tris(*o*-methylphenyl)methanol, 6922-86-7; bis(*o*-methylphenyl)methanol, 2845-91-2; diphenylmethanol, 91-01-0; bis(*p*-methylphenyl)methanol, 885-77-8; 1,1-diphenyl-1-ethanol, 599-67-7; α,α-diphenylcyclopropanemethanol, 5785-66-0; α,α-dicyclopropylcyclopropanemethanol, 23719-88-2; 9-methyl-9-fluorenol, 6311-22-4; bis(*p*-chlorophenyl)methanol, 90-97-1; bis(*p*-fluorophenyl)methanol, 365-24-2; tricyclo[3.3.1.1^{3,7}]dec-1-ylium, 19740-18-2; bicyclo[2.2.1]hept-2-ylium, 24321-81-1; 1,1-dimethylethylium, 14804-25-2; 1-methylcyclopentylium, 17106-22-8; 1-methylcyclohexylium, 26378-05-2; 1,1-dimethylpropylium, 17603-15-5; 1-ethyl-1-methylpropylium, 17603-16-6; 2-methylbicyclo[2.2.1]hept-2-ylium, 3197-78-2; 1-methyl-1-phenylethylium, 16804-70-9; 1-methyl-1-(3-methylphenyl)ethylium, 20605-65-6; 1-methyl-1-(4-methylphenyl)ethylium, 20605-66-7; 1-(3-bromophenyl)-1-methylethylium, 77826-66-5; 1-(4-bromophenyl)-1-methylethylium, 67595-62-4; 1-(4-chlorophenyl)-1-methylethylium, 41912-29-2; 1-methyl-1-[3-(trifluoromethyl)phenyl]ethylium, 77826-67-6; 1-[3,5-bis(trifluoromethyl)phenyl]-1-methylethylium, 67595-63-5; 1-(2,3-dihydrobenzofuran-5-yl)-1-methylethylium, 82955-09-7; triphenylmethylium, 13948-08-8; (4-methylphenyl)diphenylmethylium, 13947-74-5; bis(4-methylphenyl)phenylmethylium, 34073-85-3; tris(4-methylphenyl)methylium, 14039-17-9; tris(2-methylphenyl)methylium, 84988-00-1; bis(2-methylphenyl)methylium, 84988-01-2; diphenylmethylium, 709-82-0; bis(4-methylphenyl)methylium, 58493-75-7; 1,1-diphenylethylium, 16805-85-9; cyclopropyldiphenylmethylium, 38252-94-7; tricyclopropylmethylium, 25940-78-7; 9-methylfluoren-9-ylium, 20685-25-0; bis(4-chlorophenyl)methylium, 15876-05-8; bis(4-fluorophenyl)methylium, 39769-55-6.

Communications to the Editor

Molecular Structure of Silicon Dichloride and Silicon Dibromide from Electron Diffraction Combined with Mass Spectrometry

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Direct information on the structure and reactivity of carbene analogues and their derivatives is of great importance.[1,2] Experimental determination of the molecular structure of the carbene analogues is usually hindered, however, by their high reactivity and polymerization at ordinary temperatures. The recently developed combined electron diffraction/mass spectrometric technique with a high-temperature reactor nozzle system[3,4] has opened new possibilities in this respect. Recently, the molecular structures of germanium dichloride[4] and germanium dibromide[5] have been communicated. On the basis of available experimental structural data, the geometries for several other carbene analogues have been predicted,[5] among them silicon dichloride and silicon dibromide. Here we report the molecular structures of these two molecules.

Parallel quadrupole mass spectrometric and electron diffraction experiments were carried out on the products of the reactions.

