Communications to the Editor

Dicobalt Octacarbonyl as a Catalyst for Hydrosilation of Olefins

Sir:

The extensive work of Speier and co-workers[1] 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 $IrCl_3$ and $RuCl_3$, but it is not clear whether this activity was intrinsic or due to trace impurities of platinum.[1a] 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.[2] 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,[3] 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,[2] 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.[4] The silicon hydride appears to be ᶜcleaved homolytically by dicobalt octacarbonyl

to yield cobalt hydrocarbonyl and a silyl cobalt carbonyl.

$$Co_2(CO)_8 + R_3SiH \longrightarrow R_3Si\text{—}Co(CO)_4 + HCo(CO)_4 \quad (1)$$
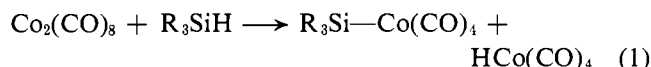
In the absence of olefin the cobalt hydrocarbonyl decomposes at room temperature to give hydrogen and dicobalt octacarbonyl. However, in the presence of olefins, the formation of alkylcobalt carbonyls is expected, thus[3]

$$HCo(CO)_n + R'CH{=}CH_2 \rightleftharpoons$$
$$R'CH_2CH_2Co(CO)_n \quad (2)$$
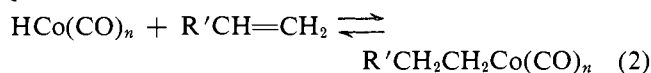
where $n = 3$ or 4.

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

$$R'CH_2CH_2Co(CO)_n + R_3SiH \longrightarrow$$
$$R_3SiCH_2CH_2R' + HCo(CO)_n \quad (3)$$

or

$$R'CH_2CH_2Co(CO)_n + R_3SiCo(CO)_4 \longrightarrow$$
$$R_3SiCH_2CH_2R' + Co_2(CO)_{4+n} \quad (4)$$

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.[3]

Nesmayanov, *et al.*,[5] 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).

J. F. Harrod, A. J. Chalk
General Electric Research Laboratory
Schenectady, New York

Reactions between Dicobalt Octacarbonyl and Silicon Hydrides

Sir:

In a previous paper[1] we drew attention to the similarity between hydrogen and silicon hydrides in their

(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).

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

Table I. Carbonyl Absorptions of Silylcobalt Carbonyl[a,b]

Parent silane	Si–H stretch, cm.⁻¹	C–O stretch, cm.⁻¹					
Cl₃SiH	2250	2120 (s)	2070 (sh)	2070 (s)	2040 (vssh)	2030 (vs)	2000 (msh)
C₆H₅SiCl₂H	2220	2120 (s)	2070 (sh)	2060 (s)	2040 (vs)	2030 (vs)	1990 (sh)
(CH₃O)₃SiH	2200	2105 (s)	2060 (sh)	2040 (vs)	2025 (vs)	2010 (vssh)	
(CH₃(H)SiO)₄	2180	2105 (s)		2040 (s)	2020 (vs)	2010 (vssh)	
(C₆H₅)₃SiH	2130	2100 (s)		2040 (s)	2015 (vs)	2010 (ssh)	1975 (wsh)
(C₂H₅)₃SiH	2100	2090 (s)		2030 (s)	2000 (vs)	1995 (vssh)	1960 (wsh)

[a] Cobalt hydrocarbonyl shows the following absorptions (cm.⁻¹): 2119 (m), 2070 (sh), 2053 (vs), 2030 (vs), 1996 (m), 1957 (sh), 1934 (sh) (I. Wender, H. W. Sternberg, R. A. Friedel, S. J. Metlin, and R. E. Markby, Bureau of Mines, Bulletin 600, 1962). [b] Spectra measured in heptane solution.

reactions with transition metal complexes. Pursuing this similarity further, we have studied the reactions of silanes with dicobalt octacarbonyl and used these reagents to effect catalyses which are formally analogous to certain reactions encountered in the "oxo" process.[2]

Dicobalt octacarbonyl can homolytically cleave molecular hydrogen to yield cobalt hydrocarbonyl,[3] thus

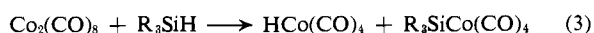$$Co_2(CO)_8 + H_2 \rightleftharpoons 2HCo(CO)_4 \qquad (1)$$
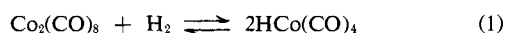
Furthermore, it is probable that, under the conditions of the oxo reaction, cobalt hydrocarbonyl can effect the homogeneous hydrogenation of olefins, aldehydes, and ketones.[4]

