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PHOTOCHEMICAL REACTION OF
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MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY
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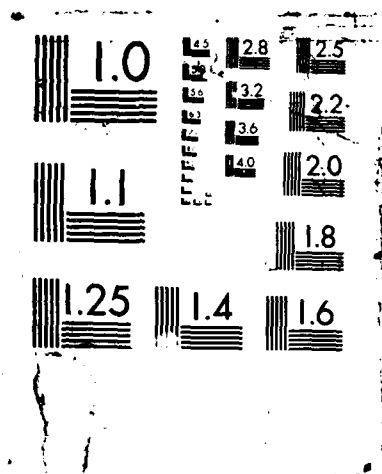
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Summary ✓

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Photochemical Reaction of Triethylsilyl(tetracarbonyl)-
cobalt with Ethylene: Implications for Cobalt
Carbonyl-Catalyzed Hydrosilation of Alkenes

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

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

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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 CH_4 , not SiMe_4 , when $(\text{CO})_4\text{Co-Me}$ is reacted with Me_3SiH , 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.

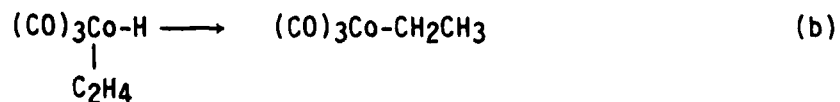
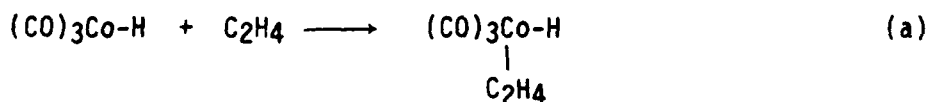
The commonly proposed Chalk-Harrod mechanism,[1-3] Scheme I, for transition metal catalyzed hydrosilation of alkenes involves as the key steps the insertion of an alkene into a M-H bond, step (3), and the reductive elimination of an alkyl and a silyl ligand to form an alkylsilane, step (5). Whereas the insertion of alkenes into M-H bonds is well documented,[4] the reductive elimination of an alkylsilane has only been reported for $(CO)_4Fe(alkyl)(SiR_3)$,[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] $M_3(CO)_{12}$ ($M = Fe, Ru, Os$)[7] or $(CO)_4Co-SiR_3$ [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 $(\eta^5-C_5Me_5)-(CO)_3Fe-SiR_3$. [10] We have now extended these investigations to $(CO)_4Co-SiR_3$ which is known to be an efficient hydrosilation catalyst under irradiation.[8]

It has been shown[11] that near UV photolysis of $(CO)_4Co-SiEt_3$ at 77 K in a methylcyclohexane (MCH) matrix yields the 16-electron complex $(CO)_3Co-SiEt_3$ 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 $(CO)_3Co-SiEt_3$ 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 $(CO)_4Co-SiEt_3$ and ethylene in MCH at 210 K. We attribute the bands at 1968 and 1961 cm^{-1} to $(CO)_3(C_2H_4)Co-SiEt_3$, formed by addition of ethylene to photogenerated $(CO)_3Co-SiEt_3$. Coordination of ethylene is

also evidenced by $^1\text{H-NMR}$ spectroscopy.[13]

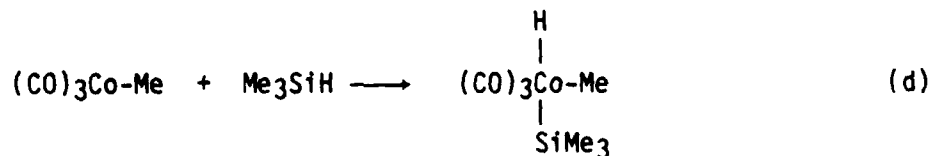
According to Scheme II the next step in the catalytic cycle is insertion of the coordinated alkene into the Co-Si bond, step (3). To investigate this reaction a solution of $(\text{CO})_3(\text{C}_2\text{H}_4)\text{Co-SiEt}_3$ was slowly warmed to 298 K and monitored by FTIR. Above 265 K a slow reaction is observed. The unexpected reaction product is the acyl complex $(\text{CO})_4\text{Co-C}(\text{O})\text{C}_2\text{H}_5$, 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_3SiH necessary for step (4) is present, $\beta\text{-SiR}_3$ 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 $(\text{CO})_4\text{Co-C}(\text{O})\text{C}_2\text{H}_5$, reactions (a-c). Consistent



