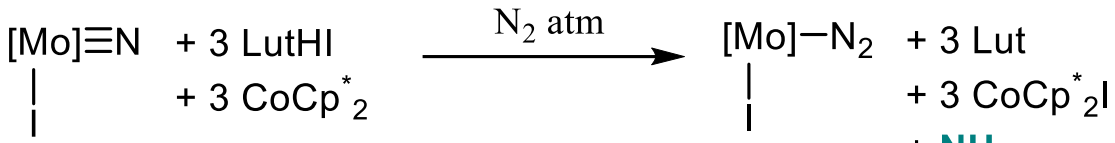


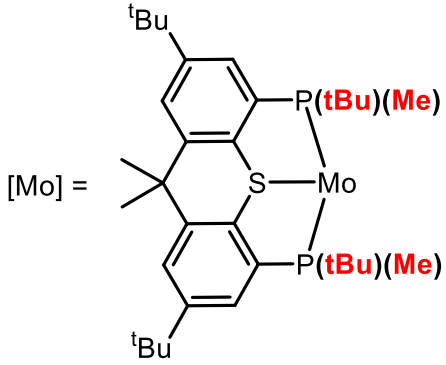
Proposed pathway
Minimum energy pathway

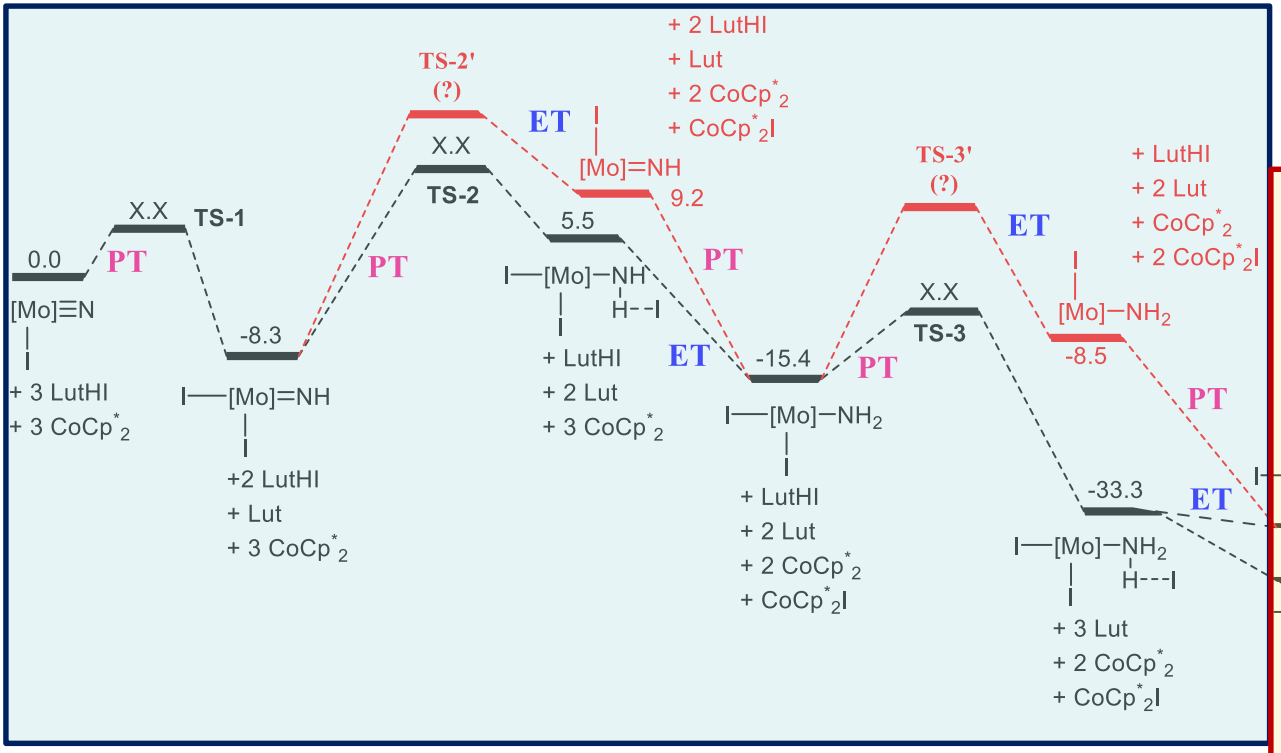
Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Nitride protonation to give NH_3 with (PSP)Mo. ($X^- = I^-$)







