

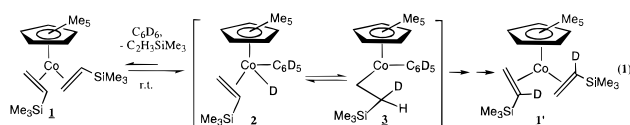
Co(I)-Catalyzed Inter- and Intramolecular Hydroacylation of Olefins with Aromatic Aldehydes

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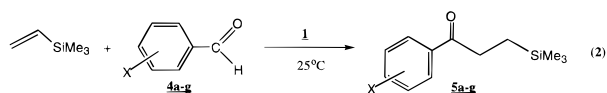
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Intramolecular hydroacylation of olefins using Rh(I) catalyst precursors has been extensively studied by Bosnich^{1–6} and others;^{7–16} however, intermolecular versions have received little attention.^{9,10,17–20} The most notable example of intermolecular catalysis is Marder's and Milstein's report²⁰ of addition of benzaldehyde to ethylene catalyzed by η^5 -C₈H₇Rh(C₂H₄)₂ (4 TO/h, 100 °C, 70 atm C₂H₄). Recently we reported that Co(I) complex **1** containing bulky, highly labile vinyltrimethylsilane ligands exhibits H/D exchange in C₆D₆ presumably via intermediate **2** involving oxidative addition of benzene to a Co(I) species²¹ (eq 1). The formation of olefin-coupled aromatic products was not observed.



We report here the use of complex **1** as a precatalyst for both *intra*- and *intermolecular* hydroacylation of certain substrates together with a mechanistic study of these reactions.

Initial studies involved hydroacylation of vinyltrimethylsilane using a series of aromatic aldehydes in benzene or acetone as shown in eq 2.²² Results are summarized in Table 1.



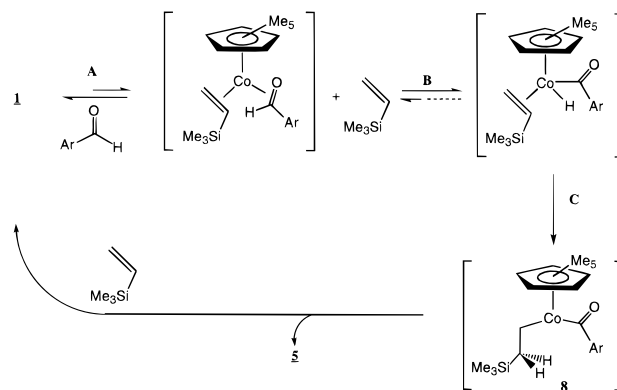
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Table 1. Hydroacylation of Vinyltrimethylsilane by Substituted Aromatic Aldehydes (X-ArC(O)H)

entry	aromatic aldehyde (X)	ratio of aldehyde to olefin to catalyst			
		20:20:1		30:50:1	100:100:1
		TOF, ^a [TO/h]	convn, ^b %	convn, ^b %	convn, ^c %
1 (a)	4-Me ₂ N-	6.7	100	100	100, (65) ^d
2 (b)	4-Me-O-	6.2	100	100	100, (82) ^d
3 (c)	4-Me-	6.1	100	100	90, (75) ^d
4 (d)	3,4-(MeO) ₂ -	4.0	77	85	70, (33) ^d
5 (e)	3,4,5-(MeO) ₃ -	3.2	30	45	45, (85) ^d
6 (f)	3-Me-	4.4	35	42	52, (83) ^d
7 (g)	H	2.9	19	25	38, (85) ^d

^a Initial TOF determined by ¹H NMR; 0.7 mL of benzene-*d*₆ at 35 °C, 0.005 g of **1** (1.27 × 10⁻⁵ mol). ^b Catalysis competes with aldehyde decarbonylation generating **6** and **7** except for entries 1–3. ^c Conversion based on ¹H NMR analysis of a scaled up reaction in 3.5 mL of toluene, 0.01 g of **1** (2.54 × 10⁻⁵ mol). ^d Isolated yield based on conversion after chromatography on silica with hexane/ethyl acetate.

