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ARTICLE

Cationic Rhenium(III) Complexes: Synthesis, Characterization, and Reactivity for Hydrosilylation of Aldehydes

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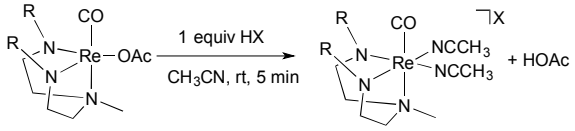
Abstract: A series of novel cationic Re(III) complexes [(DAAm)Re(CO)(NCCH$_3$)$_2$][X] [DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C_6F_5 (**a**), Mes (**b**)] [X = OTf (**2**), BAr^F_4 [BAr^F_4 = tetrakis[3,5-(trifluoromethyl)phenyl]borate)] (**3**), BF_4 (**4**), PF_6 (**5**)], and the analogue [(DAmA)Re(CO)(Cl)$_2$] [DAmA = N,N-bis(2-arylamineethyl)methylamino; aryl = C_6F_5] (**6**) were synthesized. The catalytic efficiency for the hydrosilylation reaction of aldehydes using **4a** (0.03 mol%) has been demonstrated to be significantly more active than previous rhenium catalysts reported in the literature. The data suggest that electron-withdrawing substituents at the diamido amine ligand increases the catalytic efficiency of the complexes. Excellent yields were achieved at ambient temperature in neat conditions using dimethylphenylsilane. The reaction affords TONs of up to 9,200 and a TOF of up to 126 h^{-1}. Kinetic and mechanistic studies were performed, and the data suggest that the reaction is *via* a non-hydride ionic hydrosilylation mechanism.

INTRODUCTION

Hydrosilylation reactions of organic carbonyls are useful because a protected alcohol can be generated in a single step under mild conditions.[1] These reactions are more attractive and convenient than the conventional two-step methodology of reduction by a metal hydride followed by silyl protection. In recent years several examples of mono-oxorhenium, dioxorhenium, and mono-oxomolybdenum complexes were shown to be highly active for the hydrosilylation of aldehydes and ketones.[2-24] In general, cationic rhenium(V) mono-oxo complexes exhibit the highest activities for catalytic hydrosilylation reactions compared to their neutral rhenium(V) complexes counterparts.[10, 15] However, recently our group reported a rhenium(III) complex that is significantly more active that its rhenium(V) metal mono-oxo precursors,[25] and we hypothesized 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 the organosilane. Here, we report the synthesis of cationic rhenium(III) complexes that are efficient catalysts for the hydrosilylation of aldehydes. A few examples of low-valent rhenium complexes not bearing an oxo ligand have been shown to be efficient catalysts for hydrosilylation reaction of carbonyl compounds.[26, 27]

RESULTS AND DISCUSSION

Synthesis and Characterization of Cationic DAAm Rhenium(III) Complexes. A series of cationic [(DAAm)Re(CO)(NCCH$_3$)$_2$][X] [DAAm = N,N-bis(2-arylaminoethyl)methylamine; aryl = C_6F_5 (**a**), Mes (**b**)] [X = OTf (**3**), BAr^F_4 [BAr^F_4 = tetrakis[3,5-(trifluoromethyl)phenyl]borate)] (**4**), BF_4 (**5**), PF_6 (**6**)] complexes were synthetized from the DAAm rhenium(III) acetate complex [(DAAm)Re(CO)(OAc)] (**1a** or **1b**)[28] by treatment with 1 equiv of a non-coordinating acid in acetonitrile (Scheme 1).



(**1a**) R = C_6F_5
(**1b**) R = Mes

(**2a**) R = C_6F_5, X = OTf; (**2b**) R = Mes, X = OTf
(**3a**) R = C_6F_5, X = BAr^F_4; (**3b**) R = Mes, X = BAr^F_4
(**4a**) R = C_6F_5, X = BF_4; (**4b**) R = Mes, X = BF_4
(**5a**) R = C_6F_5, X = PF_6; (**5b**) R = Mes, X = PF_6

Scheme 1. Synthesis of Cationic DAAm Rhenium(III) Complexes

X-ray quality crystals were obtained by the slow diffusion of ether into a concentrated acetonitrile solution of **3a** (Figure 1). The geometry around rhenium is best described as a distorted octahedron with the carbonyl ligand and amine nitrogen occupying the apical position. The acetate ligand is replaced by two acetonitrile ligands in the equatorial plane and the Re1-N4

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Electronic Supplementary Information (ESI) available: Additional NMR spectra and experimental details and X-ray experimental for **3a**, **4b**, and **6**. CCSD 1528990, 1528991 and 1528992 for **3a**, **4b** and **6**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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(2.168 Å) and Re1-N5 (2.120 Å) bond lengths are comparable to cationic Re-acetonitrile bond lengths.[29]

The ^{1}H NMR spectrum of **4a** is shown in Figure 2 and is representative of the series of cationic complexes. The methylene protons from the ligand backbone resonate as three distinct multiplets at δ 4.05 (2H), δ 3.72 (2H) and δ 3.01 (4H) ppm. A singlet at δ 2.85 ppm is assigned to the methyl group on the amine from the ligand backbone. The singlet corresponding to the methyl groups from the acetonitrile ligands resonate at δ 2.14 ppm (6H). The IR stretch of the carbonyl ligand in **4a** is observed at 1882 cm^{-1}. This stretch is at higher frequency than the average CO stretch in **1a** (1872).[28]

