

Hydrosilylation of Carbon Dioxide catalysed by Ruthenium Complexes

By HIDEOMI KOINUMA,* FUMIAKI KAWAKAMI, HIROHIKO KATO, and HIDEFUMI HIRAI

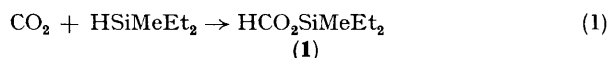
(Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo,

Hongo, Bunkyo-ku, Tokyo 113, Japan)

Summary Carbon dioxide was found to be catalytically fixed into silyl esters of formic acid by the reaction with hydrosilanes in the presence of some ruthenium phosphine complexes.

In view of its significance in organosilane chemistry, the hydrosilylation of carbonyl compounds with transition-metal catalysts has been extensively studied using aldehydes and ketones. However, little information is available on the reactivity in, or even the possibility of, hydrosilylation of other carbonyl compounds, including heterocumulenes. In order to extend our studies on new fixation reactions of carbon dioxide using noble metal complexes as catalysts,^{1,2} we have investigated the reactions of carbon dioxide with hydrosilanes and found that it can be hydrosilylated using ruthenium and palladium complexes as catalysts.

Typically, a solution of diethylmethylsilane (20 mmol) and $\text{RuCl}_2(\text{PPh}_3)_3$ (0.2 mmol) in 5 ml of benzene was placed in a 50 ml stainless steel autoclave and constantly stirred at 100 °C under a pressure of carbon dioxide of 30 kg/cm². After 20 h, the solution was separated by distillation into two fractions. The fraction which distilled below 80 °C was composed mostly of unchanged silane and benzene. The fraction involatile at 80 °C was separated further by g.l.c. and was shown to contain diethylmethylsilyl formate (**1**) as the main product [reaction (1)]. ¹H n.m.r. (CDCl_3)



δ 0.24 (s, 3H), 0.60—1.10 (m, 10H), and 8.00 (s, 1H); i.r. (liquid film) 1710 ($\nu_{\text{C=O}}$), 1020 ($\nu_{\text{Si-O-C}}$), 1260, and 800 cm^{-1} ($\nu_{\text{Si-C}}$).

The Table summarizes the results of reactions carried out under various conditions. Since the catalyst concentration was 1 mole % of the concentration of the hydrosilane in the feed, reactions giving (**1**) in more than 1 mole % yields are catalytic.

TABLE. Reactions of carbon dioxide with hydrosilanes by catalysts of transition-metal complex catalysts.^a

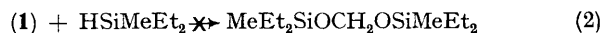
Hydrosilane	Catalyst ^b	Temp./°C	HCO_2SiR_3 ^c mole %
HSiMeEt_2	$\text{RuCl}_2(\text{PPh}_3)_3$	100	14 ^d
"	"	80	1
"	"	120	4
"	$\text{RuH}_2(\text{PPh}_3)_4$	100	6
"	$\text{Pd}(\text{PPh}_3)_4$	100	1
$\text{HSiMe}(\text{OMe})_2$	$\text{RuCl}_2(\text{PPh}_3)_3$	100	1

^a Hydrosilane, 20 mmol; catalyst, 0.2 mmol; CO_2 , 30 kg/cm²; solvent, benzene; time, 20 h. ^b $\text{RhCl}(\text{PPh}_3)_3$, $\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2$, and PdCl_2 were inactive as catalysts for the formation of HCO_2SiR_3 at 100 °C. ^c Based on hydrosilane. ^d In the absence of CO_2 or $\text{RuCl}_2(\text{PPh}_3)_3$, no reaction took place.

The ruthenium complexes $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuH}_2(\text{PPh}_3)_4$ catalysed the synthesis of the silyl ester (**1**), the former being the most effective of the catalysts used. $\text{Pd}(\text{PPh}_3)_4$ also afforded the hydrosilylation product, but in low yield. In sharp contrast to the ruthenium complexes, $\text{RhCl}(\text{PPh}_3)_3$

was inactive as catalyst for the fixation of carbon dioxide by hydrosilylation under the conditions employed. This observation is noteworthy since it indicates a somewhat unusual reactivity of carbon dioxide compared with other carbonyl compounds. For the hydrosilylation of ketones and aldehydes, $\text{RhCl}(\text{PPh}_3)_3$ was also effective, and more active than $\text{RuCl}_2(\text{PPh}_3)_3$.^{3,4} Svoboda *et al.* reported that $\text{RhCl}(\text{PPh}_3)_3$ was carbonylated stoichiometrically with carbon dioxide in the presence of hydrosilane to give $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$,^{5,6} a complex we confirmed to be inactive for the present reaction. The relatively low yields of (1) presumably resulted from partial carbonylation of $\text{RuCl}_2(\text{PPh}_3)_3$ to $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$.⁵ The optimum temperature for the reaction catalysed by $\text{RuCl}_2(\text{PPh}_3)_3$ was about 100 °C and below 80 °C the hydrosilylation hardly occurred at all. 1,1-Dimethyl-1,1,3,3-tetraethylidisiloxane and formaldehyde were also detected as minor products (yields < 4 mole %) in some of the reactions by g.l.c. and either ¹H n.m.r. spectroscopy or chromotropic acid assay using the absorption maximum at 575 nm.⁷ There was no evidence for reaction

(2) occurring to give a further hydrosilylation product of



(1). This result indicates that the hydrosilane has a higher reactivity towards carbon dioxide than towards (1). Ester carbonyl groups have rarely been hydrosilylated⁸ unless they were conjugated with a vinyl group.^{9,10}

Thus, the present reaction may be considered to be the first example of the catalytic addition of a silicon-hydrogen bond to a carbon-oxygen double bond which is cumulative with another double bond. Although isocyanates were recently reported to react with hydrosilanes in the presence of catalytic amounts of transition-metal compounds, the reaction took place exclusively at the carbon-nitrogen double bond.^{11,12}

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