Crystals of the title compound are monoclinic with space group Pn and cell constants a = 13.760 (2) Å, b = 7.950 (2) Å, c = 7.245 (2) Å, β = 103.20 (4)°, V = 772 (2) Å^3, Z = 2, D(calcd) = 2.122 g cm^{-3}, and F(000) = 468 electrons. From the total of 2232 reflections, measured on an Enraf-Nonius CAD 4 diffractometer using graphite-monochromated Mo Kα radiation, 182 were less than 2.5$\sigma(I)$ and were treated as unobserved. No absorption correction was applied. Refinement proceeded by anisotropic block diagonal least-squares calculations resulting in a final R value of 0.039.[5]

In Figure 1 is shown the molecular geometry of the complex along with the adopted numbering scheme. Some relevant bond lengths and bond angles are given in Table I. The platinum center has a distorted octahedral geometry having a *mer* coordination of the *o,o′*-$(Me_2NCH_2)_2C_6H_3$ ligand *via* C(1) [1.96 (3) Å] and the two mutually trans positioned NMe_2 groups.[6] The principal distortion of the octahedral geometry results from the N(1)–Pt–N(2) angle of 160.7 (6)°, which is due to the intrinsically small N–Pt–C(1) bite angles of the two five-membered chelate rings. There is a significant difference in Pt–Cl bond lengths between the axial Cl atoms [2.330 (5) and 2.334 (5) Å] and meridial Cl atom [2.454 (8) Å] that points to a strong trans effect of the carbon ligand:[7] IR and Raman spectra show ν(Pt–Cl) at 260, 330, and 333 cm^{-1}.

The formation of the platinum(IV) complexes **2a** and **2b**, using the copper(II) reagents, is the result of an overall two-electron ligand transfer oxidation[8] which is preferred to Pt–C bond cleavage. It is noteworthy that the analogous reaction of $[Ni^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ with CuX_2 stops at the stage of stable $[Ni^{III}X_2(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$, having a square-pyramidal structure.[9] These reactions can be envisaged as one-electron ligand transfer oxidations possibly involving transient formation of a M^{II}–Cu^{II} heterobimetallic intermediate (cf. $[PtAgX(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(\mu\text{-}\{RNC(H)NR\})]$ (R = *p*-tolyl). In the platinum reaction a subsequent one-electron tranfer and bonding of a third halogen occurs, thus completing an octahedral geometry. This provides evidence that the constraints of the terdentate ligand can not be the factor responsible for preventing further oxidation in the corresponding nickel reactions. Further studies on the properties of these novel platinum(IV) species as well as the reactions of $[M^{II}X(C_6H_3(CH_2NMe_2)_2\text{-}o,o')]$ species (M^{II} = Ni, Pd, or Pt) with oxidizing reagents are in progress.

Acknowledgment. Thanks are due to Prof. K. Vrieze for helpful discussions and to Dr. D. M. Grove for critically reading the manuscript.

Registry No. **1a**, 82112-96-7; **1b**, 67507-09-9; **1c**, 83311-96-0; **2a**, 87555-29-1; **2b**, 87555-30-4; **2c**, 87555-31-5.

Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters, and interatomic distances and bond angles (3 pages). Ordering information is given on any current masthead page.

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(5) The position of Pt was derived from a Patterson synthesis. The other non-hydrogen atoms were found from a subsequent ΔF synthesis.

(6) With the related ligand *o,o′*-$(t\text{-}Bu_2PCH_2)_2C_6H_3$ hexacoordinate Pt(IV) complexes so far has not been made, but indications were obtained that octahedral $[IrHCl(CO)(C_6H_3(CH_2PBu\text{-}t_2)_2\text{-}o,o')]$ exists. Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

(7) A review covering this subject is: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 423.

(8) Reaction of equimolar amounts of 1 and CuX_2 affords a 1/1 mixture of 2 and unreacted 1. The 1/2 reaction of $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o')(\mu\text{-}\{RNC(H)NR\})]$ (R = *p*-tolyl) (cf. ref. 1d) with CuX_2 afforded **2a** (or **2b**), Cu^IX, and $Cu^I(RNC(H)NR)$ (R = *p*-tolyl).

(9) Grove, D. M.; van Koten, G.; Zoet, R. *J. Am. Chem. Soc.* **1983**, *105*, 1379.

