correlation; however, there has not been any indication so far that these are of significant importance for χ or σ.

We have not cared too much about comparison with previous theoretical values. For the molecules of this study, except the smaller ones, previous ab initio calculations hardly exist. One may mention that our calculations are probably the first to give the right order of the proton shifts in propene (cf. ref 11).

Forthcoming applications of the present method will be devoted to (a) a study of the effect of hydrogen bonding on χ and σ, (b) accurate calculations on some small moleucles such as CO, CO_2, N_2, etc.[44] (c) carbonium ions, (d) chemical shifts of fluorine, and (e) chemical shifts of phosphorus.

Acknowledgment. The computations have been carried out at the INTERDATA (Perkin-Elmer) 8-32 minicomputer sponsored by the Deutsche Forschungsgemeinschaft.

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(44) M. Schindler and W. Kutzelnigg, *Mol. Phys.*, in press.

Communications to the Editor

Conversion of Alkyl Acetates to (Siloxymethylene)alkanes by $Co_2(CO)_8$-Catalyzed Reaction with a Hydrosilane and Carbon Monoxide

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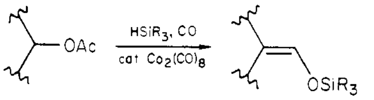
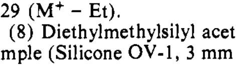
In the study of the new $Co_2(CO)_8$-catalyzed reaction of aldehydes[1a,b] and cyclic ethers[1b,c] with hydrosilanes and carbon monoxide, we found a novel method of introducing various functional groups such as formyl, (trialkylsiloxy)methylene, and 1,2-bis(trialkylsiloxy)vinyl. It was suggested that tetracarbonyl(trialkylsilyl)cobalt [$R_3SiCo(CO)_4$ (**1**)], which was formed in situ by the reaction of $Co_2(CO)_8$ with hydrosilanes,[2] played a key role in these catalytic reactions of oxygenated compounds.[3] The high affinity of the silicon in **1** for an oxygen atom would be the driving force for the cleavage of the carbon–oxygen bond in the oxygenated compounds to give intermediates having a carbon–cobalt bond. This line of thought has provided a new and promising methodology for the formation of carbon–transition metal bonds.[3,4] Since it seemed plausible that the reaction of an alkyl acetate with **1** might give a tetracarbonylalkylcobalt, (vide infra, **2** → **22** → **23** in eq 4), it was anticipated that the catalytic reaction of an alkyl acetate with a hydrosilane and carbon monoxide in the presence of $Co_2(CO)_8$ (a precursor of **1**) might result in catalytic incorporation of carbon monoxide into the carbon atom bearing the acetoxy group. This is the case. In this paper, we describe the unprecedented transformation of alkyl acetates into [(trialkylsiloxy)methylene]alkanes (eq 1).[5] This synthetically useful reaction is also applicable to lactones.

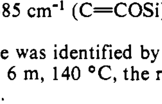


(1)

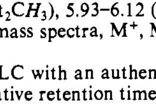
The representative results are given in Table I. A typical experimental procedure is illustrated below for the reaction of 2-adamantyl acetate (**4**, entry 6 in Table I). In a 100-mL stainless steel autoclave were placed 10 mmol of **4**, 30 mmol of $HSiEt_2Me$, 0.4 mmol of $Co_2(CO)_8$, and 20 mL of benzene.[6] The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring in an oil bath at 200 °C for 6 h. Analysis of the reaction mixture by GLC showed it to contain 2-[(diethylmethylsiloxy)methylene]adamantane (**12**) in 95% yield. Distillation gave pure enol silyl ether **12**, bp 103–104 °C (0.25 mmHg), in 90% yield.[7] Various cyclic and acyclic alkyl acetates (entries 1–7) underwent the incorporation of carbon monoxide to give (trialkylsiloxy)methylenated compounds **7**–**13** (enol silyl ethers). In all cases diethylmethylsilyl acetate was obtained as a byproduct.[8] Trimethylsilane ($HSiMe_3$) and triethylsilane ($HSiEt_3$) can also be used in place of $HSiEt_2Me$[9] and gave comparable product yields (entry 2). Since enol silyl ethers are known as extremely useful synthetic intermediates,[10] all the products obtained in the present reaction are expected to be amenable to further synthetic elaboration. For example, treatment of **11** and **12** with KF in CH_3OH at 25 °C gave quantitatively aldehydes **19** and **20**, respectively.[11] The overall transformation of **3** and



19



20



21

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[1] (a) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393. (b) Seki, Y.; Murai, S.; Sonoda, N. *Ibid.* **1978**, *17*, 119. (c) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Ibid.* **1977**, *16*, 789.

