$Mo(OSi(tBu)_3)_3$: Structure and Reactivity

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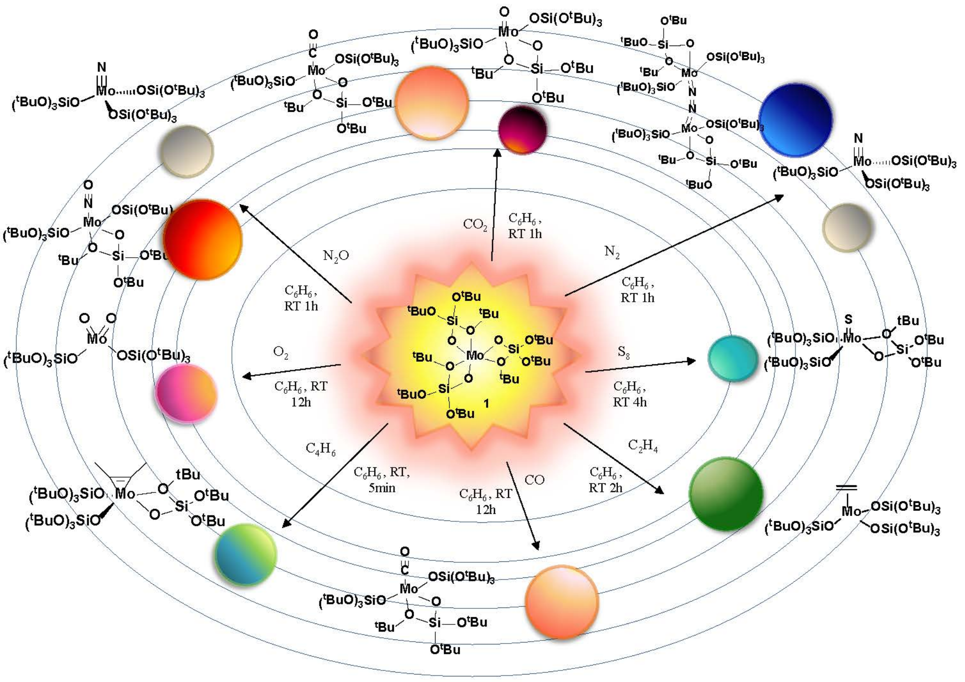
Cr(III) surface species, prepared from Cr(III) siloxide molecular precursor, are highly active catalysts for olefin polymerization and alkane dehydrogenation.[1,2] We have thus become interested in generating low coordinated isoelectronic Mo(III) surface to investigate their corresponding reactivity. To date, low coordinate Mo(III) compounds are rare; they typical require large somewhat rigid ligands like in $Mo[N(R)Ar]_3$ (R= tBu, Ar= 3,5-$C_6H_5Me_2$)[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, N_2O, O_2, S_8, ethylene and N_2). The complex **1** has three siloxy ligands adopting a k^2-coordination, yielding an overall distorted octahedral geometry. This complex reacts at room temperature with N_2 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 react with N_2O, but does not lead to the splitting of N-O bond as expected from metal mediated decomposition of nitrous oxide[4], but rather of N-N bond, leading to [Mo-h^1-NO] with NO in linear fashion and Mo(VI)-N. Similarly, reaction with CO_2 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 S_8 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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