The $Co_2(CO)_8$-Catalyzed Hydrosilylation of Oxygen-Containing Olefins: Silylmetalation as a Key Step

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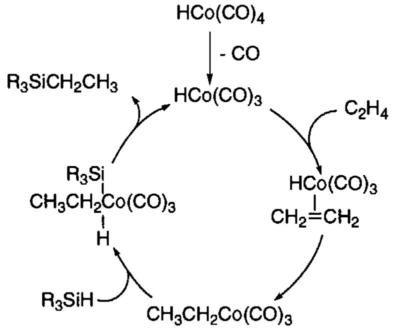
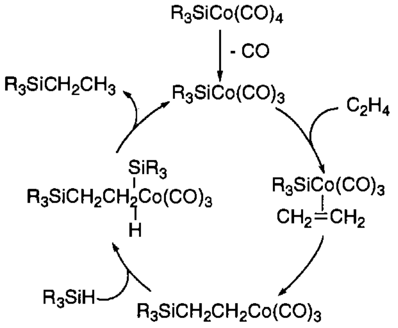
The hydrosilylation of oxygen-containing olefins in the presence of $Co_2(CO)_8$ was carried out. The $Co_2(CO)_8$-catalyzed hydrosilylation of allyl acetate with $HSiEt_2Me$ is consistent with proceeding via a silylmetalation mechanism rather than a classical hydrometalation (Chalk-Harrod mechanism).

The transition-metal-catalyzed hydrosilylation of olefins represents one of the most important and straightforward methods for the preparation of organosilicon compounds.[1] The reaction mechanism for this reaction has been discussed in terms of two distinct mechanisms, namely hydrometalation (Scheme 1) and silylmetalation (Scheme 2). The well known Chalk-Harrod mechanism (hydrometalation) involves the insertion of the olefin into the H-Co bond of $HCo(CO)_3$, leading to the formation of an alkylcobalt complex as a key step. The subsequent reactions are the oxidative addition of a hydrosilane to the alkylcobalt complex followed by the reductive elimination to form an alkylsilane (Scheme 1).[2] Chalk and Harrod proposed the above hydrometalation mechanism based on the facts that an increase in the concentration of $HSiEt_3$ resulted in a decrease in the reaction rate and that the catalytic reaction was accompanied by the isomerization of the olefin in the case of the $Co_2(CO)_8$-catalyzed hydrosilylation with $HSiEt_3$ of simple olefins such as 1-hexene.[2a] This mechanism gained wide acceptance until recently, when Wrighton pointed out the possibility of a silylmetalation mechanism (Scheme 2) on the basis of a series of stoichiometric reactions.[3] The key step in this mechanism is the insertion of an olefin into a Si-Co bond in $R_3SiCo(CO)_3$ leading to a β-silylethylcobalt complex, from which, via the successive steps shown in Scheme 2, the hydrosilylation product is formed and $R_3SiCo(CO)_3$ is regenerated. This mechanism offers a reasonable explanation for the formation of vinylsilanes as significant by-products under hydrosilylation conditions.[4] In some cases vinylsilanes, which are formed by β-hydride elimination from a β-silylethylmetal complex, are obtained as the main product.[5] We found that $Fe_3(CO)_{12}$ was an efficient catalyst for the dehydrogenative silylation of styrene leading to (*E*)-β-silylstyrene,[6] $Ru_3(CO)_{12}$ for styrene,[7] $Co_2(CO)_8$ for acrylic acid esters,[8] and $RhCl(PPh_3)_3$ for 1,5-hexadiene,[9] all of which must involve silylmetalation as a key step. Recently, several reports have appeared on the hydrosilylation of olefins in which the catalytic cycle is proposed to involve silylmetalation.[10] We wish to report here that the $Co_2(CO)_8$-catalyzed hydrosilylation of allyl acetate with $HSiEt_2Me$ very likely proceeds via a silylmetalation mechanism, rather than hydrometalation.



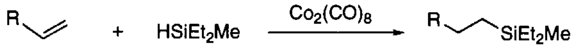
Scheme 1. Hydrometalation Mechanism.

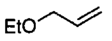
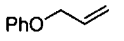
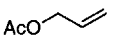
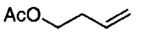
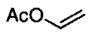


Scheme 2. Silylmetalation Mechanism.

