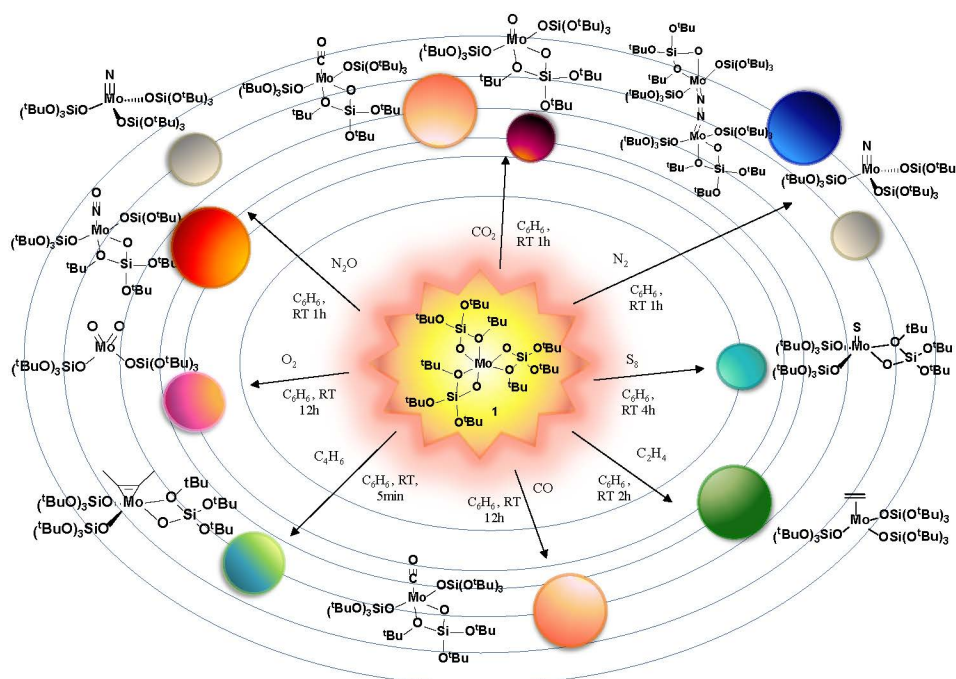


Mo(OSi(tBu)₃)₃: Structure and Reactivity

M. Pucino¹, F. Allouche¹, M. Wörle², C. Copéret^{1*}

¹ETH Zurich, ²ETH Zürich

Cr(III) surface species, prepared from Cr(III) siloxide molecular precursor, are highly active catalysts for olefin polymerization and alkane dehydrogenation.^{1,2} We have thus become interested in generating low coordinated isoelectronic Mo(III) surface to investigate their corresponding reactivity. To date, low coordinate Mo(III) compounds are rare; they typically require large somewhat rigid ligands like in Mo[N(R)Ar]₃ (R= tBu, Ar= 3,5-C₆H₅Me₂)² and Mo(OSi^tBu)₃.³ Here, we have developed the synthesis of Mo(OSi(OtBu)₃)₃ (**1**) and investigated its reactivity towards a broad range of small molecules (CO_x, N₂O, O₂, S₈, ethylene and N₂). The complex **1** has three siloxy ligands adopting a k²-coordination, yielding an overall distorted octahedral geometry. This complex reacts at room temperature with N₂ to give the corresponding Mo(VI)-nitrido compound by dinitrogen splitting via [Mo=N=N=Mo] intermediate, which was isolated at low temperature and fully characterized. This complex also reacts with N₂O, but does not lead to the splitting of N-O bond as expected from metal mediated decomposition of nitrous oxide⁴, but rather of N-N bond, leading to [Mo-h¹-NO] with NO in linear fashion and Mo(VI)-N. Similarly, reaction with CO₂ yields Mo(III)-CO and Mo(V)-O. The former can also be obtained from the reaction of **1** with CO. Reaction of **1** with S₈ yields Mo(V)-S complex. Finally, the reaction of **1** and ethylene generates the corresponding p-complex as it does by reaction with 2-butyne.



[1] M. F. Delley, F. Nunez-Zarur, M. P. Conley, C. Copéret et al., *PNAS*, **2014**, 111 (32), 11624-11629.

[2] M. P. Conley, M. F. Delley, C. Copéret et al., *Inorg. Chem.*, **2015**, 54 (11), 5065-5078.

[3] C. E. Laplaza, C. C. Cummins, *Angew. Chem. Int. Ed.*, **1995**, 34, 2042; D. Kuiper, P. Wolczanski, T. Cundari, *JACS*, 130, **2008**, 12931-12943.

[4] W.B. Tolman, *Angew. Chem., Int. Ed.*, **2010**, 49, 1018-1024.