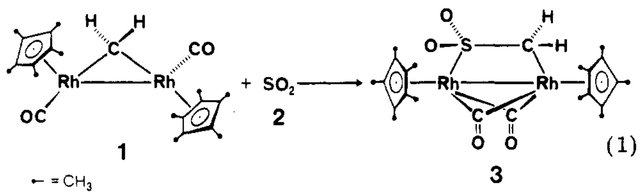

(1)

unambiguous proof that compound **3** represents a C_s symmetrical μ-η^2-sulfene complex that originates from electrophilic insertion of sulfur dioxide into the three-membered backbone of the precursor compound **1**.

(1) The IR spectra (KBr)[6] exhibit a very strong absorption at 1807 cm^{-1}. Both the position of this band and its observed long-wave shift occurring upon ^{13}CO labeling of **3** (1776 cm^{-1})[7] underline its assignment to carbon monoxide bridges, the presence of which latter groups being once more evident from a characteristic low-field triplet in the ^{13}C NMR spectrum (δ(CO) 228.0 (^1J(Rh–C) = 40 Hz)).[6]

(2) Convincing proof of loss of the dimetallacyclopropane geometry of compound **1** upon reaction with sulfur dioxide comes from ^1H NMR spectroscopy: as a result of SO_2 insertion into one of the rhodium–methylene bonds, the methylene protons give rise to a A_2X system centered at δ 2.96 (relative intensity 2 H; $CDCl_3$, 25 °C, 400 MHz), with the observed coupling constant (^2J(Rh–H) = 3.5 Hz) being typical of Rh–CH_x functionalities (x = 1–3).[5a,8] In addition, the methylene carbon resonance is no longer found within the shift range of μ-methylene complexes[3b,c] but is rather close to that of metal alkyls (δ(CH_2) 68.8 (d)); again, the corresponding coupling constant (^1J(Rh–C) = 28 Hz) is in the order commonly observed for alkylrhodium complexes.[5a,8] The positions of two intense IR absorptions found at 1197 cm^{-1} [$\nu_{as}(SO_2)$, KBr] and 1063 cm^{-1} [$\nu_s(SO_2)$, KBr] are diagnostic of *S*-sulfinato derivatives that are structurally closely related to the methylenesulfene bridge of compound **3**.[9,10]

(3) The unequal chemical environment of the metal centers arising from C,S coordination of the sulfene ligand across the dimetal frame accounts for the appearance of separate, well-resolved signals for each set of the methyl protons as well as the ring carbon atoms in the ^1H and ^{13}C NMR spectra, respectively.[6] Based upon the well-documented structural details of triply bridged (η^5-C_5Me_5)Rh–Rh(η^5-C_5Me_5) dimetal fragments, we should expect both C_5Me_5 ligands to be oriented perpendicular to the metal-to-metal vector and also parallel to each other.[3c,11,12]

The reactivity of the dimetallacyclopropane **1** is in marked contrast to related systems that display a metal–metal double bond in addition to a methylene bridge. Thus, the cobalt derivative (μ-CH_2)(μ-CO)[(η^5-C_5Me_5)Co]$_2$ instantaneously reacts with sulfur dioxide even at low temperatures to give the triply bridged species (μ-CH_2)(μ-CO)(μ-SO_2)[(η^5-C_5Me_5)CO]$_2$.[1] Furthermore, both electronic and structural details seem to decidedly govern SO_2-induced reaction pathways of dimetallacyclopropanes: for example, the μ-diphenylmethylene derivative of the parent compound **1** undergoes ring opening instead of ring expansion, with the single product formed in this particular case being the diphenylcarbene complex of composition (μ-SO_2)[(η^5-C_5Me_5)$_2$$Rh_2$(CO){C($C_6H_5$)$_2$}].[13]

This paper demonstrates for the first time the feasibility of electrophilic SO_2 insertion into methylene bridges with concomitant metal-centered formation of the parent sulfene, $CH_2{=}SO_2$. This latter species—a highly reactive formal analogue of ketene[14]—has to the best of our knowledge escaped all previous attempts of stabilization through metal coordination. We are presently in the process of applying this promising straightforward synthetic method to related dimetallacyclopropanes.

