Reductive Oligomerization of Carbon Monoxide by Rhodium-Catalyzed Reaction with Hydrosilanes

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The production of specific organic compounds via the hydrogenation of carbon monoxide represents an important pathway to row chemical material production and promises to be critically important in the coming decades, given the world situation relative to crude oil.[1,2] Extensive efforts have been made toward this goal, but the number of processes available remain limited and the mechanisms for these reactions remain unclear.[3,4] Many of the mechanisms proposed thus far are based on studies of stoichiometric reactions involving discrete isolable complexes,[4] such as acyl complexes,[5] α-oxyalkyl complexes,[6] and related materials.[7,8] Although stoichiometric approaches give useful and important information, they often deviate from actual catalytic processes. We have designed a novel catalytic reaction of CO using hydrosilanes in place of H_2. The advantage of using hydrosilanes is that otherwise unstable intermediates, such as enols, can survive as a silyl derivative without isomerization to the stable keto isomer (e.g., tautomerization) at the experimental conditions used. Hydrosilanes have been used as a promoter for reductive coupling of CO to ethylene glycol from H_2/CO[9] and used for a stoichiometirc model for the hydrogenation of CO.[5,8] To our knowledge, there has been only one report[10] on a transition-metal-catalyzed reaction of CO with a hydrosilane. We now report a novel Rh-catalyzed reductive oligomerization of CO with a hydrosilane. The reaction is intrinsically interesting and useful as a synthetic method. Moreover, the reaction provides an entirely novel

model that may be useful for a better understanding of the mechanism of such catalytic reductions.

A variety of transition-metal carbonyl complexes such as $Mo(CO)_6$, $W(CO)_6$, $PdCl_2$, $Ru_3(CO)_{12}$, $RuCl_2(PPh_3)_3$, $Co_2(CO)_8$, $Rh_6(CO)_{16}$, $[RhCl(CO)_2]_2$, $RhCl(PPh_3)_3$, and $Ir_4(CO)_{12}$ have been examined for their catalytic activity with respect to reactions of CO with $HSiEt_2Me$ under a variety of reaction conditions (2.5 mol % of catalyst to $HSiEt_2Me$, 100−180 °C, CO 10−50 atm), but CO-incorporated products were not detected in GC. In most cases, the sole product obtained was $MeEt_2SiOSiEt_2Me$. As a result of extensive examination of catalysts and additives, we have ultimately discovered that a reaction of CO with hydrosilanes can be achieved by using a Rh/amine catalytic system to give CO-incorporated products. Thus, the reaction of CO (50 atm) with $HSiEt_2Me$ (2.5 mmol) at 140 °C in the presence of $[RhCl_2(CO)_2]_2$ (0.05 mmol)/Et_3N (7.5 mmol) in C_6H_6 (5 mL) for 1 day in a 50-mL stainless steel autoclave gave $MeEt_2SiOSiEt_2Me$[11] as the main product (31% yield), along with reductive coupling of CO which gave diethylmethylsiloxymethane (**1a**, 2%), 1,2-bis(diethylmethylsiloxy)ethene[12] (**2a**, 18%, $Z/E = 93/7$), and 1,2,3-tris(diethylmethylsiloxy)-propene (**3a**, 5%, $Z/E = 10/1$). In addition, products that corresponded to four and five molecules of CO were also observed by GCMS (eq 1). Yields are based on the $HSiEt_2Me$
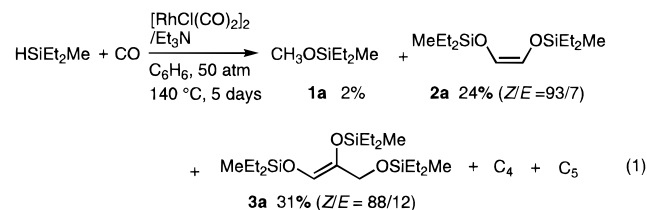
charged. Increasing (200 °C) or decreasing (80 °C) the reaction temperature failed to improve the product yields and selectivities. When the reaction was run for 5 days, the yields were 2% for **1a**, 24% ($Z/E = 93/7$) for **2a**, and 31% ($Z/E = 88/12$) for **3a**.