[2] Chalk, A. J.; Harrod, J. F. *J. Am. Chem Soc.* **1967**, *89*, 1640. Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986.

[3] Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

[4] Recently, this methodology has also been shown to be effective in the stoichiometric reactions of $Me_3SiMn(CO)_5$ by Gladysz. Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. Maris, M.; Gladysz, J. A. *Tetrahedron Lett.* **1982**, *23*, 631 and references cited therein.

[5] A portion of this study has been presented at the 26th Symposium on Organometallic Chemistry, Kyoto, Japan, Oct 1979, abstr 151, and also described briefly in our first state of the art report.[3]

[6] Toluene can also be used as a solvent.

[7] All new compounds were characterized by IR, NMR, and mass spectral data and elemental analyses. These data are given in the supplementary material. Characteristic spectral data include the following: ^1H NMR (CCl_4) δ 0.07–0.12 (s, $C{=}COSiEt_2CH_3$), 0.20–0.21 ($COOSiEt_2CH_3$), 5.93–6.12 (m, $C{=}CHOSi$); IR (neat) 1675–1685 cm^{-1} ($C{=}COSi$); mass spectra, M^+, $M^+ - 29$ ($M^+ -$ Et).

[8] Diethylmethylsilyl acetate was identified by GLC with an authentic sample (Silicone OV-1, 3 mm × 6 m, 140 °C, the relative retention time to a standard, n-$C_{14}H_{30}$, was 0.18).

[9] $HSiEt_2Me$ has an appropriate boiling point for handling with syringe (bp 77–78 °C). $HSiMe_3$ (bp 6.7 °C), $HSiEt_2Me$, and $HSiEt_3$ (bp 107–108 °C) are all commercially available (e.g., Petrarch Systems Co., PA).

[10] Rasmussen, J. K. *Synthesis* **1977**, 91. Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981; pp 198–287. Fleming, I. In "Comprehensive Organic Chemistry"; Barton, D., Ollis, D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, Part 13, pp 584–592. Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 96.

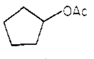
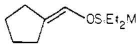
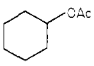
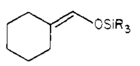
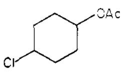
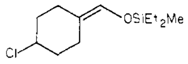
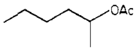
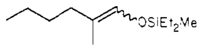
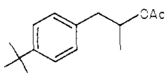
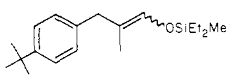
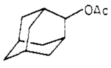
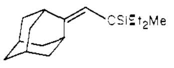
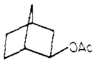
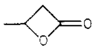
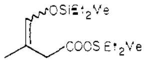
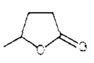
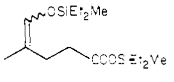
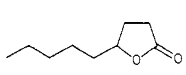
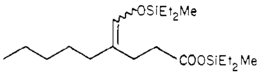
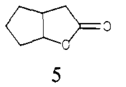
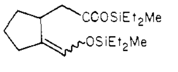
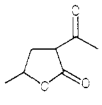
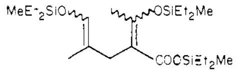
[11] Aldehyde **19** is important not only as a perfume component[12] but also as an intermediate for pharmacological active amines,[13] and **20** has been reported to be somewhat difficult to prepare.[14]

[12] Aldehyde **19** has been known as Lirial and used in place of cyclamenaldehyde: Heilen, G.; Nissen, A.; Koernig, W.; Horner, M.; Fliege, W.; Boettger, G. Ger. Offen. 2832699; *Chem. Abstr.* **1980**, *93*, 26108. Sokolskii, D. V.; Pak, A. M.; Konuspaev, S. R.; Ginzburg, M. A.; Turganbaeva, S. M.; Pogorelskii, A. P. *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* **1980**, 26; *Chem. Abstr.* **1981**, *94*, 4126. Virgilio, J. A.; Heilweil, E. *Org. Prep. Proc. Int.* **1982**, *14*, 9.

[13] For recent synthesis via **19**, see: Goetz, N.; Hupfer, L. Ger. Offen. 2830999; *Chem. Abstr.* **1980**, *93*, 95288. Bohnen, K.; Pfiffner, A. Eur. Pat. Appl. 5541; *Chem. Abstr.* **1980**, *93*, 8027. Pommer, E. H.; Himmele, W. Ger. Offen. 2921131; *Chem. Abstr.* **1981**, *94*, 116004. Himmele, W.; Heberle, W.; Kohlmann, F. W.; Wesenberg, W. Ger. Offen. 2921221; *Chem. Abstr.* **1981**, *95*, 7302.

