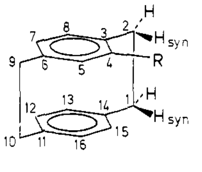
Table I. Deuterium Isotope Effects on ^{13}C Chemical Shifts in Deuterated Methylcyclophanes[a-c]

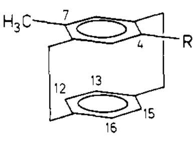
carbon	1b	1c	1d	2c	3c
C-1	n.m.[d]	+10	+13	n.m.	+10
C-2	n.m.	−6	−10	n.m.	−6
C-3	+12	+17	+26	+16	+13
C-4	−26	−52	−80	−52	−43
C-5				+6	+13
C-6		br[e]	−7	−3	
C-7			+10	+5	+12
C-8		−11	−15	−9	
C-9	n.m.	br	+4	n.m.	
C-13				[f]	+30
C-15	+11	+23	+35	+22	

[a] Values given in ppb (1 ppb = 0.001 ppm); positive sign denotes deshielding in the deuterated compound. [b] Measured at 100.6 MHz, solvent $CDCl_3$, relative to the chemical shifts of 1a, **2**a, and 3**a**, respectively. [c] Digital resolution 1.2 ppb. A conservative error estimate for the isotope shifts is ±3 ppb. [d] Not measured. [e] Only line broadening observed; chemical shift difference not resolved. [f] $|\delta_{13} - \delta_{16}| = 4$ ppb. The resonances for C-13 and C-16 in **2**c could not be assigned individually.

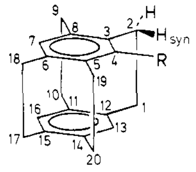
which were obtained from mixtures of the deuterium and protium analogues.



1a - d



2a,c



3a,c

(R= CH_3(a); CH_2D(b); CHD_2(c); CD_3(d))

The isotope shifts over two and four bonds at the carbons ipso and meta to the methyl substituents are found to be shielding.[10] Ortho and para carbons, however, are deshielded,[11] and we interpret this by decreased electron donation of the benzylic C–D relative to the C–H bonds, i.e., we are dealing with the same "hyperconjugative" effect (though smaller by two orders of magnitude) as advanced by Servis[3h] to explain the shifts in his static classical β-deuteriocarbocations. Indeed, we suggest the same mechanism also to be responsible for a number of previously reported deshielding deuterium isotope effects, viz., on the carbonyl carbon in acetone-d_6[3a] and in 3,3-dideuteriocamphor derivatives,[3b] on C-β in N-deuterioenamines,[3c] on C-4 in O-deuteriophenols,[3g] and on C-1 in 3-deuteriocyclobutene.[3i] In all these cases, the X–D bond (X = C, N, O) is either adjacent to an electron-deficient carbon atom or to an unsaturated C=C fragment.

The most remarkable finding in the cyclophane systems are the deshielding isotope effects upon the carbons pseudogeminal to the deuterated methyl groups, formally seven bonds apart. Clearly, these are through-space effects, due to the close proximity of the interacting nuclei. This is the first occurrence of isotope effects on ^{13}C chemical shifts which are not transmitted through chemical bonds[12] and which are not of conformational origin. Conformational factors can be excluded for two reasons. Firstly, the effects are of similar magnitude both in the relatively flexible molecules **1c** and **2c** and in the very rigid framework of **3c**. Secondly, as pointed out by Andrews et al.,[5] lifting of conformational degeneracy by isotopic substitution must leave unchanged the average shift of nuclei which can be interchanged by symmetry operations on the average structure. Thus, if the assumption were correct that the deshielding of C-15 in **2c** is caused by a change of the average distance between C-4 and C-15, then increased shielding of the same magnitude would be expected for C-12, which is not observed. Further, yet much smaller, through-space isotope effects are found on C-1 and C-2 of the ethano bridges. The effect on C-2 is shielding which may indicate that the relative orientation of the carbon affected and the deuterium-containing group governs both sign and magnitude of the through-space isotope effect.

