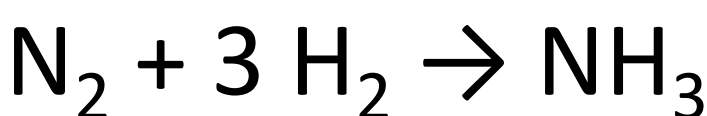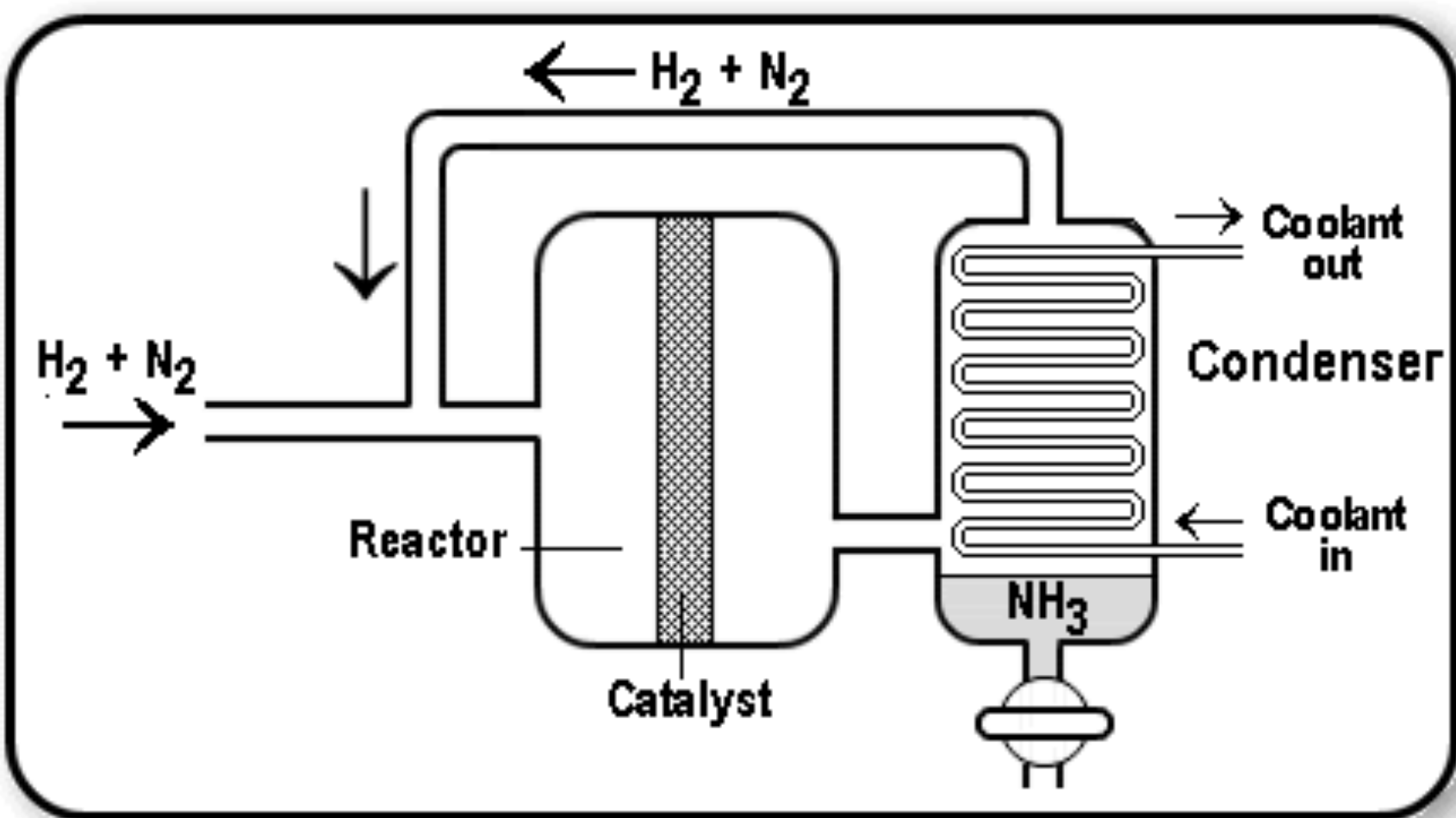# Computational Review of Pincer-Ligated Molybdenum Catalysts for Ammonia Production