Registry No. 1, 76545-02-3; 2, 7446-09-5; 3, 82264-78-6; Rh, 7440-16-6.

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[6] Procedure. A magnetically stirred solution of 273 mg (0.5 mmol) of **1** in 50 mL of rigorously dried tetrahydrofuran is treated at −78 °C (dry ice/acetone) with a vigorous stream of high-quality dry SO_2 gas for ca. 3 min (100-mL Schlenk tube). The Schlenk tube is then connected with a mercury-filled pressure relief valve, and the solution is allowed to slowly warm up to room temperature. After the color change from deep red to brownish yellow has gone to completion (30–60 min at ca. 25 °C), the solvent is stripped off in a water aspirator. The remaining brown residue is first washed with *n*-pentane and subsequently with diethyl ether. Product **3** is finally crystallized from a nearly saturated solution in acetone/diethyl ether (+25 to −35 °C) to give brownish red lustrous crystals: yield 283 mg (93%); mp 100 °C (sealed capillary). The compound is air stable both in solution and in the solid state, very soluble in benzene, methylene chloride, acetone, and tetrahydrofuran, and insoluble in *n*-pentane and diethyl ether. Anal. Calcd for $C_{23}H_{32}O_4Rh_2S$ (610.38): C, 45.26, H, 5.28 Rh, 33.71, S, 5.25. Found: C, 45.33, H, 5.58, Rh, 33.81, S, 5.29; mol wt, 610 (field desorption mass spectrometry). Spectroscopic data of **3**: IR (KBr) 1807 (vs) ($\nu(^{12}CO)$), 1776 ($\nu(^{13}CO)$); 1197 (vs) [$\nu_{as}(SO_2)$], 1063 (vs) [$\nu_s(SO_2)$]; further typical bands: 2912 (m), 2899 (m), 1003 (s), 727 (s); IR (THF) 1813 (vs) ($\nu(^{12}CO)$), 1784 ($\nu(^{13}CO)$); ^1H NMR (90 MHz, $CDCl_3$, 25 °C, internal Me_4Si) $\delta(CH_3)$ 1.83 (d, 15 H, ^3J(Rh–H) = 0.6 Hz), $\delta(CH_3)$ 1.80 (d, 15 H; ^3J(Rh–H) = 0.7 Hz), $\delta(CH_2)$ 2.96 (d, 2 H, ^2J(Rh–H) = 3.5 Hz); $^{13}C\{^1H\}$ NMR (67.88 MHz, $CDCl_3$, 28 °C, internal Me_4Si) δ(CO) 228.0 (t, ^1J(Rh–C) = 40 Hz), $\delta(CH_3)$ 8.7 (s), $\delta(C_5Me_5)$ 105.0 (s) and 103.9 (s), $\delta(CH_2)$ 68.8 (d, ^1J(Rh–C) = 28 Hz). The CH_2 signal expectedly appears as a doublet of triplets in the off-resonance decoupled ^{13}C NMR spectrum. Systematic nomenclature: [μ-η^2(*C,S*)-sulfene]bis[(μ-carbonyl)(η^5-pentamethylcyclopentadienyl)rhodium](*Rh–Rh*).

[7] **3**-[^{13}CO] has been synthesized from **1**-[^{13}CO] and sulfur dioxide according to the above preparation (ca. 30% ^{13}CO).

[8] (a) Werner, H.; Feser, R.; Buchner, W. *Chem. Ber.* **1979,** *112,* 834. (b) Schmidt, G. F.; Muetterties, E. L.; Beno, M. A.; Williams, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **1981,** *78,* 1318. (c) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. *J. Chem. Soc., Chem. Commun.* **1981,** 809.