We also observed deuterium isotope effects on the chemical shifts of some protons close in space to the deuterium nuclei. In **1d**, H-2_{syn} and H-15 are shielded relative to **1a** by 4.0 ± 0.1 and 6.0 ± 0.2 ppb, respectively. The signals for H-1_{syn} are only broadened so that an effect of ca. 1 ppb can be estimated. In **3c**, isotope effects are discernible on the chemical shifts of H-2_{syn} (−4.7 ± 0.1 ppb) and H-13 (−5.8 ± 0.3 ppb). Further studies of the dependence of deuterium isotope effects on ^{13}C and ^{1}H chemical shifts are required to define their dependence on geometrical factors.

Acknowledgment. S.E. thanks the DAAD for a dissertation scholarship. Support of part of this work by the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. 1a, 24262-07-5; **1b**, 80028-60-0; **1c**, 80028-61-1; **1d**, 80028-62-2; **2a**, 35117-18-1; **2c**, 80028-63-3; **3a**, 80028-64-4; **3c**, 80028-65-5.

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[10] For convenience, this effect of the deuterons has occasionally been termed "inductive"[3h] because hydrogen and deuterium *act* as if their electronegativities were different. One referee disagrees with the use of this term and, to avoid confusion, stresses that all isotope effects arise because the different isotope masses cause differences in the amplitudes of zero-point motions on the potential-energy surface of the isotopomers.

[11] Similarly, successive replacement by deuterium of the benzylic protons in toluene causes decreased shielding of the para carbon (+13 ppb for $PhCD_3$); unpublished results from our laboratory.

[12] Anet[4] reported steric deuterium isotope effects on ^{1}H chemical shifts in two systems in which the distances between the interacting protons and deuterons were estimated to be 1.6 and 2.0 Å, respectively. No influence of deuterium on the ^{13}C shifts could be observed in these cases. Molecular models indicate that the corresponding internuclear distances in our systems are larger than in Anet's.

Crystal Structure of Tetrakis(trimethylsilyl)ethylene at −70 °C[1]

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The molecular structures of overcrowded olefins are of interest in order to determine how the molecules relieve their inherent repulsive nonbonded interactions. Widening bond angles, nonplanar distortions of the double bond, and/or carbon atom pyramidalization can be factors determining the most stable conformations of the molecules.[2]

We have recently reported the preparation and some interesting properties of tetrakis(trimethylsilyl)ethylene (**1**).[3,4] Preliminary investigations indicate that the olefin should be twisted from planarity. We now wish to report the molecular structure of **1** which shows several unusual features.

Tetrakis(trimethylsilyl)ethylene was prepared as described before,[3,5] and crystals appropriate for the X-ray diffraction study were grown from hexane. Since **1** sublimes quickly at room temperature under X-ray irradiation, diffraction data were collected at −70 °C by using a specimen coated with thin layers of

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[1] Chemistry of Organosilicon Compounds. 151.

[2] For reviews, see: (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Tidwell, T. T. *Tetrahedron* **1978**, *34*, 1855.

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[5] Low temperature (0 °C) reaction improved the yield of **1** up to 74%.

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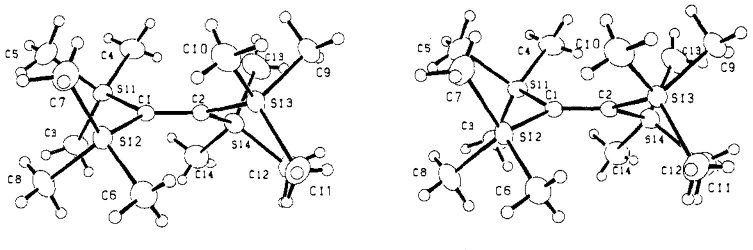

Figure 1. Stereoscopic view of the molecular structure of tetrakis(trimethylsilyl)ethylene at −70 °C.