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The Industrial Haber Process


$$N_2 + 3 H_2 \rightarrow NH_3$$

The method of choice for modern day Ammonia production is the Haber-Bosch Process (A brief overview is shown above). The process generally makes use a vanadium catalyst, in addition to high temperature and pressure to push the reaction towards Ammonia. Because ammonia is used to make fertilizer which is used ubiquitously, the energy required to power the Haber-Bosch process worldwide may account for 1-2 % of the world's carbon emissions.

Pincer-Ligated Molybdenum Catalysts

In the search for alternative methods to produce Ammonia, Pincer-Ligated Transition metal catalysts have been the subject of research in the recent past. A research team based in the University of Tokyo, Japan published a paper in Nature: Chemistry on the use of these catalysts to produce ammonia from nitrogen gas, using water a proton source and samarium diiodide as a reducing agent. (pictured above are some catalysts from the literature, and the proposed mechanistic pathway for the reduction of N_2)

Further Computational Exploration

Abstract: in the previous literature, the negative ions complexed with the molybdenum catalysts have been shown to have an effect on yield and turn over rate of the reaction. Using the Gaussian software, geometry optimizations were performed on three different possible substituents besides the previously examined halides. These groups were an acetoxide, a phenyloxide, and ethoxide ions.
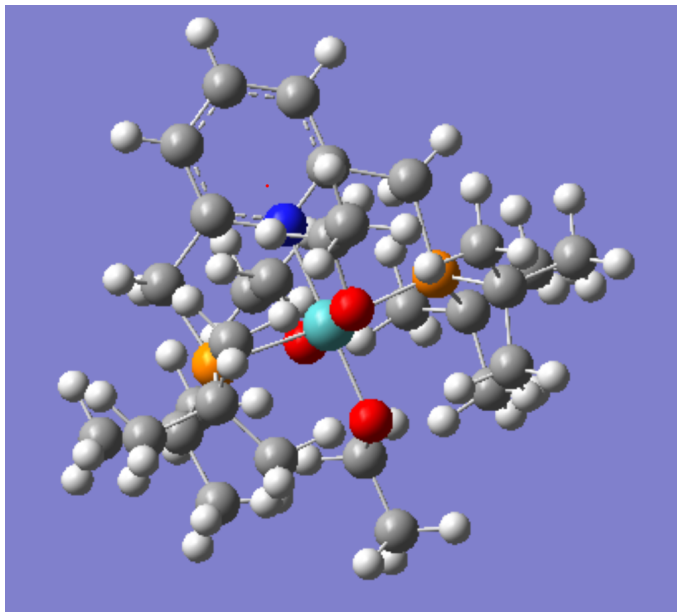
Results: (pictured below are the gaussian images of the optimized geometries):
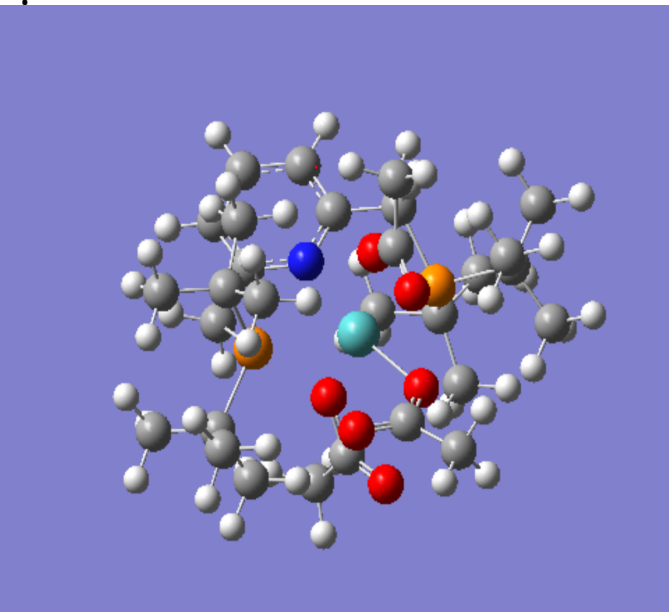
PNPMoOAc3
Ground state energy from DFT: -2392 AU
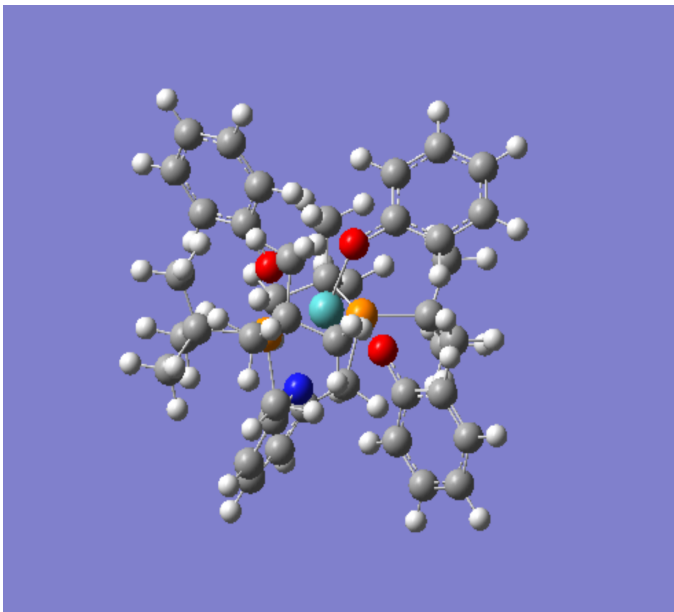
PNPMoOPh3
Ground state energy from DFT: -2627 AU