0002-7863/83/1505-1370$01.50/0

Table I. $Co_2(CO)_8$-Catalyzed Reactions of Alkyl Acetates and Lactones with $HSiR_3$ and CO^a

entry	substrate	product	yield,^{b} %
1	 2	 7	75
2		 8	82^c 75 72^d
3		 9	60
4		 10	91^g
5	 3	 11	63^{e,h}
6	 4	 12	95 (90)
7		 13	68^i
8		 14	88 (73)^{f,j}
9		 15	87^{f,k}
10		 16	81 (73)^{f,i}
11	 5	 17	70^{f,l}
12	 6	 18	92 (84)^{e,f,i}

[a] Reaction conditions: an alkyl acetate or a lactone (10 mmol), $HSiEt_2Me$ (30 mmol), CO (50 atm at 25 °C), $Co_2(CO)_8$ (0.4 mmol), C_6H_6 (20 mL), 200 °C, 6 h, unless otherwise noted. Characterization of the products are given in the supplementary material. [b] GLC yields. Isolated yields are in parentheses. [c] $HSiMe_3$ (30 mmol) was used as a hydrosilane. [d] $HSiEt_3$ (30 mmol) was used as a hydrosilane. [e] $HSiEt_2Me$ (50 mmol) was used. [f] Pyridine (2 mmol) was added, and the reactions were run at 140 °C. [g] A mixture of stereoisomers (43:57). [h] A mixture of stereoisomers (40:60). [i] A mixture of stereoisomers, the ratio of which was not determined. [j] A mixture of stereoisomers (48:52). [k] A mixture of stereoisomers (37:63). [l] A mixture of stereoisomers (34:66).

4 to aldehydes (**19** and **20**) is the replacement of an acetoxy group with a formyl group (via the siloxymethylene compound). In this context, it may be worth mentioning that various attempts to replace a ketonic oxygen with a (trialkylsiloxy)methylene group using Wittig-type reagents have been made recently in vain.[15]

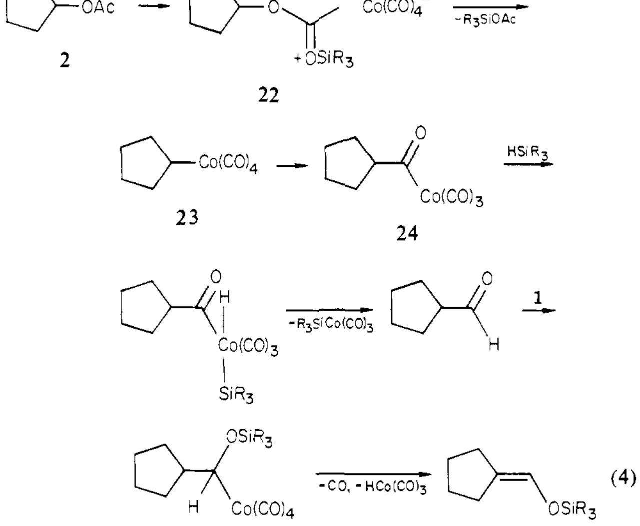
The siloxymethylenation of β- and γ-lactones (entries 8–12) proceeded similarly to that of alkyl acetates. In these cases, the silyl ester part remained in the products. A new method of carbafunctionalization of a cyclopentane ring is illustrated by the reaction of **5** (entry 11). Compound **18** contains a masked aldehyde unit and a masked β-keto acid unit. Indeed, hydrolysis of **18** (without purification, 1 N HCl/THF, 25 °C, 30 min) proceeded with decarboxylation to give a 1,5-keto aldehyde **21** in 60% overall yield from **6**.

We suggest the mechanism of the present catalytic siloxymethylenation as depicted in Scheme I. The key catalyst species would be $R_3SiCo(CO)_4$ (**1**). High affinity of the silicon center in **1** for an oxygen atom may bring about the activation of the acetoxy group into a good leaving group (**2** → **22**) and force a carbon–cobalt bond formation to give an alkylcobalt complex (**22** → **23**). The subsequent steps would be similar to those proposed previously.[16,17] Regeneration of **1** from $HCo(CO)_3$ and CO to close the catalytic cycle may be performed as in eq 3.

