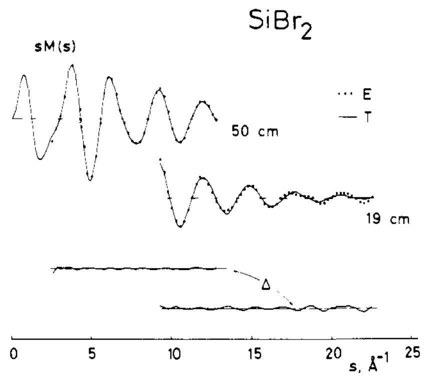

Figure 3. Experimental (E) and theoretical (T; cf. Table I) molecular intensities and their differences for silicon dibromide; 50 and 19 cm are the two camera ranges.

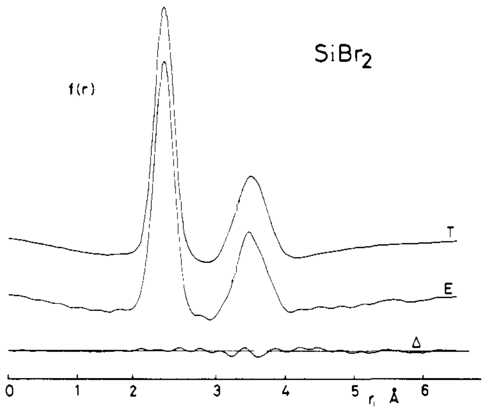

Figure 4. Experimental (E) and theoretical (T) radial distributions and difference curve for silicon dibromide. The curves correspond to those in Figure 3.

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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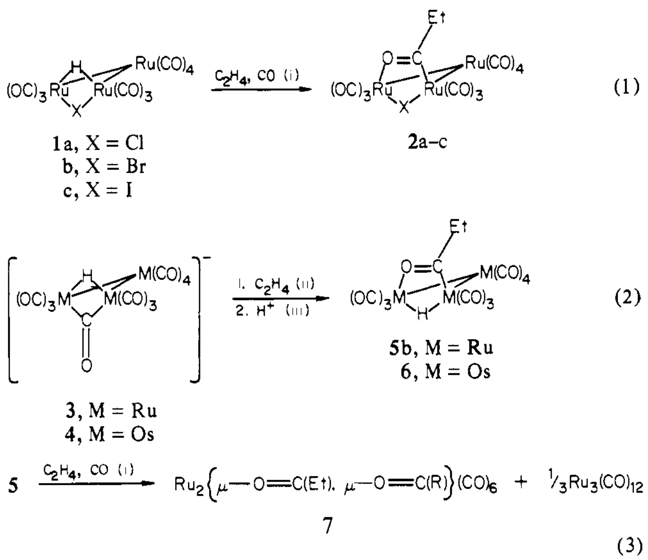
Scheme I[a]



5 or 7	a	b	c	d
R =	Me	Et	Ph	N(Me)$_2$

[a] (i) C_2H_4, 3 atm; CO, 1 atm; 26 °C in hexane. (ii) C_2H_4, 3 atm; 26 °C in THF. (iii) $HBF_4 \cdot 2Et_2O$.

even less than by) other routes,[6] but important in demonstrating this reaction path.

Further reaction of ethylene with any of the acyl- or amido-bridged trinuclear hydride complexes **5a-d** gives the result represented in eq 3 of Scheme I. Mass balance is achieved nearly quantitatively (95–100%). $Ru_3(CO)_{12}$ is crystallized out at −20 °C; when the solution is warmed back to room temperature, half the solvent removed under vacuum, and the solution again cooled to −20 °C, complexes **7a–d** (respectively) are now crystallized out. These compounds can be separated on silica gel columns with 50/50 petroleum ether/CH_2Cl_2.[4b] By ^{13}C NMR[7] and similarity of their IR absorptions to the complex $(OC)_3Fe\{O{=}C(Ph)\}_2Fe(OC)_3$[8] we believe them to be dimers as indicated in Scheme I.

The bridging acyl groups are three-electron donors, and the presence of two of these along one edge of a trimer would require loss of the metal–metal bond between the ruthenium atoms thus bridged.[9] *Instead*, we observe loss of an $Ru(CO)_4$ group giving $Ru_3(CO)_{12}$ and a metal–metal-bonded dimer. The instability of the trinuclear unit with the two bridging μ-acyl groups is an important observation of relevance to the question of the stability of cluster complexes under catalytic conditions.[10]

Acknowledgment. This work was supported by a grant from the National Science Foundation (CHE-79-08406) and an SERC Fellowship to N.M.B.

Registry No. 1a, 85220-73-1; **1b**, 85220-74-2; **1c**, 85220-75-3; **2a**, 85220-76-4; **2b**, 85220-77-5; **2c**, 85220-78-6; **3**, 85220-79-7; **4**, 85220-80-0; **5a**, 85220-81-1; **5b**, 85220-82-2; **5c**, 85220-83-3; **5d**, 85220-83-3; **6**, 85220-85-5; **7a**, 85220-86-6; **7b**, 85220-87-7; **7c**, 85220-88-8; **7d**, 85220-89-9; $Ru_3(CO)_{12}$, 15243-33-1; $Ru_3(\mu\text{-Br},\mu\text{-O}{=}C(n\text{-}C_3H_7))(CO)_{10}$, 85220-90-2; $Ru_3(\mu\text{-Br},\mu\text{-O}{=}(iso\text{-}C_3H_7))(CO)_{10}$, 85220-91-3; C_2H_4, 74-85-1; propene, 115-07-1.