[9] (a) Vitzthum, G.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1971,** *10,* 315. (b) Wojcicki, A. *Adv. Organomet. Chem.* **1974,** *12,* 31. (c) Lindner, E.; von Au, G.; Eberle, H.-J.; Hoehne, S. *Chem. Ber.* **1982,** *115,* 513.

[10] Bridging SO_2 complexes of type (μ-SO_2)[ML_x]$_2$ display a fairly different IR pattern: cf. Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Wülknitz, P. *Chem. Ber.* **1981,** *114,* 716. See also: Herrmann, W. A.; Plank, J.; Bauer, Ch.; Ziegler, M. L.; Guggolz, E.; Alt, R. *Z. Anorg. Allg. Chem.*, in press.

[11] Herrmann, W. A.; Bauer, Ch.; Kriechbaum, G.; Kunkely, H.; Ziegler, M. L.; Speth, D.; Guggolz, E. *Chem. Ber.* **1982,** *115,* 878 and references cited therein.

[12] Several attempts to obtaining single-crystals of **3** for the purpose of an X-ray structure analysis were unsuccessful. We are presently trying to solve this problem by synthesizing alkyl derivatives of **3**.

[13] Herrmann, W. A.; Bauer, Ch., unpublished results, 1981.

[14] Review: Opitz, G. *Angew. Chem., Int. Ed. Engl.* **1967,** *6,* 107.

Hydrosilane-Induced Reductive Coupling of Carbon Monoxide

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Summary: A remarkable acceleration by hydrosilanes of the transition-metal-catalyzed reduction of carbon monoxide to compounds containing methoxy and 1,2-ethanedioxy groups has been discovered.

We wish to report the remarkable acceleration by a hydrosilane of the transition-metal-catalyzed reduction of carbon monoxide to compounds containing methoxy and

Table I. Reaction[a] of CO + H_2 with $(n\text{-}C_6H_{13})_3SiH$/Metal Carbonyl

metal carbonyl	pressure, psi		product, mol/[(g-atom of metal)h][b,c]		
	CO	H_2	$-OCH_2CH_2O-$	CH_3O-	$n\text{-}C_6H_{13}CH_2O-$
$Co_2(CO)_8$	~1200	~1200	0	0	0
	2000	2000	1.0	2.2	0
	3000	3000	2.6	3.7	0
	4000	4000	3.3	4.0	0
$Rh(CO)_2acac$	4000	4000	2.7	4.2	0
$Ru_3(CO)_{12}$	0	~3300	0	1.7	trace
	3500	0	0.2	1.0	1.5
	500	500	0	trace	6
	1000	1000	0	1.4	5
	2000	2000	0.3	4.8	6
	3000	3000	1.7	17	29
	4000	4000	2.2	15	?

[a] 80 mL (0.22 mol) of $(n\text{-}C_6H_{13})_3SiH$, 270 °C, 1 h (The turnover rate usually decreased with time), 3 mg-atom of metal. [b] Products were determined as $PhCO_2CH_2CH_2O_2CPh$, $PhCO_2Me$, and $n\text{-}C_7H_{15}O_2CPh$ by use of vapor-phase chromatography and NMR and mass spectroscopy after treatment of the reaction mixture with benzoic anhydride. This treatment is based on a report of the reaction $Et_3SiOEt + Ac_2O \rightarrow Et_3SiOAc + EtOAc$.[d] The numbers reported in this Table are lower limits because the reaction with Bz_2O is not quantitative; for example, treatment of Me_3SiOEt and $(n\text{-}C_6H_{13})_3SiOCH_2CH_2OSi(n\text{-}C_6H_{13})_3$[e] gave conversions to the corresponding benzoates of 77 and 60%, respectively. [c] The experiments were not all performed in the sequences in which they are grouped in this table; trends should be viewed qualitatively, not quantitatively. [d] Ladenburg, A. *Ber. Dtsch. Chem. Ges.* **1872**, *5*, 319. [e] Prepared by reaction of ethylene glycol with $(n\text{-}C_6H_{13})_3SiCl$/pyridine. NMR ($CHCl_3$): 3.63 (s, 2.0 H), 5.6-7.2 (m, 39 H) ppm, upfield from $CHCl_3$. Chemical ionization (isobutane) mass spectrum: calcd for $C_{38}H_{82}O_2Si_2$ 626.5853 and for $C_{38}H_{82}O_2Si_2-C_6H_{13}$ 541.4835; found 626.5198 ± 66 ppm (parent), 541.4828 ± 1.3 ppm (base).