Scheme I

$$\underset{\textstyle\mathbf{1}}{}Co_2(CO)_8 + HSiR_3 \longrightarrow \underset{\textstyle\mathbf{1}}{R_3SiCo(CO)_4} + HCo(CO)_4 \quad (2)$$

$$HCo(CO)_4 + HSiR_3 \longrightarrow \mathbf{1} + H_2 \quad (3)$$



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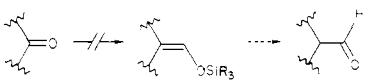
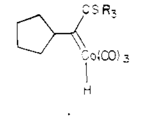
[14] Scharp, J.; Wynberg, H.; Strating, J. *Recl. Trav. Chim.* **1970**, *89*, 18. Farcasiu, D. *Synthesis* **1972**, 615. Bernaert, E.; Danneels, D.; Anteunis, M.; Verhegge, G. *Tetrahedron* **1973**, *29*, 4127. Reichardt, C.; Wurthwein, E.-U. *Synthesis* **1973**, 604. See also for a recent synthesis: Magnus, P.; Roy, G. *Organometallics* **1982**, *1*, 553.

[15] The attempted reactions and the reagents used were as follows:



(a) $(EtO)_2P(O)CH_2OSiMe_2$-*t*-Bu/LiN(*i*-Pr)$_2$: Kluge, A. F.; Cloudsdale, I. S. *J. Org. Chem.* **1979**, *44*, 4847. (b) $(EtO)_2P(O)CH(Ph)OSiMe_3$/LiN(*i*-Pr)$_2$: Koenigkramer, R. E.; Zimmer, H. *Tetrahedron Lett.* **1980**, *21*, 1017. (c) $PPh_3^+CH_2OSiMe_3I^-$/base: Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5866. For a review of the conversion of ketones to aldehydes via enol alkyl ethers, see: Martin, S. F. *Synthesis* **1979**, 633.

[16] An alternative mechanism involving i in place of the aldehyde intermediate may exist.



i

[17] It has been shown that $Co_2(CO)_8$-catalyzed reactions of cycloalkenes with $HSiR_3$ and carbon monoxide gave similar products ((siloxymethylene)cycloalkanes) via alkylcobalt complexes. The mechanism of the reaction of olefins has been fully discussed.[3]

The studies on the scope and limitation of the catalytic reaction of alkyl esters[18] as well as the further application of the new methodology for the formation of a carbon–transition metal bond are in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research 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. 2, 933-05-1; **3**, 84454-49-9; **4**, 19066-22-9; **5**, 5745-61-9; **6**, 3620-18-6; **7**, 61490-90-2; **8** (R = Me), 53282-55-6; **8** (R = Et), 7030-75-3; **9**, 84454-50-2; **10** (isomer 1), 65167-91-1; **10** (isomer 2), 65138-39-8; **11** (isomer 1), 84472-74-2; **11** (isomer 2), 84472-75-3; **12**, 84454-51-3; **13** (isomer 1), 84454-52-4; **13** (isomer 2), 84454-53-5; **14** (isomer 1), 84454-54-6; **14** (isomer 2), 84454-55-7; **15** (isomer 1), 84454-56-8; **15** (isomer 2), 84454-57-9; **16** (isomer 1), 84472-76-4; **16** (isomer 2), 84498-61-3; **17** (isomer 1), 84454-58-0; **17** (isomer 2), 84454-59-1; **18**, 84454-60-4; $HSiMe_3$, 993-07-7; $HSiEt_3$, 617-86-7; $HSiEt_2Me$, 760-32-7; $Co_2(CO)_8$, 10210-68-1; CO, 630-08-0; cyclohexanol acetate, 622-45-7; 4-chlorocyclohexanol acetate, 84454-61-5; 2-hexanol acetate, 5953-49-1; 2-norbornanol acetate, 34640-76-1; 4-methyl-2-oxetanone, 3068-88-0; 5-methyldihydro-2-furanone, 108-29-2; 5-pentyldihydro-2-furanone, 104-61-0.

Supplementary Material Available: GLC data and characterization of **7–18** (12 pages). Ordering information is given on any current masthead page.

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[18] The present catalytic reaction so far is limited to secondary alkyl esters. Primary alkyl esters gave a mixture of several products. In the case of tertiary alkyl acetates, no incorporation of carbon monoxide was observed.