Cobalt Carbonyl Catalyzed Reaction of Tetrahydrofurans with a Hydrosilane and Carbon Monoxide at Atmospheric Pressure

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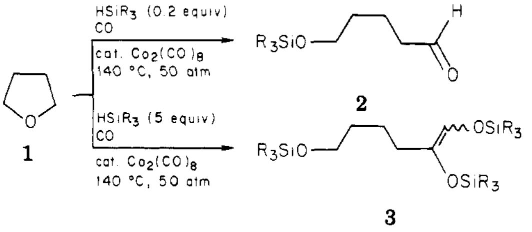
Received September 27, 1983

Summary: The reaction of various tetrahydrofurans with $HSiR_3$ (3 equiv) and CO (1 atm) at 25–40 °C in the presence of $Co_2(CO)_8$ (0.08 equiv) gave the corresponding diol disilyl ethers with incorporation of CO in 56–94% yield. The catalytic reaction begins with the ring opening of tetrahydrofurans with a key catalyst species, $R_3SiCo(CO)_4$, to give tetracarbonylalkylcobalt.

We have reported a series of new $Co_2(CO)_8$-catalyzed reactions with a hydrosilane ($HSiR_3$) and carbon monoxide,[1] by which incorporation of carbon monoxide into olefins,[2] aldehydes,[3,4] cyclic ethers,[4,5] and alkyl acetates[6] has been achieved. Interestingly, when tetrahydrofuran (THF), a five-membered cyclic ether, was employed as substrate, two types of products were obtained, both selectively by simply changing the molar ratio of the substrate to the hydrosilane $HSiEt_2Me$ (eq 1 and 2).[4,5] These reactions generally proceeded under *50 atm* of carbon monoxide and at *140 °C*.

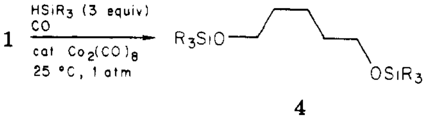


(1)

(2)

$R_3Si = MeEt_2Si$

In our efforts to clarify the basic features of these reactions, we have now found another type of $Co_2(CO)_8$-catalyzed reaction of THF with a hydrosilane and carbon monoxide that gives neither **2** nor **3** but a homologated diol derivative **4**[7] (eq 3). More remarkable is that the catalytic incorporation of carbon monoxide proceeds at *atmospheric pressure* and at *room temperature*. To our knowledge, only a few cases have been recorded of a catalytic reaction of carbon monoxide at 1 atm with the aid of a cobalt catalyst.[8]



(3)

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(1) For a review, see: Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

(2) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Seki, Y.; Hidaka, A.; Makino, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361.

(3) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393.

(4) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 119.

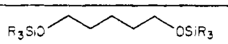
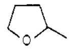
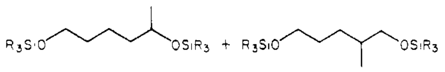
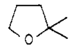
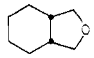
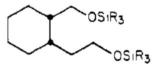
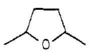
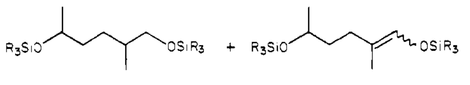
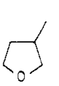
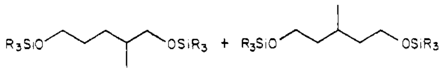
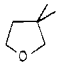
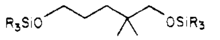
(5) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(6) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370.

(7) All new compounds have been adequately characterized by spectral data and elementary analyses. Details are given in the supplementary material.

0276-7333/83/2302-1883$01.50/0

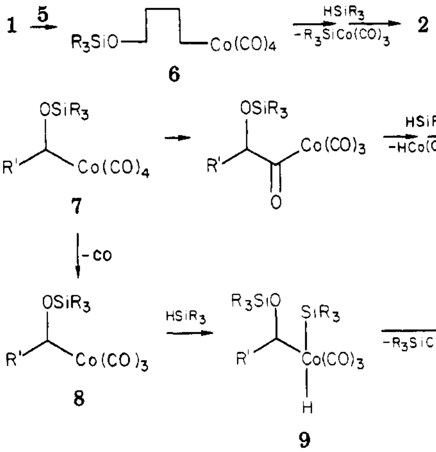
Table I. $Co_2(CO)_8$-Catalyzed Reaction of Tetrahydrofurans with $HSiR_3$ and CO[a]