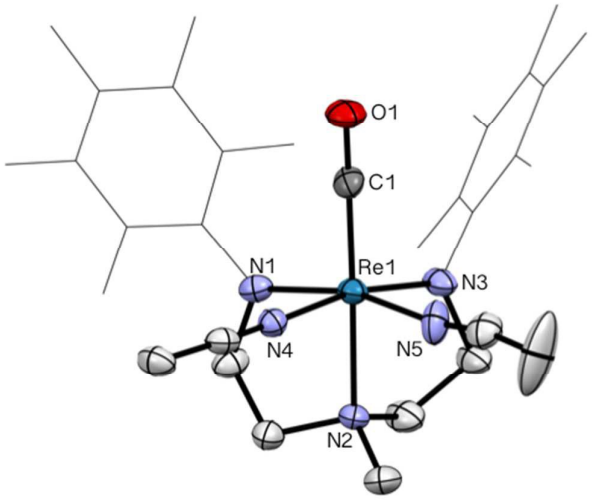


Figure 1. X-ray structure of **3a**. Thermal ellipsoids are at 50% probability level. Hydrogen atoms and counter ion were omitted and the pentafluorophenyl groups on the ligand are shown in wireframe format for clarity. Selected bond lengths (Å) and angles (deg.): Re1-C1, 1.867(4); Re1-N1, 1.932(3); Re1-N2, 2.220(3); Re1-N3, 1.928(1); Re1-N4, 2.167(3); Re1-N5, 2.120(2), N1-Re1-N3, 10.04(15); N1-Re1-N2, 80.79(13); N1-Re1-C1, 94.26(16); N2-Re1-C1, 172.91(16); N1-Re1-N4, 85.09(13); N1-Re1-N5, 160.96(15); Re1-N1-C8, 119.2(2); Re1-N3-C12, 116.9(3)

The synthesis of **2-5** provided a diverse set of cationic rhenium(III) complexes bearing either electron-withdrawing (R = C_6F_5) or electron-donating (R = Mes) analogues of the DAAm ligand framework. These complexes are easily synthesized, are air and moisture stable, and a direct comparison of the reactivity could be made based on the electronics and sterics of the ligand framework.

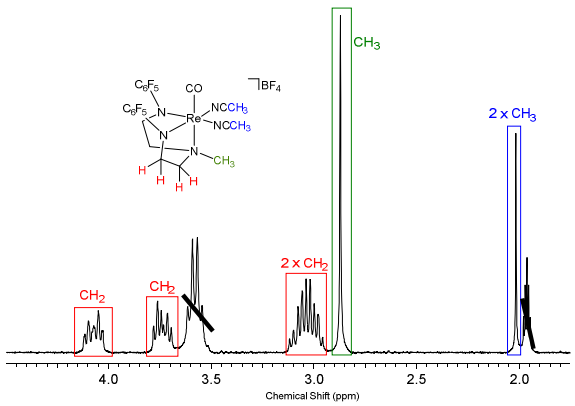
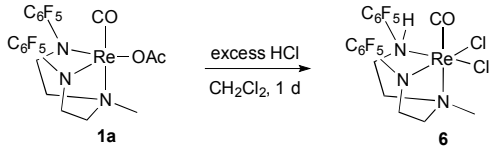


Figure 2. ^{1}H NMR spectrum for **4a** formation after addition of $HBF_4{\cdot}OEt_2$ to **1a** in CD_3CN at room temperature. Peaks at 3.6 and 1.9 ppm are from Et_2O.

Synthesis and Characterization of DAmA Rhenium(III) Complex. The complex [(DAmA)Re(CO)(Cl)$_2$] [DAmA = N,N-bis(2-arylamineethyl)methylamino; aryl = C_6F_5] (**6**) was synthetized by treating **1a** with excess hydrochloric acid (HCl) in methylene chloride at room temperature (Scheme 2).



Scheme 2. Synthesis of DAmA rhenium(III) dichloride complex **6**.

X-ray quality crystals were obtained by the slow diffusion of pentanes into a concentrated reaction mixture of **6** in methylene chloride (Figure 3). The geometry around rhenium in **6** is best described as distorted octahedral. The acetate ligand is replaced by two chloride ligands in the equatorial plane. The X-ray crystal structural data suggest that one of the chelating ligand nitrogen atoms has been protonated. Evidence for this protonation and the change in hybridization from sp^2 to sp^3 is provided by the analysis of the angles around N1 and N3 in **6**. A comparison between **1a** and **6** reveals a decrease in the Re-N1-C8 angle from 118° to 108°. Also in **6**, the Re-N1 bond length (2.2 Å) is longer than Re-N3 bond length (1.92 Å).

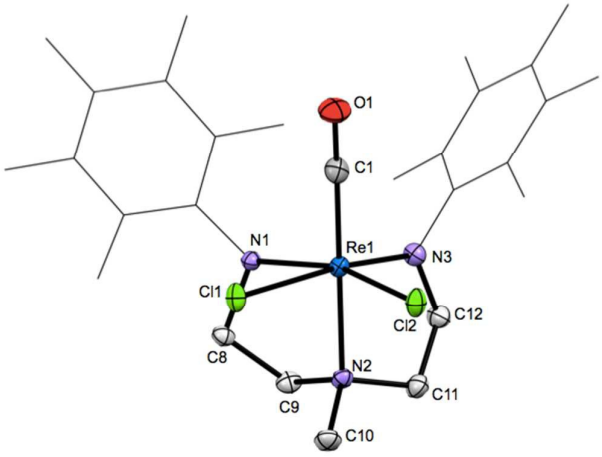


Figure 3. X-ray structure of **6**. Thermal ellipsoids are at 50%. Hydrogen atoms and counter ion were omitted and the pentafluorophenyl groups on the ligand are shown in wireframe format for clarity. Selected bond lengths (Å) and angles (deg.): Re1-C1, 1.862(3); Re1-N1, 2.200(2); Re1-N2, 2.262(2); Re1-N3, 1.920(2); Re1-Cl1, 2.4361(6); Re1-Cl2, 2.3685(6), N1-Re1-N3, 93.97(8); N1-Re1-N2, 78.18(7); N1-Re1-C1, 98.15(9); N2-Re1-C1, 174.44(9); N1-Re1-Cl1, 80.01(6); N1-Re1-Cl2, 163.79(5); Re1-N1-C8, 107.95(14); Re1-N3-C12, 120.44(16).

In the ^{1}H NMR spectrum of **6** (S37) a singlet at 3.36 ppm is observed for the methyl group on the amine nitrogen. The methylene protons from the ligand backbone are observed as three distinct multiplets at δ 4.16 (2H), δ 3.45 (2H) and δ 3.31 (4H) ppm. The amine proton was not observed by ^{1}H NMR spectroscopy.

