Hydrolysis of the Organometallic Aqua Ion *fac*-Triaquatricarbonylrhenium(I). Mechanism, pK_a, and Formation Constants of the Polynuclear Hydrolysis Products

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Hydrolytic pathways of the organometallic aqua ion $[Re(CO)_3(H_2O)_3]^+$ (**2**) in aqueous media were investigated by means of potentiometric titration experiments. The aqua complex **2** was obtained quantitatively by dissolving $(NEt_4)_2[Re(CO)_3Br_3]$ (**1**) in water. Conventional alkalimetric titrations (0.1 M KNO_3, 25 °C) allowed the determination of the formation constants of $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ (**3**) and $[Re_2(CO)_6(\mu_2\text{-}OH)_3]^-$ (**4**). The neutral dinuclear $[Re_2(CO)_6(\mu_2\text{-}OH)_2(H_2O)_2]$ (**5**) was observed as a minor species. A fast titration technique was used to investigate a rapid preequilibrium, consisting of the formation of the mononuclear deprotonation products $[Re(CO)_3(OH)(H_2O)_2]$ (**6**) and $[Re(CO)_3(OH)_2(H_2O)]^-$ (**7**). The corresponding pK_a values are 7.5(2) and 9.3(3). The immediate extraction of an aqueous solution of **2** with diethyl ether after base addition (1 equiv) led to the quantitative isolation of the well-known cubane cluster $[Re(CO)_3(OH)]_4$ (**8**), which was obtained as a DMF (**8b**) or $OPPh_3$ adduct (**8c**). Attempts to isolate the aqua complex **2** as a crystalline material by precipitating the bromo ligands of **1** with $AgCF_3COO$ resulted in the formation of $(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$ (**9**). The structures of **8b**, **8c**, and **9** were elucidated by single-crystal X-ray analysis.

Introduction

For a long time, organometallic chemistry was predominantly restricted to nonaqueous media. However, due to the significant ecological advantages of water as a solvent in industrial processes, the aqueous chemistry of organometallic compounds has lately been receiving increased attention. In the last few years, considerable effort has gone into developing organometallic compounds which could be used as catalysts in water.[1] A basic mode of reactivity of such complexes is the substitution of labile ligands by solvent molecules. However, reports on organometallic aqua complexes are still rare.[2−4] In a recent publication, we reported the facile formation of $[Re(CO)_3(H_2O)_3]^+$ (**2**) by simple dissolution of $(NEt_4)_2[Re(CO)_3Br_3]$ (**1**) in water.[5] Due to the lability of the three H_2O ligands, this complex could serve as a powerful synthon for novel complexes of the $[Re^I(CO)_3]^+$ moiety and could be of interest for applications in nuclear medicine.[6] Some of us have recently presented a convenient and effective one-pot, low-pressure carbonylation method for **1** with perrhenate as starting material, which provides easy access to the aqua complex **2**.[7]

In our previous report, we also demonstrated that **2** reacts as a weak acid.[5] However, addition of KOH to an aqueous solution of **2** yielded the trinuclear $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ (**3**) and the dinuclear $[Re_2(CO)_6(\mu_2\text{-}OH)_3]^-$ (**4**) (Figure 1) rather than the simple deprotonation product $[Re(CO)_3(OH)(H_2O)_2]$ (**6**). Clearly, complexes **3** and **4** can be regarded as hydrolytic condensation products which require, however, the formation of the mononuclear **6** as a short-lived intermediate. This interpretation was supported by characteristic slow kinetics of formation of **3**. The reaction scheme in aqueous solution should thus be separable into a fast preequilibrium, consisting of a simple deprotonation reaction, and the much slower hydrolytic polymerization.