run	tetrahydrofuran	conditns	product	ratio	% yield[b]
1	 1	$HSiEt_2Me$, C_6H_6, 40 °C, 20 h			87
		$HSiEt_2Me$, CH_2Cl_2, 25 °C, 20 h			86
		$HSiMe_3$,[c] CH_2Cl_2, 25 °C, 20 h			70
2		$HSiEt_2Me$, C_6H_6, 25 °C, 20 h		62:38[d]	77
3		$HSiEt_2Me$, C_6H_6, 25 °C, 20 h	no reaction		
		$HSiEt_2Me$, C_6H_6, 60 °C, 20 h	*e*		
4		$HSiEt_2Me$, C_6H_6, 25 °C, 20 h			56
5		$HSiEt_2Me$, CH_2Cl_2, 25 °C, 6 days		60:40[d]	94
		$HSiMe_3$,[c] CH_2Cl_2, 25 °C, 20 h		100:0[d]	71
6		$HSiEt_2Me$, C_6H_6, 25 °C, 20 h		90:10[g]	78
7		$HSiEt_2Me$, C_6H_6, 25 °C, 20 h			84

[a] Molar ratio of reactions are described in the text. $HSiR_3$ = $HSiEt_2Me$ or $HSiMe_3$. Characterization of products is given in the supplementary material. [b] Determined by GLC analysis. [c] The hydrosilane ($HSiMe_3$, bp 9.6 °C, 25 mmol) was charged to the reaction vessel by trap to trap distillation. [d] The ratio was determined by ^1H NMR. [e] Products without incorporation of CO, see text. [f] A mixture of diastereomers. [g] The ratio was determined by ^{13}C NMR.

Experimentally, the present atmospheric pressure reaction requires no pressure apparatus; an ordinary glass flask connected to a balloon containing carbon monoxide suffices. A representative example follows. In a 10-mL flask was placed $Co_2(CO)_8$ (0.2 mmol), and the flask was filled with carbon monoxide (1 atm), and then $HSiEt_2Me$ (7.5 mmol) was added at 25 °C. In about 5 min, the $Co_2(CO)_8$ dissolved and the solution became light brown. This operation corresponds to the conversion of $Co_2(CO)_8$ to $MeEt_2SiCo(CO)_4$ (**5**).[9] A solvent (CH_2Cl_2, 5 mL) and THF (0.324 mL, 2.5 mmol) were added, and the mixture was stirred at 25 °C for 20 h under CO (1 atm). The product formed was a disilyl ether of 1,5-pentanediol **4** (86%, GLC, based on THF).

Scheme I[a]



[a] R_3Si = $MeEt_2Si$ or Me_3Si; R' = $R_3SiO(-CH_2-)_4$.

The disilyl ether **4** apparently consists of one molecule of THF, one molecule of carbon monoxide, and two molecules of the hydrosilane. The transformation of eq 3 would be rationalized by assuming two successive reactions, i.e., formation of the aldehyde **2** as an intermediate and the hydrosilylation of the thus formed **2** to give the product **4**. The mechanism of the formation of **2** and **3** has already been discussed[1] and is outlined in Scheme I. A silylcobalt carbonyl, $MeEt_2SiCo(CO)_4$ (**5**),[9,10] would have played a key role in the formation of the carbon–cobalt bonds in **6** as well as in **7**. In the present reaction providing **4** (Scheme I), dissociation of a CO ligand from **7** to form **8** and subsequent oxidative addition of $HSiEt_2Me$ to give

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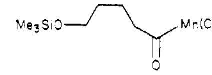
[8] The known examples are limited to the carbonylation of organic halides: (a) Brunet, J. J.; Sidot, C.; Loubinoux, B.; Caubere, P. *J. Org. Chem.* **1979**, *44*, 2199. (b) Cassar, L.; Chiusoli, G. P.; Guerrieri, F. *Synthesis* **1973**, 509. (c) Alper, H.; Amaratunga, S. *J. Org. Chem.* **1982**, *47*, 3595 and related works cited therein. For general reviews of Co-catalyzed reactions, see: (d) Pino, P.; Piacenti, F.; Bianchi, M. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II. (e) Orchin, M. *Acc. Chem. Res.* **1981**, *9*, 259. (f) Colquhoun, H. W. *Chem. Ind.* (*London*) **1982**, 747.

[9] A well-known reaction, $2HSiR_3 + Co_2(CO)_8 \rightarrow 2R_3SiCo(CO)_4 + H_2$: (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *89*, 1640. (b) Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986. (c) Morrison, D. L.; Hagen, A. P. In "Inorganic Syntheses"; Cotton, F. A., Ed.; MacGraw-Hill: New York, 1972; Vol. XIII, p 65.