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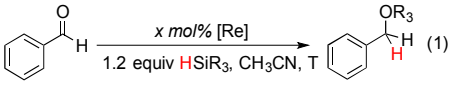
Catalytic Hydrosilylation of Aldehydes. The catalytic competency of complexes **4a-b** and **6** for the hydrosilylation reaction of benzaldehyde were examined according to Equation 1. Reactions were conducted at different temperatures, catalyst loadings, and with different silane reagents in acetonitrile or under neat conditions. The results are shown in Table 1.

Table 1. Catalytic hydrosilylation of benzaldehyde according to equation **1**.



Entry[a]	[Re]	mol %	R_3	T (°C)	Time (h)	Conversion (%)[b]
1[c]	**6**	1	Me_2Ph	80	95	79
2[d]	**4a**	0.10	Me_2Ph	40	118	41
3[d]	**4a**	0.10	Me_2Ph	60	48	46
4[d]	**4a**	0.10	Me_2Ph	80	48	49
5[e]	**4a**	0.50	Me_2Ph	rt	8	95
6[d]	**4b**	0.10	Me_2Ph	rt	24	NR
7[d]	**4b**	0.10	Me_2Ph	40	34	NR
8[d]	**4a**	0.10	Ph_3	rt	114	NR
9[e]	**4a**	0.50	Et_3	rt	48	51
10[e]	**4a**	0.50	Ph_3	rt	46	12
11[f,k]	**4a**	0.01	Me_2Ph	rt	72	92
12[g,k]	**4a**	0.03	Me_2Ph	rt	24	100
13[h,k]	**4a**	0.05	Me_2Ph	rt	16	100
14[d,k]	**4a**	0.10	Me_2Ph	rt	9	100
15[e,k]	**4a**	0.50	Me_2Ph	rt	2.5	100
16[i,k]	**4a**	1	Me_2Ph	rt	1	100
17[g,k]	**4a**	0.03	OEt_3	rt	18	100
18[g,k]	**4a**	0.03	$MePh_2$	rt	240	71

[a]General Reaction Conditions: 2 mg of the catalyst, 1.2 equiv silane, 0.5 equiv 2-bromomesitylene (internal standard), 0.35 mL CH_3CN, and under an N_2 atmosphere. [b]NMR yield. [c]Re (0.003 mmol), and aldehyde (0.3 mmol). [d]Re (0.003 mmol), and aldehyde (3 mmol). [e]Re (0.003 mmol), and aldehyde (0.6 mmol). [f]Re (0.003 mmol), and aldehyde (28 mmol). [g]Re (0.003 mmol), and aldehyde (9 mmol). [h]Re (0.003 mmol), and aldehyde (6 mmol). [i]Re (0.007 mmol), and aldehyde (0.7 mmol). [k]Neat Conditions. rt = room temperature. NR = no reaction.

Complex **4a** is the most efficient catalyst in the series: 100% conversion was attained at room temperature with 0.03 mol% catalyst loading under neat conditions achieving a TON 3,000 and a TOF 138 h^{-1} (Table 1, entry 12); with 0.01 mol% catalyst loading, 92% conversion was observed and TONs 8,586 and a TOF 119 h^{-1} was achieved (Table 1, entry 11). These data suggests that cationic catalysts are significantly more active than the neutral rhenium acetate precursors. For example, the data at room temperature with **4a** at 0.01 and 0.03 mol% catalyst loadings, suggest that this catalyst is more efficient at catalytic hydrosilylation than the precursor **1a**, which was reported to attain a yield of 93.5% (TON = 935; TOF = 62.3 h^{-1}) under similar reaction conditions.[25, 28] Higher temperatures did not improve the catalytic competency of **4a** (Table 1, entries 2-4) presumably due to catalyst decomposition.

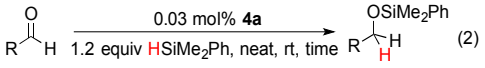
Complex **6** is not as active as **4a** (Table 1, entry 1) and requires heating because of the poor solubility of the complex. The difference in reactivity may also be attributable to the fact that **6** does not contain open coordination sites or L-type ligands that can easily dissociate.

Reactivity was not observed when **4b** was utilized as the catalyst (Table 1, entries 6 and 7). These results suggest that the electronics of the diamido amine ligand are crucial for the reactivity of the complex. Alternatively, the decreased reactivity may be a result of the increased steric demands of the mesityl substituents.

The effect of various silane substrates was investigated. The data suggest that **4a** performed efficiently in the hydrosilylation of benzaldehyde with $HSiMe_2Ph$ and $HSiOEt_3$ (Table 1, entry 17). Conversion was poor when $HSiPh_3$ and $HSiEt_3$ were utilized as substrates (Table 1, entries 8–10). The reaction with $HSiMePh_2$ (Table 1, entry 18) was slower than the reactions using $HSiMe_2Ph$ (24 h) or $HSiOEt_3$ (18 h). Presumably the poor catalytic reactivity of **4a** with $HSiPh_3$ and $HSiMePh_2$ are due to the steric bulk of these silanes. Similar results using these reagents were observed previously by our group with the precursor **1a**.[25, 28]

The optimized conditions for the hydrosilylation of benzaldehyde using **4a** as the (Table 2). A catalyst loading of 0.03 mol% was chosen with $HSiMe_2Ph$ or $HSiOEt_3$ at room temperature under neat conditions as. Catalysis with a variety of aldehydes was efficient, and most reactions were complete in 24 h (Table 2).