Table I. Bond Lengths and Bond Angles with Estimated Standard Deviations for Tetrakis(trimethylsilyl)ethylene at −70 °C

Bond Length, Å			
Si(1)–C(1)	1.913 (2)	Si(2)–C(8)	1.880 (3)
Si(2)–C(1)	1.918 (2)	Si(3)–C(9)	1.873 (3)
Si(3)–C(2)	1.918 (2)	Si(3)–C(10)	1.864 (3)
Si(4)–C(2)	1.909 (2)	Si(3)–C(11)	1.874 (3)
Si(1)–C(3)	1.874 (3)	Si(4)–C(12)	1.873 (3)
Si(1)–C(4)	1.863 (3)	Si(4)–C(13)	1.884 (3)
Si(1)–C(5)	1.872 (3)	Si(4)–C(14)	1.855 (3)
Si(2)–C(6)	1.870 (3)	C(1)–C(2)	1.368 (3)
Si(2)–C(7)	1.875 (3)		
Bond Angles, deg			
C(1)–Si(1)–C(3)	116.9 (1)	C(9)–Si(3)–C(10)	102.4 (1)
C(1)–Si(1)–C(4)	113.1 (1)	C(9)–Si(3)–C(11)	107.5 (1)
C(1)–Si(1)–C(5)	106.9 (1)	C(10)–Si(3)–C(11)	109.1 (1)
C(3)–Si(1)–C(4)	110.0 (1)	C(2)–Si(4)–C(12)	107.1 (1)
C(3)–Si(1)–C(5)	107.1 (1)	C(2)–Si(4)–C(13)	116.2 (1)
C(4)–Si(1)–C(5)	101.5 (1)	C(2)–Si(4)–C(14)	113.4 (1)
C(1)–Si(2)–C(6)	112.8 (1)	C(12)–Si(4)–C(13)	108.1 (1)
C(1)–Si(2)–C(7)	116.0 (1)	C(12)–Si(4)–C(14)	101.8 (1)
C(1)–Si(2)–C(8)	107.1 (1)	C(13)–Si(4)–C(14)	109.0 (1)
C(6)–Si(2)–C(7)	110.6 (1)	Si(1)–C(1)–Si(2)	112.0 (1)
C(6)–Si(2)–C(8)	101.6 (1)	Si(3)–C(2)–Si(4)	111.8 (1)
C(7)–Si(2)–C(8)	107.6 (1)	Si(1)–C(1)–C(2)	123.8 (1)
C(2)–Si(3)–C(9)	107.5 (1)	Si(2)–C(1)–C(2)	124.3 (1)
C(2)–Si(3)–C(10)	113.6 (1)	Si(3)–C(2)–C(1)	124.3 (1)
C(2)–Si(3)–C(11)	115.7 (1)	Si(4)–C(2)–C(1)	123.9 (1)

starch and epoxy resin.[6] A total of 4049 independent reflections with $|F_o| > 3\sigma(|F_o|)$ and $2\theta_{\mathrm{MoK}\alpha} < 60°$ was collected on a Rigaku AFC-5 automated diffractometer with graphite-monochromatized Mo radiation by using an attached variable temperature apparatus based on a continuous nitrogen gas flow method. The structure was solved by a direct method (MULTAN). Block-diagonal least-squares refinement including all hydrogen atoms with isotropic temperature factors gave $R = 0.045$ and $R_w = 0.054$. Bond lengths and angles are listed in Table I, and the molecular structure of the crystal at −70 °C, together with the numbering of atoms, is given in Figure 1.

Several interesting facts can be pointed out. The bond length of the central double bond [1.368 (3) Å] is significantly longer than the ordinary values (1.337 ± 0.006 Å).[8] Atoms Si(1), Si(2), C(1), and C(2) and Si(3), Si(4), C(2), and C(1) are strictly coplanar (±0.001 Å). Therefore, no pyramidalization effect to relieve the strain exists. However, the dihedral angle between these two planes corresponds to a twist of the double bond by 29.5°.