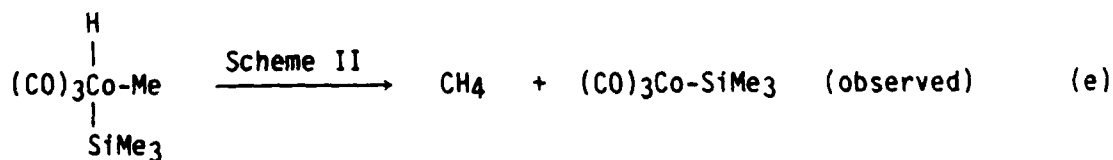
with consumption of two molecules of CO for one metal complex, the formation of $(\text{CO})_4\text{Co-C}(\text{O})\text{C}_2\text{H}_5$ stops, once 40% of photogenerated $(\text{CO})_3(\text{C}_2\text{H}_4)\text{Co-SiEt}_3$,

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 is presumably followed by reaction of (CO)₃Co-H with R₃SiH to regenerate (CO)₃Co-SiR₃ and H₂.

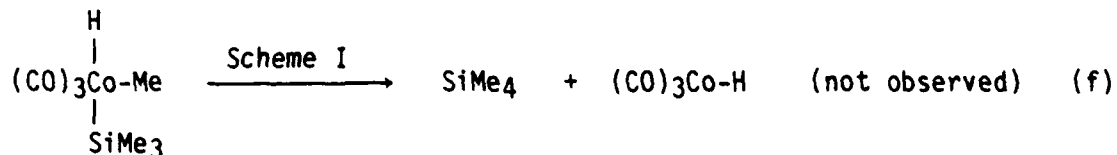
We have so far demonstrated steps (1)-(3) and (6) and (7) of Scheme II. To obtain evidence for steps (4) and (5), we turned to (CO)₄Co-Me as a model complex for the alkyl complex (CO)₄Co-CH₂CH₂SiR₃. Due to the lability of cobalt alkyl complexes, the reactions could not be spectroscopically monitored. 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).



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



of the silyl and the alkyl ligand to yield SiMe_4 and $(\text{CO})_3\text{Co-H}$, reaction (f). We find CH_4 , not SiMe_4 by $^1\text{H-NMR}$ ($\delta = 0.18$ ppm) and $(\text{CO})_4\text{Co-SiMe}_3$ 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.