PNPMoOEt3
Ground state energy from DFT: -2170 AU

Discussion: Computational models obtained through density functional calculations, like the structures obtained here, can help to guide research into certain directions. The aim of this analysis is to begin to compile calculated results in order to better understand the catalytic activity of molybdenum in the role of nitrogen reduction into ammonia. Using these models as starting points in a theoretical catalytic reaction may help to predict the kinds of substituents that will have better yields, and may give insight into the reaction mechanism of these catalysts.

Possible reaction to examine using energies obtained via DFT:
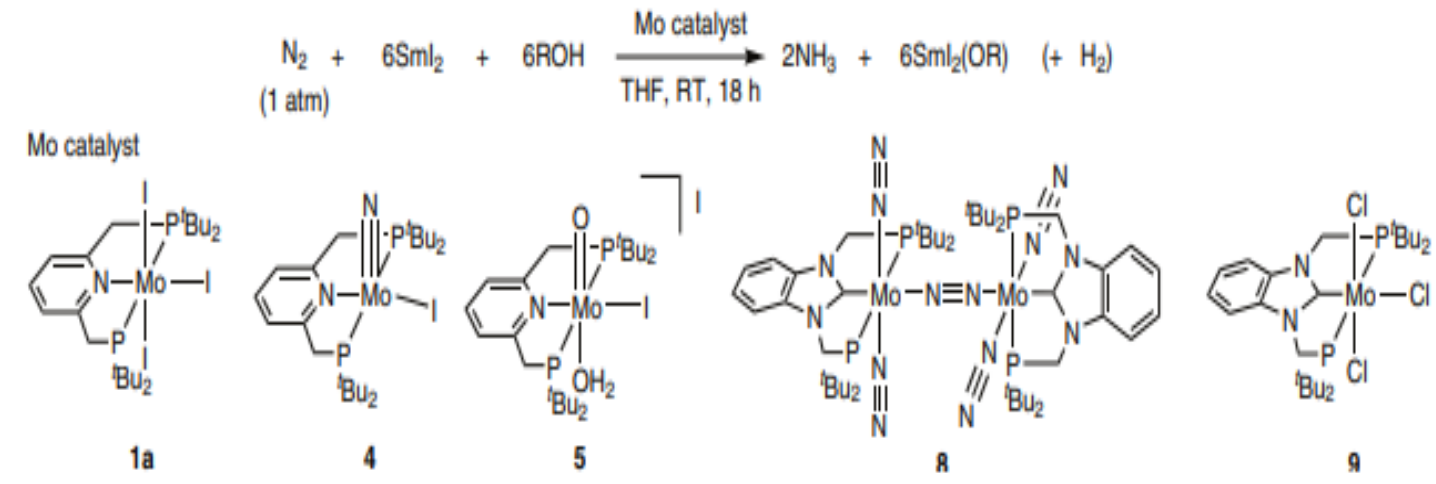
$$CoCp^* + (PNP)MoX3 + N_2 \rightarrow + (PNP)MoXN_2$$
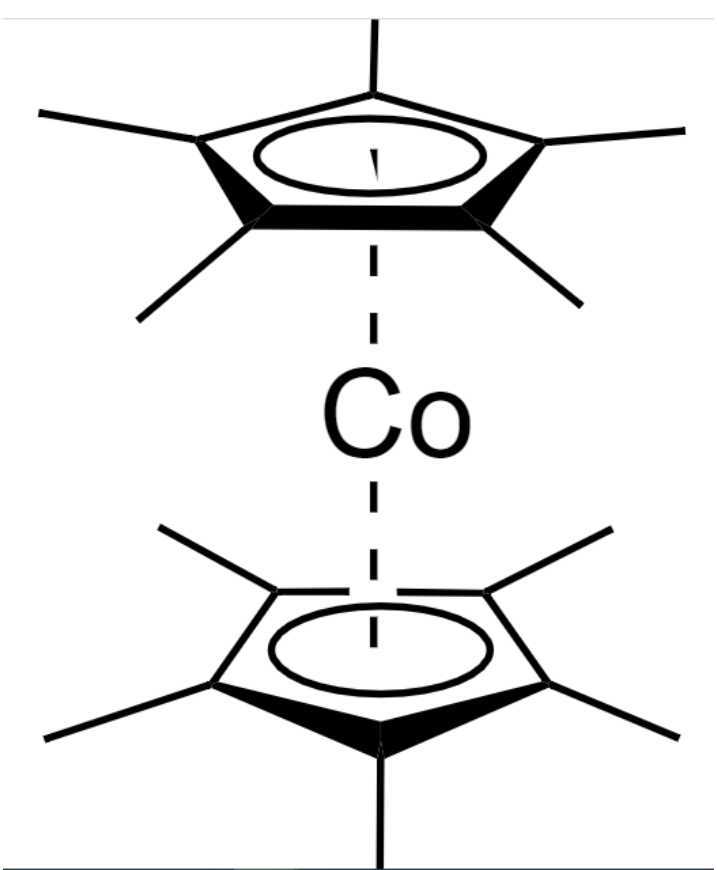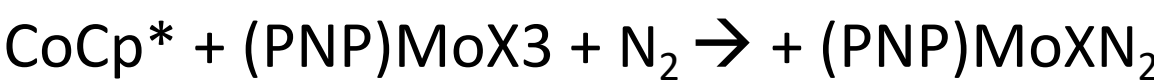
Decamethylcobaltocene (CoCp*; a literature tested reducing agent)
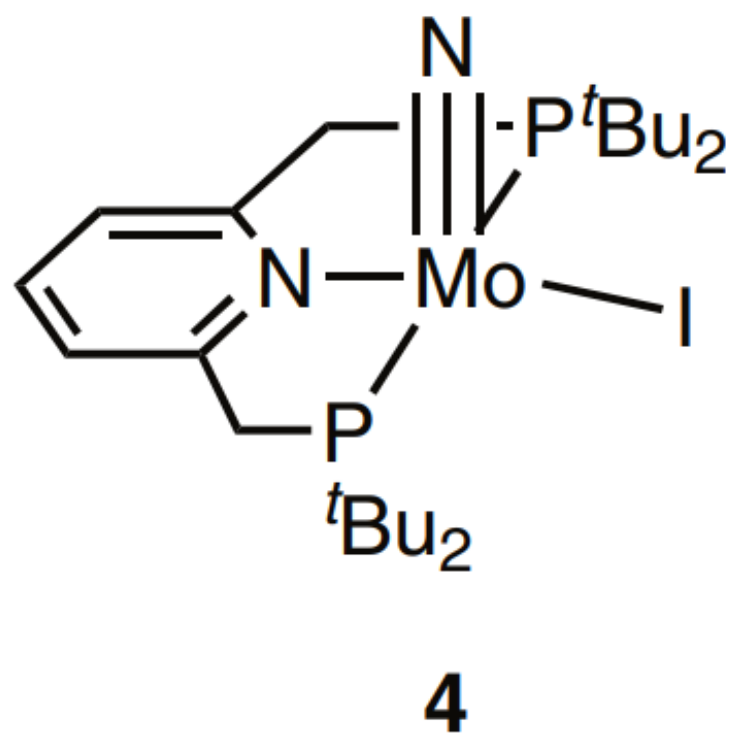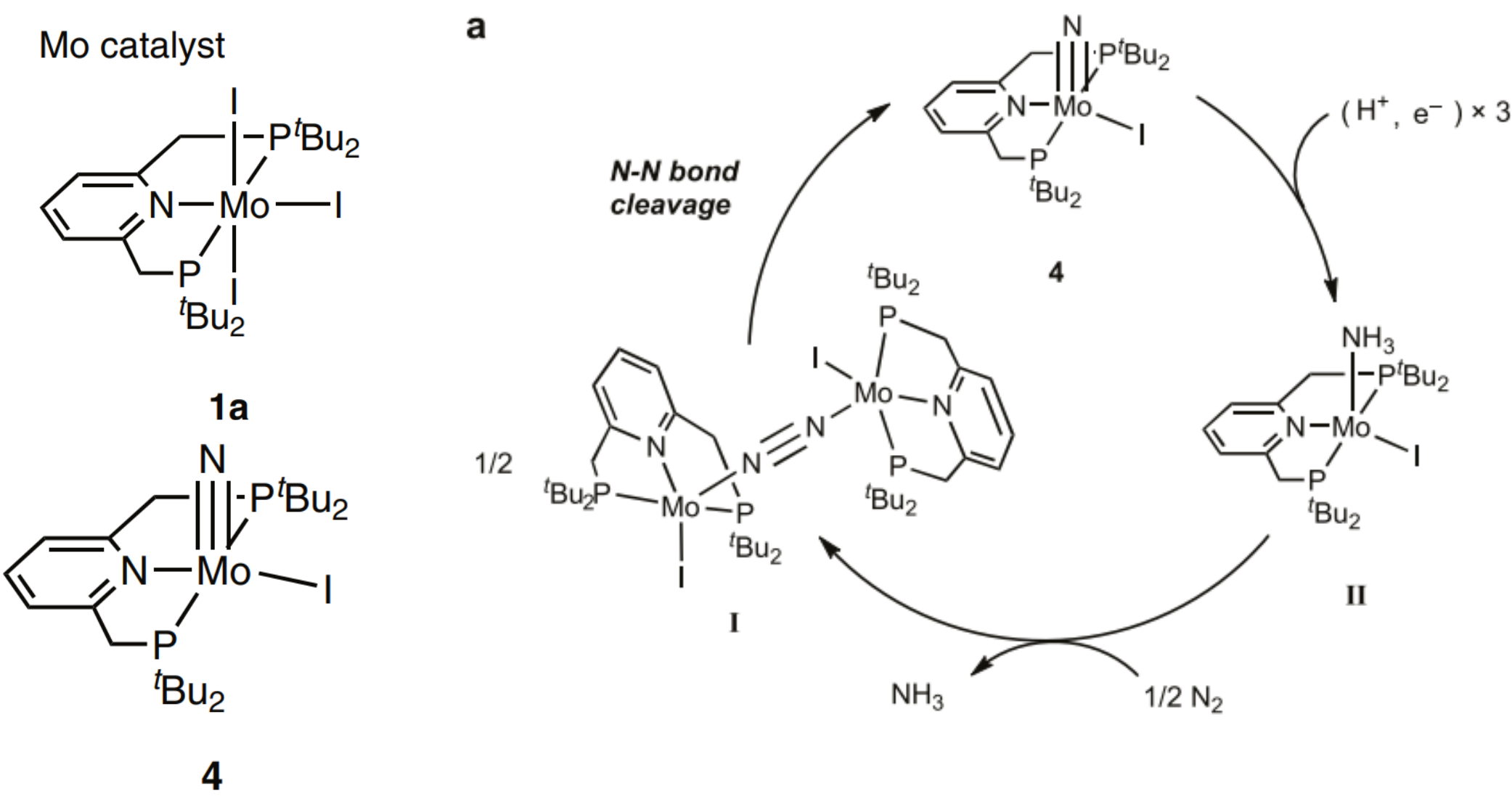
Reacts With proton source to make ammonia