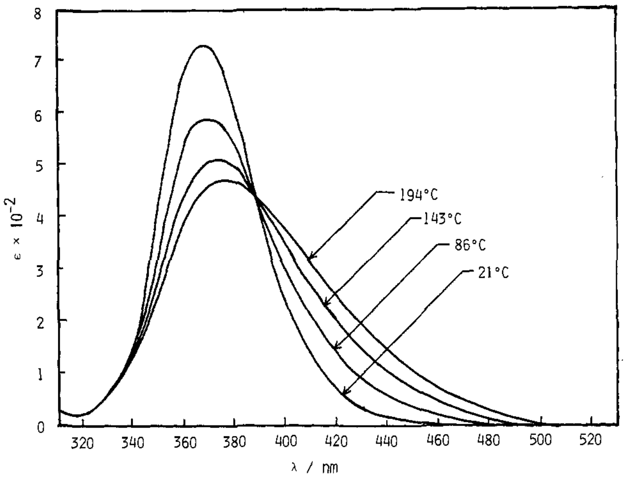

Figure 2. Temperature-dependent electronic spectra of tetrakis(trimethylsilyl)ethylene in decalin in the 320–520-nm region.

Although some cyclic conjugated olefins such as bifluorenylidene[9] and octachloropentafulvalene[10] have larger tortional angles about the olefinic linkages, the value reported here is the largest among acylic olefins. 1,1-Diphenyl-2,2-di-*tert*-butylethylene has a tortional angle of 24°,[11] but the apparently crowded bi[adamantylidene],[12] tetraisopropylethylene,[13] and bi[tricyclo[3.3.1.0^{1,5}]non-9-ylidene][14] are planar.

Another interesting point worth mentioning is the Si–C(sp^2) bond length of **1**. The Si–C(sp^2) bond lengths reported for $H_3SiCH{=}CH_2$ and $PhSiH_3$ are 1.853 (microwave spectra)[15] and 1.843 Å (electron diffraction),[16] respectively. A slightly longer Si–C(sp^2) bond length has been reported for Ph_4Si by X-ray crystallographic analysis (1.872[17] and 1.863 Å[18]). These are comparable to or shorter than $Si–CH_3$ bonds of CH_3SiH_3[19] and $(CH_3)_2SiH_2$[20] (1.867 and 1.871 Å, microwave spectra). Although the mean $Si–CH_3$ bond length of **1** [1.871 (8) Å] is rather normal, the mean Si–C(sp^2) bond length [1.915 (4) Å] of **1** is exceedingly long, obviously due to overcrowding.

The molecular overcrowding, however, is not reflected strongly relative to a widening of bond angles. Thus the mean C═C—Si angle [124.1 (4)°] is not very much enlarged with respect to the olefinic bond angle. The C═C—Si angle of $H_3SiCH{=}CH_2$ determined by microwave spectra is 122°53′.[15]

Interestingly, **1** (yellow at room temperature) shows reversible thermochromism. At −70 °C, **1** is colorless, but it becomes orange

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(6) Crystallographic data: $C_{14}H_{36}Si_4$, M_r 316.78, monoclinic, $P2_1/n$, $z = 4$. Cell constants at −70 °C: $a = 17.841$ (3), $b = 12.432$ (2), $c = 9.598$ (1) Å; $\beta = 92.88$ (1)°; $V = 2126.1$ (5) Å^3. At 20 °C: $a = 17.902$ (3), $b = 12.595$ (2), $c = 9.722$ (2) Å, $\beta = 92.85$ (2)°; $V = 2189.4$ (6) Å^3. D_{calcd} (20 °C) = 0.961 g·cm^{-3} D_{obsd} (flotation in H_2O–MeOH, at 23.5 °C) = 0.961 g·cm^{-3}; μ(Mo Kα) = 2.63 cm^{-1}. A platelike crystal with dimensions 0.45 × 0.35 × 0.30 mm was used for the intensity measurement. Weighting scheme employed was $w = [\sigma_{\mathrm{count}}^2 + (0.015|F_o|)^2]^{-1}$. No absorption correction was applied. All the calculations were carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with a universal crystallographic computation program system, UNICS III.[7]