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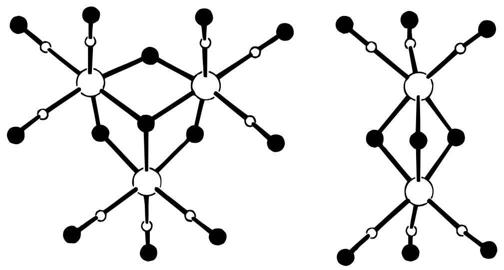

3 **4**

Figure 1. Crystal structures (from ref 5) of the hydrolysis products $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ (**3**) and $[Re_2(CO)_6(\mu_2\text{-}OH)_3]^-$ (**4**). Re, O, and C atoms are shown as spheres with decreasing diameter in this order. H-atoms are omitted for clarity.

Organometallic complexes with a polynuclear, "inorganic" metal oxide or hydroxide core are well-known,[8,9] although their formation from a mononuclear aqua complex by analogy with the olation of Werner-type complexes seems not to be common.[4] Moreover, a search of the literature revealed a complete lack of thermodynamic data for such processes. In this paper, we present pK_a values for the aqua complex **2** and thermodynamic formation constants for the hydrolysis products **3** and **4**. These data allow the calculation of the species distribution as a function of pH, which is of crucial relevance for the understanding of the reactivity of such systems. We also discuss a possible mechanism for the formation of these two species. In addition, we present X-ray structures of the tetranuclear $[Re(CO)_3(OH)]_4$ (**8**) and the mononuclear complex $(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$ (**9**).

Experimental Section

Materials, Analyses, and Spectroscopy. All chemicals were of reagent grade quality and were used without further purification. $(NEt_4)_2[ReBr_3(CO)_3]$ was prepared as described previously.[5] IR spectra (KBr disks) were recorded on a Perkin-Elmer FT-IR PC 16 infrared spectrometer. Elemental analyses were performed by D. Manser and M. Schneider, Laboratorium für Organische Chemie, ETH Zürich. FAB$^+$ mass spectra were measured on a VG ZAB VSEQ instrument. Test solutions were prepared by dissolving the sample in water or alcoholic solvents and mixing the resulting solution with a 3-nitrobenzyl alcohol matrix prior to the introduction in the spectrometer. ES$^+$ mass spectra were measured on a Fisons VG Trio 2000 quadrupole instrument with direct inlet (capillary voltage set at 2.85 kV, cone voltage at 12 V, ion voltage at 2.3 V) with H_2O as solvent (100 μL min^{-1} flow rate).

$[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]\cdot 4H_2O$ (8a). A solution of $(NEt_4)_2[Re(CO)_3Br_3]$[5] (154 mg, 0.2 mmol) in 20 mL of H_2O was layered with 30 mL of diethyl ether, and 10 mL of 0.02 M NaOH was added rapidly with vigorous stirring. After 5 min, the two phases of the reaction mixture were separated. Removal of the ether *in vacuo* yielded 57 mg of **8a** as a white solid (93%). Anal. Calcd for $C_{12}H_{12}Re_4O_{20}$: C, 11.80; H, 0.99. Found: C, 12.26; H, 1.15. IR (cm^{-1}): 3578 s, 3428 br, 3218 br, 2032 vs, 1926 vs, 1896 vs, 662 m, 544 m, 510 m, 464 m. FAB MS: *m/z* 1149.8 (7.2) $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]^+$.

$[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]\cdot 4DMF$ (8b). **8a** (20 mg) was dissolved in 2 mL of DMF and layered with 8 mL of water. After 2 weeks, 12 mg of colorless crystals, suitable for X-ray analysis, was isolated. IR (cm^{-1}): 3422 br, 2814 w, 2022 vs, 1910 vs, 1646 s, 1436 w, 1418 w, 1384 m, 1256 w, 1104 m, 662 m, 556 m, 510 m, 486 m.

$[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]\cdot 4OPPh_3$ (8c). The preparation was performed as described for **8a**; however, 1 equiv of triphenylphosphine was added to the ether extract. The solution was evaporated and the resulting residue redissolved in CH_2Cl_2 and layered with hexane. After 24 h, 50 mg of colorless crystals, suitable for X-ray analysis, was isolated.

