PHOTOCHEMICAL REACTION OF TRIETHYLSILYL(TETRACARBONYL)-COBALT WITH ETHYLE... (U)
MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY

UNCLASSIFIED F SEITZ ET AL. 07 JAN 88 TR-10
<table>
<thead>
<tr>
<th>1a. REPORT SECURITY CLASSIFICATION</th>
<th>Unclassified</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a. SECURITY CLASSIFICATION AUTHORITY</td>
<td>None</td>
</tr>
<tr>
<td>2b. DECLASSIFICATION/DOWNGRADING SCHEDULE</td>
<td>Unlimited</td>
</tr>
<tr>
<td>3. DISTRIBUTION/AVAILABILITY OF REPORT</td>
<td>Unlimited</td>
</tr>
<tr>
<td>4. PERFORMING ORGANIZATION REPORT NUMBER(S)</td>
<td>Office of Naval Research</td>
</tr>
<tr>
<td>5. MONITORING ORGANIZATION REPORT NUMBER(S)</td>
<td>Office of Naval Research</td>
</tr>
<tr>
<td>6a. NAME OF PERFORMING ORGANIZATION</td>
<td>Department of Chemistry</td>
</tr>
<tr>
<td>6b. OFFICE SYMBOL</td>
<td>Office of Naval Research</td>
</tr>
<tr>
<td>6c. ADDRESS (City, State, and ZIP Code)</td>
<td>Chemistry Division</td>
</tr>
<tr>
<td>7a. NAME OF MONITORING ORGANIZATION</td>
<td>800 N. Quincy Street</td>
</tr>
<tr>
<td>6d. ADDRESS (City, State, and ZIP Code)</td>
<td>Arlington, VA 22217</td>
</tr>
<tr>
<td>8a. NAME OF FUNDING/SPONSORING ORGANIZATION</td>
<td>Office of Naval Research</td>
</tr>
<tr>
<td>8b. OFFICE SYMBOL</td>
<td>N00014-84-K-0553</td>
</tr>
<tr>
<td>8c. ADDRESS (City, State, and ZIP Code)</td>
<td>Chemistry division</td>
</tr>
<tr>
<td>9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER</td>
<td>800 N. Quincy Street</td>
</tr>
<tr>
<td>10. SOURCE OF FUNDING NUMBERS</td>
<td>Arlington, VA 22217</td>
</tr>
<tr>
<td>11. TITLE (Include Security Classification)</td>
<td>Prepared for publication in Angewandte Chemie</td>
</tr>
<tr>
<td>12. PERSONAL AUTHOR(S)</td>
<td>Friedrich Seitz and Mark S. Wrighton</td>
</tr>
<tr>
<td>13a. TYPE OF REPORT</td>
<td>technical interim</td>
</tr>
<tr>
<td>13b. TIME COVERED</td>
<td>FROM 1/7/88 TO 1/7/88</td>
</tr>
<tr>
<td>16. SUPPLEMENTARY NOTATION</td>
<td>See Attached Sheet</td>
</tr>
<tr>
<td>17. COSATI CODES</td>
<td></td>
</tr>
<tr>
<td>18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)</td>
<td>photocatalysis, hydrosilation, olefin insertion, catalysis</td>
</tr>
<tr>
<td>19. ABSTRACT (Continue on reverse if necessary and identify by block number)</td>
<td></td>
</tr>
<tr>
<td>20. DISTRIBUTION/AVAILABILITY OF ABSTRACT</td>
<td>DTIC File Code</td>
</tr>
<tr>
<td>21. ABSTRACT SECURITY CLASSIFICATION</td>
<td>Unlimited</td>
</tr>
<tr>
<td>22a. NAME OF RESPONSIBLE INDIVIDUAL</td>
<td>Mark S. Wrighton</td>
</tr>
<tr>
<td>22b. TELEPHONE (Include Area Code)</td>
<td>617-253-1597</td>
</tr>
<tr>
<td>22c. OFFICE SYMBOL</td>
<td></td>
</tr>
</tbody>
</table>

**DD FORM 1473, 84 MAR**

83 APR edition may be used until exhausted.

All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
For the first time, insertion of an unactivated alkene into the metal-silicon bond of a catalytically active transition metal complex has been demonstrated. In addition, formation of CH₄, not SiMe₄, when (CO)₄Co-Me is reacted with Me₃SiH, is clearly inconsistent with the traditional Chalk-Harrod mechanism for transition metal catalyzed hydrosilation of olefins. Both reactions are key steps in a new mechanism for hydrosilation.
Photochemical Reaction of Triethylsilyl(tetracarbonyl)-cobalt with Ethylene: Implications for Cobalt Carbonyl-Catalyzed Hydrosilation of Alkenes

by

Friedrich Seitz
BASF AG
Kunststofflaboratorium
6700 Ludwigshafen
West Germany

and

Mark S. Wrighton
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Prepared for publication in Angewandte Chemie