Table 2. Hydrosilylation of Various Aldehydes Catalyzed by **4a.**



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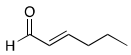
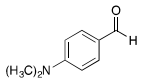
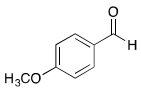
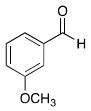
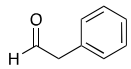
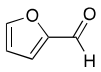
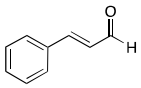
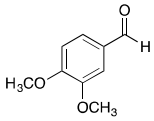
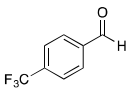
Entry[a]	Substrate	Time (h)	Conversion (%)[b]
1		24	100
2		24	100
3		18	100
4		20	91
5		24	92
6		24	100
7		24	65
8[c]		24	100
9[c]		24	90
10		48	73
11		24	65
12		29	100
13[c]		20	100

[a]General Reaction Conditions: Re (0.00277 mmol), aldehyde (9.21 mmol), 1.2 equiv $HSiMe_2Ph$, 0.5 equiv 2-bromomesitylene, neat, and under an N_2 atmosphere. [b]NMR yield. [c]Silane: $HSiOEt_3$. *Note: Solid aldehydes were dissolved in a minimum amount of CH_3CN.*

Kinetic Studies. Kinetic experiments were performed to determine the dependences with respect to each reagent. The time profile for this reaction under pseudo-first order conditions as monitored by ^1H NMR spectroscopy is depicted in Figure 4. The results suggest a first-order overall rate law (Figure 4 (left)). A first order dependence on [**4a**] was also obtained by plotting the observed rate constants (k_{obs}) versus the concentration of rhenium (Figure 4 (right)).

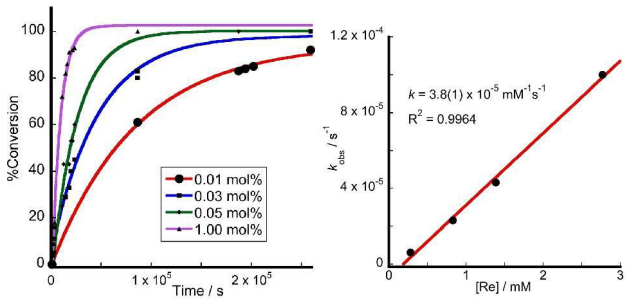


Figure 4. Left: Time profile for the catalytic hydrosilylation of benzaldehyde by **4a**. Reaction Conditions: [Benzaldeyde] = 2.77 M; [$HSiMe_2Ph$] = 3.324 M; [2-bromomesitylene] = 1.385 M; [**4a**] = 0.0279 mmol (0.01 mol%), 0.829 mM (0.03 mol%), 1.385 mM (0.5 mol%), 2.77 (1 mol%). Reactions were performed in a vial under neat conditions at room temperature in a N_2 atmosphere for a fixed time. Each point represents a representative aliquot of the reaction mixture at a different time point. The percent conversion was determined by ^1H NMR spectroscopy by integrating the product peak against the internal standard. Observed rate constants (k_{obs}) 6.2 x 10^{-6} s^{-1}, 2.3 x 10^{-5} s^{-1}, 4.31 x 10^{-5} s^{-1} and 1.0 x 10-4 s^{-1} were obtained. Right: Plot k_{obs} (s^{-1}) vs Concentration (mM) of **4a** for determination of the order with respect to **4a**

The order with respect to [benzaldehyde] was determined by performing the kinetic experiments in neat $HSiMe_2Ph$. The decay of benzaldehyde was monitored by GC with 2-bromomesitylene as the internal standard. As shown in A linear decay over time was observed with suggest a pseudo-zeroth order dependence with respect to [benzaldehyde] (Figure 6).

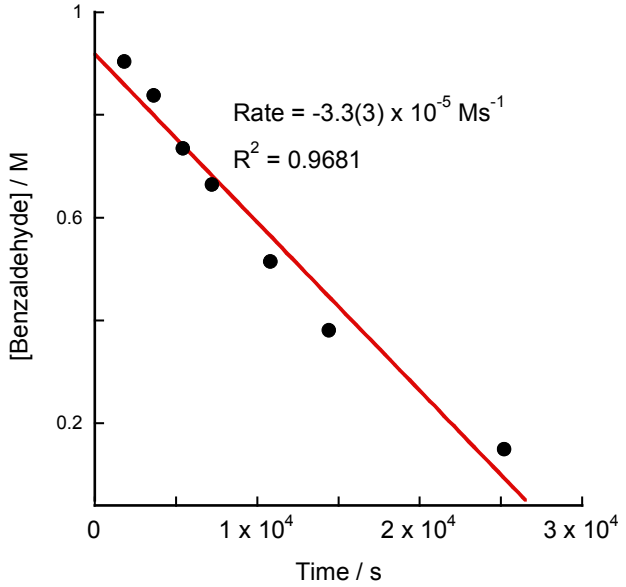


Figure 5. Kinetic plot of [Benzaldehyde] vs time (s). Reaction Conditions: [**4a**] = 0.921 mM; [Benzaldehyde] = 0.921 M; [$HSiMe_2Ph$] = 5.48 M. Benzaldehyde concentration was determined by GC by integrating the benzaldehyde peak versus the internal standard, 2-bromomesitylene (0.438 M). The reaction was performed under neat conditions at room temperature in 10 different 4 mL screw cap vials for a fixed period of time.

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Given that the reaction is first order overall, a zeroth order dependence on [benzaldehyde] suggests that the reaction is first order with respect to silane. Based on the kinetic experiments the rate equation for the hydrosilylation of benzaldehyde catalyzed by **4a** is given by:

$$\frac{d[\mathrm{PhCH_2OSiMe_2Ph}]}{dt} = k[\mathbf{4a}][\mathrm{HSiMe_2Ph}] \quad (1)$$

Hammett Correlation. Competition experiments between benzaldehyde and the corresponding *para*-substituted benzaldehyde (*para*-OCH_3, -Cl, -CF_3, -NO_2) were monitored by ^{1}H NMR spectroscopy after 1 d at room temperature. As shown in Figure 6, the Hammett plot obtained showed a linear correlation with a positive slope (ρ) of 0.36. The slope suggests that for the product-forming step, electron-withdrawing substituents accelerate the rate of the reaction.