1,2-ethanedioxy groups (eq 1). We report also the transition-metal-catalyzed desilylative α-oxymethylation of the alkyl group of a hydrosilane (eq 2).

$$CO + H_2 \xrightarrow[>SiH]{\text{transition metal}} -OCH_2CH_2O- + CH_3O- \quad (1)$$

$$R_3SiH + CO + H_2 \xrightarrow{\text{transition metal}} RCH_2O- \quad (2)$$

After a long hiatus following the original reports[1] of the transition-metal-catalyzed reductive coupling of CO to ethylene glycol and its derivatives, such reactions have become commonplace. However, in the absence of a Lewis base as cocatalyst or carboxylic acid as solvent, either great pressure or great patience is required for their observation. The most active catalysts contain cobalt, rhodium, or ruthenium.

Motivated by the well-known hydrosilylation of carbonyl groups and by our observation that silanes such as Ph_3SiH and $(MeSiHO)_x$ converted formaldehyde to compounds containing $-OCH_2CH_2O-$,[2] we investigated transition-metal-catalyzed reactions of CO with H_2 in the presence of a hydrosilane[3a] and discovered reaction 1. Results obtained with trihexylsilane are in Table I; the use of triphenylsilane with $Co_2(CO)_8$ at 6000 psi also led to compounds containing CH_3O- and $-OCH_2CH_2O-$, but more slowly. The acceleration of the formation of $-OCH_2CH_2O-$ brought about by a high concentration (2.7 M) of $>SiH$[16] is large: similar experiments done in the absence of $>SiH$ with $Co_2(CO)_8$ and $Ru_3(CO)_{12}$ in sulfolane, dibutyl ether, and tetraethylsilane as solvents and experiments done with $Rh(CO)_2acac$ in a wide variety of solvents gave no detectable compounds containing $-OCH_2CH_2O-$; although the use of 0.07 M $(n\text{-}C_6H_{13})_3SiH$, Et_2SiH_2, Ph_3SiH, Ph_2SiH_2, $PhSiH_3$, and $(EtO)_3SiH$ with $Co_2(CO)_8$ in sulfolane led to no compounds containing CH_3O- or $-OCH_2CH_2O-$, the significance of such results in sulfolane is unclear since the possibility of a solvent-induced transformation of the catalyst system has not been excluded. Use of $ClRh(CO)(Ph_3P)_2$, $Mn_2(CO)_{10}$, Cu_2O, H_2PtCl_6, H_2OsCl_6, $(Ph_3P)_2PdCl_2$, and no metal compound in 2.7 M $(n\text{-}C_6H_{13})_3SiH$ at 8000 psi led to no compounds containing $-OCH_2CH_2O-$ or $n\text{-}C_6H_{13}CH_2O-$. Note also in Table I that compounds containing $-OCH_2CH_2O-$ and CH_3O- are produced even when H_2 is not introduced.