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yellow at ca. 200 °C. The electronic spectra of **1** in a 320–520-nm range is shown in Figure 2. Clearly an isosbestic point is observable at 389 nm. The mechanism of this spectral change is not clear at this moment but indicates that the double bond of **1** must be more twisted at higher temperatures than in the solid state at −70 °C.

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Registry No. 1, 74465-53-5.

Supplementary Material Available: A stereoview of packing of molecules in crystal, tables of atomic parameters, anisotropic temperature factors, mean-square displacement tensor of atoms, and structure factors (27 pages). Ordering information is given on any current masthead page.

Reactions of Carbon Monoxide and Alkyl Isocyanides with Rhodium Octaethylporphyrin Species: Metalloformyl and Formimidoyl Complexes

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Metalloformyl species are frequently invoked as a key intermediate in the metal-catalyzed reduction of CO by H_2.[1] We have recently observed that RhOEP(H) reacts with CO to produce RhOEP(CHO) (I), which is the first reported formyl complex prepared by the reaction of a metal hydride complex with carbon monoxide.[2] We now wish to report on the alternate preparation of I by using H_2O as a source of hydrogen, the molecular structure of I, and the formation of a metalloformimidoyl complex from the reaction of RhOEP(H) with an alkyl isocyanide.

The metalloformyl complex RhOEP(CHO) (I) can be alternatively prepared by reactions 1, 2, or 3.[3] Substitution of D_2 and

$$\mathrm{RhOEP(H)} + \mathrm{CO} \rightleftarrows \mathrm{RhOEP(CHO)} \tag{1}$$

$$(\mathrm{RhOEP})_2 + \mathrm{H_2} + 2\mathrm{CO} \rightleftarrows 2\mathrm{RhOEP(CHO)} \tag{2}$$

$$(\mathrm{RhOEP})_2 + \mathrm{H_2O} + 3\mathrm{CO} \rightarrow 2\mathrm{RhOEP(CHO)} + \mathrm{CO_2} \tag{3}$$

D_2O, respectively, in reactions 2 and 3 produces the deuterated formyl RhOEP(CDO) and identifies D_2 and D_2O as alternate sources of the formyl hydrogen. Reaction 2 undoubtedly occurs through formation of RhOEP(H) by reaction 4. Reaction 3 is

$$(\mathrm{RhOEP})_2 + \mathrm{H_2} \xrightleftharpoons{\mathrm{C_6H_6}} 2\mathrm{RhOEP(H)} \tag{4}$$

thought to occur by formation of RhOEP(H) in the water gas shift (WGS)[4] reaction (reactions 5–7). Some of the intermediate

$$(\mathrm{RhOEP})_2 + \mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{RhOEP(CO_2H)} + \mathrm{RhOEP(H)} \tag{5}$$

$$\mathrm{RhOEP(CO_2H)} \rightleftarrows \mathrm{RhOEP(H)} + \mathrm{CO_2} \tag{6}$$

$$2\mathrm{RhOEP(H)} \rightleftarrows (\mathrm{RhOEP})_2 + \mathrm{H_2} \tag{7}$$

RhOEP(H) formed in the WGS reaction is utilized by reaction 1 in producing the formyl complex I. This system is capable of catalyzing the WGS reaction even though most of the active catalyst, $(RhOEP)_2$, is converted to compound I, because reactions 1 and 2 are reversible. A transient species observed in the ^1H NMR spectrum for reaction 3 is tentatively assigned to the intermediate metallocarboxylic acid complex, $RhOEP(CO_2H)$.