January 7, 1983

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.
PHOTOCHEMICAL REACTION OF TRIETHYL-SILYL(TETRACARBONYL-COBALT)
WITH ETHERYLENE: IMPLICATIONS FOR COBALT CARBONYL-CATALYZED
HYDROSILATION OF ALKENES*

Friedrich Seitz*
BASF AG
Kunststofflaboratorium
6700 Ludwigshafen
West Germany

and

Mark S. Wrighton*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 U.S.A.

*Dedicated to Prof. Dr. Helmut Dörfel on the occasion of his 60th birthday.

*Address correspondence to either author.
Summary

For the first time, insertion of an unactivated alkene into the metal-silicon bond of a catalytically active transition metal complex has been demonstrated. In addition, formation of CH₄, not SiMe₄, when (CO)₄Co-Me is reacted with Me₃SiH, is clearly inconsistent with the traditional Chalk-Harrod mechanism for transition metal catalyzed hydrosilation of olefins. Both reactions are key steps in a new mechanism for hydrosilation.
The commonly proposed Chalk-Harrod mechanism,[1-3] Scheme I, for transition metal catalyzed hydrosilation of alkenes involves as the key steps the insertion of an alkene into a M-H bond, step (3), and the reductive elimination of an alkyl and a silyl ligand to form an alkylsilane, step (5). Whereas the insertion of alkenes into M-H bonds is well documented,[4] the reductive elimination of an alkylsilane has only been reported for (CO)₄Fe(alkyl)(SiR₃),[5] and this is a slow reaction at 298 K. More importantly, the mechanism in Scheme I cannot explain the formation of alkenyl-silanes, that are frequently observed as by-products of hydrosilation reactions.[6-9]

An alternative mechanism, Scheme II, has been suggested for the photocatalyzed hydrosilation of alkenes using Fe(CO)₅,[6] M₃(CO)₁₂ (M = Fe, Ru, Os)[7] or (CO)₄Co-SiR₃[8] as catalysts. The key steps of this mechanism are the insertion of an alkene into a M-Si bond, step (3), and the reductive elimination of an alkyl and a hydrido ligand, step (5). Evidence for all steps required by this mechanism has been obtained for (η⁵-C₅Me₅)-(CO)₃Fe-SiR₃.[1⁰] We have now extended these investigations to (CO)₄Co-SiR₃ which is known to be an efficient hydrosilation catalyst under irradiation.[8]

It has been shown[1¹] that near UV photolysis of (CO)₄Co-SiEt₃ at 77 K in a methylcyclohexane (MCH) matrix yields the 16-electron complex (CO)₃Co-SiEt₃ and CO as the only species detectable by FTIR.[1²] The same coordinatively unsaturated complex is obtained at 77 K, when the matrix contains ethylene. However, in this case warmup of the matrix leads to disappearance of bands attributed to (CO)₃Co-SiEt₃ and formation of new bands at 1968 (sh) and 1961 cm⁻¹. These bands are also observed upon near-UV irradiation of a solution of (CO)₄Co-SiEt₃ and ethylene in MCH at 210 K. We attribute the bands at 1968 and 1961 cm⁻¹ to (CO)₃(C₂H₄)Co-SiEt₃, formed by addition of ethylene to photogenerated (CO)₃Co-SiEt₃. Coordination of ethylene is
also evidenced by \textsuperscript{1}H-NMR spectroscopy.\cite{13}