Comparison of the productivities in Table I with those in the literature indicates that they are exceptionally superior for cobalt, almost as high[5k] for ruthenium, and inferior for rhodium: the most productive cobalt systems, $Co_2(CO)_8$ in CF_3CH_2OH[4a,b] and HOAc[4c] solvent, gave compounds containing $-OCH_2CH_2O-$ at a rate of ~0.04 and ~0.01 mol/[(g-atom of Co)h], respectively, at 4900 and 4500 psi, respectively. The most productive ruthenium systems involve the use as cocatalysts of salts in an "inert" solvent,[5a,b] carboxylic acids as solvent with[5c-e,l] and without salts, and molten 'onium salts as solvents;[5g,h] the highest rates calculable from the data published for each of these classes of cocatalyst at pressures of ~6000 psi and below are ~1.5 (5000 psi),[5a] 0.7 (6300 psi),[5c,l] ~0.4 (6000 psi),[5a,f] and 4.6 (6300 psi)[5h] mol/[(g-atom of Ru)h], respectively.[5i] The most productive rhodium systems such as the CsOAc/*N*-methylmorpholine cocatalyzed system in 18-crown-6/Pr_3PO,[6a] Et_3PO, and 1,3-dimethyl-2-imidazolidinone[6b] solvents can produce ethylene glycol at rates of 25, 25, and 18 mol/[(g-atom of Rh)h], respectively, at 8000 psi.

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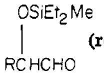
(1) (a) Gresham, W. F. British Patent 655 237 1951 (application in U.S., 1947). (b) Gresham, W. F.; Schweitzer, C. E. U.S. Patent 2 534 018, 1950. (c) Gresham, W. F. U.S. Patent 2 636 046 1953.

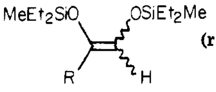
(2) Kaplan, L. U.S. Patent 4 283 578 1981.

(3) (a) The reduction of CO_2 to formaldehyde by $RuCl_2(PPh_3)_3$/$MeEt_2SiH$[3b] and the $Co_2(CO)_8$/PPh_3-catalyzed hydroformylation of RCHO by $MeEt_2SiH$/CO to give



$$\overset{\displaystyle OSiEt_2Me}{\overset{|}{RCHCHO}}$$

(ref 3c)



(ref 3d)

have since been reported. (b) Koinuma, H.; Kawakami, F.; Hirai, H. "Abstracts of the 9th International Conference on Organometallic Chemistry", Dijon, 1979, p C26. Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. commun.* 1981, 213. (c) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Honolulu, HI, Apr 1979; American Chemical Society: Washington, DC, 1979; No. 262. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. (d) Seki, Y.; Murai, S.; Sonoda, N. *Ibid.* **1978**, *17*, 119.

(4) (a) Feder, H. M.; Rathke, J. W. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 45. (b) Rathke, J. W.; Feder, H. M. In "Catalysis of Organic Reactions"; Moser, W. R., Ed.; Marcel Dekker: New York, 1981; p 219. (c) Knifton, J. F. U.S. Patent 4 268 689 1981.

Although we have made no observations which indicate how >SiH acts to accelerate these cobalt-, ruthenium-,[7a] and rhodium-catalyzed reactions, we believe that the following facts provide a framework which facilitates thought about possible mechanisms. (1) Neutral and anionic mono- and oligonuclear transition metal carbonyl compounds containing silyl groups as ligands are well-known, and their reactivity toward $\mathrm{CO/H_2}$, solubility, and stability under the reaction conditions would differ from those of the compounds which would exist in the absence of hydrosilane. (2) Fachinetti has suggested and provided evidence for the reaction $\mathrm{HCo(CO)_4 + Co_2(CO)_8 \rightarrow Co_3(CO)_9COH}$, i.e., for the idea that the common cobalt/$\mathrm{H_2}$/CO system contains as a matter of course a small cluster in which a CO is already en route to products of reduction, and has concluded that it is possible that $\mathrm{Co_3(CO)_9COH}$ can be an intermediate in the reduction of CO by $\mathrm{H_2}$.[8] (3) The existence of $\mathrm{HRu_3(CO)_{10}COH}$ has been suggested.[9] (4) The alcoholysis of silanes, $\mathrm{>C{-}OH + H{-}Si< \rightarrow >C{-}OSi<}$, in the presence of a variety of transition-metal compounds is well-known. (5) The reaction of $\mathrm{Co_2(CO)_8}$ with $\mathrm{R_2SiH_2}$ to produce $\mathrm{Co_3(CO)_9COSiR_2Co(CO)_4}$ has been reported.[10] (6) The reaction $\mathrm{Co_3(CO)_9COR + CO/H_2 \rightarrow ROCH_2CH_2OH}$ has been reported.[11] (7) It has been reported that an α-(trimethylsilyloxy) substituent can accelerate carbonylation of an alkyl group.[12]