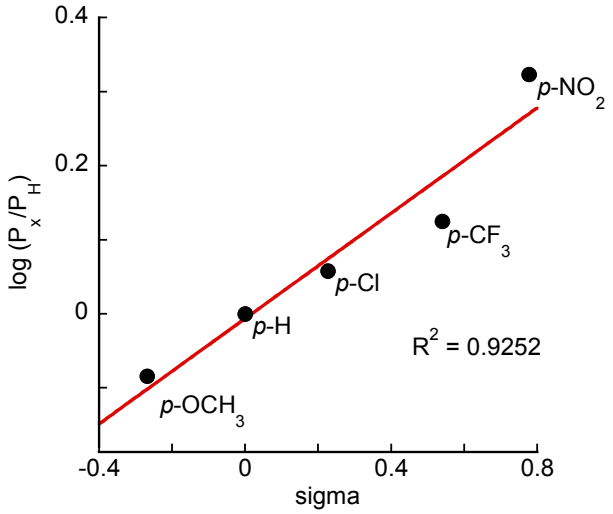
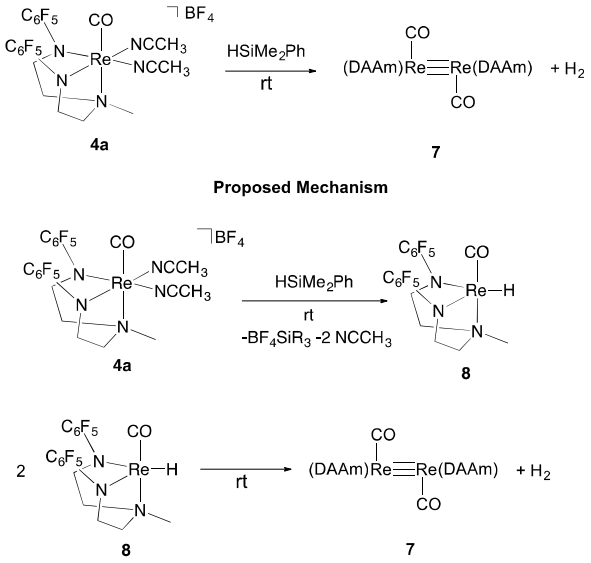


Figure 6. Hammett Plot for the hydrosilylation of various *para* substituted benzaldehydes catalyzed by **4a**. Reaction Conditions: [**4a**] = 0.00277 mmol; [Benzaldehyde] = 0.554 mmol; [*para*-substituted benzaldehyde] = 0.554 mmol; [$HSiMe_2Ph$] = 0.277 mmol; [2-bromomesitylene] = 0.274 mmol. Monitored by ^{1}H NMR spectroscopy at room temperature.

Determination of the Activation Parameters. Kinetic experiments were performed to investigate the activation parameters in a temperature range of 25-80 °C. The enthalpy of activation, $\Delta H^{\ddagger}$, was found to be 13.1(4) kcal/mol, and the entropy of activation, $\Delta S^{\ddagger}$, was found to be -34(1) cal/mol·K. Thus, the overall free energy of activation, $\Delta G^{\ddagger}$ (298 K) was 23.5 kcal/mol.

Possible Intermediates. Attempts were made to isolate possible intermediates in the reaction. The stoichiometric reaction of **4a** with $HSiMe_2Ph$ resulted in the formation of a DAAm dirhenium(II) complex **7** (Scheme 3).



Scheme 3. Stoichiometric reaction of **4a** and $HSiMe_2Ph$ and Proposed Mechanism for the Hydrosilylation Reaction Catalyzed by **4a**

This result suggests that $HSiMe_2Ph$ is activated in the absence of benzaldehyde. Complex **7** has been reported and characterized previously by our group in the stoichiometric reaction of **1a** with $HSiMe_2Ph$ at 80 °C,[25] and was shown to exhibit minimal activity in hydrosilylation reactions described (< 5% conversion in 5 h). A similar pathway for its formation is proposed here and is depicted in Scheme 3. In this mechanism, $HSiMe_2Ph$ is activated to produce the rhenium hydride complex **8**, in the absence of benzaldehyde two molecules react to produce H_2 and **7**. Consistent with the kinetic data, no reactivity was observed in the stoichiometric reaction of **4a** with benzaldehyde in the absence of $HSiMe_2Ph$.

Proposed Mechanism. The following mechanism has been proposed for the catalytic hydrosilylation of benzaldehyde by **4a** (Scheme 4) based on kinetic data, the Hammett correlation, and mechanistic observations. Kinetic data suggest that the turnover-limiting step is the activation of the silane as no dependence was observed on [benzaldehyde] and a first order dependence on [silane] was observed. Activation of the silane could occur *via* η^1 or η^2 coordination. Treatment of **4a** with $HSiMe_2Ph$ in the absence of benzaldehyde results in the formation of **7**. The electronic dependence on the benzaldehyde substrate, suggest that for the product-forming step, electron-withdrawing substituents in the para position of the benzaldehyde substrate accelerate the formation of the reduced carbonyl products.

In recent years, an ionic hydrosilylation mechanism has been proposed by Oestreich[18] and computationally studied by Wei[11-13, 22, 23, 30] for catalysis by oxorhenium and oxomolybdenum complexes. In this mechanism aldehyde does not coordinate to the metal center; instead, silane is activated by coordination to rhenium, this is followed by nucleophilic S_N2-Si attack of the carbonyl substrate at the activated silicon leading to the cleavage of the Si-H bond and formation of an ion pair. Product formation results from transfer of the hydride from

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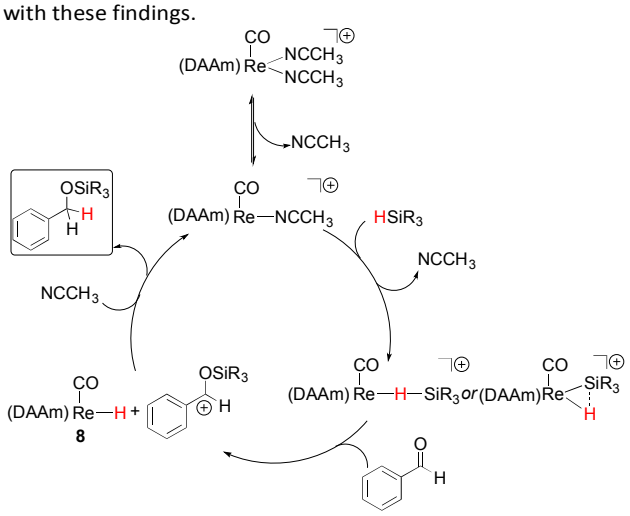
rhenium to the carbonyl carbon of the resultant ion-pair. As shown in Scheme 4, the proposed mechanism is consistent with these findings.



