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DFT study on mechanism of carbonyl hydrosilylation catalyzed by high-valent molybdenum (IV) hydrides

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ABSTRACT

Density functional theory (DFT) calculations have been employed to investigate hydrosilylation of carbonyl compounds catalyzed by three high-valent molybdenum (VI) hydrides: Mo(NAr)H(Cp)(PMe$_3$) (**1A**), Mo(NAr)H(PMe$_3$)$_3$ (**1B**), and Mo(NAr)H (Tp)(PMe$_3$) (Tp = tris(pyrazolyl) borate) (**1C**). Three independent mechanisms have been explored. The first mechanism is “carbonyl insertion pathway”, in which the carbonyls insert into Mo–H bond to give a metal alkoxide complex. The second mechanism is the “ionic hydrosilylation pathway”, in which the carbonyls nucleophilically attacks η^1-silane molybdenum adduct. The third mechanism is [2 + 2] addition mechanism which was proposed to be favorable for the high-valent di-oxo molybdenum complex MoO$_2$Cl$_2$ catalyzing the hydrosilylation. Our studies have identified the “carbonyl insertion pathway” to be the preferable pathway for three molybdenum hydrides catalyzing hydrosilylation of carbonyls. For Mo(NAr)H (Tp)(PMe$_3$) (Tp = tris(pyrazolyl) borate), the proposed nonhydride mechanism experimentally is calculated to be more than 32.6 kcal/mol higher than the “carbonyl insertion pathway”. Our calculation results have derived meaningful mechanistic insights for the high-valent transition metal complexes catalyzing the reduction reaction.

1. Introduction

Recently, significantly progress has been made in the use of high-valent transition metal complexes in the catalytic reductions.[1–6] A series of high valent rhenium/molybdenum complexes, Re(O)$_2$I(PPh$_3$)$_2$,[4k] Re(O/NAr)Cl$_3$(PPh$_3$)$_2$,[5a] Re(O)(H)Cl$_2$(PPh$_3$)$_2$,[5a] Re(N)Cl$_2$(PPh$_3$)$_2$,[5a] Re(O)(hoz)$_2^+$ (hoz = 2-(2′-hydroxylphenyl)-2-oxazlin),[5d,5e] HReO$_4$, Re$_2$O$_7$[6e] and MoO$_2$Cl$_2$[6a,6b] have been identified as powerful catalysts for activating X–H bond (X = Si, B, P and H), and for reduction of carbonyls, imine, ester groups, etc. This new reactivity represents a complete reversal from the traditional role of these complexes acting as oxidation catalysts[7] and opened a new research area for the high-valent transition metal complexes. The first example of high-valent transition metal complex catalyzing reduction reaction was reported by Toste et al.[4k] It involved catalysis hydrosilylation of the carbonyl compounds by high valent rhenium(V)-di-oxo complex, ReO$_2$I(PPh$_3$)$_2$. To account for the unusual catalytic activity of Re(O)$_2$(I)(PPh$_3$)$_2$, Toste et al. proposed an unconventional [2 + 2] addition mechanism: the Si–H bond adding across one of Re═O bond in a [2 + 2] fashion to generate the hydrido-oxo intermediate: Re(O)(OSiR$_3$)(H)I(PPh$_3$)$_2$, which is the active species in the reduction of carbonyl substrates, shown in Scheme 1.[4a] This unconventional [2 + 2] addition mechanism was later explored computationally by Wu et al. and confirmed to be the preferred reaction pathway.[8] Likewise, the [2 + 2] addition mechanism was proposed to be the most favorable pathway for the catalysis hydrosilylation of the carbonyl compounds by di-oxo-molybdenum (VI) complex: MoO$_2$Cl$_2$.[9,10]

This proposed [2 + 2] addition mechanism was in contrast to the traditional oxidative addition proposed for the low-valent metal complexes catalyzed catalytic reactions, shown in Scheme 2,[11,12] which generally involves oxidative addition of the silicon-hydrogen bond to the metal center forming the metal hydrides.

While, the following steps in the catalytic cycles of [2 + 2] addition and oxidative addition pathways are similar, both requiring the forming metal hydride intermediates to reduce the carbonyl compounds. First, the carbonyl substrate coordinates to the transition metal center, following by insertion of the carbonyl substrate into metal–hydrogen bond to generate the metal alkoxide intermediate. Therefore, both types of mechanism rely on the ability of metal hydride bond to insert carbonyl substrates.

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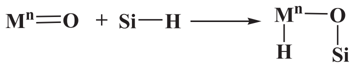
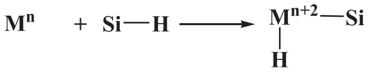


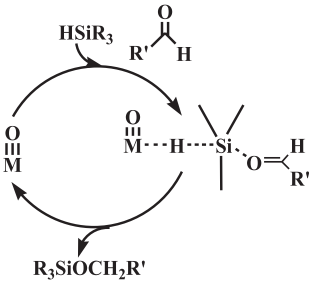
Scheme 1. The [2 + 2] addition mechanism proposed for the catalysis hydrosilylation of the carbonyl compounds by di-oxo-molybdenum (VI) complex: MoO2Cl2.



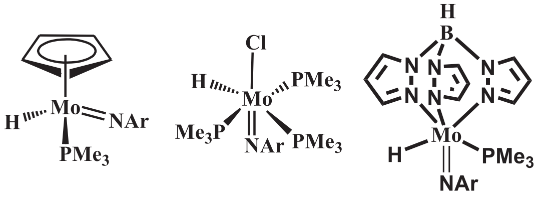
Scheme 2. The traditional oxidative addition proposed for the low-valent metal complexes catalyzed catalytic reactions.