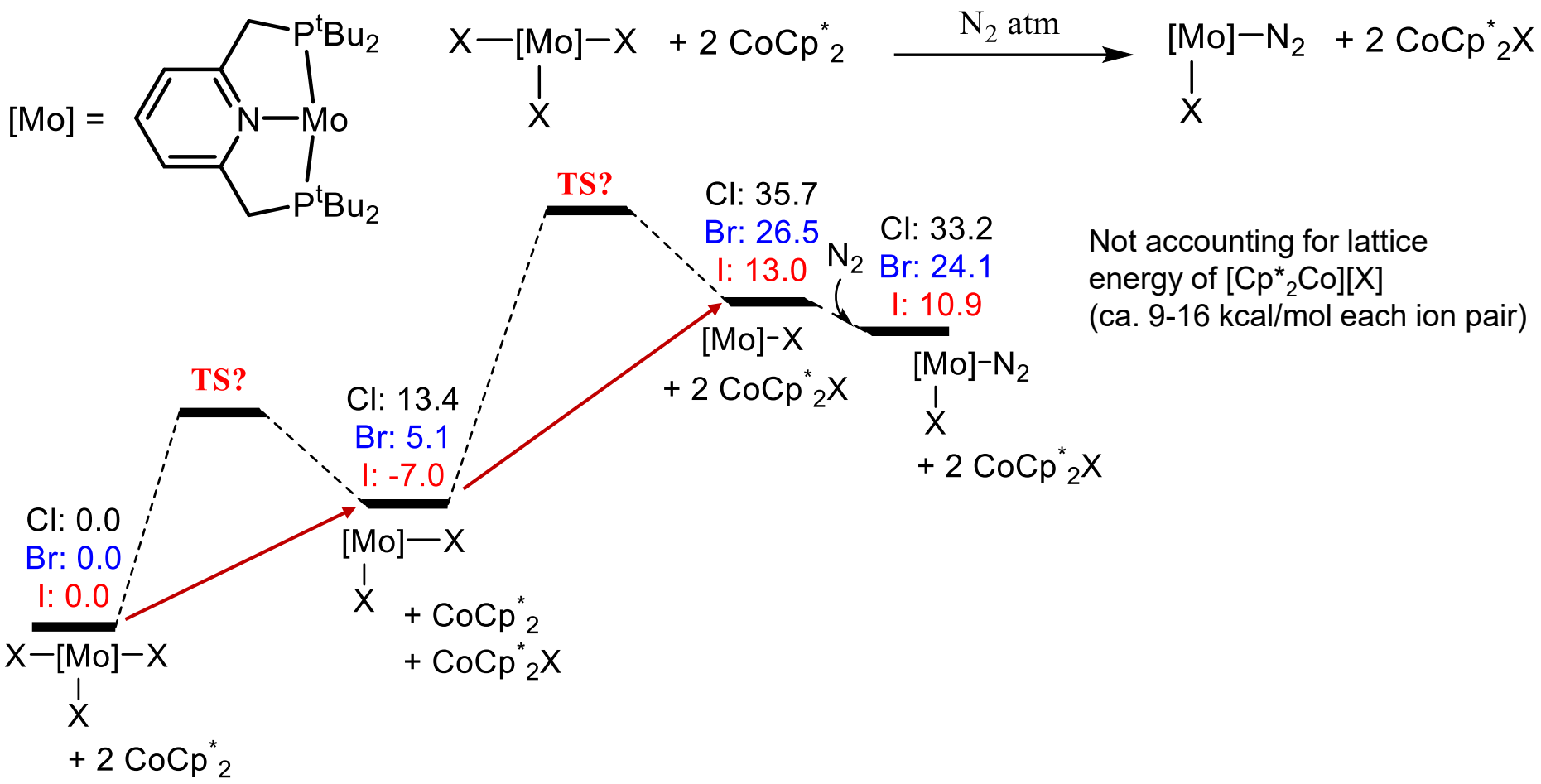
Proposed pathway

Minimum energy pathway

Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

(^{tBu}PNP)MoX_3: Reduction to give N_2 complex



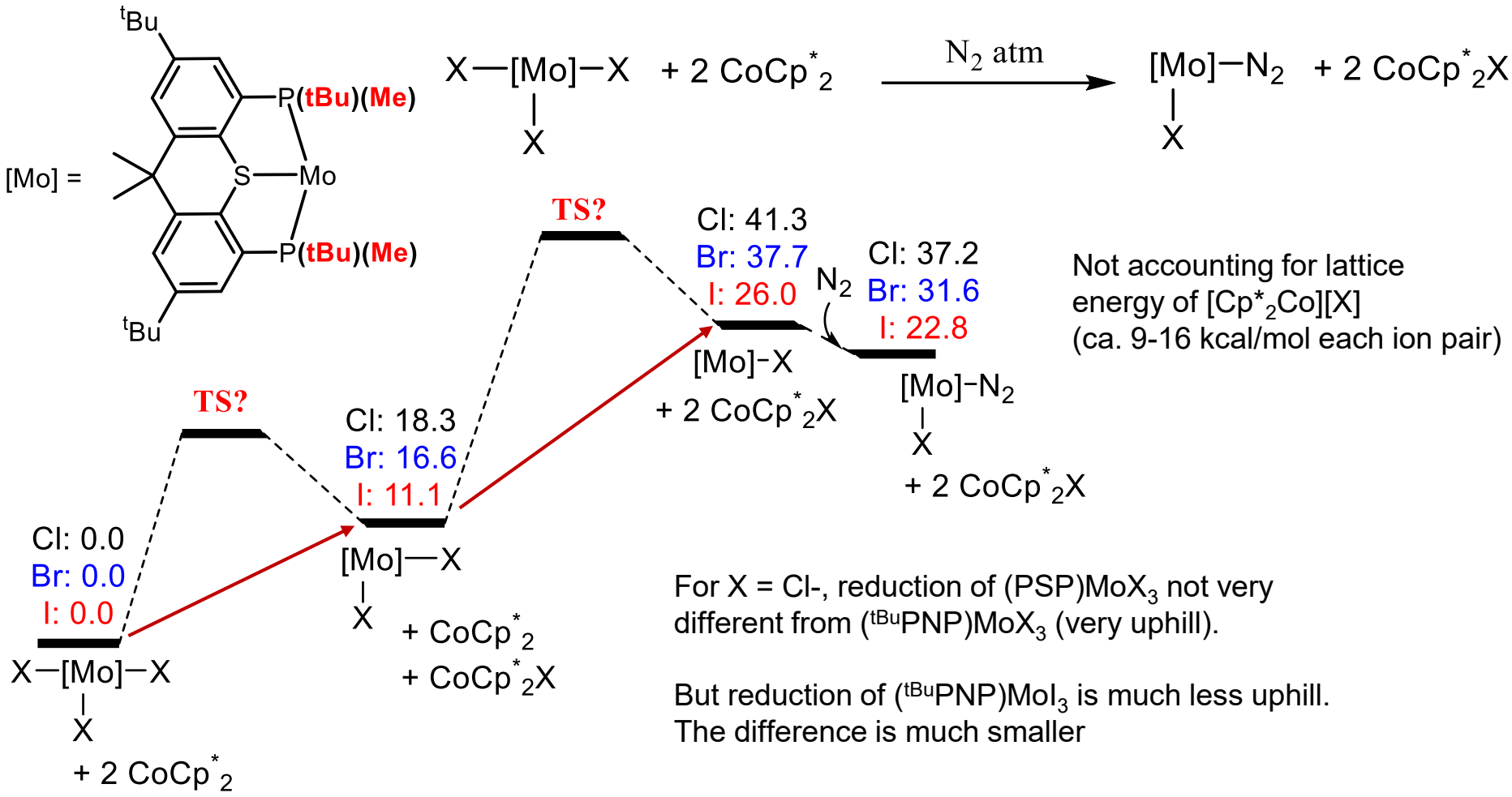
Not accounting for lattice energy of [Cp*$_2$Co][X] (ca. 9-16 kcal/mol each ion pair)

	Chloride		Bromide		Iodide	
	1e$^-$ redn.	2e- redn.	1e$^-$ redn.	2e- redn.	1e$^-$ redn.	2e- redn.
(^{tBu}PNP)MoX_3	13.4	35.7	5.1	26.5	-7.0	13.0

Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

(PSP)MoX_3: Reduction to give N_2 complex



Not accounting for lattice energy of $[Cp^*_2Co][X]$ (ca. 9-16 kcal/mol each ion pair)

For X = Cl-, reduction of (PSP)MoX_3 not very different from (^{tBu}PNP)MoX_3 (very uphill).