Scheme 4. Proposed Mechanism for the Hydrosilylation Reaction Catalyzed by **4a**.

CONCLUSION

In conclusion, we have demonstrated that cationic DAAm rhenium(III) complexes are highly efficient catalysts for the hydrosilylation of aldehydes. Kinetic data revealed that the reaction rate is 1st order in [silane] and [**4a**], and is independent of aldehyde concentration. A Hammett correlation suggests that electron-withdrawing substituents on the para position of benzaldehyde accelerate the reaction rate. Based on this data, a non-hydride ionic outer-sphere hydrosilylation mechanism has been proposed.

EXPERIMENTAL SECTION

General Considerations. **1a-b**[28] and $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-$ $[H(OEt_2)_2]^+$ ($HBAr^F{}_4$)[31, 32] were prepared according to previous procedures. All reactions were carried out in a nitrogen filled glove box unless otherwise noted. All reagents were purchased from commercial sources, placed in a nitrogen filled glove box and used as received without further purification. ^{1}H, ^{13}C and ^{19}F spectra were acquired on a Varian Mercury 700 MHz, Varian Mercury 400 MHz or Varian Mercury 300 MHz spectrometer. NMR chemical shifts are listed in parts per million (ppm) and are referenced to residual protons or carbons of the deuterated solvents, respectively at room temperature unless otherwise noted. The FTIR spectra were obtained in KBr thin films on a JASCO FT/IR-4100 instrument. Gas Chromatography was performed on an Agilent 7820A GC/FIC using HP-5MS columns. Elemental analyses were performed by Atlantic Micro Laboratories Inc. X-ray crystallography was performed at the X-ray Structural Facility at North Carolina State University by Dr. Roger D. Sommer and Paul D. Boyle.

General Synthesis [(DAAm-aryl)Re(CO)($NCCH_3$)$_2$][X] (aryl = C_6F_5, Mes) (X = OTf, $BAr^F{}_4$, BF_4, PF_6); 2a-b, 3a-b, 4a-b, 5a-b.

In a nitrogen filled glove box, the corresponding [(DAAm-aryl)Re(CO)(OAc)] (aryl = C_6F_5 (**1a**), Mes(**1b**)) (**1a** = 50 mg, 0.07 mmol; **1b** = 50 mg, 0.08 mmol) was added to a screw cap vial and dissolved in 0.35 mL of acetonitrile. Then, the corresponding acid HX (X = HOTf, $HBAr^F{}_4$, $HBF_4{\cdot}OEt_2$, $HPF_6{\cdot}H_2O$) (1 equiv) was added to the solution. The solvent was removed under pressure. The resulting oil was dissolved in diethyl ether and the corresponding bisacetonitrile product was precipitated with excess of hexanes. The final powder was collected *via* vacuum filtration.

[(DAAm-C_6F_5)Re(CO)($NCCH_3$)$_2$][OTf], **2a.** Following the general synthesis, complex **2a** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN) δ: 4.05 (m, 2H), 3.71 (m, 2H), 3.01 (m, 4H), 2.85 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ: 188.2, 172.9, 143.5, 142.7, 142.1, 141.3, 140.3, 139.0-138.2, 137.8, 137.5, 65.9, 59.1, 55.2. ^{19}F NMR (376 MHz, CD_3CN) δ: -79.4 (s, 3F), -149.8 (dd, *J* = 22.1, 5.7 Hz, 2F), -150.8 (dd, *J* = 14.0, 8.0 Hz, 2F), -162.9 (t, *J* = 20.9 Hz, 2F), -165.8 (m, 2F), -166.7 (m, 2F). IR (FTIR, cm^{-1}): ν(CO) 1882. Anal. Calc. for $C_{23}H_{17}F_{13}N_5O_4ReS$: C, 30.95; N, 7.85; H, 1.92. Found: C, 30.39; N, 7.74; H, 1.90.

[(DAAm-Mes)Re(CO)($NCCH_3$)$_2$][OTf], **2b.** Following the general synthesis, complex **2b** was synthetized in quantitative yield. ^{1}H NMR (400 MHz, CD_3CN) δ: 6.87 (s, 2H), 6.76 (s, 2H), 4.03 (m, 2H), 3.56 (m, 2H), 3.07 (m, 2H), 2.91 (m, 5H), 2.33 (s, 6H), 2.25 (s, 6H), 1.96 (m, 6H), 1.84 (s, 6H). ^{13}C NMR (126 MHz, CD_3CN) δ: 193.4, 159.2, 135.3, 132.1, 131.6, 130.4, 129.7, 66.5, 60.2, 49.4, 20.4, 20.3, 20.0. ^{19}F NMR (376 MHz, CD_3CN) δ: -79.6 (s, 3F). IR (FTIR, cm^{-1}): ν(CO) 1890. Anal. Calc. for $C_{29}H_{39}F_3N_5O_4ReS{\cdot}H_2O$: C, 43.71; N, 8.79; H, 4.93. Found: C, 42.50; N, 8.69; H, 5.00.

[(DAAm-C_6F_5)Re(CO)($NCCH_3$)$_2$][$BAr^F{}_4$], **3a.** Following the general synthesis, complex **3a** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN) δ: 7.69 (m, 12H), 4.03 (m, 2H), 3.72 (m, 2H), 2.99 (m, 4H), 2.84 (s, 3H), 1.96 (s, 6H). ^{13}C NMR (175 MHz, CD_3CN) δ: 188.1, 163.0, 162.7, 162.4, 162.1, 143.7, 142.9, 142.2, 141.4, 140.4, 139.2-138.6, 137.9, 137.6, 130.2, 130.0, 129.8, 129.6, 127.7, 126.2, 124.6, 123.1, 66.2, 59.3, 47.5. ^{19}F NMR (376 MHz, CD_3CN) δ: -63.25 (s, 24F), -149.8 (m, 2F), -150.8 (m, 2F), -162.9 (m, 2F), -165.8 (t, *J* = 20.7 Hz, 2F), -166.2 (m, 2F). IR (FTIR, cm^{-1}): ν(CO) 1925. Anal. Calc. for $C_{54}H_{29}BF_{34}N_5ORe{\cdot}H_2O$: C, 39.92; N, 4.31; H, 1.92. Found: C, 39.11; N, 4.80; H, 2.02.