We have now found that dicobalt octacarbonyl reacts rapidly at room temperature with a variety of silicon hydrides to give approximately 1 mole of hydrogen per 2 moles of a trisubstituted silicon hydride. The reaction appears to be

$$2R_3SiH + Co_2(CO)_8 \longrightarrow 2R_3SiCo(CO)_4 + H_2 \qquad (2)$$

Presumably, there is an initial reaction analogous to (1).

$$Co_2(CO)_8 + R_3SiH \longrightarrow HCo(CO)_4 + R_3SiCo(CO)_4 \qquad (3)$$

Production of hydrogen may arise from the reverse of eq. 1 which occurs readily at room temperature or by reaction of the hydrocarbonyl with silane

$$HCo(CO)_4 + R_3SiH \longrightarrow R_3SiCo(CO)_4 + H_2 \qquad (4)$$

The reactions were initially carried out on a vacuum line. In one experiment an excess of trichlorosilane was distilled onto dicobalt octacarbonyl (0.96 × 10⁻³ mole) on a vacuum transfer line. On warming the reaction mixture from liquid nitrogen to room temperature it turned from deep amber to pale yellow and evolved 1.3 × 10⁻³ mole of gas. *Anal.* Found: Cl₃SiH, 20; H, 78; CO, 2. Volatile material was distilled off at 25° and collected. The residue was a gray solid (I) weighing 60% more than the original dicobalt octacarbonyl. *Anal.* Calcd. for Cl₃SiCo(CO)₄: C, 15.7; H, 0; Si, 9.2; Cl, 34.9; Co, 19.3. Found: C, 15.5; H, 0.3; Si, 9.1; Cl, 34.9; Co, 19.2.

Clean separations of the cobalt silyl and the parent silane were in general difficult to obtain using simple vacuum line distillations. Later experiments were carried out under nitrogen using a commercially sup-

plied solution of dicobalt octacarbonyl. The reactions were followed by gas evolution and by changes in infrared spectra. Reaction was accompanied by the disappearance of the bands due to SiH and the bridging CO of the dicarbonyl. The cobalt silyl was conveniently isolated by fractional crystallization from heptane using a cooling bath of solid carbon dioxide and acetone. The lower molecular weight silyls could be further purified by vacuum distillation or sublimation. The triethylsilyl derivative was obtained as a liquid. The trichlorosilyl, the phenyldichlorosilyl, and the triphenylsilyl derivatives were obtained as crystalline solids (m.p. 44°, 34–35°, and 135–140°, respectively). An analysis on the last compound gave Si, 6.2; C, 60.8; H, 3.9; and Co, 12.9. (C₆H₅)₃SiCo(CO)₄ requires Si, 6.5; C, 61.4; H, 3.5; and Co, 13.7. Solutions in hexane appear to be monomolecular.

The infrared spectra of the silyl cobalt carbonyls were similar to that of cobalt hydrocarbonyl in the CO region 2200–1800 cm.⁻¹ (Table I). It can be readily seen that ν_{CO} is very sensitive to the electronegativity of the groups on silicon which affect the charge on the metal. A similar effect was noted for the iridium silyl derivatives reported earlier.[1] The trichlorosilyl derivative has approximately the same ν_{CO} as the hydrocarbonyl, signifying the similar electronegativity of H– and Cl₃Si–. This is consistent with the low polarity of the Si–H bond in trichlorosilane.[5] As less electronegative groups are substituted on the silicon ν_{CO} moves to progressively lower frequencies. This weakening of the C–O bonding is expected, since decreasing positive charge on the metal tends to increase donation by the metal into the antibonding π-orbital of the carbonyl group.

The remainder of the infrared spectra are similar to those of the parent silanes except for the disappearance of absorptions at ~2200 and 800 cm.⁻¹ associated with SiH stretching and bending and the appearance of other bands associated with the Co(CO)₄ group.

In contrast to the corresponding alkyl compounds, all of these compounds show a considerable degree of stability and react only very slowly with air or moisture. The greater stability of the silicon–metal bond is ascribed to π-bonding between d-orbitals, similar to that found with the isoelectronic phosphine complexes.

Alkyl cobalt carbonyls have recently been synthesized by Heck and Breslow,[6] but to our knowledge the only previously reported compound containing a

(2) J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **87**, 1133 (1965).
(3) M. Orchin, L. Kirch, and I. Goldfarb, *ibid.*, **78**, 5450 (1956); I. Wender, H. W. Sternberg, and M. Orchin, *ibid.*, **75**, 3041 (1953); M. Orchin, *Advan. Catalysis*, **5**, 385 (1953).
(4) L. Marko, *Chem. Ind.* (London), 260, (1962); *Proc. Chem. Soc.*, 17 (1962); I. Wender, R. Levine, and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4375 (1950).