Benz[*b*]homoheptalene. Consequences of Ring Fusion between Benzene and a Bridged [12]Annulene

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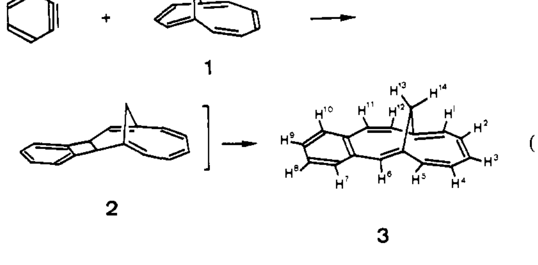
We have recently discovered[1] that addition of an electron-deficient acetylene to homoazulene (**1**)[2] results in ring expansion of **1** to generate the homoheptalene ring system.[3] This novel route to structurally interesting [12]annulene derivatives has now been extended to a remarkably simple synthesis of benz[*b*]homoheptalene (**3**)[3] as illustrated in eq 1. Thus benzyne (generated in situ from excess benzenediazonium-2-carboxylate at 80 °C in 1,2-dichloroethane[4]) reacts with homoazulene to produce the stable orange hydrocarbon **3** in 51% yield, presumably via an initial [2 + 2] cycloadduct (**2**). The previously unknown title compound (**3**) incorporates both a benzene ring ($4N + 2$ π electrons) and a [$4N$]annulene derivative into a single bicyclic π system, and we report here several consequences of that unusual union. Table I summarizes some of the properties of benz[*b*]homoheptalene.

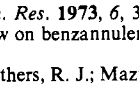


(1)

Table I. Some Properties of Benz[*b*]homoheptalene (**3**)

mp	53–54 °C
^{1}H NMR	(400 MHz, CD_3CN) perimeter δ(1) 5.90, δ(2) 5.73, δ(3) 5.66, δ(4) 5.61, δ(5) 6.22, δ(6) 6.47, δ(11) 6.16, δ(12) 6.06; benzo ring δ(7) 6.96, δ(8) 7.14, δ(9) 7.12, δ(10) 6.78; bridge δ(13) 4.52, δ(14) 4.43.
^{13}C NMR	($CDCl_3$) δ 145.9, 143.3, 138.7, 137.5, 136.3, 133.3, 132.9, 132.7, 130.9, 130.6, 130.4, 129.9, 128.5, 127.4 (2 C), 126.9, 31.2.
IR (KBr)	2995, 1475, 1445, 842 (s), 812, 775, 763, 727 (s), 707, 678, 640 (s) cm^{-1}
UV(CH_3CN)	λ_{max} 226 (sh), 274, 379 nm

The parent homoheptalene molecule **4** was first prepared in an elegant ten-step synthesis by Vogel et al. nearly a decade ago.[5] The π system of this bridged [12]annulene, unlike that in benzene, was found to deviate significantly from planarity[6] and to be characterized by alternating short and long bonds.[5,6] Nevertheless, ^{1}H NMR spectroscopy reveals that hydrocarbon **4** shares with other [$4N$]annulenes the ability to support an induced *paramagnetic* ring current:[7] the methylene bridge protons of **4** resonate at abnormally low field (δ 6.1), whereas the protons attached to the perimeter resonate at relatively high field (δ 5.1–5.8).[5] Ring puckering and bond alternation undoubtedly reduce the ring current to a level below that in a pure [12]annulene,[8] as predicted by theory,[7] but some cyclic conjugation still remains. The same structural features likewise reduce the instability ("antiaromaticity") normally associated with [$4N$]annulenes[9] and thereby endow homoheptalenes with an ideal balance between paratropicity and isolability.



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Fusion of a benzene ring onto one bond of a [$4N + 2$]annulene causes bond-length alternation, weakens the ring current, and diminishes the resonance energy in the annulene ring.[10–13] The consequences of uniting a benzene ring with a [$4N$]annulene, however, have been difficult to assess experimentally, owing to the lack of stable [$4N$]annulene/benzannulene pairs.[10,14] The

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[2] Scott, L. T.; Brunsvold, W. R.; Kirms, M. A.; Erden, I. *J. Am. Chem. Soc.* **1981**, *103*, 5216–5220 and references cited therein. Homoazulene (**1**) may also be named 1,5-methano[10]annulene or bicyclo[5.3.1]undeca-1,3,5,7,9-pentaene.

[3] Homoheptalene (**4**) may also be named 1,7-methano[12]annulene or bicyclo[5.5.1]trideca-1,3,5,7,9,11-hexaene. Benz[*b*]homoheptalene (**3**) may also be named 3,4-benzo-1,7-methano[12]annulene or 3,4-benzobicyclo-[5.5.1]trideca-1,3,5,7,9,11-hexaene.

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