Surprisingly, the reaction of CO with $HSiMe_2Ph$ afforded 1,2-bis(dimethylphenylsiloxy)ethene (**2b**)[13] in yields as high as 62% ($Z/E = 90/10$) (eq 2). Reaction 2 is so efficient for this type of

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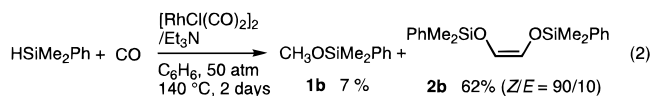
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(10) Sisak reported that the reaction of CO with a hydrosilane in the presence of $Co_2(CO)_8$ gave numerous products in low yields with low selectivities. Sisak, A.; Marko, L.; Angyalossy, Z.; Ungvary, F. *Inorg. Chim. Acta* **1994**, *222*, 131.

(11) Some portion of the siloxane ($MeEt_2SiOSiEt_2Me$) arises from the transition metal catalyzed reaction of $HSiEt_2Me$ with H_2O, which may be eventually produced with the concomitant formation of H_2. Another possibility is the reaction of $HSiEt_2Me$ with CO leading to $MeEt_2SiOSiEt_2$-Me and CH_4 as was reported by Vollhardt. Vollhardt, K. P. C.; Yang, J.-Y. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 460. No effort was made to identify (these small amounts of) H_2 or CH_4. In addition, some portion of the siloxane came from reduction of the allylic siloxy group in C3, C4, C5, and higher (such as **3a**) products by $HSiEt_2Me$.

(12) All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra.
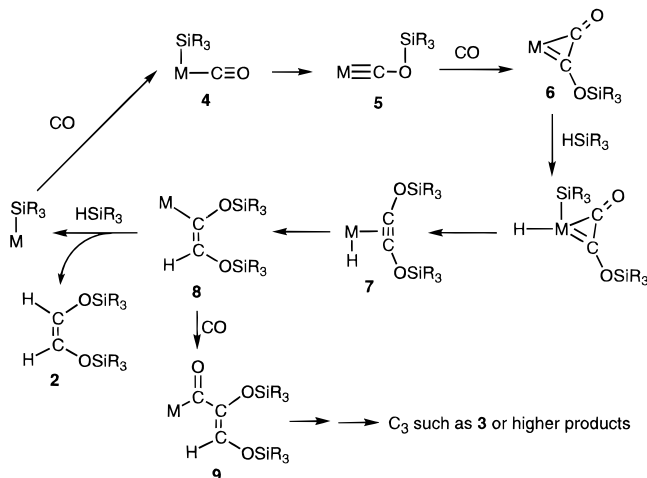
(13) 1,2-Bis(dimethylphenylsiloxy)ethene (**2b**): bp 200 °C (1.5 Torr); ^{1}H NMR (CDCl$_3$) δ 0.43 (s, 12 H, SiCH$_3$), [5.51 (s, *Z*-isomer), 6.36 (s, *E*-isomer), 2 H, =CH], 7.49 (m, 10 H, Ph); ^{13}C NMR (CDCl$_3$) δ −1.60, 124.98, 127.90, 129.72, 133.47, 137.08; IR (neat) 3056, 2968, 2812, 1960, 1888, 1826, 1668, 1594, 1492, 1432, 1390, 1294, 1254, 1144, 1120, 1076, 1000, 896, 834, 790; MS, *m/z* 328 (23, M$^+$), 197 (12), 137 (19), 136 (14), 135 (100), 107 (10); exact mass for $C_{18}H_{24}O_2Si_2$ (M$^+$), calcd 328.1315, found, 328.1341.