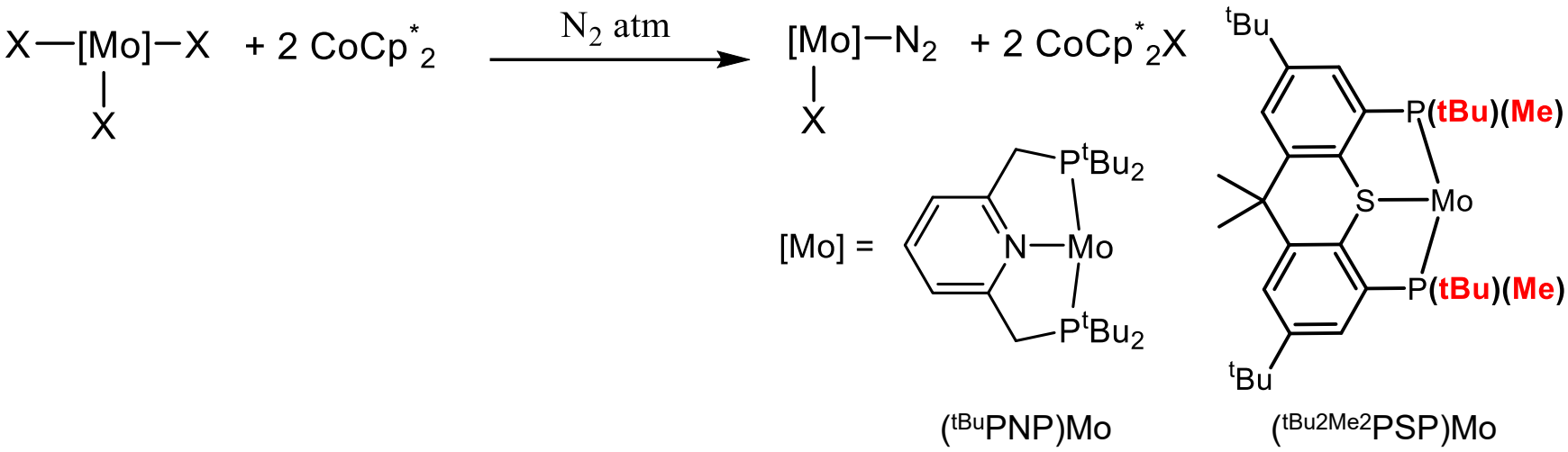
But reduction of (^{tBu}PNP)MoI_3 is much less uphill. The difference is much smaller

	Chloride		Bromide		Iodide	
	1e- redn.	2e- redn.	1e- redn.	2e- redn.	1e- redn.	2e- redn.
(^{tBu2Me2}PSP)MoX_3	18.3	41.3	16.6	35.7	11.1	22.8

Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Reduction to give N_2 complex: $^{tBu\text{-}Me}$PSP vs ^{tBu}PNP



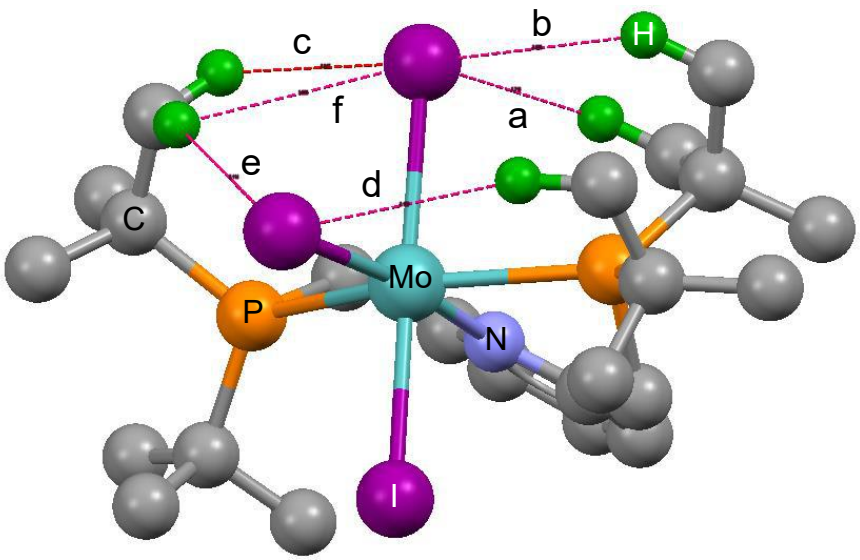
	Chloride		Bromide		Iodide	
	1e- redn.	2e- redn.	1e- redn.	2e- redn.	1e- redn.	2e- redn.
(^{tBu}PNP)MoX$_3$	13.4	35.7	5.1	26.5	-7.0	13.0
(^{tBu2Me2}PSP)MoX$_3$	18.3	41.3	16.6	35.7	11.1	22.8

No clear trend between (^{tBu2Me2}PSP) and (^{tBu}PNP)
Underlying structural features?