In the course of this work we have observed with $\mathrm{Ru_3(CO)_{12}}$ an unprecedented desilylative reductive carbonylation, i.e., α-oxymethylation, of the alkyl group of a hydrosilane (reaction 2). Results are in Table I; compounds containing n-$\mathrm{C_6H_{13}O}$– or (n-$\mathrm{C_5H_{11}}$)MeCHO– were not detected. The use at 6000 psi of triphenylsilane with $\mathrm{Co_2(CO)_8}$ and of tetraethylsilane with $\mathrm{Co_2(CO)_8}$ and $\mathrm{Ru_3(CO)_{12}}$ did not lead to compounds containing $\mathrm{PhCH_2O}$– or $\mathrm{CH_3CH_2CH_2O}$–. Such an α-oxymethylation reaction[13] involves the cleavage of what was a silicon–carbon bond and the bonding to that carbon of what was CO.[14] Although the cleavage of a Si–C bond by a transition metal is well-known, the "insertion" of a transition metal into a Si–C bond has actually been observed only for compounds whose Si–C bond is part of a small strained ring.[15]

Acknowledgment. We are grateful to Wilbur L. Berry for expert technical assistance. The high pressure experiments were performed under the general supervision of B. J. Argento.

Registry No. CO, 630-08-0; $\mathrm{Co_2(CO)_8}$, 10210-68-1; $\mathrm{Rh(CO)_2acac}$, 14874-82-9; $\mathrm{Ru_3(CO)_{12}}$, 15243-33-1; (n-$\mathrm{C_6H_{13})_3SiH}$, 2929-52-4; $\mathrm{Ph_3SiH}$, 789-25-3; (n-$\mathrm{C_6H_{13})_3SiOCH_2CH_2OSi(C_6H_{13}}$-$n$)$_3$, 82294-11-9.

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[5] (a) Dombek, B. D. European Patent Application 13 008 1980. (b) Dombek, B. D. *J. Am. Chem. Soc.* **1981**, *103*, 6508. (c) Knifton, J. F. *J. Chem. Soc., Chem. Comm.* **1981**, 188. (d) Knifton, J. F. U.S. Patent 4 268 689 1981. (e) Knifton, J. F. British Patent Application 20 586 00A 1981. (f) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855. (g) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. (h) Knifton, J. F. U.S. Patent 4 265 828 1981. (i) Also, we have studied a $\mathrm{Ru_3(CO)_{12}}$ (10 mmol)/NaI (15–180 mmol) system in 18-crown-6[5j] and N-methylpyrrolidone as solvents in the range 170–250 °C at 6000 psi of 1/1 $\mathrm{CO/H_2}$. Rates (1.9 and 1.3 mol/[(g-atom of Ru)h], respectively) and selectivities to ethylene glycol (accompanied by methanol and ethanol at rates of 8 and 6 mol/[(g-atom of Ru)h], respectively, in both solvents) equal to the best which we observed were obtained at 210 °C by use of 180 mmol of NaI. Similar results were obtained in a less thorough study with KI. (j) Kaplan, L. U.S. Patent 4 162 261 1979. (k) See footnote *b* to Table I. (l) Knifton, J. F. *J. Catal.* **1982**, *76*, 101.

[6] (a) Kaplan, L. U.S. Patent 4 197 253 1980. (b) Hart, P. W. U.S. Patent 4 302 547 1981.