[10] High reactivity of THF toward $Me_3SiCo(CO)_4$[11] or a related reagent combination ($HSiR_3$ + $Co_2(CO)_8$[12] or R_3SiCl + $NaCo(CO)_4$[13]) has been noted. The reaction of $Me_3SiMn(CO)_5$ with THF under 200 psi of CO has been studied by Gladysz to afford i.[14]



i

[11] Ingle, W. M.; Preti, G.; MacDiarmid, A. G. *J. Chem. Soc., Chem. Commun.* **1973**, 497.

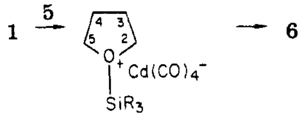
[12] Chalk, A. J. *J. Chem. Soc. D* **1970**, 847.

[13] Nicholson, B. K.; Simpson, J. *J. Organomet. Chem.* **1978**, *155*, 237.

[14] Brinkman, K. C.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1260.

9 would have become favorable at the lower pressure and temperature.

The $Co_2(CO)_8$-catalyzed reaction of tetrahydrofurans having substituents at various positions has been studied, and the results are given in Table I. Generally, incorporation of carbon monoxide took place at 25 °C and 1 atm with benzene or dichloromethane as the solvent. The product distributions in the cases where formation of isomers was possible were greatly effected by the substitution patterns. The results suggest that the regiochemistry would be determined in the ring-opening step of an appropriate silyloxonium ion (**10**) by $Co(CO)_4^-$. For 2-methyltetrahydrofuran (run 2) the ring opening at C-5 (a primary center) is likely to involve S_N2-like attack of $Co(CO)_4^-$, while cleavage at C-2 (a secondary center) would be accounted for by assuming the development of partial positive charge at C-2 in the transition state.[15,16] Since the development of the partial positive charge is expected to be highly enhanced at a tertiary center, it was not surprising to observe 2,2-dimethyltetrahydrofuran (run 3) undergoing exclusive cleavage at C-2 (a teritary center) to give a mixture of products (2-methyl-5-(diethylmethylsiloxy)pentane, 26%, 2-methyl-5-(diethylmethylsiloxy)-2-pentene, 47%, 2-methyl-5-(diethylmethylsiloxy)-1-pentene, 26%) without incorporation of carbon monoxide.[17] Introduction of substituents at the C-3 position of THF has resulted in the incorporation of carbon monoxide predominantly (run 6) or exclusively (run 7) at C-5, probably due to sterically unfavorable approach of $Co(CO)_4^-$ to C-2 in the oxonium ion corresponding to **10**. The presence of a byproduct having an unsaturated bond in run 5 may be ascribed to β-hydride elimination from the intermediate similar to **8**. In such a case, the use of $HSiMe_3$ instead of $HSiEt_2Me$ was found to be effective in suppressing the byproduct formation (run 5). The less bulky $HSiMe_3$ would undergo oxidative addition (see **8** and **9** in Scheme I) more easily than $HSiEt_2Me$ to give the desired product exclusively.



10

The present work not only demonstrates a new method of using carbon monoxide under mild conditions but also suggests a new room-temperature entry to alkylcobalt carbonyls.[10] It should be also noted that the overall transformation described is formally a nucleophilic introduction of an oxymethyl group which is not an easy task from the viewpoint of organic synthesis.[18] Further studies are in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research No. 57118002 provided by The Ministry of Education, Science, and Culture, Japan. We gratefully acknowledge Shin-Etsu Chem. Ind. Ltd., for generous gift of chlorosilanes.