[(DAAm-Mes)Re(CO)($NCCH_3$)$_2$][$BAr^F{}_4$], **3b.** Following the general synthesis, complex **3b** was synthetized in quantitative yield. ^{1}H NMR (376 MHz, CD_3CN) δ: 7.69 (m, 12H), 6.87 (s, 2H), 6.75 (s, 2H), 4.02 (m, 2H), 3.55 (m, 2H), 3.07 (m, 2H), 2.91 (m, 5H), 2.33 (s, 6H), 2.25 (s, 6H), 1.96 (m, 6H), 1.84 (s, 6H). ^{19}F NMR (376 MHz, CD_3CN) δ: -63.4 (s, 24F). IR (FTIR, cm^{-1}): ν(CO) 1890. The complex was not characterized by ^{13}C NMR due to its very poor stability. Elemental Analysis was not attempted on this complex because of its instability.

[(DAAm-C_6F_5)Re(CO)($NCCH_3$)$_2$][BF_4], **4a.** Following the general synthesis, complex **4a** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN) δ: 4.05 (m, 2H), 3.72 (m, 2H), 3.01 (m, 4H), 2.85 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (176 MHz, CD_3CN) δ: 188.2, 143.5, 142.7, 142.1, 141.3, 140.2, 139.0-138.4, 137.8, 137.6-137.3, 66.0, 59.1, 47.3. ^{19}F NMR (376 MHz, CD_3CN) δ: -149.8 (dd, *J* = 22.1, 5.8 Hz, 2F), -150.8 (m, 2F), -

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151.7 (d, *J* = 20.2 Hz, 4F), -162.9(t, *J* = 20.9 Hz, 2F), -165.8 (m, 2F), -166.2 (m, 2F). IR (FTIR, cm^{-1}): ν(CO) 1882. Anal. Calc. for $C_{22}H_{17}BF_{14}N_5ORe$: C, 31.82; N, 8.43; H, 2.06. Found: C, 31.40; N, 7.90; H, 2.12.

[(DAAm-Mes)Re(CO)(NCCH$_3$)$_2$][BF$_4$], **4b.** Following the general synthesis, complex **4b** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN) δ: 6.87 (s, 2H), 6.75 (s, 2H), 4.03 (m, 2H), 3.55 (m, 2H), 3.07 (m, 2H), 2.91 (m, 5H), 2.33 (s, 6H), 2.25 (s, 6H), 1.84 (d, 12H). ^{13}C NMR (126 MHz, CD_3CN) δ: 193.4, 159.3, 135.3, 132.1, 131.6, 130.4, 129.7, 66.5, 60.2, 49.42, 20.43, 20.30, 20.02. ^{19}F NMR (376 MHz, CD_3CN) δ: -151.3 (s, 4F). IR (FTIR, cm^{-1}): ν(CO) 1878. Anal. Calc. for $C_{28}H_{39}BF_4N_5ORe{\cdot}H_2O$: C, 44.68; N, 9.30; H, 5.49. Found: C, 43.80; N, 8.99; H, 5.38.

[(DAAm-C$_6$F$_5$)Re(CO)(NCCH$_3$)$_2$][PF$_6$], **5a.** Following the general synthesis, complex **5a** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN) δ: 4.07 (m, 2H), 3.74 (m, 2H), 3.05 (m, 4H), 2.87 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ: 188.1, 144.1, 143.3, 141.6, 140.8, 139.3, 138.5, 137.8, 136.9, 66.0, 59.2, 47.3. ^{19}F NMR (376 MHz, CD_3CN) δ: -72.0 (s, 3F), -73.9 (s, 3F), -150.0 (dd, *J* = 22.1, 5.6 Hz, 2F), -150.9 (dt, *J* = 16.1, 4.7 Hz, 2F), -163.0 (t, *J* = 20.9 Hz, 2F), -165.8 (t, *J* = 20.0 Hz, 2F), -166.2 (m, 2F). IR (FTIR, cm^{-1}): ν(CO) 1882. Anal. Calc. for $C_{22}H_{17}F_{16}N_5OPRe$: C, 29.74; N, 7.88; H, 1.93. Found: C, 29.62; N, 7.19; H, 2.03.

[(DAAm-Mes)Re(CO)(NCCH$_3$)$_2$][PF$_6$], **5b.** Following the general synthesis, complex **5b** was synthetized in quantitative yield. ^{1}H NMR (300 MHz, CD_3CN, δ): 6.88 (s, 2H), 6.75 (s, 2H), 4.03 (m, 2H), 3.55 (m, 2H), 3.07 (m, 2H), 2.97 (m, 5H), 2.33 (s, 6H), 2.25 (s, 6H), 1.84 (m, 6H), 1.86 (s, 6H). ^{13}C NMR (101 MHz, CD_3CN, δ): 193.37, 159.31, 135.36, 132.15, 131.60, 130.40, 129.70, 66.52, 60.21, 49.47, 20.48, 20.34, 20.07. ^{19}F NMR (376 MHz, CD_3CN, δ): -71.96 (s, 3F), -73.84 (s, 3F). IR (FTIR, cm^{-1}): ν(CO) 1878. Elemental Analysis was not attempted on this complex because of its instability.

Synthesis of complex [(DAAm-C$_6$F$_5$)Re(CO)(Cl)$_2$], 6.