$$\mathrm{Si(solid)} + \mathrm{Si_2Cl_6(gas)} \rightarrow \mathrm{SiCl_2(gas)}$$

$$\mathrm{Si(solid)} + \mathrm{SiBr_4(gas)} \rightarrow \mathrm{SiBr_2(gas)}$$

The former reaction has been found to produce higher $SiCl_2$ yield than the reduction of $SiCl_4$ with Si. The optimum experimental conditions were reached in both cases at a temperature of about 1200 °C of the molybdenum reactor nozzle.[3,4] The other experimental conditions as well as the data treatment were similar to those employed earlier.[4,5] The molecular intensities and radial distributions are presented in Figures 1–4. The two principal maxima on the radial distribution curves correspond to the silicon–halogen and halogen–halogen contributions. The experimental data on silicon dibromide could be well approximated by $SiBr_2$ species only. The somewhat poorer agreement for silicon dichloride necessitated that the possible presence of other species also be considered, viz., Si_2Cl_6, $SiCl_4$, and Si_2Cl_4. Some improvement in the agreement with reasonable structural implications could be achieved by supposing a small amount of Si_2Cl_4 species. The molecular parameters obtained from the electron diffraction analysis are presented in Table I. The Cl–Si–Cl angle is in good

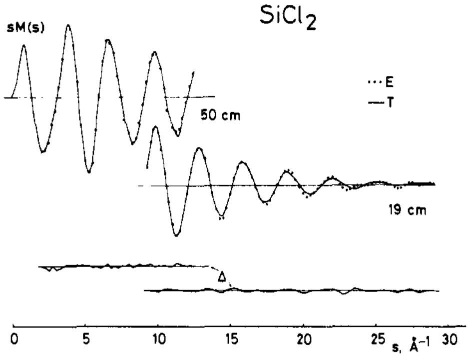

Figure 1. Experimental (E) and theoretical (T; cf. Table I) molecular intensities and their differences for silicon dichloride; 50 and 19 cm are the two camera ranges.

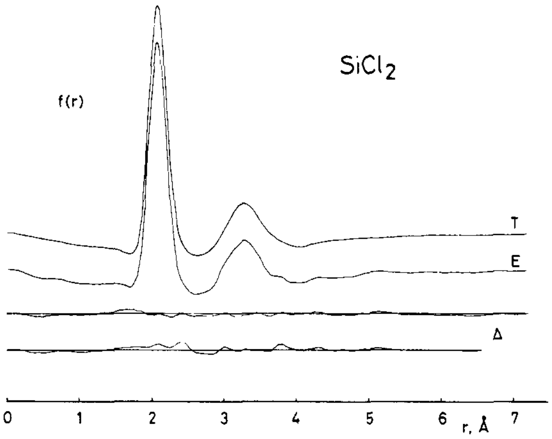

Figure 2. Experimental (E) and theoretical (T) radial distributions and difference curves for silicon dichloride. The first three curves correspond to those in Figure 1. The lower difference curve refers to a model with $SiCl_2$ monomeric species only.

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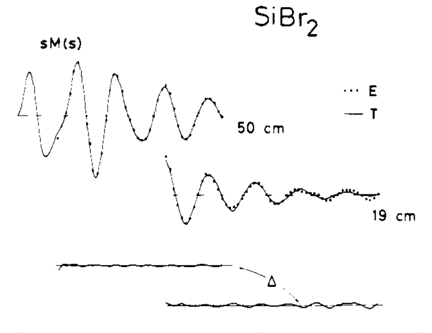

Figure 3. Experimental (E) and theoretical (T; cf. Table I) molecular intensities and their differences for silicon dibromide; 50 and 19 cm are the two camera ranges.

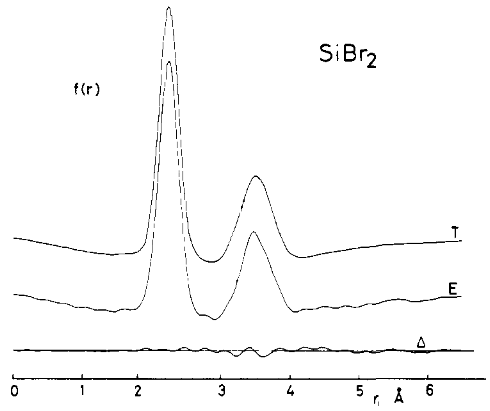

Figure 4. Experimental (E) and theoretical (T) radial distributions and difference curve for silicon dibromide. The curves correspond to those in Figure 3.