$(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$ (9). Solid **1** (77 mg, 0.1 mmol) and 66.3 mg (0.3 mmol) of $AgCF_3COO$ were suspended in 20 mL of THF. The mixture was stirred at room temperature for 14 h, and the precipitated AgBr was filtered off. The solvent was then removed *in vacuo*, and the residue was dissolved in CH_2Cl_2 and layered with hexane. After 2 weeks, 15 mg of octahedrally shaped, colorless crystals, suitable for X-ray analysis, was collected. Anal. Calcd for ($C_{25}H_{40}F_9N_2O_9Re$): C, 34.52; H, 4.64; N, 3.22. Found: C, 34.56; H, 4.64; N, 3.26.

Potentiometric Titrations. The formation constants of the hydrolysis products were determined by continuous titrations of solutions (100 mL), containing 10^{-3} M **2**, using an Orion 720 pH-meter, a Phillips GAH 420 glass electrode, and an Ag/AgCl reference electrode, fitted with a salt bridge (0.1 M KNO_3). The ionic strength was adjusted to 0.1 M using KNO_3 as inert electrolyte. The sample solutions were titrated with 0.1 M KOH, dispensed from a Metrohm 665 piston buret. The potential measurements were performed in a water-jacketed beaker at 25 °C under an atmosphere of nitrogen (which had previously been passed through an aqueous solution of 0.1 M KNO_3). Slow reaction at acidic pH required an equilibration time of 1 h/point. The electrode system was checked by calibration titrations (100 mL of 2×10^{-3} M HNO_3, 0.1 M KOH) both before and after the measurements. Back-titrations were performed with the same equipment, using 0.1 M HNO_3 as titrant.

pK_a determinations of the aqua ion **2** were performed with solutions containing 10^{-3} M **2** and 3×10^{-3} M HNO_3. In order to measure acid dissociation of the aqua ion in the absence of any hydrolytic polymerization reaction, new sample solutions were used for every point of the titration curve. A fast injection system was applied to add the entire amount of KOH required at once to the vigorously stirred sample solution. The pH of the mixture was then recorded as a function of time using a fast-response glass electrode from Möller (Zürich), an Orion 720 pH-meter, and a personal computer (IBM) equipped with an AD converter (IPK 341) with a maximal sampling rate of 30 kHz (Figure 2). To achieve minimal mixing delay, a sample size of only 5 mL was used. A dead time of ≤ 2 s was established by calibration experiments (addition of 0.1 M KOH to 10^{-3} M HNO_3 solutions). Values for $t = 0$ were obtained from a total of 20 experiments ($0 <$ equiv < 2, equiv $=$ added base:total Re) by extrapolation of the pH−time profile. However, the last four values (equiv > 1.5, pH > 9.5) were not considered because the formation of dinuclear species occurred already at such a high rate that a reliable extrapolation was not possible.

Evaluation of Equilibrium Constants. All equilibrium constants were calculated as concentration constants, and pH is defined as $-\log$ [H]. A pK_W of 13.79(1) (0.1 M KNO_3, 25 °C) was obtained from several calibration titrations. The data were evaluated by using the computer programs SUPERQUAD and BEST (Table 1).[10] The formation constants of the hydrolysis products were initially calculated by refining only the constants of the Re-containing species with fixed values for pK_W, the total amount of the reactants (total H, total Re), and the concentration of the titrant. Additional refinements were then performed where total Re was also allowed to vary. This resulted in an improved fit σ_{pH}[11] and a slight increase