Literature Data Table

Table 1 | Catalytic nitrogen fixation using typical alcohols as proton sources in the presence of molybdenum complexes as catalysts

Entry	Mo catalyst	Alcohol	NH₃ production (equiv. based on Mo)	NH₃ yield (%)[a]	H₂ production (equiv. based on Mo)	H₂ yield (%)[a]
1	1a	HOCH₂CH₂OH	42.8 ± 1.5[b]	70 ± 2[b]	22.2 ± 4.5[b]	24 ± 4[b]
2	1a	MeOH[c]	17.2 ± 1.1[b]	28 ± 1[b]	40.7 ± 1.9[b]	44 ± 12[b]
3	1a	EtOH[c]	14.5	24	41.6	45
4	1a	ᶦPrOH[c]	11.8	19	52.2	57
5	1a	ᵗBuOH[c]	7.7	13	41.2	45
6	1a	CF₃CH₂OH[c]	13.8	22	55.4	60
7	1a	PhOH[c]	16.5	27	46.1	50
8	1a	[CoH][OTf][c]	14.4	23	63.0	68
9[d]	1a	HOCH₂CH₂OH	0	0	0	0
10	4	HOCH₂CH₂OH	50.0 ± 0.1[b]	85 ± 1[b]	7.7 ± 1.0[b]	9 ± 1[b]
11	5	HOCH₂CH₂OH	44.1	76	17.9	20
12	8	HOCH₂CH₂OH	53.3 ± 2.1[b]	88 ± 4[b]	9.1 ± 0.7[b]	10 ± 1[b]
13	9	HOCH₂CH₂OH	55.0 ± 0.9[b]	92 ± 2[b]	4.0 ± 0.8[b]	5 ± 1[b]

SmI₂(THF)₂ was used as the source of SmI₂.
[a] Yield based on SmI₂.
[b] Data are mean of multiple individual experiments (at least 2) with error bars representing the s.d.
[c] A proton source (0.72 mmol; 360 equiv. based on the molybdenum atom of 1a) was used.
[d] CoCp*₂ was used as the reducing reagent instead of SmI₂.

References

1. Ashida, Y.; Arashiba, K.; Nakajima, K.; Nishibayashi, Y. Nature 2019, 568 (7753), 536–540.

2. Modak, J. M. Resonance 2002, 7 (9), 69–77.

Acknowledgments