(5) C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, p. 199.
(6) D. S. Breslow and R. F. Heck, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

Co–Si bond is vinylsilane tris(cobalt tricarbonyl), a rather unusual compound resulting from the reaction of tetravinylsilane and dicobalt octacarbonyl.[7]

(7) S. F. A. Kettle and I. A. Khan, *Proc. Chem. Soc.*, 82 (1962).

A. J. Chalk, J. F. Harrod
General Electric Research Laboratory
Schenectady, New York

## The Chemistry of C_1 Ground State, ^3P

Sir:

Carbon vapor deposited in paraffin hydrocarbon matrices shows no diminution of C_1 or C_3 content after remaining at $-196°$ for several hours. Additions of methanol to aged matrices result in formation of methylal and 1,3-dimethoxyallene. Additions of olefins result in formation of spiropentanes and bisethanoallenes,[1] and *no other product* other than minor components which have a composition indicating they are derived from C_2 + 2olefins.
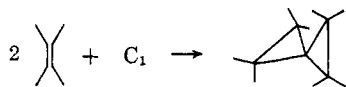
We report here on the products obtained from the reactions of ground-state C_1 with the *cis*- and *trans*-2-butenes. The spiropentane product mixtures were analyzed and separated by gas chromatography. They are resistant to permanganate oxidations, and have infrared and mass spectra consistent with the assigned structures of isomeric 1,2,1′,2′-tetramethylspiropentanes. Strong spectroscopic evidence has not been adduced for the configurations assigned below; the assignments follow from the assumption of a mechanism for additions, comprising one stereospecific and one nonstereospecific addition.[2]

The observations for the reactions of *cis*- and *trans*-2-butenes with ground-state carbon atoms can be summarized by Scheme I, the spiropentane structures being

Scheme I
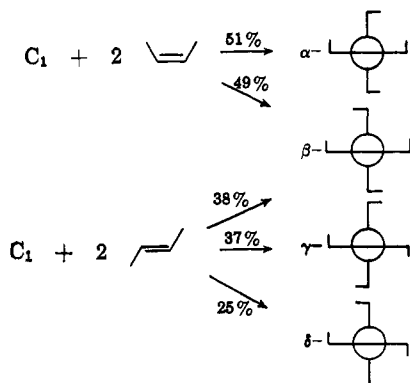
viewed along their major axes. The β-spiropentane is the only common product obtained, no α- being prod-

(1) P. S. Skell and L. D. Wescott, *J. Am. Chem. Soc.*, **85**, 1023 (1963).
(2) (a) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

uced from *trans*-2-butene, nor any γ- or δ- from *cis*-2-butene.[3]

A triplet C_1 reagent I, is required for the pictured reaction scheme, and this assignment is in accord with the spectroscopically identified ^3P ground state.

I
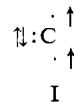
That ring formation by stereospecific mode precedes ring formation by the nonstereospecific mode follows from the observation $[\beta/\alpha]_{cis} \neq [(\gamma + \delta)/\beta]_{trans}$. For the reversed sequence of steps these ratios must be identical. Although these considerations do not lead to a unique mechanistic description, the preferred one is
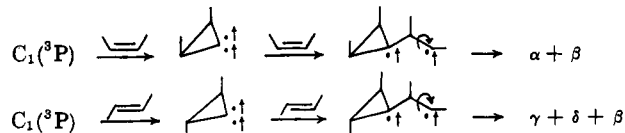
This rationalization is given additional support by the observation that C_1 in singlet D and S states react with 2-butenes to produce spiropentanes *via* two stereospecific steps.[4]

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research and the Army Research Office (Durham).

(3) The choice of structures for the γ- and δ-spiropentane products was made by assigning the more probable reaction mode to the least-hindered structure.
(4) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).
(5) National Science Foundation Cooperative Graduate Fellow, 1963–1965.

P. S. Skell, R. R. Engel[5]
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania

The Chemistry of C_1 Metastable States, ^1D and ^1S

Sir:

A series of experiments in which C_1 was allowed to age in a paraffin hydrocarbon matrix prior to reaction with an olefin revealed a striking alteration of product composition with the age of the C_1. These experiments have revealed the presence of two metastable states in addition to the ^3P ground state.[1]

Carbon vapor was generated in a carbon arc. In the high vacuum system employed the flight to the wall has a duration of approximately 10^{-5} sec. With simultaneous deposition of olefin and carbon vapor the elapsed life of the C_1 (departure from the arc plasma chosen as $t = 0$) is approximately 10^{-5} sec. if reaction occurs on contact with the olefin. Under these circumstances the products from C_1 and *cis*-2-butene are those listed (in area %) as A through J (increasing retention times over a dioctyl phthalate gas chromatography column): A, 15; B, 28; C, 12; D, 4; E, 10; F, 2; G, 11; H, 6; I, 3; and J, 9. A, C, and D have been identified and the others are the subjects of current investigations.

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).