In a screw cap vial, complex **1a** (50 mg, 0.07 mmol) was dissolved in a minimal amount of methylene chloride. Excess 12 M HCl (5.0 µL, 60.0 µmol) was added to the screw cap vial. The solution was shaken and let to stand overnight. The product precipitates out of solution as green crystals (21.9 mg, 43.0% yield). ^{1}H NMR (400 MHz, CD_3CN) δ: 4.16 (m, 2H), 3.45 (m, 2H), 3.36 (s, 3H), 3.31 (m, 4H). The amine proton in the ligand backbone was not observed either at room temperature or -60 °C indicating that the proton is too fast to be observed on the NMR time scale. ^{19}F NMR (376 MHz, CD_3CN) δ: -150.1 (m, 2F), -150.5 (dd, *J* = 23.5, 6.6 Hz, 2F), -162.9 (m, 2F), -167.2 (m, 4F). The complex was not characterized by ^{13}C NMR due to its very poor solubility in acetonitrile-d_3 or methylene chloride-d_2. IR (FTIR, cm^{-1}): ν(CO) 1873. Anal. Calc. for $C_{18}H_{13}Cl_2F_{10}N_3ORe$: C, 29.48; N, 5.73: H, 1.65. Found: C, 29.79; N, 6.01: H, 1.59.

General Procedure for Catalytic Hydrosilylation Reactions of Aldehydes with 4a and 4b.

In a nitrogen-filled glove box, the corresponding [(DAAm-aryl)Re(CO)(OAc)] (aryl = C_6F_5 (**1a**), Mes (**1b**)) (**1a** = 2 mg, 0.003 mmol; **1b** = 0.003 mmol) was added to a screw cap vial and dissolved in 0.35 mL of acetonitrile. $HBF_4{\cdot}OEt_2$ (1 equiv) was added to the solution. The solvent was removed under reduced pressure to afford the corresponding oil. The aldehyde (27.7 mmol, 0.01 mol%; 9.23 mmol, 0.03 mol%; 5.54 mmol, 0.05 mol%; 2.77 mmol, 0.1 mol%; 0.554 mmol, 0.5 mol%; 0.277 mmol, 1 mol%), silane (33.2, 11.1, 6.65, 3.32, 0.665 and 0.332 mmol respectively) and 2-bromomesitylene (0.20 mL, 1.39 mmol) were sequentially added to the screw cap vial. The reaction was stirred at room temperature for the designated amount of time. An aliquot of the crude reaction mixture was dissolved in $CDCl_3$ or CD_3CN. The percent conversion was determined by the ^{1}H NMR ratio of the product and starting material: ((integration of methylene protons/2)/((integration of aldehyde peak) + (integration of methylene protons/2))).

General Procedure for Catalytic Hydrosilylation Reactions of Aldehydes with 6.

In a nitrogen-filled glove box complex **6** (2 mg, 0.003 mmol) was added to a screw cap NMR tube and dissolved in 0.35 mL of acetonitrile. The aldehyde (28 µL, 0.274 mmol), silane (50 µL, 0.326 mmol) and 2-bromomesitylene (21 µL, 0.136 mmol) were sequentially added to the screw cap NMR tube. The reaction was heated at 80 °C for the designated amount of time. The percent conversion was determined by the proton NMR ratio of the product and starting material ((integration of methylene protons/2)/((integration of aldehyde peak) + (integration of methylene protons/2))).

General Procedure to Obtain Order with Respect to Benzaldehyde by Gas Chromatography.

In a nitrogen filled glove box complex **1a** (2 mg, 0.003 mmol), and $HBF_4{\cdot}OEt_2$ (1 equiv) were added to a screw cap vial and dissolved in 0.35 mL of acetonitrile. The solvent was removed under reduced pressure to afford the corresponding oil. Then, benzadehyde (2.8 mmol, 0.28 mL), dimethylphenylsilane (17 mmol, 2.5 mL), and 2-bromomesiltylene (1.4 mmol, 0.20 mL) were added to the screw cap vial and mixed. The reaction mixture was divided into 10 small screw cap vials equipped with a stir bar. The reactions were stirred at room temperature for the designated amount of time. At that time, the ratio benzaldehyde:2-bromomesitylene was determined by GC using a calibration curve.

General Procedure to Competition Reaction for Hammett Plot.

In a nitrogen-filled glove box complex **1a** (2 mg, 0.003 mmol), and $HBF_4{\cdot}OEt_2$ (1 equiv), benzaldehyde (0.55 mmol, 56 µL), the indicated *para*-substituted benzaldehyde (0.55 mmol), dimethylphenylsilane (0.28 mmol, 42 µL), and 2-bromomesiltylene (0.27 mmol, 42 µL) were added to the screw cap vial. The reaction mixture was dissolved in CD_3CN (0.35 mL) and stirred for 24 h at room temperature. An aliquot of the reaction mixture was placed in CD_3CN. The ^{1}H NMR integration against the internal standard (2-bromomesitylene) of the methylene protons of the *para*-substituted silyl ether and the benzyloxydimethylphenylsilane were used to determine the product ratio value (P_H/P_X).

General Procedure for Eyring Plot Data.

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In a nitrogen-filled glove box complex **1a** (2 mg, 0.003 mmol) was added to a screw cap NMR tube and dissolved in 0.35 mL of CD_3CN. Then $HBF_4{\cdot}OEt_2$ (0.3 µL, 0.003 mmol) was added to the solution and mixed. The benzaldehyde (0.554 mmol, 56 µL), dimethylphenylsilane (0.665 mmol, 0.1 mL) and 2-bromomesitylene (0.277 mmol, 42 µL) were sequentially added to the mixture. The reaction was heated at the respective temperature (25–80 °C). The percent conversion was determined by the proton NMR ratio of the product and starting material.

Acknowledgements

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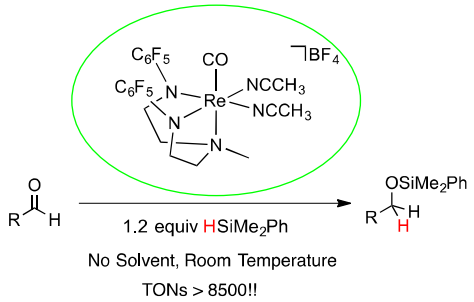

Cationic Re(III) complexes are shown to be more active for the catalytic hydrosilylation of benzaldehydes than their neutral acetate precursors.