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Role of Low-Valent Rhenium Species in Catalytic Hydrosilylation Reactions with Oxorhenium Catalysts

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Supporting Information

ABSTRACT: The catalytic competency of a Re(III) complex has been demonstrated. In the presence of silane, oxorhenium(V) catalysts are deoxygenated to produce species that are significantly more active than the metal oxo precursors in hydrosilylation reactions. The results presented suggest that, in evaluating mechanisms for catalytic hydrosilylation reactions that involve high-valent metal oxo complexes, the activity of species that may be generated by deoxygenation of the metal with silane should also be systematically investigated as potential catalysts.



O ver the past decade, several research groups have investigated the catalytic competency of high-oxidationstate Re(V) and Re(VII) oxo complexes in hydrosilylation reactions.¹ In these systems, the role of the terminal oxo ligand(s) has been investigated, and it has been shown that the oxo ligand either stabilizes the high-valent metal center but does not participate directly in the catalytic reaction or is activated with silane to generate a new catalytically active species.^{1c,f,i,2} However, in any of these systems, the catalyst may be deoxygenated by silane to generate a low-valent Re species that is capable of catalysis. Recently, low-valent Re species not bearing terminal oxos have also been shown to be efficient catalysts for hydrosilylation.³

In this paper we provide evidence for the catalytic competency of a Re(III) complex. We show that, in the presence of silane, oxorhenium(V) catalysts are deoxygenated to produce species that are significantly more active than the metal oxo precursors in hydrosilylation reactions. The results presented suggest that in evaluating mechanisms for catalytic hydrosilylation reactions that involve high-valent metal oxo complexes, the activity of species that may be generated by deoxygenation of the metal with silane should also be systematically investigated as potential catalysts.

Recently we reported the synthesis of the rhenium(III) acetate complex [DAAmRe(CO)(OAc)] (1; DAAm = N_iN_i bis(2-arylaminoethyl)methylamine; aryl = C_6F_5). As shown in Scheme 1, the reaction proceeds by treating the oxorhenium-(V) complex [DAAmRe(O)(CH₃)] (3) with CO to produce

Scheme 1



the rhenium(V) acyl intermediate $[DAAmRe(O)(C(O)CH_3)]$ (2), followed by the treatment of 2 with CO to generate 1.^{2b,4}

The catalytic competency of complexes 1-3 for the hydrosilylation of aldehydes with dimethylphenylsilane was investigated (Table 1). Complexes 1-3 catalyze the hydrosilylation of benzaldehyde with neat dimethylphenylsilane at 80 °C. Complex 1 is the most efficient catalyst in the series, and 100% conversion is attained in 2.5 h with 0.1 mol % catalyst loading (entry 1); 100% conversion is attained in 14 h with 0.01 mol % catalyst loading (entry 2). The Re(V) complexes 2 and 3 are not as active; 98.0% and 83.5% yields are achieved with 0.1 mol % catalyst loading in 2 and 3 days, respectively (entries 3 and 4). At room temperature, quantitative conversion of benzaldehyde to benzyloxydimethyl(phenyl)silane by 1 was observed in 15 h (entry 5). Complexes 2 and 3, however, achieved <12% yield after 15 days at room temperature (entries 6 and 7).

Catalyst 1 also performed efficient hydrosilylations with various other silanes, such as MePh₂SiH (entry 8), Et₃SiH (entry 10), and Pr₃SiH (entry 11). Hydrosilylation was not observed when Ph₃SiH was utilized as a substrate (entry 9), presumably due to the steric bulk of this silane. Catalysis of various para-substituted benzaldehydes with varied functionalities (CF₃, Cl, Me; entries 12–15) was efficient, and reactions were complete in <2 h.