According to Scheme II the next step in the catalytic cycle is insertion of the coordinated alkene into the Co-Si bond, step (3). To investigate this reaction a solution of (CO)\textsubscript{3}(C\textsubscript{2}H\textsubscript{4})Co-SiEt\textsubscript{3} was slowly warmed to 298 K and monitored by FTIR. Above 265 K a slow reaction is observed. The unexpected reaction product is the acyl complex (CO)\textsubscript{4}Co-C(0)C\textsubscript{2}H\textsubscript{5}, established spectroscopically by comparison with independently synthesized material.\cite{14} We assume that insertion into the Co-Si bond, step (3), does indeed take place, but, since no R\textsubscript{3}SiH necessary for step (4) is present, R-SiR\textsubscript{3} transfer takes place instead, step (6). The complex obtained is expected to undergo loss of vinyl(triethyl)ilane, step (7). Free vinyl(triethyl)ilane can be detected in the reaction mixture by gas chromatography. We have thus demonstrated formation of an alkenylsilane. Since we have used a large excess of ethylene the 16-electron metal complex formed in step (7) undergoes addition of ethylene, followed by insertion into the Co-H bond and addition of two molecules of CO to form (CO)\textsubscript{4}Co-C(0)C\textsubscript{2}H\textsubscript{5}, reactions (a-c). Consistent with consumption of two molecules of CO for one metal complex, the formation of (CO)\textsubscript{4}Co-C(0)C\textsubscript{2}H\textsubscript{5} stops, once 40% of photogenerated (CO)\textsubscript{3}(C\textsubscript{2}H\textsubscript{4})Co-SiEt\textsubscript{3},

\[
\begin{align*}
(CO)\textsubscript{3}Co-H + C\textsubscript{2}H\textsubscript{4} & \rightarrow (CO)\textsubscript{3}Co-H \quad \text{(a)} \\
                                       & + C\textsubscript{2}H\textsubscript{4} \\
(CO)\textsubscript{3}Co-H & \rightarrow (CO)\textsubscript{3}Co-CH\textsubscript{2}CH\textsubscript{3} \quad \text{(b)} \\
                                       & + C\textsubscript{2}H\textsubscript{4} \\
(CO)\textsubscript{3}Co-CH\textsubscript{2}CH\textsubscript{3} + 2CO & \rightarrow (CO)\textsubscript{4}Co-C(0)CH\textsubscript{2}CH\textsubscript{3} \quad \text{(c)}
\end{align*}
\]
i.e. 80% of CO, reacts. The rate limiting step in this reaction sequence appears to be the ethylene insertion into the Co-Si bond, since none of the intermediates could be observed. Insertion of ethylene into the Co-Si bond (step (3)) is the first example of insertion of an unactivated alkene into the M-Si bond of a catalytically active complex. In the presence of R₃SiH step (7) in Scheme II in presumably followed by reaction of (CO)₃Co-H with R₃SiH to regenerate (CO)₃Co-SiR₃ and H₂.

We have so far demonstrated steps (1)-(3) and (6) and (7) of Scheme II. To obtain evidence for steps (4) and (5), we turned to (CO)₄Co-Me as a model complex for the alkyl complex (CO)₄Co-CH₂CH₂SiR₃. Due to the lability of cobalt alkyl complexes, the reactions could not be spectroscopically monitored. We therefore reacted (CO)₄Co-Me with Me₃SiH and analyzed products by ¹H-NMR.[15] We assume thermal CO loss occurs from (CO)₄Co-Me giving (CO)₃Co-Me, corresponding to the intermediate (CO)₃Co-CH₂CH₂SiR₃ in Scheme II, but also to (CO)₃Co-C₂H₅ in Scheme I. In both cases, as well as with our model complex, the next step is oxidative addition of the silane, reaction (d).

\[
\begin{align*}
  \text{(CO)}_3\text{Co-Me} + \text{Me}_3\text{SiH} & \rightarrow \text{(CO)}_3\text{Co-Me} + \text{Me}_3\text{SiMe}_3 \\
  \text{(CO)}_3\text{Co-Me} & \rightarrow \text{CH}_4 + \text{(CO)}_3\text{Co-SiMe}_3
\end{align*}
\]

In Scheme II this is followed by elimination of the alkyl and the hydrido ligand to yield, in the case of our model compound, CH₄ and (CO)₃Co-SiMe₃, reaction (e). In contrast, from Scheme I we would expect elimination

\[
\begin{align*}
  \text{(CO)}_3\text{Co-Me} & \rightarrow \text{CH}_4 + \text{(CO)}_3\text{Co-SiMe}_3 \\
  \text{SiMe}_3
\end{align*}
\]
of the silyl and the alkyl ligand to yield SiMe₄ and (CO)₃Co-H, reaction (f).
We find CH₄, not SiMe₄ by ¹H-NMR (δ = 0.18 ppm) and (CO)₄Co-SiMe₃ by FTIR. We

\[
\begin{align*}
\text{SiMe}_3 & \quad \text{Scheme I} \quad \text{SiMe}_4 + (\text{CO})_3\text{Co-H} \quad \text{(not observed)} \quad (f) \\
(CO)_3\text{Co-Me} & \quad \text{H} \\
\end{align*}
\]

cannot completely rule out the possibility that some SiMe₄ is also formed, but formation of CH₄ is certainly the predominant reaction.