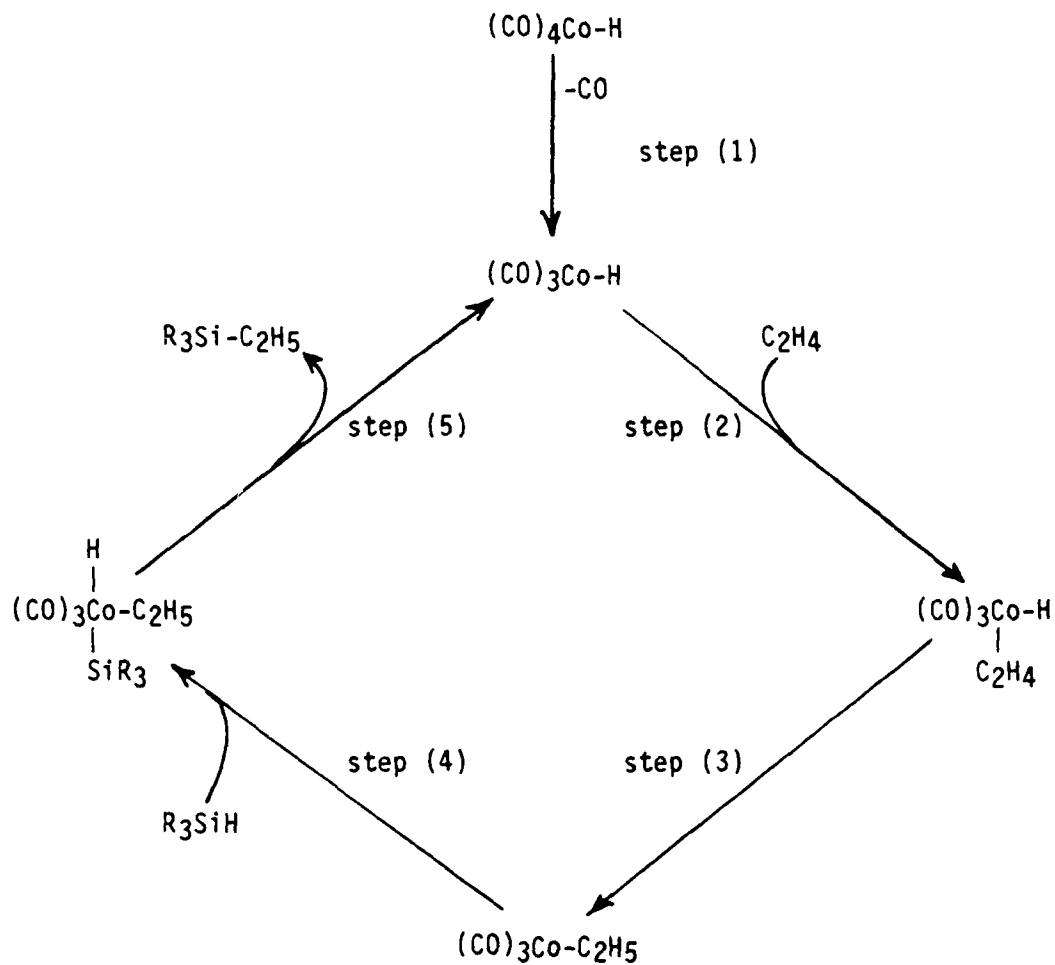
We have thus found evidence for all steps postulated in Scheme II. Formation of CH_4 , not SiMe_4 , in the reaction of $(\text{CO})_4\text{Co-Me}$ with Me_3SiH is clearly inconsistent with the Chalk-Harrod mechanism, Scheme I. We therefore propose the mechanism depicted in Scheme 2 for hydrosilation 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.