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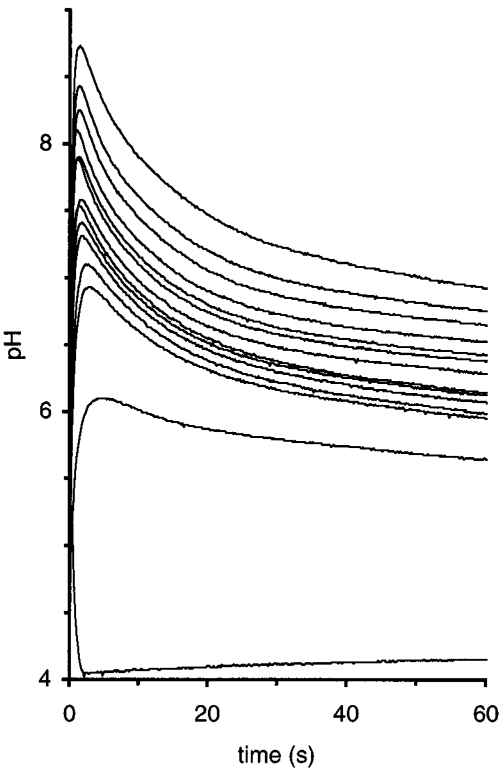

Figure 2. pH versus time curves as sampled in the fast titration experiment. From bottom to top the lines correspond to 0.0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, and 1.5 equiv of added base/total Re.

Table 1. Potentiometric Data (25 °C, 0.1 M KNO_3) and Evaluated Formation Constants with Estimated Standard Deviations in Parentheses[a]

		fast titration	
	continuous	$t = 120$ s	$t = 0^b$
evaluated range			
equiv	0−2.6	0−1.5	0−1.5
pH	4.64−10.85	4.19−9.00	4.02−9.40
no. of data points	41	16	16
$\log \beta^*_{xy}{}^c$			
x y			
1 1			$-7.5(2)^d$
1 2			$-16.8(3)^d$
3 4	−15.06(3)		
2 3	−14.7(1)	−14.9(2)	
2 2	−8.7(3)	−8.9(3)	
$\sigma_{pH}{}^e$	0.0017	0.033	0.069

[a] Total Re: 10^{-3} mol dm^{-1}. Titrant: 0.1 mol dm^{-1} KOH. In addition to the usual statistical analysis of the titration curve, the esds comprise estimated uncertainties due to the extrapolation procedure ($t = 0$) and the small amounts of the added increments of base in the fast titration experiment as well as a possible drift in $E°$ of the electrode due to the long measuring time in the continuous titration. [b] Evaluation of extrapolated data. [c] The constants were evaluated as dissociation quotients, according to the equation $x\mathrm{Re(CO)_3} \rightarrow \mathrm{Re}_x\mathrm{(CO)}_{3x}\mathrm{(OH)}_y + y\mathrm{H}$; $\beta^*_{xy} = [\mathrm{Re}_x\mathrm{(CO)}_{3x}\mathrm{(OH)}_y][\mathrm{H}]^y[\mathrm{Re(CO)_3}]^{-x}$; the corresponding formation constants $\beta_{xy} = [\mathrm{Re}_x\mathrm{(CO)}_{3x}\mathrm{(OH)}_y][\mathrm{OH}]^{-y}[\mathrm{Re(CO)_3}]^{-x}$ are $\beta_{34} = 40.1(1)$, $\beta_{23} = 26.7(2)$, and $\beta_{22} = 18.9(3)$, using $pK_W = -13.79(1)$. [d] $pK_1 = 7.5(2)$, $pK_2 = 9.3(3)$. [e] For the definition of σ_{pH}, see ref 11.

for total Re of about 4−5%. However, the formation constants did not change significantly. We attribute the slight increase for total Re to traces of the dimeric $(NEt_4)[(CO)_3Re(\mu\text{-}Br)_3Re(CO)_3]$, which is formed as a byproduct of $(NEt_4)_2[Re(CO)_3Br_3]$.[12]