Under these reaction conditions, catalyst 1 is more efficient than the previously reported Re(V) complex $[{\rm Re}(O)_2({\rm I})-({\rm PPh}_3)_2]$ (4)^{1d} (entry 16) and is comparable to $[{\rm Re}(O)-({\rm hoz})_2({\rm NCCH}_3)]^+$ (5)^{1f} (entries 17 and 18). Importantly, 1 performs as well as, or better than, the best oxorhenium catalysts reported thus far. The specific highlights of this particular catalytic system include: (1) the catalytic system employs a Re(III) catalyst that does not incorporate a metal

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Table 1. Catalytic Hydrosilylation of Aldehydes According to Eq 1

| x | | H ⁺ | 1.2 HSiR ₃ — | [Re] neat X [^] | ► O ^{SIR} H | (1) |
|--------------------|-------|----------------|-------------------------|--------------------------------|-------------------------|--------------------------|
| entry ^a | cat. | Х | R ₃ | time | $T(^{\circ}C)$ | yield (%) ^{b,c} |
| 1 | 1 | Н | Me ₂ Ph | 2.5 h | 80 | 94.6 ^b |
| 2 | 1^d | Н | Me_2Ph | 14 h | 80 | 92.7 ^b |
| 3 | 2 | Н | Me_2Ph | 2 days | 80 | 98.0 ^c |
| 4 | 3 | Н | Me_2Ph | 3 days | 80 | 83.5 ^c |
| 5 | 1 | Н | Me_2Ph | 15 h | room temp | 93.5 ^b |
| 6 | 2 | Н | Me_2Ph | 15 days | room temp | 11.1 ^c |
| 7 | 3 | Н | Me_2Ph | 15 days | room temp | 3.4 ^c |
| 8 | 1 | Н | $MePh_2$ | 8 h | 80 | quant ^c |
| 9 | 1 | Н | Ph_3 | 22 h | 80 | 0 ^c |
| 10 | 1 | Н | Et ₃ | 27 h | 80 | 86.9 ^b |
| 11 | 1 | Н | Pr ₃ | 53 h | 80 | 78.6 ^c |
| 12 | 1 | CF_3 | Me_2Ph | 2 h | 80 | 96.3 ^b |
| 13 | 1 | Cl | Me_2Ph | 2 h | 80 | 85.0 ^b |
| 14 | 1 | Me | Me ₂ Ph | 2 h | 80 | 98.4 ^b |
| 15 | 1 | OMe | Me_2Ph | 2 h | 80 | 81.6 ^b |
| 16 | 4 | Н | Me_2Ph | 5 h | 80 | 59.6 ^c |
| 17 | 5 | Н | Me_2Ph | 1 h | 80 | quant ^c |
| 18 | 5^d | Н | Me_2Ph | 24 h | 80 | 73.8 ^c |
| | | | | | | |

^{*a*}Reaction conditions: Re (0.00989 mmol), aldehyde (9.89 mmol), and silane (11.87 mmol) under an N_2 atmosphere. ^{*b*}Isolated yield. ^{*c*}NMR yield. ^{*d*}Re (0.000989 mmol, 0.01 mol %)

oxo, (2) the reaction can be performed with low catalyst loadings and short reaction times, (3) reactions can be performed without a solvent, and (4) the catalyst is air and moisture stable and can be easily handled on the benchtop.

In order to compare the catalytic activity of rhenium complexes in two oxidation states (3 and 2, Re(V); 1, Re(III)) bearing the same DAAm ancillary ligands, the time profile for product formation by each of the catalysts was monitored by ¹H NMR spectroscopy (1, 0.01 mol %; 2 and 3, 0.1 mol %) (Figure 1). Catalysis with 1 and 2 ensues without an induction period, with catalyst 1 ~17 times more active than catalyst 2 ($k_{obs} = 0.54$ and 0.032 s⁻¹ for 1 and 2, respectively). Catalysis



Figure 1. Time profile for the catalytic hydrosilylation of benzaldehyde (9.89 mmol) with dimethylphenylsilane (11.87 mmol) with 1 (red circles; 0.989 μ mol, 0.01 mol %); 2 (blue diamonds; 9.89 μ mol, 0.1 mol %), and 3 (green squares; 9.89 μ mol, 0.1 mol %) at 80 °C under an N₂ atmosphere. Yields were obtained by ¹H NMR spectroscopy.

with 3 is initially very sluggish (\sim 24 h). During this time the reaction mixture undergoes a series of color changes (blue-green-red). Once the reaction mixture turns red (\sim 24 h), rapid catalysis ensues, which implies that 3 is not the catalytically active species but is transformed in situ by the substrates to a more active catalyst.