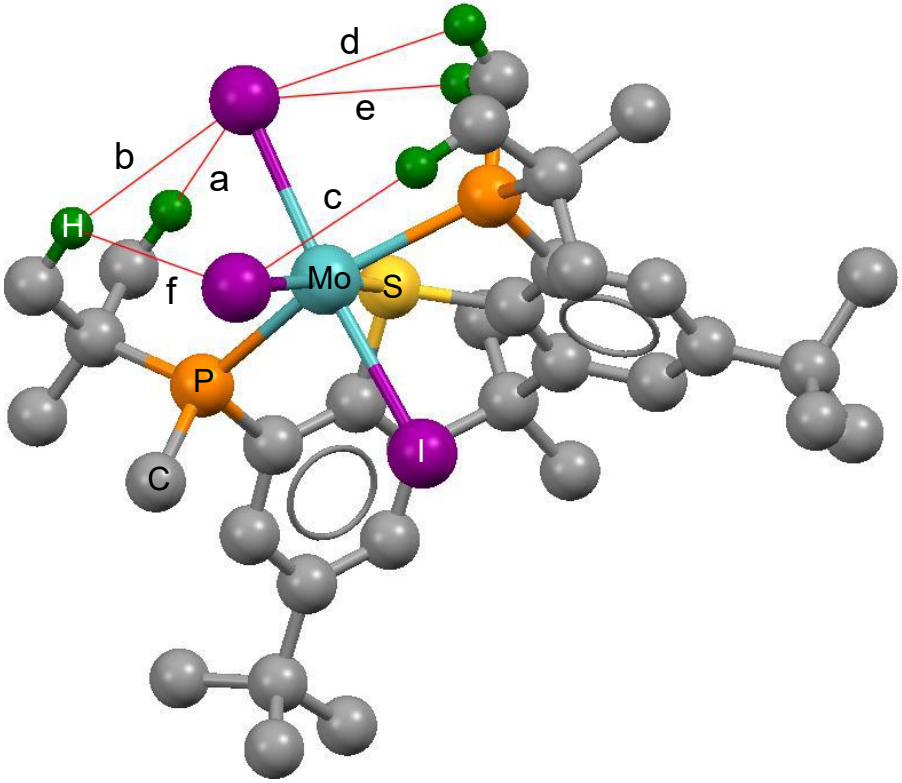
Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Structural Features of (PXP)Mo^{III} Tri-Iodides: Interactions



C_2 symmetric : 2x interactions



Comparison of similar intramolecular interactions

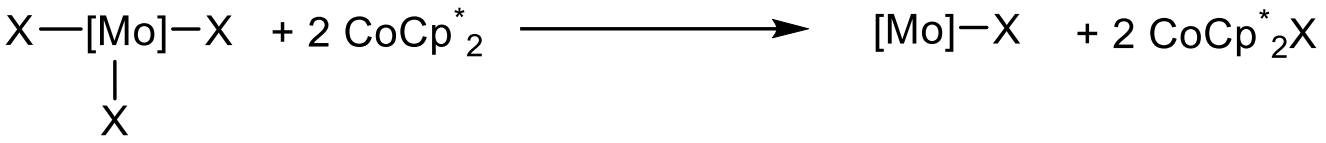
	a	b	c	d	e	f
^{tBu}PNP	2.71	2.85	3.03	3.15	3.11	3.22
^{tBu2Me2}PSP	2.93	3.03	3.06	3.28	3.30	3.92

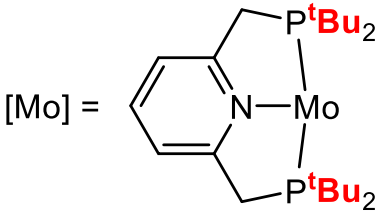
Is the steric crowding of (PNP)MoI$_3$ responsible for its energetic favorability for reduction?

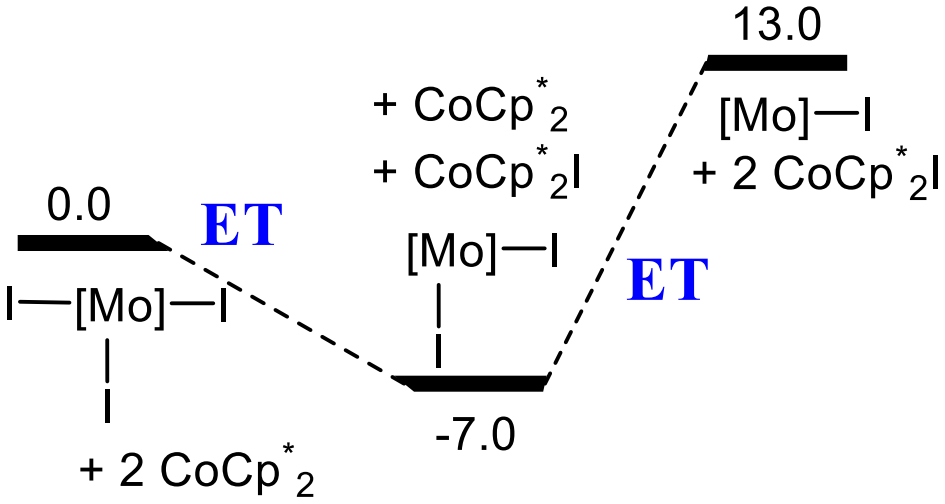
Gibbs free energies in kcal/mol

Level of theory: SMD$_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Quantifying the Steric Effect of tBu-groups (?)

