PHOTOCHEMICAL REACTION OF TRIETHYLSILYL(TETRACARBONYL)-COBALT WITH ETHYLE... (U)

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UNCLASSIFIED  F SEITZ ET AL.  07 JAN 88 TR-10  F/G 7/3  NL
REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION  
Unclassified

1b. RESTRICTIVE MARKINGS  
None

2a. SECURITY CLASSIFICATION AUTHORITY  

2b. DECLASSIFICATION/DOWNGRADE SCHEDULE  

3. DISTRIBUTION/AVAILABILITY OF REPORT  
Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)  

5. MONITORING ORGANIZATION REPORT NUMBER(S)  

6a. NAME OF PERFORMING ORGANIZATION  
Department of Chemistry

6b. OFFICE SYMBOL  
(if applicable)

7a. NAME OF MONITORING ORGANIZATION  
Office of Naval Research

7b. ADDRESS (City, State, and ZIP Code)  
Chemistry Division  
800 N. Quincy Street  
Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION  
Office of Naval Research

8b. OFFICE SYMBOL  
(if applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER  
N00014-84-K-0553

10. SOURCE OF FUNDING NUMBERS  

PROGRAM ELEMENT NO.  PROJECT NO.  TASK NO.  WORK UNIT ACCESSION NO.  

11. TITLE (Include Security Classification)  
Photochemical Reaction of Triethylsilyl(tetracarbonyl)cobalt with Ethylene: Implications for Cobalt Carbonyl-Catalyzed Hydroisilation of Alkenes

12. PERSONAL AUTHOR(S)  
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13a. TYPE OF REPORT  
technical interim

13b. TIME COVERED  
FROM  
TO  
1/7/88

14. DATE OF REPORT (Year, Month, Day)  
1/7/88

15. PAGE COUNT  
13

16. SUPPLEMENTARY NOTATION  
Prepared for publication in Angewandte Chemie

17. COSATI CODES  

FIELD  GROUP  SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)  
photocatalysis, hydrosilation, olefin insertion, catalysis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)  
See Attached Sheet

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT  
Unclassified/Unlimited  

21. ABSTRACT SECURITY CLASSIFICATION  
Unlimited

22a. NAME OF RESPONSIBLE INDIVIDUAL  
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22b. TELEPHONE (Include Area Code)  
617-253-1597

22c. OFFICE SYMBOL  

DD FORM 1473, 84 MAR  
83 APR edition may be used until exhausted.  
All other editions are obsolete.  

SECURITY CLASSIFICATION OF THIS PAGE
Summary

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Photochemical Reaction of Triethyldimethylsilyletetracarbonyl-cobalt with Ethylene: Implications for Cobalt Carbonyl-Catalyzed Hydrosilation of Alkenes

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Prepared for publication in *Angewandte Chemie*

January 7, 1983

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PHOTOCHEMICAL REACTION OF TRIETHYLSILYL(TETRACARBONYL)COBALT
WITH ETHYLENE: IMPLICATIONS FOR COBALT CARBONYL-CATALYZED
HYDROSILATION OF ALKENES*

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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 \((\text{CO})_4\text{Fe(alkyl)}(\text{SiR}_3)\),[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 \((\eta^5-\text{C}_5\text{Me}_5)-\text{(CO)}_3\text{Fe-SiR}_3\).[10] We have now extended these investigations to \((\text{CO})_4\text{Co-SiR}_3\) which is known to be an efficient hydrosilation catalyst under irradiation.[8]

It has been shown[11] that near UV photolysis of \((\text{CO})_4\text{Co-SiEt}_3\) at 77 K in a methylcyclohexane (MCH) matrix yields the 16-electron complex \((\text{CO})_3\text{Co-SiEt}_3\) 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 \((\text{CO})_3\text{Co-SiEt}_3\) 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 \((\text{CO})_4\text{Co-SiEt}_3\) and ethylene in MCH at 210 K. We attribute the bands at 1968 and 1961 cm⁻¹ to \((\text{CO})_3(\text{C}_2\text{H}_4)\text{Co-SiEt}_3\), formed by addition of ethylene to photogenerated \((\text{CO})_3\text{Co-SiEt}_3\). Coordination of ethylene is...
also evidenced by $^1$H-NMR spectroscopy.[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)$_3$(C$_2$H$_4$)Co-SiEt$_3$ 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)$_4$Co-C(O)C$_2$H$_5$, established spectroscopically by comparison with independently synthesized material.[14] We assume that insertion into the Co-Si bond, step (3), does indeed take place, but, since no R$_3$SiH necessary for step (4) is present, R-SiR$_3$ transfer takes place instead, step (6). The complex obtained is expected to undergo loss of vinyl(triethyl)silane, step (7). Free vinyl(triethyl)silane 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)$_4$Co-C(O)C$_2$H$_5$, reactions (a-c). Consistent