Table I. Molecular Parameters of $SiCl_2$ and $SiBr_2$ from Electron Diffraction with Estimated Total Errors[a]

parameters/SiX_2	$SiCl_2$	$SiBr_2$
r_a(Si–X), Å	2.083 ± 0.004	2.243 ± 0.005
∠X–Si–X, deg	102.8 ± 0.6	102.7 ± 0.3
r_a(X···X), Å	3.257 ± 0.011	3.503 ± 0.009
l(Si–X), Å	0.108 ± 0.003	0.117 ± 0.003
l(X···X), Å	0.218 ± 0.013	0.225 ± 0.005
$10^5\kappa$(Si–X), Å^3	3.3 (assumed)[b]	5.7 ± 1.0
amt of SiX_2, %	97.4 ± 0.3	100

[a] See: (8) Hargittai, M.; Hargittai, I. *J. Chem. Phys.* **1973**, *59*, 2513. In estimating the total errors of the $SiCl_2$ parameters, one additional term was included, viz., the half of the differences in the parameters obtained when ignoring and when taking into account the species that might be present in addition to the $SiCl_2$ molecules. [b] When refined, assuming the presence of $SiCl_2$ molecules only, κ was obtained 3.9 (7) × 10^{-5} Å^3.

agreement with that (102°) obtained from the matrix infrared spectra of silicon dichloride.[6] The geometrical variations in dihalocarbene molecules and their analogues AX_2 (A = Si, Ge, Sn, Pb; X = F, Cl, Br) appear to indicate the importance of both electron pair repulsions and ligand–ligand interactions in agreement with previous considerations.[4,5]

Spectroscopic calculations paralleled the electron diffraction structure analysis. Force fields suggested by Svyatkin et al.[6] and Maass et al.[7] were used for $SiCl_2$ and $SiBr_2$, respectively. These force fields were based on experimental frequencies and an assumed bending frequency for $SiBr_2$ (ν_2 120 cm^{-1}).[7] The calculated amplitudes, viz., l(Si–Cl) 0.096 Å, l(Cl···Cl) 0.200 Å, and l(Si–Br) 0.105 Å, are somewhat lower than those obtained from electron diffraction (Table I). The value of l(Br···Br) is essentially determined by the assumption for the bending frequency of $SiBr_2$. The electron diffraction l(Br···Br) value is reproduced by assuming ν_2 122.5 cm^{-1}.

Registry No. $SiCl_2$, 13569-32-9; $SiBr_2$, 14877-32-8.

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(6) Svyatkin, V. A.; Maltsev, A. K.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 2236.

(7) Maass, G.; Hauge, R. H.; Margrave, J. L. *Z. Anorg. Allg. Chem.* **1972**, *392*, 295.

Reaction of Ethylene with Trinuclear Hydrido Cluster Complexes: Formation and Subsequent Fragmentation of μ-Acyl Complexes

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In studies of the chemistry of the newly isolated edge double-bridged complexes $Ru_3\{\mu\text{-}H,\mu\text{-}X\}(CO)_{10}$ (X = Cl, Br, or I, **1a–c**),[1] we observe a reaction with ethylene and carbon monoxide to yield the corresponding haloacyl complexes $Ru_3\{\mu\text{-}X,\mu\text{-}O{=}C(C_2H_5)\}(CO)_{10}$, **2a–c**[2] (see eq 1 in Scheme I). These results prompted us to investigate whether other trinuclear hydrido complexes would give the same reaction, and we have observed the two transformations indicated as eq 2 and 3 in Scheme I. Salts of the anion **3**$^-$ are known to catalyze the hydroformylation reaction;[3] μ-acyl complexes were not observed under the catalytic conditions. Finally, it is worth noting that the trinuclear ruthenium complexes **5a–d** undergo dissociation in their further reaction with ethylene, shown in eq 3 in Scheme I.

Formulation of the complexes **2a–c** is achieved by a combination of ^1H and ^{13}C NMR[4a] and elemental analyses;[4b] their carbonyl absorptions in the infrared[4c] are analogous to those of the hydrido acyl complex **5b**.[4d]

With propene (1.63 atm) and CO (1 atm), **1b** (0.60 g, 0.90 mmol) yields the corresponding propionyl halide complex $Ru_3(\mu\text{-}Br,\mu\text{-}O{=}C(R))(CO)_{10}$, R = *n*- or *iso*-$C_3H_7$, (0.45 g, 0.61 mmol, 76% based on reacted **1b**) with an *n*-/*iso*- ratio of 10.