Scheme 1



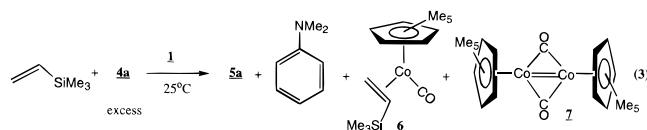
Using *p*-dimethylaminobenzaldehyde, **4a**, a large number of turnovers (>250) can be achieved without significant catalyst decomposition, thus mechanistic studies were carried out using this electron-rich benzaldehyde derivative. Monitoring initial turnover frequencies (benzene-*d*₆, 35 °C) as a function of olefin and aldehyde concentrations established that the TO rate is first-order in aldehyde and inverse order in olefin, turnover frequency (TOF) = *k*[aldehyde]/[olefin]. For example, the initial TOF (35 °C, C₆D₆) at ratios of olefin:aldehyde:catalyst of 20:20:1, 50:20:1, and 20:50:1 are 6.7/h, 2.2/h, and 14.8/h, respectively. More extensive data and kinetic plots appear in the Supporting Information. At a 1:1 molar ratio of aldehyde:olefin the TO frequency is invariant with percent conversion and linear plots of turnover number vs reaction time are observed up to 100% conversion. The sole cobalt species detected by *in situ* NMR spectroscopy during catalysis, the catalyst resting state, was complex **1**. Based on these results the mechanism of hydroacylation must involve a rapid pre-equilibrium between **1** and an olefin/aldehyde adduct prior to the turnover-limiting step. A possible catalytic cycle is shown in Scheme 1.

Use of deuterated aldehyde, *p*-NMe₂C₆H₄C(O)D, results in formation of *p*-Me₃SiCHDC₂H₂C(O)C₆H₄NMe₂; no evidence for H/D scrambling in the product is seen.²⁰ Following the reaction by ¹H NMR spectroscopy revealed no formation of protio aldehyde, *p*-NMe₂C₆H₄C(O)H, during the reaction which suggests that a species such as **8** in which the methylene hydrogens are equivalent does not form prior to the transition state. (However, note that formulation of **8** as an η^2 -acyl complex results in the methylene hydrogens being diastereotopic and thus

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remaining inequivalent.) An alternative mechanism for ketone formation, the migration of the acyl moiety to olefin, as opposed to the migration of the hydride to olefin seems unlikely based on the observed exclusive regiochemistry of aldehyde addition and the site selectivity for H/D exchange in this system.²¹

Using excess olefin, complex **1** is the only organometallic species present after complete catalytic conversion of **4a** to **5a**. With excess aldehyde, complete conversion of olefin to ketone is observed; however, the cobalt species present reacts with excess aldehyde to produce decarbonylation products (*N,N*-dimethylaniline) and the cobalt carbonyl complexes **6**²² and **7**^{22,23–25} (eq 3). Increasing the aldehyde:olefin ratio increases the **7**:**6** ratio. Reaction of **1** with 15 equiv of **4a** produces only **5a**, *N,N*-dimethylaniline, and **7**. Complexes **6** and **7** are not active in hydroacylation catalysis. Thermolysis of **6** does not yield **7** (benzene-*d*₆, 12 h, 35 °C), and treatment of **7** with vinyltrimethylsilane under the reaction conditions does not give **6**. These results suggest decarbonylation reactions and formation of inactive cobalt carbonyl complexes are major routes for catalyst deactivation.



Using aromatic aldehydes with less electron-donating substituents, catalyst lifetimes are substantially decreased due to decarbonylation and catalyst deactivation, but initial turnover frequencies are not significantly affected (see Table 1). For example, with *p*-CH₃C₆H₄C(O)H complete conversion is obtained with 5% catalyst loading, but conversion drops to ca. 90% with 1% catalyst (compare entry 3, columns 1 vs 3). With unsubstituted benzaldehyde, only 19% conversion is achieved with 5% catalyst loading; however, increasing the olefin:aldehyde ratio to retard decarbonylation (see above) increases conversion to 25% with only 3.3% catalyst (see entry 7, column 2). Similar trends are evident for other aldehydes reported in Table 1.