$$HSiMe_2Ph + CO \xrightarrow[\substack{C_6H_6,\ 50\ atm \\ 140\ °C,\ 2\ days}]{\substack{[RhCl(CO)_2]_2 \\ /Et_3N}} CH_3OSiMe_2Ph + PhMe_2SiO\diagdown\!\!=\!\!\diagup OSiMe_2Ph \qquad (2)$$

1b 7 %   **2b** 62% (Z/E = 90/10)

reaction that it satisfies the requirement for a synthetic method for the synthesis of disiloxyethylenes **2**.[14] It might be assumed that **2** and **3** are produced by the consecutive reactions of **1**, giving **2** and then **3**, with a hydrosilane and CO. However, this possibility can be excluded by the following results. The reaction of CH_3OSiMe_2Ph (**1b**) with $HSiEt_2Me$ and CO did not give a cross-diol derivative $PhMe_2SiOCH{=}CHOSiEt_2Me$, but rather **1a**, **2a**, and **3a** as in eq 2. The formation of Me_3-$SiOCH_2C(OSiMe_3){=}COSiEt_2Me$ was not observed in the reaction of $Me_3SiOCH{=}CHOSiMe_3$ (E/Z = 1/1) (separately prepared)[14] with $HSiEt_2Me$ and CO.

What is most impressive is the high stereoselectivities leading to **2** and **3**. Such selectivities cannot be thermodynamicaly controlled, and this is the first case of the observation of kinetic products for a catalytic reduction of CO. We propose the mechanism of the present reaction as shown in Scheme 1.[15] The key intermediates are a carbyne–metal complex **5** and dioxyacetylene–metal complex **7**. These two intermediates have also been proposed in our recent study of the Ru-catalyzed synthesis of catechols from two CO's, $HSiR_3$, and two acetylenes.[16] The carbyne complex **5** is formed via a 1,3-silicon (or hydrogen) shift (step **4** → **5**).[17] The conversion of **5** to **7** is well precedented as a carbyne/CO coupling.[18,19] *syn*-Hydrometalation in **7** leads to the final product, **2**. Lippard reported that exposure of the disiloxyacetylene–vanadium complex

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(15) We thank referee ml for suggesting a way not to involve Rh(V).

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Scheme 1

(similar to **7**) under 100 psi of H_2 in THF at 25 °C gave (Z)-disiloxyethylene.[19c] This reaction supports the possibility of the step **7** → **2** and accounts for the high Z-selectivity. The formation of **3** initiated by the insertion of CO in **8** also accounts for the Z-stereoselectivity of **3a**.

The reaction of paraformaldehyde with $HSiEt_2Me$ and CO in the presence of $[RhCl(CO)_2]_2/Et_3N$ for 1 day gave $MeEt_2$-$SiOSiEt_2Me$, **1a** (1%), **2a** (10%), and **3a** (5%), in yields comparable to those observed for reactions without paraformaldehyde. This result shows that formaldehyde does not represent a primary product in the present reaction.

Nicholas proposed that a 1,3-hydrogen shift from a metal to the oxygen atom of the CO ligand in $HM(CO)_n$ leading to $HOC{\equiv}M(CO)_{n-1}$ might be an important step in the homogeneous transition-metal-catalyzed CO reduction. This mechanism is an alternative to the conventionally proposed 1,2-hydrogen shift leading to the formyl complex $HC(O)M(CO)_{n-1}$.[17d] Our system also suggests that catalytic hydrogenation of CO by homogeneous catalysts would proceed via a carbyne complex (i.e., $M{\equiv}C{-}OH$) as a key step.[20]

Supporting Information Available: Characterization of products **2a**, **2b**, and **3a** (2 pages). See any current masthead page for ordering and Internet access instructions.

JA9631561

(20) The present results suggest that the catalytic synthesis of ethylene glycol from CO and H_2 might involve an intermediate similar to **8**, i.e., $MC(OH){=}CGH(OH)$.