To investigate the modes of substrate activation with catalysts 1-3, stoichiometric reactions between the complexes and the substrates were investigated. Catalysts 1-3 did not exhibit stoichiometric reactivity with benzaldehyde but did react stoichiometrically with the dimethylphenylsilane. The reaction of 1 and 2 with dimethylphenylsilane (Scheme 2)





resulted in the formation of the dirhenium(II) species 6. Complex 6 was characterized by ¹H and ¹⁹F NMR and IR spectroscopy, as well as X-ray crystallography (Figure 2). The electron configuration for 6 ($\sigma^2 \pi^4 \delta^2 \delta^{*2}$) is consistent with a Re–Re bond order of 3. The Re–Re bond length in 6 is 2.4722(2) Å, which is comparable to those in related dirhenium complexes reported by Walton and co-workers where the Re– Re triple bond is weakened by π -back-bonding to the CO π^* orbitals.⁵ The geometry at each Re center is a distorted trigonal bypyramid, with the CO and amine nitrogen occupying the axial planes. The C1–Re1–Re2–C2 dihedral angle is –113.7° between the two halves of the dimer.

The stoichiometric reaction of 3 with dimethylphenylsilane was also investigated. As shown in Scheme 3, heating 3 (80 °C) in the presence of Me₂PhSiH resulted in the formation of the dirhenium complex 7. Complex 7 is isostructural with 6, except that N₂ replaces CO as the terminal ligand. CO stretches are observed by IR spectroscopy for 6 at 1886 and 1868 cm⁻¹, while N₂ stretches are observed at 2031 and 2015 cm⁻¹ for 7. An X-ray crystal structure of 7 was also obtained (Figure 2). The Re–Re bond length in 7 is 2.4447(5) Å.

Catalysis with 6 was investigated and resulted in <5% yield in 5 h. Complex 3 was allowed to react with Me_2PhSiH for 24 h to generate 7 in situ. Once 7 was generated, it was used as the catalyst for the hydrosilylation of benzaldehyde with Me_2PhSiH . Catalysis with 7 proceeded immediately, unlike the analogous reaction with catalyst 3; however, catalysis was significantly slower than with 1 or 2 (Supporting Information).

A plausible mechanism for the reaction of 1 with Me₂PhSiH is depicted in Scheme 4. In this mechanism, Me₂PhSiH is activated by 1 to produce the Re hydride 8. In the absence of aldehyde, two 8 molecules react to produce H₂ and the Re(II) dimer 6. The high activity observed for catalyst 1 (Re(III)), which does not contain a terminal oxo, and the facile formation of 6 and 7 from 2 and 3, respectively, suggest that in the



Figure 2. Thermal ellipsoid (50%) plots of **6** and 7. Hydrogen atoms are omitted, and the C_6F_5 ligands are represented in wireframe for clarity. Selected bond lengths (Å) and angles (deg) are as follows. **6**: Re1–Re2, 2.4722(2); Re1–C1, 1.880 (3); Re1–N1, 1.9668(19); Re1–N2, 2.242(2). C1–Re1–Re2, 81.93(7); N1–Re1–Re2, 120.30(6); N2–Re1–Re2, 106.98(5); C1–Re1–N2, 171.07(8); C1–Re1–N1, 95.99(9); N1–Re1–N3, 121.39(8); N1–Re1–N2, 80.28(8). 7: Re1–Re2, 2.4447(5); Re1–N1, 1.9280(16); Re1–N5, 1.9780(17); Re1–N6, 2.1895(16); N1–N2, 1.127(2). N1–Re1–Re2, 86.81(5); N5–Re1–Re2, 119.94(5); N6–Re1–Re2, 104.25(5); N5–Re1–N7, 122.80(7); N5–Re1–N6, 80.74(6).