We have thus found evidence for all steps postulated in Scheme II.

Formation of CH₄, not SiMe₄, in the reaction of (CO)₄Co-Me with Me₃SiH is clearly inconsistent with the Chalk-Harrod mechanism, Scheme I. We therefore propose the mechanism depicted in Scheme 2 for hydrosilation catalysis at least with cobalt carbonyl complexes. This new mechanism involves as the key step the insertion of an olefin into a Co-Si bond.

Acknowledgements. We thank the Deutsche Forschungsgemeinschaft and the Office of Naval Research and the National Science Foundation for partial support of this research.
References


12. IR spectroscopic data (CO stretching region) for relevant complexes (cm⁻¹): (CO)₄Co-SiEt₃: 2089 m, 2026, 1995 s; (CO)₃Co-SiEt₃: 1957 s, 1953 s; (CO)₃(C₂H₄)Co-SiEt₃: 1968 sh, 1961 s; (CO)₄Co-C(O)CH₂CH₃: 2105 m, 2045 m, 2023 s, 2002 s.

13. When a solution of (CO)₄Co-SiEt₃ in ethylene containing toluene-d₈ is irradiated, signals at δ = 1.15 ppm (m) for Et₃Si and at 3.00 ppm (s) for coordinated ethylene are observed. For the resonance of coordinated ethylene cf. Y.-M. Wuu, J. G. Bentsen, C. G. Brinkley, M. S. Wrighton, Inorg. Chem. 26 (1987) 530.

14. Under 1 atm of CO at 0 °C 210 mg (0.3 mmol) of PPN[Co(CO)₄] in 2 ml of THF was added to 200 mg (1.1 mmol) of [Et₃O]BF₄. After stirring the solution for 15 min, the solvent was removed in vacuo. The residue was redissolved in 1 ml of methylcyclohexane. [PPN]BF₄ and excess [Et₃O]BF₄ was removed via filtration and the solution was used without further purification. Only signals due to (CO)₄Co-C(O)CH₂CH₃ were observed in FTIR spectrum; cf. L. Marko, G. Bor, G. Almasy, P. Szabo, Brennst. Chem. 44 (1963) 184.

15. At 0 °C 45 mg (0.3 mmol) of MeI was added to a solution of 70 mg (0.4 mmol) of Na[Co(CO)₄] in 1 ml THF-d₈. After 2 min the resulting (CO)₄Co-Me was reacted with 100 mg (1.3 mmol) of Me₃SiH. The solution was stirred for 20 min at 0 °C and then warmed up. Immediately after the solution reached room temperature, a ¹H-NMR spectrum was taken: δ = 0.18 ppm for methane. Formation of (CO)₄C(O)CH₃ accompanies formation of (CO)₄Co-Me in the synthesis [see citation in ref. 14] and the thermolysis of the (CO)₄Co-Me/(CO)₄Co-C(O)CH₃ mixture in the presence of Me₃SiH gives CH₃CHO in addition to CH₄ [cf. also R. W. Wegman, Organometallics 5 (1986) 707, which shows formation of CH₃CHO from reaction of (CO)₃(PPh₃)Co-C(O)CH₃ with Et₃SiH or Ph₃SiH].
Scheme I: Chalk-Harrod mechanism for hydrosilation catalysis by C_2H_4 insertion into a M-H bond, illustrated for (CO)_4Co-H [1-3].
Scheme II. Proposed mechanism for hydrosilation catalysis by C₂H₄ insertion into a Co-Si bond.
<table>
<thead>
<tr>
<th>Address</th>
<th>Copies</th>
<th>Address</th>
<th>Copies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000</td>
<td>2</td>
<td>Dr. David Young Code 334 NORDA NSTL, Mississippi 39529</td>
<td>1</td>
</tr>
<tr>
<td>Dr. Bernard Dawda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050</td>
<td>1</td>
<td>Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555</td>
<td>1</td>
</tr>
<tr>
<td>Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code LS2 Port Hueneme, California 93401</td>
<td>1</td>
<td>Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380</td>
<td>1</td>
</tr>
<tr>
<td>Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314</td>
<td>12</td>
<td>U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709</td>
<td>1</td>
</tr>
<tr>
<td>DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401</td>
<td>1</td>
<td>Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112</td>
<td>1</td>
</tr>
<tr>
<td>Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000</td>
<td>1</td>
<td>Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232</td>
<td>1</td>
</tr>
</tbody>
</table>