Registry No. 1, 109-99-9; 4, 87481-75-2; $MeEt_2SiO(CH_2)_4CH(CH_3)OSiEt_2Me$, 87481-76-3; $MeEt_2SiO(CH_2)_3CH(CH_3)CH_2OSiEt_2Me$, 87481-77-4; $MeEt_2SiOCH(CH_3)CH_2CH_2CH(CH_3)CH_2OSiEt_2Me$ (isomer 1), 87481-79-6; $MeEt_2SiOCH(CH_3)CH_2CH_2CH(CH_3)CH_2OSiEt_2Me$ (isomer 2), 87481-80-9; $MeEt_2SiOCH(CH_3)CH_2CH_2C(CH_3) = CHOSiEt_2Me$, 87481-81-0; $MeEt_2SiOCH_2CH_2CH(CH_3)CH_2CH_2OSiEt_2Me$, 87481-82-1; $MeEt_2SiO(CH_2)_3C(CH_3)_2CH_2OSiEt_2Me$, 87494-50-6; $HSiEt_2Me$, 760-32-7; CO, 630-08-0; $Co_2(CO)_8$, 10210-68-1; 2-methyl-5-(diethylmethylsiloxy)pentane, 87481-83-2; 2-methyl-5-(diethylmethylsiloxy)-2-pentene, 87481-84-3; 2-methyl-5-(diethylmethylsiloxy)-1-pentene, 87481-85-4; 2-methyltetrahydrofuran, 96-47-9; 2,2-dimethyltetrahydrofuran, 1003-17-4; *cis*-8-oxabicyclo[4.3.0]nonane, 13149-01-4; 2,5-dimethyltetrahydrofuran, 1003-38-9; 3-methyltetrahydrofuran, 13423-15-9; 3,3-dimethyltetrahydrofuran, 15833-75-7; *cis*-[[2-[2-[(diethylmethylsilyl)oxy]ethyl]cyclohexyl]methoxy]diethylmethylsilane, 87481-78-5.

Supplementary Material Available: Spectral and analytical data (6 pages). Ordering information is given on any current masthead page.

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(15) For example, see: Goldsmith, D. J.; Kennedy, E.; Campbell, R. G. *J. Org. Chem.* **1975**, *40*, 3571.

(16) In the reaction of 2-methyltetrahydrofuran with $Me_3SiMn(CO)_5$, only one product arising from C-5 cleavage was isolated after chromatographic purification.[14]

(17) Generally, a tertiary alkylcobalt carbonyl, if formed, would undergo β-hydride elimination rather than CO insertion.

(18) (a) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. (b) Paulsen, H.; Sumfleth, E.; Sinnwell, V.; Meyer, N.; Seebach, D. *Chem. Ber.* **1980**, *113*, 2055. (c) Corey, E. J.; Eckrich, T. M. *Tetrahedron Lett.* **1983**, *24*, 3163, 3165. (d) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 212 and references cited therein.

Cyclopentanones from Nucleophilic Addition/Carbonylation to (η^4-Diene)$Fe(CO)_3$ Complexes

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Received September 20, 1983

Summary: The addition of carbon nucleophiles to (1,3-diene)iron tricarbonyl complexes produces (homoallyl)$Fe(CO)_3$ anionic complexes; as reported earlier, CO is incorporated at 1.5 atm to give acyliron anionic complexes. With most open-chain 1,3-diene ligands, further cyclization occurs, producing cyclopentanone derivatives with the anionic substituent in the 3-position. The yields are good if the nucleophiles are sufficiently reactive, while the primary limitation is the resistance to ring closure with multiply substituted dienes. With 2-substituted 1,3-dienes, the cyclopentanone product is formed with a specific cis relationship of the substitutents at C-3 and C-4. Through deuterium labeling studies, a mechanism involving β-hydride elimination/readdition is demonstrated as the final stage of the cyclopentanone formation.

The addition of a reactive carbon nucleophile to an (η_4-1,3-diene)$Fe(CO)_3$ complex (e.g., **1**)[2] produces an intermediate that has the expected chemical properties of the homoallyl complex **2**.[3] For example, with (η^4-1,3-cyclohexadiene)$Fe(CO)_3$, addition of $LiC(CH_3)_2CN$ in the presence of CO gives a new intermediate, with the properties of an acyliron tricarbonyl anion, such as **3**.[5] However, for most open-chain 1,3-dienes, the process does not stop at **3** but leads to cyclopentanones with the anion unit in the C-3 position (after protonation, e.g., **4**). Herein, we

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(1) (a) NIH Graduate Trainee, 1980–1981; EXXON Fellow, 1982–1983. (b) Based in part on the Junior Paper of J.K.L.

(2) For a study of the scope of anion addition, see: Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363–372.

(3) We are aware of no previous examples of (η^3-but-3-en-1-yl)$Fe(CO)_3$ anion complexes such as **2**, although close parallels with the $RFe(CO)_3L$ anionic complexes can be expected.[4]

(4) Complex **2** is structurally related to the first intermediate in Collman's reaction, the organoiron tetracarbonyl anion. For a discussion, see: Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342–347.

(5) Semmelhack, M. F.; Herndon, J. W.; Springer, J. *J. Am. Chem. Soc.* **1983**, *105*, 2497–2499.

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