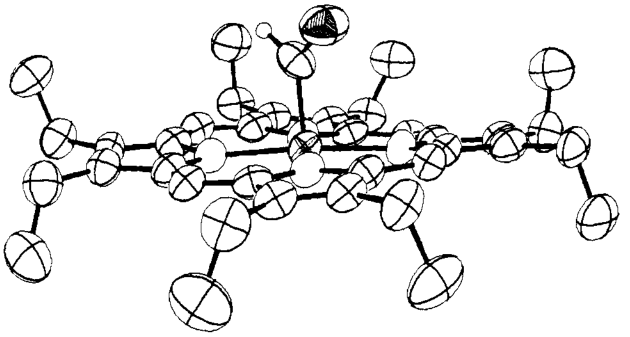

Figure 1. ORTEP representation for RhOEP(CHO). Bond lengths and angles for the RhCHO unit are as follows: Rh–C, 1.896 (6) Å; C–O, 1.175 (5) Å; C–H, 1.09 (1) Å; Rh–C–O, 129.6 (5)°; Rh–C–H, 129.9 (4)°.

RhOEP(CHO) (I) is characterized in beznene solution by ^1H and ^{13}C NMR spectroscopy (δ_{CHO} 2.90, $J_{Rh-H} = 1.75$ Hz, $J_{^{13}C-H} = 200$ Hz; $\delta_{^{13}CHO} = 194.4$). The formyl complex I has been crystallized and fully characterized by single-crystal X-ray structure determination.[5] An ORTEP representation of the molecule along with bond distances and angles for the Rh(CHO) unit is given in Figure 1.

Isocyanides (R—N≡C:) have similar reactivity patterns but generally enhanced reactivity when compared to carbon monoxide and are used to model and define the range of potential carbon monoxide reactivity. Metallohydrides of Ru,[6] Os,[7] Pt,[8] and Zr[9] are observed to react with isocyanides to produce metalloformimidoyl (M—CH=NR) species, while the corresponding reactions with carbon monoxide failed to yield observable metalloformyl complexes. We find that RhOEP(H) reacts with *n*-butyl isocyanide (BuNC) to produce the metalloformimidoyl RhOEP(—

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(3) Reactions 1, 2, and 3 are carried out in sealed NMR tubes by using C_6D_6 as the solvent at ambient laboratory temperatures. Reaction 1 is virtually quantitative (>95%) by NMR measurements when the pressure of carbon monoxide is greater than 300 torr. This reaction is complicated only by the possibility of converting RhOEP(H) into $(RhOEP)_2$ and H_2. Reaction 2 is essentially the same as 1 except that the pressure of H_2 gas (100 mm) assures complete conversion to the formyl. Reaction 3 when carried out with a fivefold excess of H_2O and $P_{CO} \sim 300$ torr again produces compound I in near quantitative yield by NMR observation. Attempts to isolate I by removal of the solvent under vacuum always results in contamination by RhOEP(H) and $(RhOEP)_2$ due to reversibility of reactions 1 and 2. Evaporation of a benzene solution of I, under a stream of CO, results in crystals of RhOEP(CHO) used in the structure determination.

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(5) RhOEP(CHO) crystallizes as a benzene solvate. The crystals are triclinic ($P\bar{1}$ space group) with lattice parameters $a = 10.564$ (4) Å, $b = 12.257$ (4) Å, $c = 15.266$ (7) Å, $\alpha = 77.38$ (3)°, $\beta = 94.31$ (4)°, and $\gamma = 100.30$ (3)°. The structure was refined by using 3843 nonzero reflections for which $I > 3\sigma(I)$ out of a total of 6609 independent reflections. Corrections were made for absorption with an absorption coefficient of 4.799. The structure was refined to an R index of 0.052 by using anisotropic temperature factors for all nonhydrogen atoms and isotropic factors for all hydrogens. All hydrogens were located by difference Fourier methods.

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