X-ray Analyses. X-ray data were collected on a Picker-Stoe (**8b**, **8c**) and an Enraf-Nonius CAD4 (**9**) diffractometer using graphite-monochromatized Mo Kα radiation (Table 2). The data of **9** were collected at 193(2) K, whereas data collection of **8a** and **8b** occurred at room temperature. Checking of the stability by monitoring standard reflections revealed no significant decay of the crystals during data collection. The data were corrected for Lorentz and polarization effects. A face-indexed numerical absorption correction was applied for **8b,** and ψ-scans were applied for **9**. The structures of **8b** and **8c** were solved by the Patterson method (SHELXTL-PLUS).[13] The structure of **9** was solved by direct methods using SHELXS 86.[14] All refinements were performed by full-matrix least-squares calculations using SHELXTL-PLUS[13] for **8b** and **8c** and SHELXL 93[15] for **9**. For **8c**, four of the six carbon atoms of the phenyl ring were found to be disordered over two sites with an occupancy of 50% each. Some disorder was also noted for the NEt_4 counterions of **9** (two positions for C(43), some unusual bond lengths and angles). Anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions. Summarized structural parameters are presented in Table 3.

Results and Discussion

Stability Constants. As shown previously by IR spectroscopy, $[Re(CO)_3Br_3]^{2-}$ (**1**) reacts quantitatively to $[Re(CO)_3(H_2O)_3]^+$ (**2**) in dilute aqueous solution.[5] This aqua complex proved to be stable indefinitely, as long as the pH was kept below 4. In the present investigation, we performed electrospray mass-spectrometric measurements to confirm the complete substitution of the ligand Br^- by H_2O. The spectrum showed only one Re-containing species, assignable to **2,** at $m/z = 325$. Two types of titration experiments were performed to shed light on the reactivity and species distribution of this complex in water: (a) formation constants of the hydrolysis products were determined by conventional titration experiments where a sample solution was neutralized by the stepwise addition of small increments of base; (b) a fast titration technique, described first by Schwarzenbach and co-workers,[16] was used to elucidate the rapid preequilibrium. A series of such experiments were performed, where the entire amount of base was added rapidly in a single step to fresh sample solutions and the pH was then recorded as a function of time (Figure 2). The data that correspond to the same time interval can be grouped to give a series of time-depending titration curves (Figure 3).

It is expected that the simple deprotonation of **2** is diffusion controlled, and the corresponding equilibria,

$$[\mathrm{Re(CO)_3(H_2O)_3}]^+\ (\mathbf{2}) \rightarrow [\mathrm{Re(CO)_3(OH)(H_2O)_2}]\ (\mathbf{6}) + \mathrm{H}^+ \quad (1)$$

$$[\mathrm{Re(CO)_3(OH)(H_2O)_2}]\ (\mathbf{6}) \rightarrow [\mathrm{Re(CO)_3(OH)_2(H_2O)}]^-\ (\mathbf{7}) + \mathrm{H}^+ \quad (2)$$

are established within much less than 1 s. The data of the fast titration experiment were therefore extrapolated to $t = 0$. The resulting curve (Figure 3) revealed

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[11] $\sigma_{pH} = (\Sigma w(pH_{obsd} - pH_{calcd})^2/\Sigma w)^{1/2}$; $w = (pH_{i+1} - pH_{i-1})^{-2}$.

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Table 2. Crystallographic Data for 8b, 8c, and 9

	8b	**8c**	**9**
formula	$C_{24}H_{32}N_4O_{20}Re_4$	$C_{21}H_{16}O_5PRe$	$C_{25}H_{40}F_9N_2O_9Re$
formula wt	1441.3	565.5	869.8
cryst syst	monoclinic	cubic	monoclinic
space group	$P2_1/c$	$I\bar{4}3m$	$P2/n$
color of crystal	colorless	colorless	colorless
a, Å	21.35(3)	16.22(7)	13.462(8)
b, Å	9.799(14)	16.22(7)	15.762(1)
c, Å	19.49(4)	16.22(7)	16.195(9)
β, deg	90.82(14)	90.0	92.06(3)
V, Å^3	4078(11)	4267(33)	3434(3)
Z	4	8	4
R[a]	0.035	0.029	0.066