Other vinylsilanes are effective substrates. Using **1** as the precatalyst, *p*-NMe₂C₆H₄C(O)H adds to vinyltriphenylsilane with higher initial TO frequencies (102 TO/h, 35 °C); complete conversion at 0.5% catalyst load is observed.²⁶ Reaction of vinyltrimethoxysilane is significantly slower (initial TOF: 0.5 TO/h, 35 °C), yet complete conversion at 1% catalyst load is observed.²⁷ Variation in these rates probably reflects the relative binding affinities of the olefins to the Co(I) center as controlled by sterics.

(22) All organic products and organometallic complexes have been characterized by NMR and IR spectroscopy, elemental analysis or mass spectroscopy; these data are summarized in the Supporting Information.

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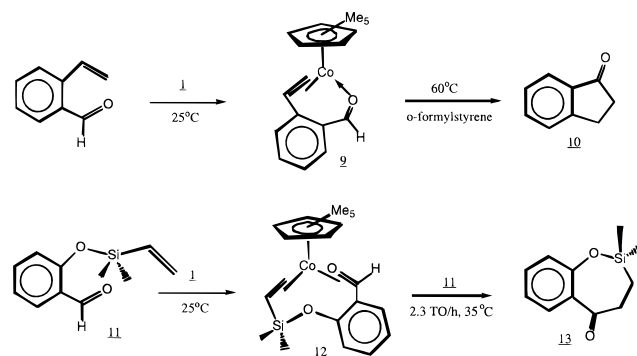
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(26) In a solution of vinyltriphenylsilane and **1** in acetone-*d*₆ the mixed olefin complex, C₃Me₅Co(C₂H₅SiMe₃)(C₂H₅SiPh₃), is generated in equilibrium with **1**. During rapid conversion of vinyltriphenylsilane to ketone in the presence of aldehyde the resting state changes and the concentration of the mixed olefin complex decreases in favor of **1**.

(27) Upon addition of vinyltrimethoxysilane, **1** is converted to a new olefin complex, C₃Me₅Co(C₂H₅Si(OMe)₃)₂. This species is the only Co-complex present during hydroacylation catalysis.

Intramolecular hydroacylation reactions of aromatic aldehydes were also examined. Treatment of **1** with *o*-formylstyrene (benzene, 25 °C) results in formation of **9** which has been isolated and characterized.²² Diagnostic for this cobalt(I) complex are the NMR features of the coordinated aldehyde (¹H, 9.35 ppm, ¹³C, 178.8 ppm).²⁸ Thermolysis of **9** with excess *o*-formylstyrene at 60 °C results in slow formation of cyclic ketone **10**, but only ca. 5 turnovers can be achieved before catalyst decomposition and formation of unidentified organometallic products. To extend the chelate ring size, compound **11** was prepared from salicylaldehyde.²² Exposure of **11** (benzene-*d*₆, 35 °C) to **1** (1%) results in quantitative catalytic conversion to the intramolecular hydroacylation product, cyclic ketone **13**.²² A turnover frequency of 2.3/h is observed and is independent of substrate concentration (a turnover vs time plot is presented in the Supporting Information). Consistent with these kinetics, analysis of the catalytic reaction by NMR spectroscopy shows that **1** is rapidly converted to **12**, the catalyst resting state, which persists throughout the reaction. Complex **12** could be characterized by ¹H and ¹³C NMR spectroscopy at –10 °C where hydroacylation is slow.²² Notable features are the ¹H and ¹³C shifts of the coordinated aldehyde (5.05 and 91.1 ppm) which suggest a π-coordination of the aldehyde moiety.²⁹



Transition metal-catalyzed intermolecular hydroacylation reactions are potentially useful general methods for carbon–carbon bond formation. Results presented here establish key mechanistic features of the hydroacylation of olefins catalyzed by Co(I) complex **1** and show that for certain substrate combinations useful catalytic lifetimes and turnover frequencies can be achieved under mild conditions. Future studies are aimed at broadening the scope of this reaction and providing additional mechanistic details.

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Supporting Information Available: Details of synthesis and characterization of organic products and organometallic complexes and descriptions and complete results of kinetic experiments (12 pages). See any current masthead page for ordering and Internet access instructions.

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