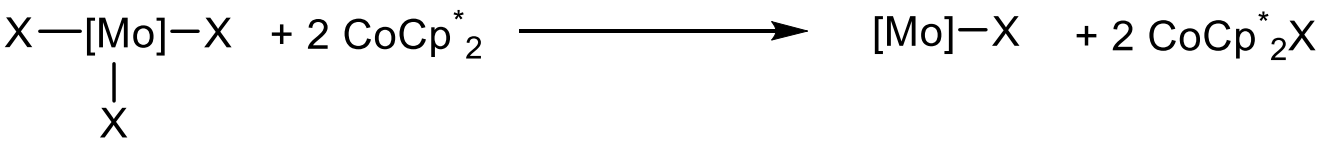


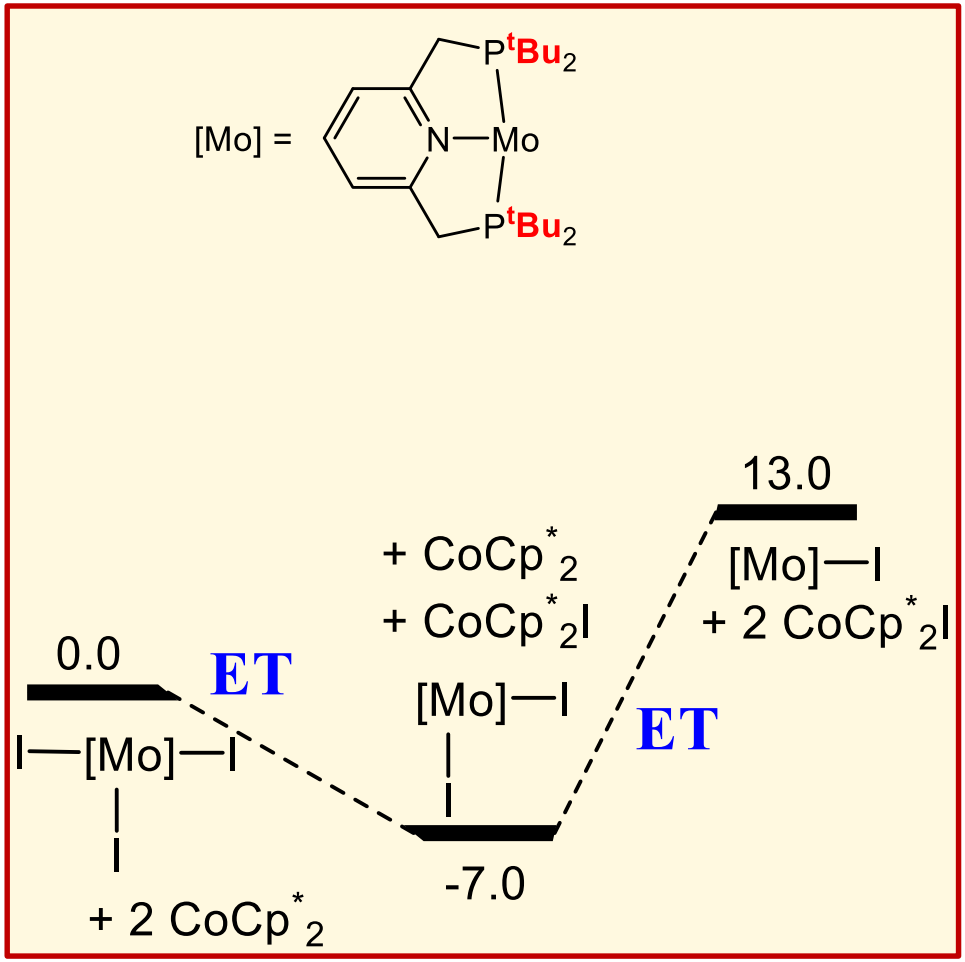


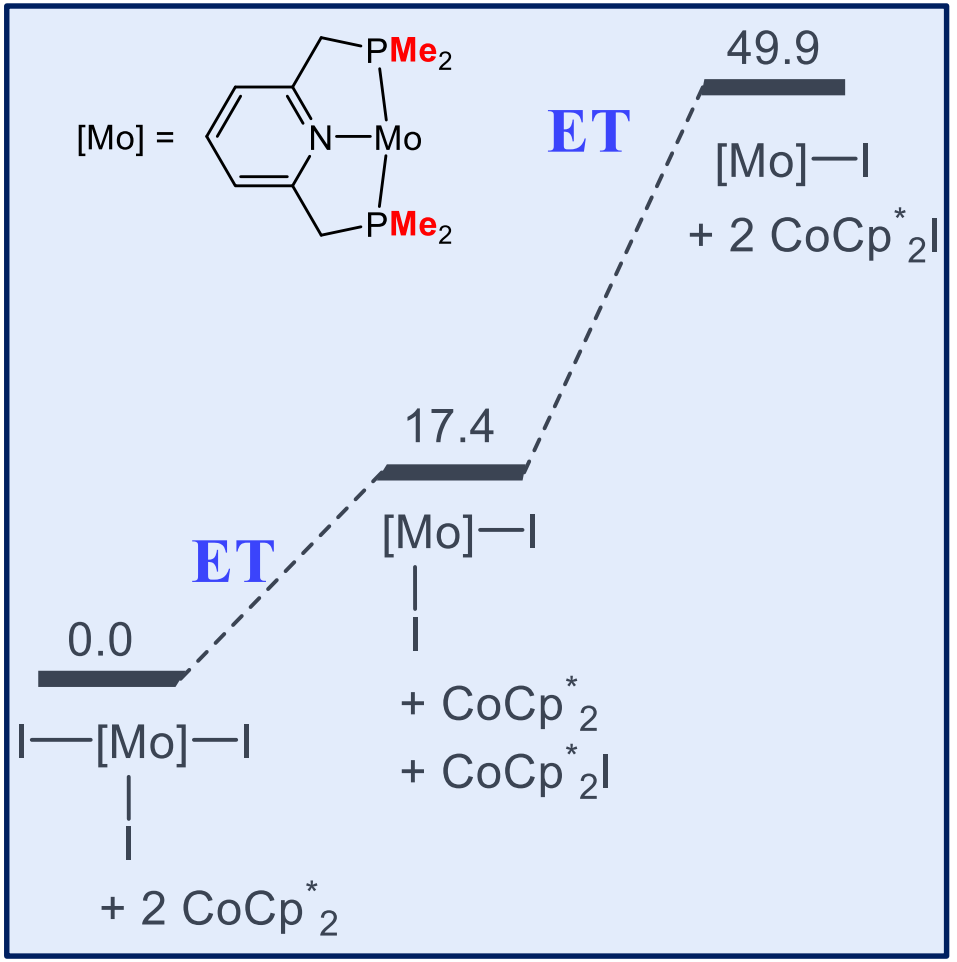


If the ^{t}Bu groups are indeed responsible for aiding the dissociation of halides from metal coordination sphere, reducing crowding should significantly change the reaction energetics