[7] (a) Our work with $\mathrm{Ru_3(CO)_{12}}$ was done as a consequence of a suggestion to that effect from R. G. Bergman which was based upon his knowledge of our results with $\mathrm{Co_2(CO)_8}$ and $\mathrm{Rh(CO)_2acac}$ and of the results[7b] of B. D. Dombek on the $\mathrm{Ru_3(CO)_{12}}$-catalyzed conversion of $\mathrm{CO/H_2}$ to $\mathrm{AcOCH_2CH_2OAc}$ in HOAc solvent. (b) Subsequently reported in ref 5f.

[8] Adams, H.-N.; Fachinetti, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 125. Fachinetti, G.; Balocchi, L.; Secco, F.; Venturini, M. *Ibid.* **1981**, *20*, 204. For a review of (alkylidyne)tricobalt nonacarbonyl complexes see: Nicholas, K. M.; Nestle, M. O.; Seyferth, D. In "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. 2, p 1.

[9] Keister, J. B. *J. Organomet. Chem.* **1980**, C36.

[10] Fieldhouse, S. A.; Cleland, A. J.; Freeland, B. H.; Mann, C. D. M.; O'Brien, R. J. *J. Chem. Soc. A* **1971**, 2536. The possible functioning of >SiH as a reagent which locks a reversibly formed intermediate into a structure which is a precursor of compounds containing $\mathrm{-OCH_2CH_2O-}$ is formally analogous to the role suggested for RCOOH in the $\mathrm{Ru_3(CO)_{12}}$/RCOOH-catalyzed reactions discussed above. ("The function of this unique solvent/promoter [RCOOH] is apparently to intercept a catalytic intermediate"[5f] and "convert it to a product not otherwise obtained."[5b]). G. Fachinetti has informed us that he has observed the reaction

$$\mathrm{CO/H_2 + Co_2(CO)_8 \xrightarrow{Me_3SiCl,\ R_3N} Me_3SiOCH_2CH_2OSiMe_3}$$

His results in the area of cobalt carbonyl chemistry aided our thinking about pathways possible for the reactions (Table I) which we had observed.

[11] Fachinetti, G.; Lazzaroni, R.; Pucci, S. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1063.

[12] Gladysz, J. A.; Selover, J.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766.

[13] An anticipation by Akhrem, I. S.; Avetisyan, D. V.; Vartanyan, R. S.; Shakhatumi, K. G.; Vol'pin, M. E. *Izv. Akad. Nauk SSSR* **1975**, 2327: "...it could be expected that cleavage of the Si–C bond [by a transition-metal compound] will lead to transfer of the organic radical to the atom of the transition metal, and consequently to the formation of exceedingly reactive σ-organic derivatives of the transition metals".

[14] Insertion, at the carbonyl group, of aldehydes and ketones into a Si–C bond is well-known. For some examples, see: Calas, R.; Dunogues, J.; Deleris, G.; Pisciotti, F. *J. Organomet. Chem.* **1974**, *69*, C15. Deleris, G.; Dunogues, J.; Calas, R. *Ibid.* **1975**, *93*, 43. Abel, E. W.; Rowley, R. J. *Ibid.* **1975**, *84*, 199. Seyferth, D.; Duncan, D. P.; Vick, S. C. *Ibid.* **1977**, *125*, C5. Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *Ibid.* **1977**, *135*, C37. Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. Gostevskii, B. A.; Kruglaya, O. A.; Albanov, A. I.; Vyazankin, N. S. *J. Organomet. Chem.* **1980**, *187*, 157 and references cited therein.

[15] Cundy, C. S.; Lappert, M. F. *Chem. Commun.* **1972**, 445; *J. Chem. Soc., Dalton Trans.* **1978**, 665; *J. Organomet. Chem.* **1978**, *144*, 317. Cundy, C. S.; Lappert, M. F.; Dubac, J.; Mazerolles, P. *J. Chem. Soc., Dalton Trans.* **1976**, 910. Kuz'min, O. V.; Bykovets, A. L.; Vdovin, V. M.; Krapivin, A. M. *Izv. Akad. Nauk SSSR* **1979**, 2815.

[16] This symbol represents a compound containing a hydrogen bonded to silicon.