However, if removing the mechanistic requirement for such an insertion reaction, then new types of catalysts could potentially be developed for delivery of the hydride based on different mechanisms. And the possibility of alternative mechanisms may be feasible by using a wider range of transition metals, including inexpensive alternatives instead of employing more expensive metals. An example of alternative hydrogenation method offers is provided by Bullock[13], Nikonov[14], and Brookhart.[15] As shown in Scheme 3, the heterolytic cleavage of Si–H bond occurs upon carbonyl substrates nucleophilically attacking the silane-transition metal adduct, resulting in formation of an ion pair composed of transition metal hydride and the carbenium ion. The last step is the hydride transferred from the transition metal to the activated carbenium ion to produce the silylether product. In this catalytic cycle, the requirement for the metal hydride bond to insert carbonyl compounds is removed. By analogous to the ionic hydrogenation mechanism, this catalytic cycle could be referring to be the ionic hydrosilylation pathway.[16]

However, other hydrogenation/hydrosilylation methods might also exist. More recently, Nikonov and co-workers have succeeded in synthesizing the high-valent molybdenum catalysts having hydride coordination, and demonstrated that these complexes can catalyze the hydrosilylation reaction with ketones, aldehyde and nitriles effectively. On the ground of stoichiometric labeling experiments, Nikonov and co-workers proposed that molybdenum hydride (ArN =)Mo (Tp)(H)(PMe_3) (Tp = tris(pyrazolyl) borate) catalyzed hydrosilylation of the carbonyl compounds proceeding via a “nonhydride pathway”, in which the hydride ligand did not participate in the reduction reaction.[17,18] However, the comparison studies on two other isolobal molybdenum hydrides: (ArN =)Mo(Cl)(H)$(PMe_3)_3$ and (ArN =)Mo(Cp)(H)(PMe_3), Nikonov and co-workers suggested that these two molybdenum hydrides catalyzed the hydrosilylation via the pathway involved of the carbonyl substrates initially coordination and then insertion into the Mo–H bond. Nevertheless, based on the experimental observations, the reaction pathways for these two complexes are quite different: (ArN =)Mo(Cl)(H)$(PMe_3)_3$ reacted by a phosphine dissociative mechanism, whereas (ArN =)Mo(Cp)(H)(PMe_3) reacted by a associative mechanism.see (scheme 4)



Scheme 3. The ionic hydrosilylation pathway proposed by Brookhart involving the heterolytic cleavage of Si–H bond.



Scheme 4. The three molybdenum hydrides investigated in the article.

Building on these reports and, most importantly, on the work of the nonhydride pathway for molybdenum hydride (ArN =)Mo (Tp)(H)(PMe_3) (**1C**) catalyzed hydrosilylation of the carbonyl compounds proposed by Nikonov and co-workers aroused our interest. What remain unclear at the present time are (1) how the high-valent molybdenum hydride (ArN =)Mo (Tp)(H)(PMe_3) (**1C**) catalyzing the hydrosilylation vi a nonhydride pathway, and (2) why the structures of three complexes of (ArN =)Mo (Tp)(H)(PMe_3) (**1C**), (ArN =)Mo(Cp)(H)(PMe_3) (**1A**) and (ArN =)Mo(Cl)(H)$(PMe_3)_3$ (**1B**) bear isolable, the mechanistic proposal is distinctively different based on the experimental investigation. To understand the difference in catalytic reduction activities displayed by those three high valent molybdenum hydrides, we initiated the detailed mechanistic studies to probe the catalytic cycle for the hydrosilylation reaction. Here, we present a computational study on illustrating all the possible activation manners of carbonyl substrate/silane by three molybdenum hydrides. Our calculations may also be considered to model the reduction action of a series of the high valent transition metal catalysts.

2. Computational methodology

All studies were performed on the catalysts (ArN =) Mo(Cp)(H)(PMe_3) (**1A**) and (ArN =)Mo(Cl)(H)$(PMe_3)_3$ (**1B**), (ArN =)Mo (Tp)(H)(PMe_3) (**1C**) (2,6-di-isopropylphenyl is simplified to benzene). Benzaldehyde was used as a model substrate for our computational study, and trimethylsilane was the model for the silane (other aldehyde/ketone substrates and silane are also employed, reported in the Supporting Information). We optimized all structures and characterized them to be transition states (TS) or energy minima at the hybrid metal exchange-correlation M06 functional[20,21] which includes medium-range correlation, as well as B3LYP level, as implemented in Gaussian 09.[19] And for M06 functional calculation, all geometries optimization were carried out using tight convergence criteria and pruned ultrafine grids.

All geometries were optimized in vacuum with the triple-ζ basis set 6-311G (d,p) on all atoms except molybdenum. For molybdenum, the double-ζ basis set LANL2DZ[22] was employed (corresponding to the Los Alamos effective core potential plus DZ), which was augmented with an extra f polarization basis function (exponent 1.043).[23] Frequency calculations were performed on all optimized structure to characterize the stationary points as minima or TSs, as well as for the calculations of zero-point energies (ZPE), enthalpies (H), entropies (S) and Gibbs free energies (G) at 298 K. And all transition states were checked to connect the respective minima by optimizations following initial intrinsic reaction coordinate calculations. Solvent effects (CH_2Cl_2 was used as the representative solvent) were taken into consideration by the MD polarizable continuum solvent model carried out at the M06 level with the M06 gas phase geometries.[24] (SMD is IEFPCM calculation