Quantifying the Steric Effect of tBu-groups



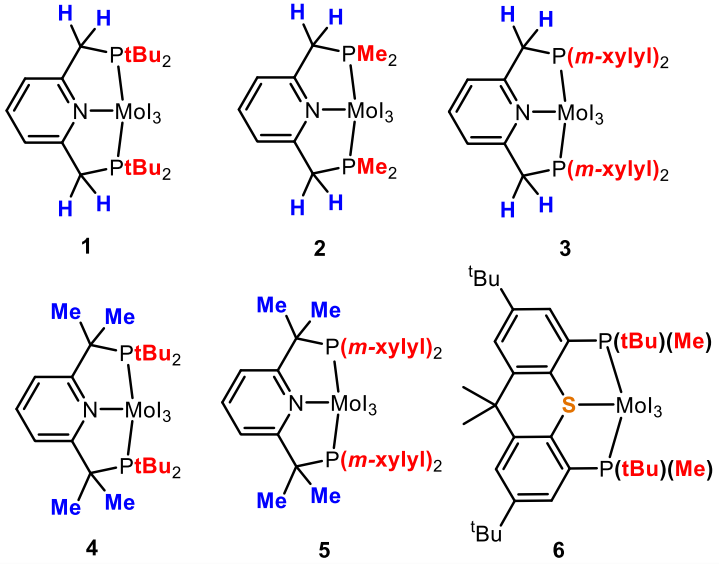




Gibbs free energies in kcal/mol

Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

(PXP)Mo^{III} Tri-Iodides: True Steric Effect (?)

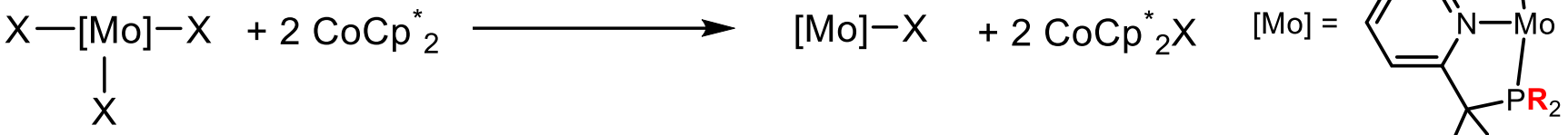


- Shorter Mo-P bond lengths for less bulky substituents on PNP for tri-iodides
- Similar Mo-P bond lengths for mono-iodides irrespective of bulk
- Similarity in bond lengths (e.g. Mo-P) of (^{Me}PNP)Mo^{I}I and ($^{m\text{-xylyl}}$PNP)Mo^{I}I indicates that differences in the analogous bond lengths of the *tri*-iodides is steric based

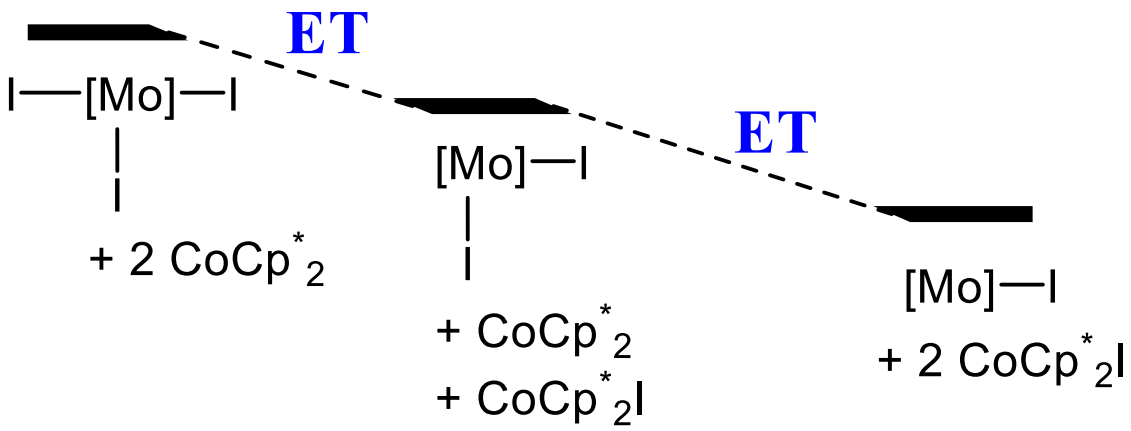
Level of theory: $SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)

Bond Length (*in Å*)	(PXP)Mo^{III}I$_3$			(PXP)Mo^{I}I		
	Mo-P	Mo-I	Mo-N or Mo-S	Mo-P	Mo-I	Mo-N or Mo-S
^{tBu}PNP (1)	2.67	2.85	2.25	2.49	2.82	2.17
^{Me}PNP (2)	2.51	2.81	2.28	2.47	2.79	2.19
$^{m\text{-xylyl}}$PNP (3)	2.70	2.84	2.26	2.46	2.79	2.21
^{tBu}P^{Me}N^{Me}P (4)	2.72	2.87	2.34	2.52	2.84	2.14
$^{m\text{-xylyl}}$P^{Me}N^{Me}P (5)	2.78	2.86	2.32	2.56	2.83	2.13
^{tBu2Me2}PSP (6)	2.58	2.82	2.55	2.47	2.79	2.35