\[
\text{(CO)}_3\text{Co-H} + \text{C}_2\text{H}_4 \rightarrow \text{(CO)}_3\text{Co-H} \quad \quad \quad \quad \quad \text{(a)}
\]

\[
\quad \quad \quad \quad \quad \text{C}_2\text{H}_4
\]

\[
\text{(CO)}_3\text{Co-H} \rightarrow \text{(CO)}_3\text{Co-CH}_2\text{CH}_3 \quad \quad \quad \quad \quad \text{(b)}
\]

\[
\quad \quad \quad \quad \quad \text{C}_2\text{H}_4
\]

\[
\text{(CO)}_3\text{Co-CH}_2\text{CH}_3 + 2\text{CO} \rightarrow \text{(CO)}_4\text{Co-C(O)CH}_2\text{CH}_3 \quad \quad \quad \quad \quad \text{(c)}
\]

with consumption of two molecules of CO for one metal complex, the formation of (CO)$_4$Co-C(O)C$_2$H$_5$ stops, once 40% of photogenerated (CO)$_3$(C$_2$H$_4$)Co-SiEt$_3$,
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).

\[
\begin{align*}
\text{(CO)₃Co-Me} + \text{Me₃SiH} & \rightarrow \text{(CO)₃Co-Me} + \text{SiMe₃} \\
\text{(CO)₄Co-Me} & \rightarrow \text{CH₄} + \text{(CO)₃Co-SiMe₃}
\end{align*}
\]

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

\[
\begin{align*}
\text{(CO)₃Co-Me} & \rightarrow \text{CH₄} + \text{(CO)₃Co-SiMe₃}
\end{align*}
\]
of the silyl and the alkyl ligand to yield SiMe$_4$ and (CO)$_3$Co-H, reaction (f). We find CH$_4$, not SiMe$_4$ by $^1$H-NMR ($\delta = 0.18$ ppm) and (CO)$_4$Co-SiMe$_3$ by FTIR. We cannot completely rule out the possibility that some SiMe$_4$ is also formed, but formation of CH$_4$ is certainly the predominant reaction.

We have thus found evidence for all steps postulated in Scheme II. Formation of CH$_4$, not SiMe$_4$, in the reaction of (CO)$_4$Co-Me with Me$_3$SiH 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)$_4$Co-SiEt$_3$: 2089 m, 2026, 1995 s; (CO)$_3$Co-SiEt$_3$: 1957 s, 1953 s; (CO)$_3$(C$_2$H$_4$)Co-SiEt$_3$: 1968 sh, 1961 s; (CO)$_4$Co-C(O)CH$_2$CH$_3$: 2105 m, 2045 m, 2023 s, 2002 s.

13. When a solution of (CO)$_4$Co-SiEt$_3$ in ethylene containing toluene-d$_8$ is irradiated, signals at $\delta = 1.15$ ppm (m) for Et$_3$Si 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 $^\circ$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 [Et$_3$O]BF$_4$. After stirring the solution for 15 min, the solvent was removed in vacuo. The residue was redissolved in 1 ml of methylcyclohexane. [PPN]BF$_4$ and excess [Et$_3$O]BF$_4$ was removed via filtration and the solution was used without further purification. Only signals due to (CO)$_4$Co-C(O)CH$_2$CH$_3$ were observed in FTIR spectrum; cf. L. Marko, G. Bor, G. Almasy, P. Szabo, Brennst. Chem. 44 (1963) 184.

15. At 0 $^\circ$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-d$_8$. After 2 min the resulting (CO)$_4$Co-Me was reacted with 100 mg (1.3 mmol) of Me$_3$SiH. The solution was stirred for 20 min at 0 $^\circ$C and then warmed up. Immediately after the solution reached room temperature, a $^1$H-NMR spectrum was taken: $\delta = 0.18$ ppm for methane. Formation of (CO)$_4$C(O)CH$_3$ accompanies formation of (CO)$_4$Co-Me in the synthesis [see citation in ref. 14] and the thermolysis of the (CO)$_4$Co-Me/(CO)$_4$Co-C(O)CH$_3$ mixture in the presence of Me$_3$SiH gives CH$_3$CHO in addition to CH$_4$ [cf. also R. W. Wegman, Organometallics 5 (1986) 707, which shows formation of CH$_3$CHO from reaction of (CO)$_3$(PPh$_3$)Co-C(O)CH$_3$ with Et$_3$SiH or Ph$_3$SiH].
Scheme I: Chalk-Harrod mechanism for hydrosilation catalysis by C2H4 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.
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