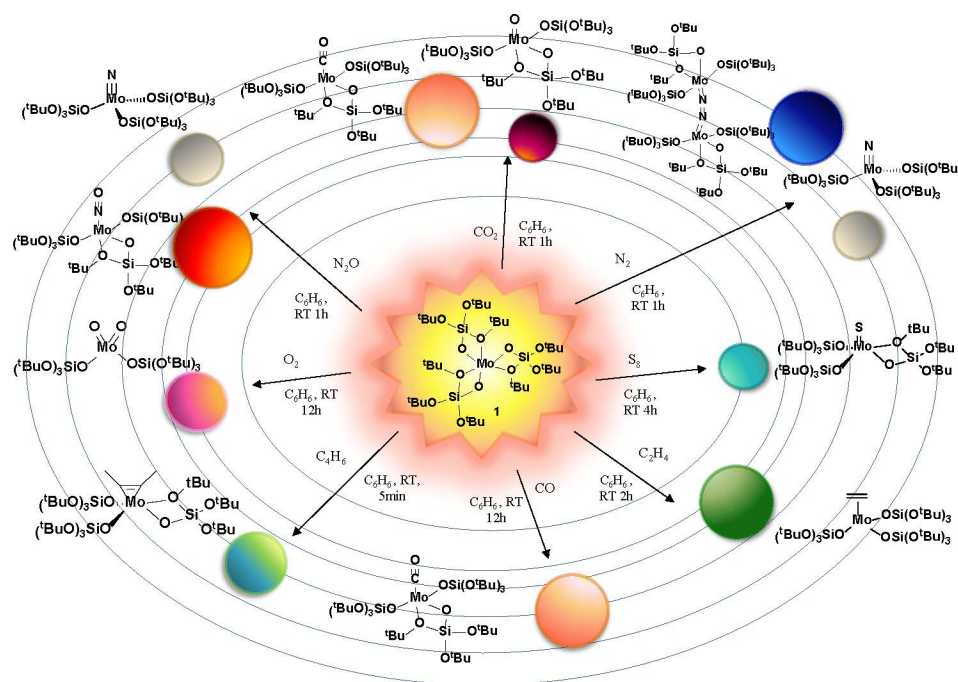


**Mo(OSi(tBu)<sub>3</sub>)<sub>3</sub>: Structure and Reactivity**M. Pucino<sup>1</sup>, F. Allouche<sup>1</sup>, M. Wörle<sup>2</sup>, C. Copéret<sup>1\*</sup><sup>1</sup>ETH Zurich, <sup>2</sup>ETH Zürich

Cr(III) surface species, prepared from Cr(III) siloxide molecular precursor, are highly active catalysts for olefin polymerization and alkane dehydrogenation.<sup>1,2</sup> 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]<sub>3</sub> (R= tBu, Ar= 3,5-C<sub>6</sub>H<sub>5</sub>Me<sub>2</sub>)<sup>2</sup> and Mo(OSi<sup>t</sup>Bu)<sub>3</sub>.<sup>3</sup> Here, we have developed the synthesis of Mo(OSi(OtBu)<sub>3</sub>)<sub>3</sub> (**1**) and investigated its reactivity towards a broad range of small molecules (CO<sub>x</sub>, N<sub>2</sub>O, O<sub>2</sub>, S<sub>8</sub>, ethylene and N<sub>2</sub>). The complex **1** has three siloxy ligands adopting a k<sup>2</sup>-coordination, yielding an overall distorted octahedral geometry. This complex reacts at room temperature with N<sub>2</sub> 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 N<sub>2</sub>O, but does not lead to the splitting of N-O bond as expected from metal mediated decomposition of nitrous oxide<sup>4</sup>, but rather of N-N bond, leading to [Mo-h<sup>1</sup>-NO] with NO in linear fashion and Mo(VI)-N. Similarly, reaction with CO<sub>2</sub> 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<sub>8</sub> 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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