Catalyst Design: Harnessing the Steric Effect

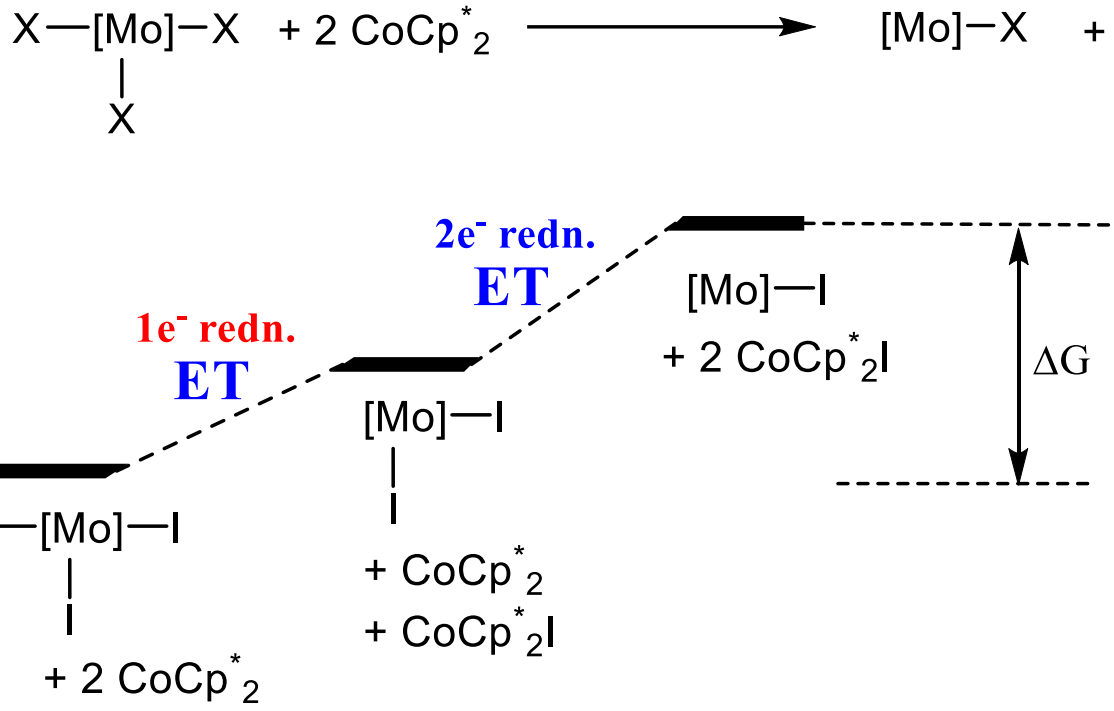


Ideal/Target Shape of Potential Energy Surface



Can we favor the energetics by increasing steric crowding?

Catalyst Design: Harnessing the Steric Effect



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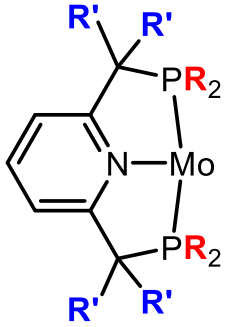
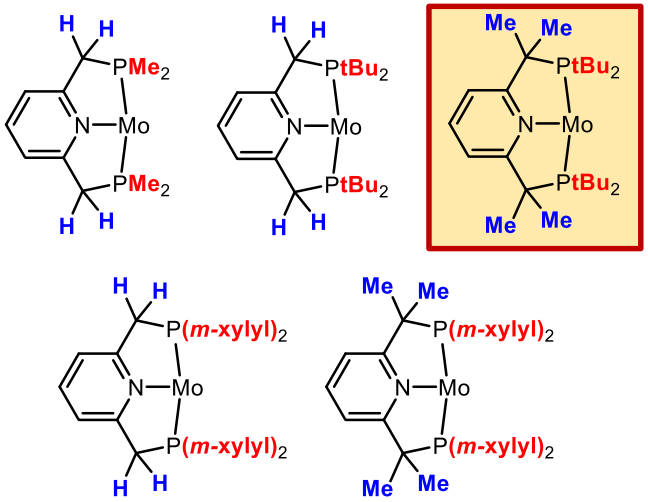




More crowding in tri-iodides : Easier halide dissociation and easier reduction

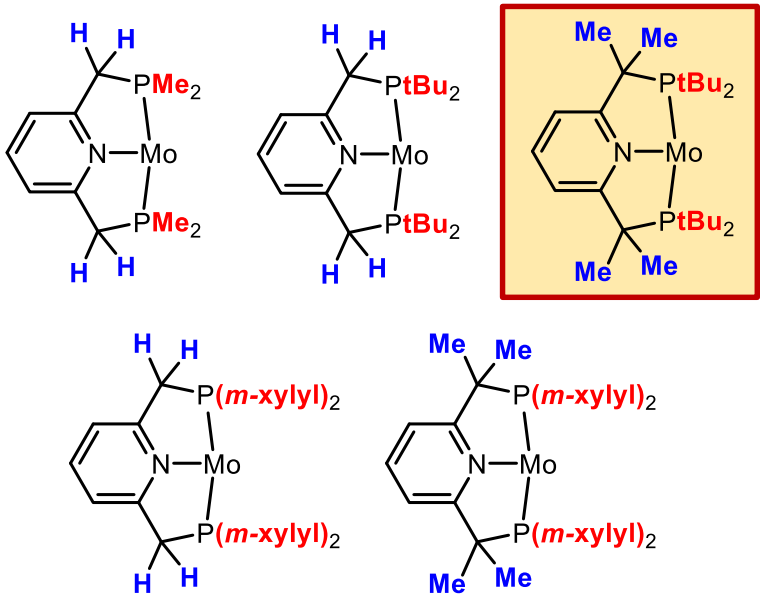
R	R'	ΔG (kcal/mol)
tBu	H	28.1 (*13.0*)
Me	H	60.5 (*49.9*)
2,6-dimethyl phenyl	H	19.7 (*4.8*)
tBu	Me	4.5 (*-8.5*)
2,6-dimethyl phenyl	Me	-2.8 (*X.X*)

Gibbs free energies in kcal/mol

Level of theory: M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)[$SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)]

Concluding the Mechanistic Insights from DFT Study

- Unanticipated proton/electron addition mechanism calculated for nitride protonation/Mo reduction
- Effect of the nature of halides determined for N_2-splitting transition states for (PSP)Mo complexes
- Rate-determining step appears to be reduction of Mo(III)X_3, subsequent to the more facile cleavage of N_2 and nitride protonation
- In the case of (^{tBu}PNP)MoI$_3$ (Nishibayashi's catalyst) steric crowding greatly favors the energetics of reduction and regeneration of the Mo^{I} active species
- Harnessing the steric effect to design better catalysts: Synthetic efforts underway