Acyl complexes **5** and **6** are characterized by ^1H and ^{13}C NMR data.[5] These are produced in 20–30% yield, comparable to (or

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(1) Boag, N. M.; Kampe, C. E.; Lin, Y. C.; Kaesz, H. D. *Inorg. Chem.* **1982**, *21*, 1706–1708.

(2) A typical procedure is given for the preparation of **2b**: **1b** (1.40 g, 2.11 mmol) is dissolved in 150 mL of dry hexane and placed in a 300-mL stainless steel Hoke cylinder. Carbon monoxide is bubbled through the solution for 30 s, after which the cylinder is pressurized with ethylene (2.86 atm). The reaction is stopped after 22 h, and the gases are vented; an IR spectrum of a solution sample indicates that only a small amount of starting material remains. Chromatographic separation is undertaken on a silica gel (SG 60) column using the same hexane as eluant. The first fraction is unreacted starting material (80 mg) followed by a smaller quantity of a yellow, as yet unidentified, material. The third and last fraction proves to be **2b** (1.13 g, 79% based on reacted **1b**).

(3) (a) Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231–242. (b) Braca, G.; Sbrana, G. *Chim. Ind.* (*Milan*) **1974**, *56*, 110.

(4) (a) ^1H NMR spectra were obtained at 26 °C on a Bruker WM-200 spectrometer and are referenced to internal tetramethylsilane (benzene-d_6). **2b**: δ 2.67 (m, 2 × 2 × 4, diastereotopic CH_2 of Et), 0.71 (t, CH_3 of Et). $^{13}C\{^1H\}$ NMR spectra were obtained at 26 °C on a JEOL FX90Q Fourier transform NMR spectrometer at 22.50 MHz relative to Me_4Si, with $Cr(acac)_3$ added as a paramagnetic relaxation agent. **2b**: δ 300.9 [O=*C*(Et)], 201.6 (1 CO), 200.7 (1 CO), 199.6 (1 CO), 199.2 (1 CO), 198.3 (1 CO), 196.6 (1 CO), 193.8 (1 CO), 193.4 (1 CO), 184.0 (1 CO), 175.9 (1 CO), 57.5 (CH_2), 8.53 (CH_3). (b) Satisfactory elemental analyses were obtained for all the designated new compounds in this work (Schwartzkopf Microanalytical Laboratories). (c) The Following IR absorptions in hexane (cm^{-1}) are observed. **2b**: ν (CO) 2105 w, 2078 vs, 2059 s, 2031 s, 2019 s, 2011 vs, 2002 m, 1983 m; ν (C=O) 1522 w; ν (Et) (KBr) 2981, 2939. (d) IR absorptions (hexane; cm^{-1}). **5b**: ν (CO) 2104 w, 2067 vs, 2054 s, 2029 s, 2017 s, 2008 m, 2004 m, 1989 w; ν (C=O) 1522 w. **6**: ν (CO) 2109 w, 2069 vs, 2058 s, 2028 s, 2012 s, 1997 m, 1982 w; ν (C=O) (KBr) 1492.

(5) **5b**: ^1H NMR (benzene-d_6, 26 °C) δ 2.89 (m, 2 × 2 × 4, diastereotopic CH_2 of Et), 0.71 (t, CH_3 of Et), −13.93 (s, Ru–μ-*H*–Ru); $^{13}C\{^1H\}$ NMR (benzene-d_6, 26 °C) δ 286.3 [O=C(Et)], 206.7 (2 CO), 201.2 (1 CO), 200.7 (1 CO), 195.9 (1 CO), 194.8 (1 CO), 191.5 (1 CO), 191.3 (1 CO), 189.3 (1 CO), 184.7 (1 CO), 55.7 (CH_2), 8.49 (CH_3). **6**: ^1H NMR (benzene-d_6, 26 °C) δ 1.98 (m, 2 × 2 × 4, diastereotopic CH_2 of Et), 0.55 (t, CH_3 of Et), −14.08 (s, Os–μ-*H*–Os).

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