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[6] Azam, A. K.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1982**, 91–98.

[7] (a) $^{13}C\{^1H\}$ NMR for **7d** (relative to Me_4Si at 26 °C in $CDCl_3$) δ 287.1 ($O{=}C$(Et)), six maxima 206.5 to 195.0, 180.4 ($O{=}CN(CH_3)_2$), 55.5 (CH_2 of Et), 40.3, 34.8 (CH_3 of $O{=}CNMe_2$), 8.19 (CH_3 of Et). (b) IR absorptions in the carbonyl region (in hexane, cm^{-1}). **7a**: 2089 w, 2053 vs, 2019 s, 2012 sh, 1983 m. **7b**: 2086 m, 2052 vs, 2018 s, 2012 sh, 1982 m. **7c**: 2088 m, 2053 vs, 2019 s, 2012 sh, 1983 m. **7d**: 2085 m, 2049 vs, 2012 s, 2008 sh, 1975 m.

[8] (a) Fischer, E. O.; Kiener, V.; Bunbury, D. Dt. P.; Frank, E.; Lindley, P. F.; Mills, O. S. *Chem. Commun.* **1968**, 1378. (b) Lindley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279–1285.

[9] The presence of two three-electron donor groups on the edge of a trinuclear complex results in *loss* of metal–metal bond order along that edge: cf.: (a) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *104*, 297–307. (b) Teo, B. K.; Hall, M. B.; Fenske, R. F.; Dahl. L. F. *Ibid.* **1974**, *70*, 413–420. (c) Mason, R.; Mingos, D. M. P. *Ibid.* **1973**, *50*, 53–61.

[10] (a) Humphries, A. P.; Kaesz, H. D. *Prog. Inorg. Chem.* **1979**, *25*, 193. (b) Pittman, C. U., Jr.; Ryan, R. C. *Chem. Technol.* **1978**, 170–175.

Dihydrogen Evolution from Aqueous Vanadium(II)-Cysteine Solutions at pH 6.0-9.5

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Few homogeneous metal ion systems[1] have been reported that are capable of reducing water thermally under mild conditions in alkaline media, and to the best of our knowledge none in neutral solutions. These systems are based on polyamine[2] and pyrochatechol ligands.[3]

We report here on another system based on a sulfur ligand. When excess cysteine is added to a V^{II} solution, substitution occurs, followed by electron transfer to electron acceptors present in the solution and to water in their absence, leading eventually to dihydrogen evolution. These reactions were investigated in the pH range 6.0–9.5 and can be represented by eq 1 and 2. The first

$$V^{II} + \text{cys} \rightarrow V^{II}\text{–cys} \qquad (1)$$

$$V^{II}\text{–cys} + H_2O \rightarrow V^{III}\text{–cys} + HO^- + {}^1/_2H_2 \qquad (2)$$

reaction is fast and is monitored by stopped flow. Before mixing, the vanadium(II) solution is acidic. Dihydrogen release is slow—it takes several minutes. During the reaction pH remains within experimental error constant; the system is a fairly good buffer. The data in Table B (supplementary material) show that the stoichiometry of the redox reaction corresponds to eq 2. Stoichiometry measurements were made in the pH range 7.5–8.5, at temperatures between 20 and 62 °C, and with initial concentrations $[V^{II}]_0 = 0.2\text{–}0.1$ M and $[\text{cys}]_0 = 0.62\text{–}1.47$ M, and $[\text{cys}]_0$ to $[V^{II}]_0$ ratios of 6.6–38.

In the pH range investigated precipitation of hydrolyzed vanadium species is avoided by using a large excess of cysteine (always larger than 20-fold). Under these conditions even small amounts of impurities in cysteine may cause extensive oxidation and lead to faulty results. It is, therefore, important to recrystallize the organic reagent (purchased from Riedel-de Haën AG) carefully, under an inert atmosphere.

V^{II}–cys is formed with a rate law first order in V^{II} and in cysteine. The kinetic data were collected in the temperature range 24–54 °C with $[V^{II}]_0 = 3 \times 10^{-4}$ M and $[\text{cys}]_0 = 0.10\text{–}0.64$ M (Table A and Figure A_1, supplementary material). The second-order rate constant depends upon pH and at 24 °C reaches a maximum value $k_2 = 1.00 \pm 0.05$ mol^{-1} L s^{-1} at pH 8.25 (Figure 1). The points in this figure are averages of many measurements. The Arrhenius activation energy (Figure A_2, supplementary material) is 10.0 ± 1.0 kcal mol^{-1}, in agreement with the value

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[1] Excluding metal hydrides.

[2] Kopple, K. D.; Svatos, G. F.; Taube, H. *Nature (London)* **1961**, 393.

[3] (a) Nikonova, L. A.; Isaeva, S. A.; Perskowa, N. I.; Shilov, A. E. *J. Mol. Cata.* **1975**, *1*, 367. (b) Schrauzer, G. N.; Palmer, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 2659.

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