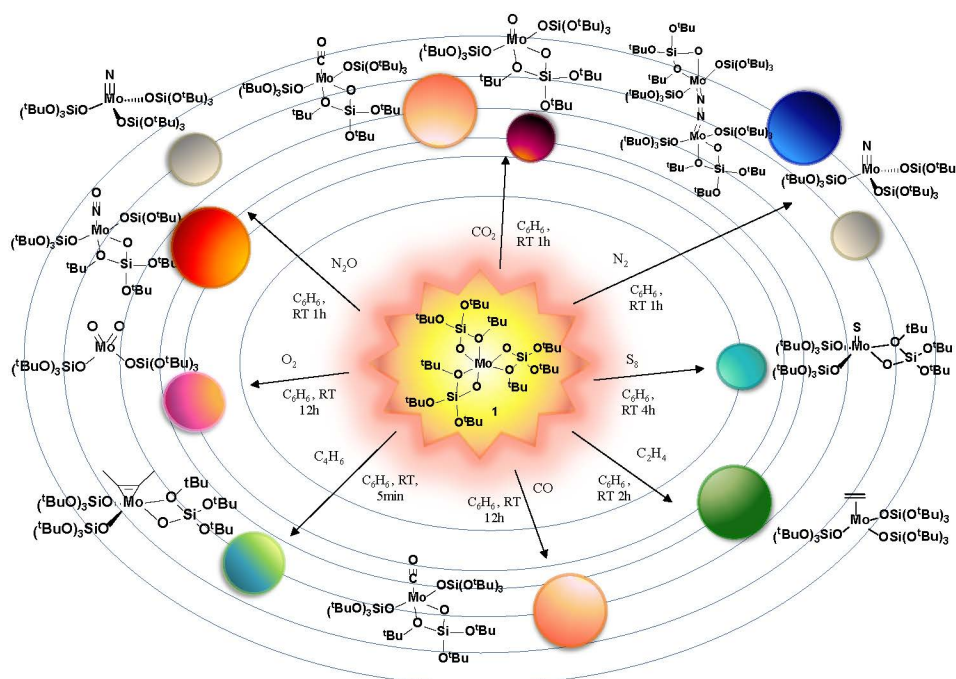


Mo(OSi(tBu)₃)₃: Structure and Reactivity

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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.



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