

## Dicobalt Octacarbonyl as a Catalyst for Hydrosilation of Olefins

Sir:

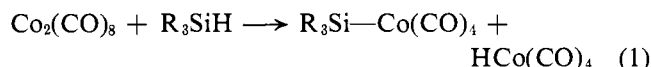
The extensive work of Speier and co-workers<sup>1</sup> has established chloroplatinic acid as a remarkably effective catalyst for the addition of silicon hydrides across unsaturated carbon-carbon bonds. A small degree of activity was observed with IrCl<sub>3</sub> and RuCl<sub>3</sub>, but it is not clear whether this activity was intrinsic or due to trace impurities of platinum.<sup>1a</sup> We have demonstrated a comparable activity between the simple olefin complexes of Pt(II) and Rh(I) as hydrosilation catalysts and have attempted to interpret the mechanism of the reaction in terms of the known chemistry of group VIII metal complexes.<sup>2</sup> On the basis of our mechanistic interpretation and a knowledge of current interpretations of the mechanisms of the various reactions occurring in the "oxo" process,<sup>3</sup> we concluded that dicobalt octacarbonyl would probably catalyze the addition of silicon hydrides to olefins. This prediction has proved to be correct.

Dicobalt octacarbonyl has been shown to be a very effective catalyst for the addition of many substituted silicon hydrides to a variety of olefinic compounds. These reactions may be conveniently carried out under nitrogen at atmospheric pressure. Under these conditions, however, the thermal instability of the catalyst requires that the temperature be kept below about 60°. The high activity of the catalyst makes it possible to carry out reactions at temperatures as low as 0° once an initial inhibition period has been overcome. Cooling is necessary to avoid the large exotherms which accompany reaction.

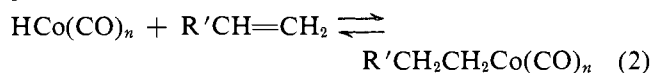
In the above temperature range and at a catalyst concentration of *ca.* 0.001 *M*, common silicon hydrides, trimethoxy-, triethyl-, and phenyldichlorosilane, add to octene-1 to give excellent yields of the terminal octyl derivatives. The only side reaction occurring is the intermediate formation of internal olefins. Isomerization occurs at a faster rate than hydrosilation, and subsequent addition is slowed to the point where long reaction times, *ca.* 24 hr., are necessary for complete reaction. Isomerization is more pronounced than with the platinum and rhodium catalysts. Even hydrosilations with trialkoxysilanes, which do not induce isomerization in the platinum-catalyzed reaction,<sup>2</sup> are accompanied by isomerization in the presence of the cobalt carbonyl catalyst.

Some indication of the mechanism of cobalt carbonyl catalyzed hydrosilation is provided by a study of the reactions of silicon hydrides with dicobalt octacarbonyl in the absence of olefin.<sup>4</sup> The silicon hydride appears to be cleaved homolytically by dicobalt octacarbonyl

to yield cobalt hydrocarbonyl and a silyl cobalt carbonyl.



In the absence of olefin the cobalt hydrocarbonyl decomposes at room temperature to give hydrogen and dicobalt octacarbonyl. However, in the presence of olefins, the formation of alkylcobalt carbonyls is expected, thus<sup>3</sup>



where  $n = 3$  or  $4$ .

The completion of hydrosilation may result either from reaction of the alkylcobalt with free silane (reaction 3) or with silyl cobalt complex (reaction 4)



or



The possibility of the addition of the silyl cobalt derivative across a double bond in a reaction analogous to (2) is discounted since catalysis appears to be reduced as the dicobalt octacarbonyl is converted to the silyl derivative. Thus the rate of reaction, including that of isomerization, is markedly reduced as the concentration of silicon hydride is raised to exceed that of the olefin. For this reason the reaction is best carried out with an excess of olefin. If the catalyst is added to the silicon hydride and allowed to react with it prior to olefin addition, catalyst activity is largely or completely reduced.

The observed isomerization of olefins accompanying the hydrosilation reaction may result from the reverse reaction of eq. 2 if the forward reaction proceeds by nonterminal metalation. Such a process has been postulated to explain the isomerization which accompanies the hydroformylation reaction.<sup>3</sup>

Nesmayanov, *et al.*,<sup>5</sup> have reported the use of iron pentacarbonyl as a catalyst for the hydrosilation of olefins, but this catalyst requires much more severe reaction conditions and is much less specific than dicobalt octacarbonyl.

(5) A. N. Nesmayanov, R. Kh. Friedlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, **17**, 61 (1962).

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## Reactions between Dicobalt Octacarbonyl and Silicon Hydrides

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In a previous paper<sup>1</sup> we drew attention to the similarity between hydrogen and silicon hydrides in their

(1) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

(1) (a) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957); (b) J. L. Speier and J. C. Saam, *ibid.*, **80**, 4104 (1958); (c) H. M. Bank, J. C. Saam, and J. L. Speier, *J. Org. Chem.*, **29**, 792 (1964).

(2) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, **87**, 16 (1965).

(3) R. F. Heck and D. S. Breslow, *ibid.*, **83**, 4023 (1961).

(4) A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 1133 (1965).