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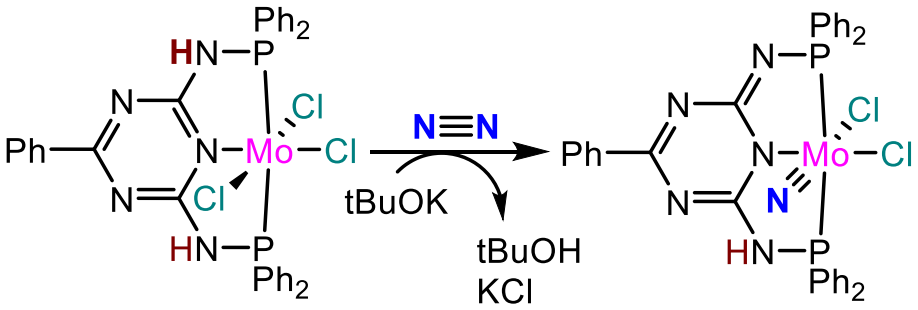
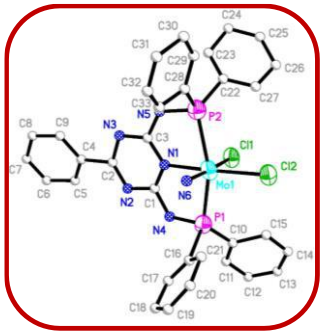
2,6-dimethyl phenyl	Me	-2.8 (*X.X*)

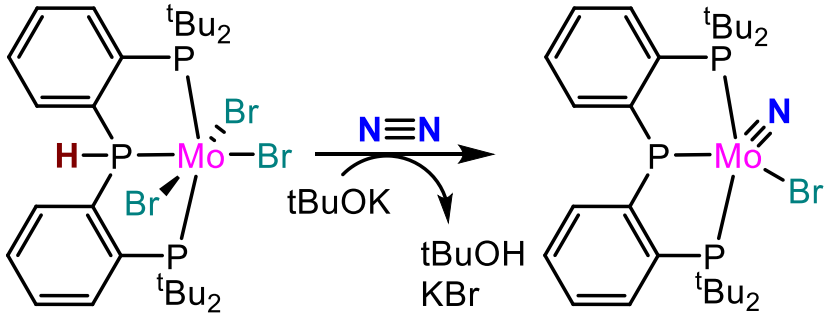
Gibbs free energies in kcal/mol

Level of theory: M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)[*$SMD_{Benzene}$/M06/Def2-QZVP//M06/6-31G(d,p)(Light atoms)/SDD(Mo,Co)*]

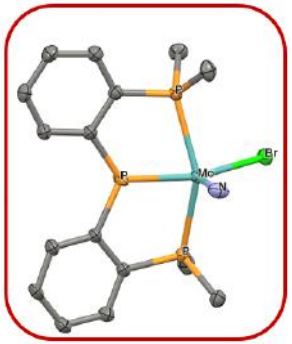
A New Paradigm in Nitrogen Splitting : Base Induced







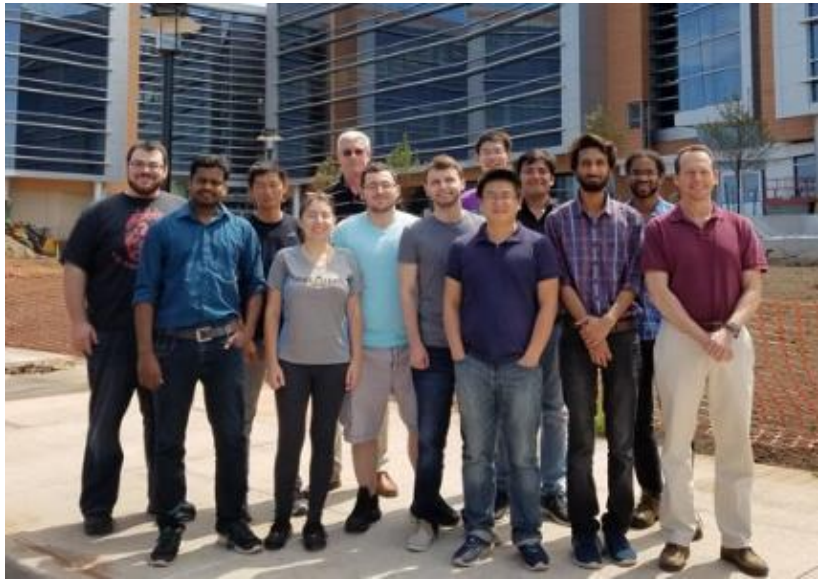
+ Mo(IV) byproduct



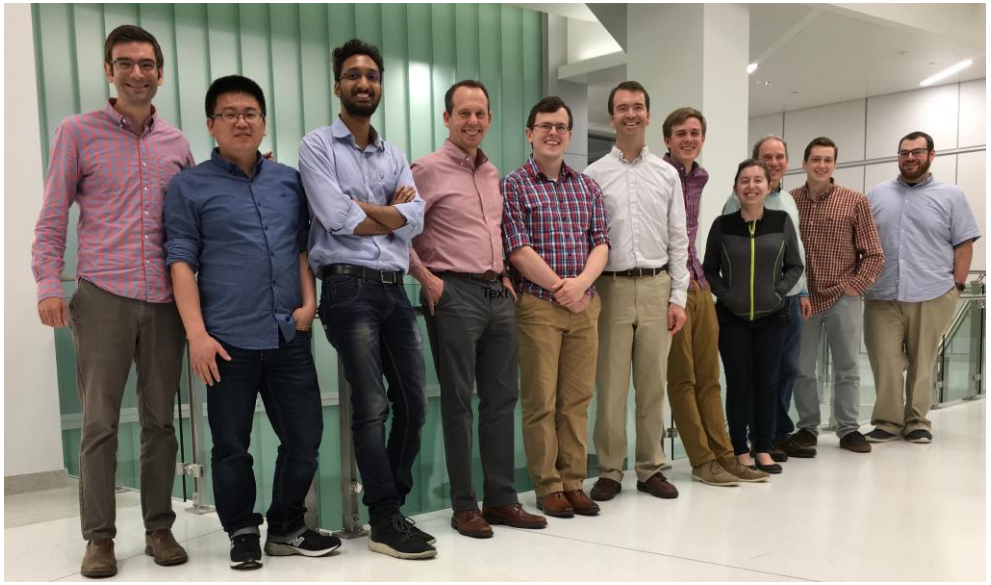
Synthetic and experimental efforts with PPP led by Benjamin Gordon

- Base induced N_2 activation for electron rich pincer molybdenum halide complexes
- No requirement for strong reductants like KC_8 or Na-Hg amalgam for nitrogen splitting

Acknowledgements



Goldman Group at Rutgers



INFEWS Collaborators at Rutgers

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- Prof. Patrick L. Holland