Scheme 3



Scheme 4





presence of silane the catalytically relevant species when the oxorhenium(V) complexes 2 and 3 are employed as catalysts are not high-valent rhenium oxos, but low-valent species that are generated upon deoxygenation with Me_2PhSiH .

In order to investigate the mechanism of the hydrosilylation reaction catalyzed by 1, several studies were performed. The relative reactivities of various para-substituted benzaldehyde substrates toward hydrosilylation were determined by a series of competition experiments, as depicted in Scheme 5 (X = H,

Scheme 5



Cl, CF₃, Me, OMe). As shown in Figure 3, the Hammett plot obtained from this experiment reveals that electron-with-drawing groups accelerate the rate of the reaction ($\rho = 0.52$).



Figure 3. Hammett plot for the benzaldehyde competition experiments.

The kinetic isotope effect (KIE) for the hydrosilylation of benzaldehyde with a 1/1 mixture of Et₃Si-H and Et₃Si-D was also investigated according to Scheme 6. A KIE of 1.4 was observed for the reaction.

Scheme 6



Finally, the influence of acetate on the catalytic reaction with 1 was investigated. Exogeneous acetate (20 equiv of $AcONBu_4$ with respect to Re) was added to the catalytic reaction with 1. The reaction was complete in 2.5 h, similar to the catalytic reactions that did not employ exogenous acetate. This suggests that the rate is not dependent on the concentration of acetate.

On the basis of the data presented, the following mechanism has been proposed for the catalytic hydrosilylation of benzaldehyde (Scheme 7). (1) Treatment of 1 with Me_2PhSiH results in the formation of the catalytically active Re–H

Scheme 7



complex 8. (2) Complex 8 subsequently reduces benzaldehyde to yield 9. The observed electronic dependence on the benzaldehyde substrate (electron-withdrawing groups accelerate the rate) is consistent with the reduction of the C=O bond with the Re-H.⁶ (3) The reaction of 9 with Me₂PhSiH results in the formation of the benzyloxydimethyl(phenyl)silane product and the regeneration of the active Re-H complex 8. The observed KIE (1.4) is consistent with Si-H cleavage occurring in the product-forming step.^{1f,6} (4) Finally, in the absence of benzaldehyde, two Re-H complexes 8 couple to yield 6. Complex 6, however, is not catalytically relevant, as catalysis with 6 is significantly slower than catalysis with 1.

To summarize, we have demonstrated that the Re(III) complex 1 is an efficient catalyst for the hydrosilylation of aldehydes. Catalysis with 1 was performed without solvent and with low catalyst loadings. Importantly, 1 is significantly more active as a catalyst than the oxorhenium(V) complexes 2 and 3 and exhibits reactivity comparable to that of the best oxorhenium(V) complexes reported thus far. Stoichiometric reactions between 1, 2, and 3 and the dimethylphenylsilane result in the dirhenium(II) complexes 6 and 7. While 6 and 7 are not catalytically relevant, their facile generation from 2 and 3 and the observed high reactivity of the Re(III) complex 1 suggests that when oxorhenium complexes are employed as catalysts, the active species are not high-valent rhenium oxos, but species that are generated upon deoxygenation with Me₂PhSiH. This work suggests that low-valent Re species that are generated by the reduction of high-valent metal oxos may be catalytically relevant and, consequently, their activity should be systematically investigated.

ASSOCIATED CONTENT

S Supporting Information

Text, figures, tables, and CIF files giving experimental procedures, crystallographic data for 6 and 7, and spectroscopic data for organic products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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