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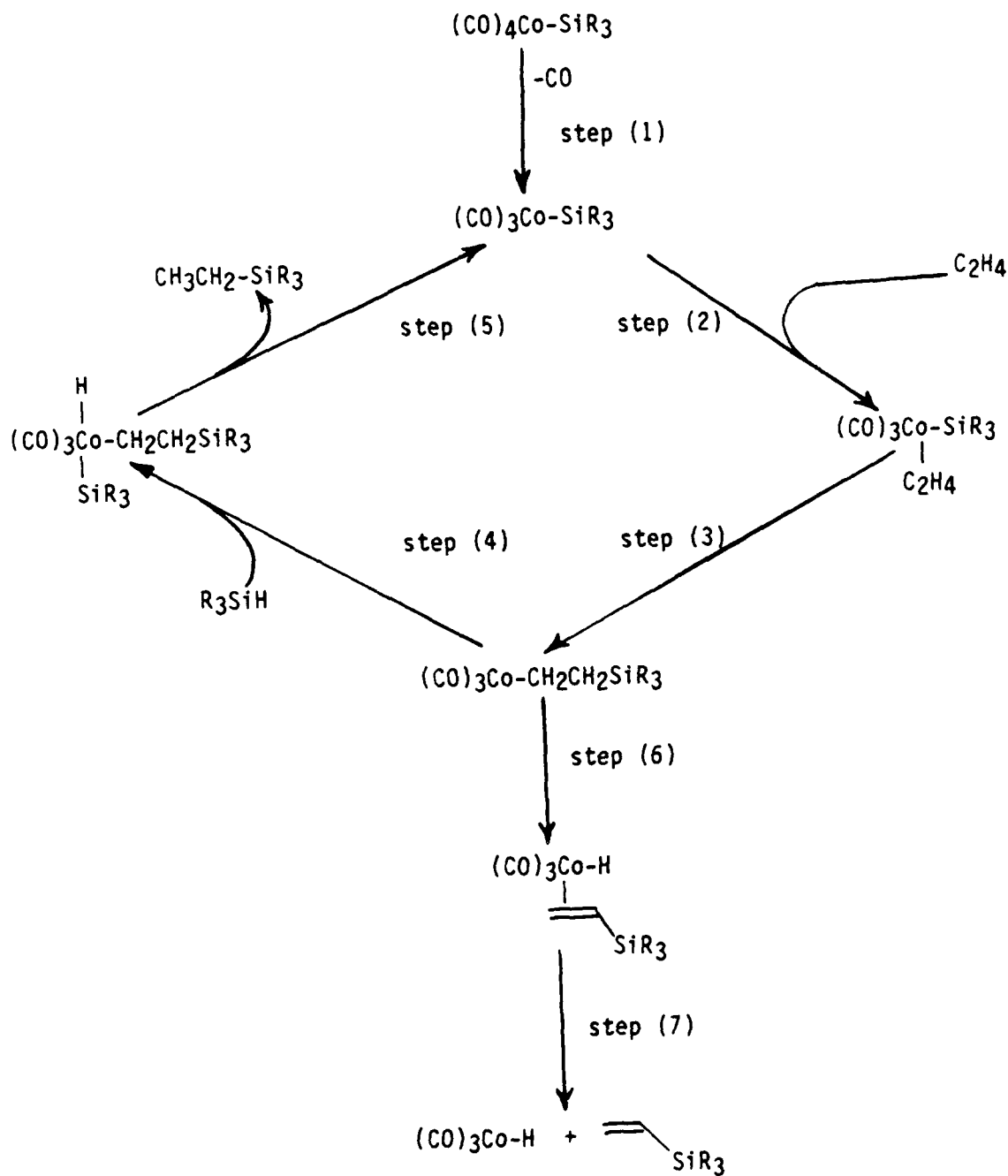
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12. IR spectroscopic data (CO stretching region) for relevant complexes (cm^{-1}): $(\text{CO})_4\text{Co-SiEt}_3$: 2089 m, 2026, 1995 s; $(\text{CO})_3\text{Co-SiEt}_3$: 1957 s, 1953 s; $(\text{CO})_3(\text{C}_2\text{H}_4)\text{Co-SiEt}_3$: 1968 sh, 1961 s; $(\text{CO})_4\text{Co-C(O)CH}_2\text{CH}_3$: 2105 m, 2045 m, 2023 s, 2002 s.
13. When a solution of $(\text{CO})_4\text{Co-SiEt}_3$ in ethylene containing toluene- d_8 is irradiated, signals at $\delta = 1.15$ ppm (m) for Et_3Si and at 3.00 ppm (s) for coordinated ethylene are observed. For the resonance of coordinated ethylene cf. Y.-M. Wu, 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 $\text{PPN}[\text{Co}(\text{CO})_4]$ in 2 ml of THF was added to 200 mg (1.1 mmol) of $[\text{Et}_3\text{O}]\text{BF}_4$. After stirring the solution for 15 min, the solvent was removed in vacuo. The residue was redissolved in 1 ml of methylcyclohexane. $[\text{PPN}]\text{BF}_4$ and excess $[\text{Et}_3\text{O}]\text{BF}_4$ was removed via filtration and the solution was used without further purification. Only signals due to $(\text{CO})_4\text{Co-C(O)CH}_2\text{CH}_3$ 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 $\text{Na}[\text{Co}(\text{CO})_4]$ in 1 ml THF- d_8 . After 2 min the resulting $(\text{CO})_4\text{Co-Me}$ was reacted with 100 mg (1.3 mmol) of Me_3SiH . The solution was stirred for 20 min at 0 C° and then warmed up. Immediately after the solution reached room temperature, a $^1\text{H-NMR}$ spectrum was taken: $\delta = 0.18$ ppm for methane. Formation of $(\text{CO})_4\text{C(O)CH}_3$ accompanies formation of $(\text{CO})_4\text{Co-Me}$ in the synthesis [see citation in ref. 14] and the thermolysis of the $(\text{CO})_4\text{Co-Me}/(\text{CO})_4\text{Co-C(O)CH}_3$ mixture in the presence of Me_3SiH gives CH_3CHO in addition to CH_4 [cf. also R. W. Wegman, Organometallics **5** (1986) 707, which shows formation of CH_3CHO from reaction of $(\text{CO})_3(\text{PPh}_3)\text{Co-C(O)CH}_3$ with Et_3SiH or Ph_3SiH].



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 C_2H_4 insertion into a Co-Si bond.

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