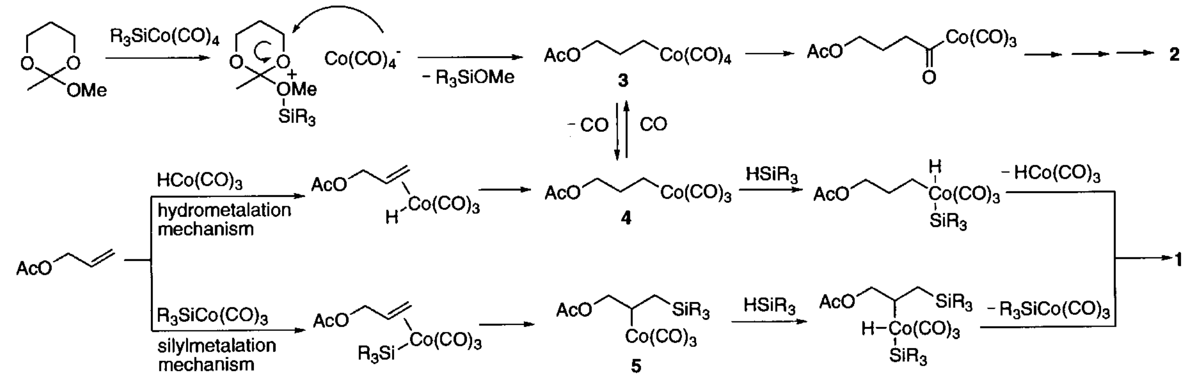
The results of the $Co_2(CO)_8$-catalyzed hydrosilylation of several olefins are summarized in Table 1. These reactions were carried out under the following three types of reaction conditions; condition A: olefin (2.5 mmol), $HSiEt_2Me$ (12.5 mmol), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (5 ml) at 25 °C under Ar;

Table 1. Hydrosilylation of olefins with $HSiEt_2Me$



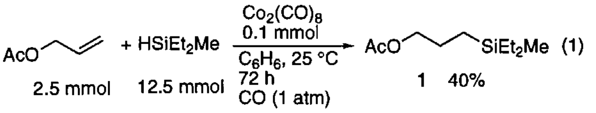
Olefin	Ar, 7 h		CO, 72 h
	HSi (xs)[a] Condition A	$RCH=CH_2$ (xs)[b] Condition B	HSi (xs)[c] Condition C
	10%	14%	—
	82%	75%	57%
	58%	63%	28%
	82%	75%	40%
	37%	32%	8%
	44%	43%	30%

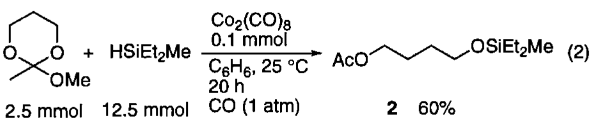
[a] Reaction conditions A: olefin (2.5 mmol), $HSiEt_2Me$ (12.5 mmol), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (5 ml) at 25 °C under Ar for 7 h. [b] Reaction conditions B: olefin (7.5 mmol), $HSiEt_2Me$ (2.5 mmol), $Co_2(CO)_8$(0.1 mmol), C_6H_6 (5 ml) at 25 °C under Ar for 7 h. [c] Reaction conditions C: olefin (2.5 mmol), $HSiEt_2Me$ (12.5 mmol), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (5 ml) at 25 °C under CO for 72 h.



Scheme 3.

condition B: olefin (7.5 mmol), $HSiEt_2Me$ (2.5 mmol), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (5 ml) at 25 °C under Ar; condition C: olefin (2.5 mmol), $HSiEt_2Me$ (12.5 mmol), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (5 ml) at 25 °C under CO. Both the reaction rate and the product yields were decreased when the reaction was run under an atmosphere of CO instead of Ar. It should be noted that oxygen-containing olefins gave higher yields of the hydrosilylation product and that 1-hexene was completely unreactive under all of those reaction conditions.





To elucidate the reaction mechanism of the $Co_2(CO)_8$-catalyzed hydrosilylation of olefins, another type of catalytic reaction that involves a different pathway to one of suspected intermediates in the hydrosilylation of an olefin was devised. For a mechanistic consideration to be meaningful, these two types of reaction should proceed catalytically under identical reaction conditions. We chose allyl acetate and a cyclic orthoester as substrates for such a purpose and these were investigated under reaction condition C. Thus, the reaction of allyl acetate afforded the hydrosilylation product **1** in 40% yield and no CO-incorporated products were observed (eq 1). The reaction of the cyclic orthoester gave 4-(diethylmethylsilyl)butyl acetate (**2**) (eq 2). The incorporation of CO into the cyclic orthoester indicates the intermediary formation of γ-acetoxy-propylcobalt carbonyl **3**,[11] which, in turn, is similar to the suspected intermediate **4** in the hydrosilylation of allyl acetate via a hydrometalation mechanism (Scheme 3).[12,13] If common intermediate is formed, same products would be obtained (eqs 1 and 2). This is not the case. This fact suggests that eq 1 does not involve a hydrometalation mechanism. It should be noted that the argument made above is based on the assumption that the interconversion of the 18e complex **3** and the 16e complex **4** is enough faster than proceeding steps. To clarify this point a further study is necessary. Although incomplete, the present study represent the first approach using a working catalytic reaction to elucidate the original Chalk-Harrod reaction, i.e., $Co_2(CO)_8$-catalyzed hydrosilylation.

In conclusion, the findings herein strongly suggest that the $Co_2(CO)_8$-catalyzed addition of $HSiEt_2Me$ to allyl acetate proceeds via a silylmetalation mechanism.

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