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 3. Summarized Bond Lengths (Å) and Angles (deg) of the Cubane Complex (8b and 8c) and of $(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$ (9)

	8b	**8c**	**9**
Re−O			
min	2.154(9)		2.139(8)
max	2.194(9)		2.166(12)
mean	2.17	2.19(1)[a]	2.15
Re−C			
min	1.81(2)		1.77(2)
max	1.93(2)		1.87(2)
mean	1.88	1.88(2)[a]	1.83
C−O			
min	1.12(2)		1.17(2)
max	1.21(2)		1.24(2)
mean	1.16	1.13(3)[a]	1.19
O−Re−O			
min	72.5(3)		77.6(3)
max	74.5(3)		81.8(4)
mean	73.4	75.8(9)[a]	79.4
C−Re−C			
min	85.2(7)		86.6(10)
max	89.4(7)		87.3(7)
mean	87.6	88.8(3)[a]	87.1
Re−O−Re			
min	103.1(3)		
max	105.8(3)		
mean	104.4	102.5(7)[a]	

[a] Only one value due to cubic symmetry.

a steady increase of pH with increasing OH:Re ratio, indicative for such a multiple-deprotonation reaction. Numerical evaluation revealed the two pK_as 7.5(2) and 9.3(3). These remarkably low values for a monovalent cation are probably a consequence of the strong π-withdrawing effect of the three carbonyl ligands.

The formation constants of the hydrolysis products could be determined by the continuous titration procedure (Figure 4). Long equilibration times (up to 1 h/point) were required, and a back-titration was performed to ensure that equilibration was complete. In contrast to the $t = 0$ curve, the continuous titration revealed two buffer regions in the ranges $5 < pH < 6$ and $10 < pH < 11$. A steep pH jump at 1.33 equiv of added base, which separated the two buffer regions, indicated that the formation of complex **3**, having a OH:Re ratio of 4:3, is the major reaction in the first buffer region. This reaction is completed at pH 6. In the second buffer region, a species with an increased OH:Re ratio must be formed. Due to the observation that the adjustment of concentrated solutions of **2** to a pH of about 11 resulted in an immediate precipitation of the dinuclear complex **4** in high yield, we concluded that the formation of **4** was the predominant reaction in this second buffer region. A numerical evaluation of the entire curve revealed an excellent fit assuming **2**, **3**, and **4** as major species.

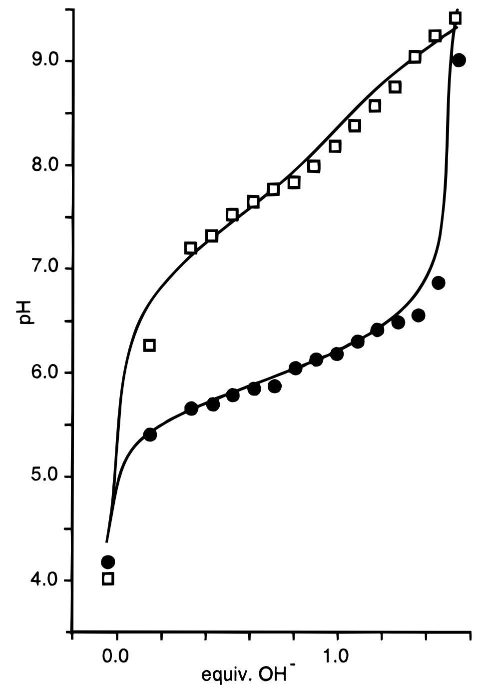

Figure 3. Data of the fast titration experiments for $t = 0$ (□) and $t = 120$ s (●). The two lines represent calculated titration curves, considering the formation of two mononuclear and two dinuclear hydrolysis products, respectively, as listed in Table 1.

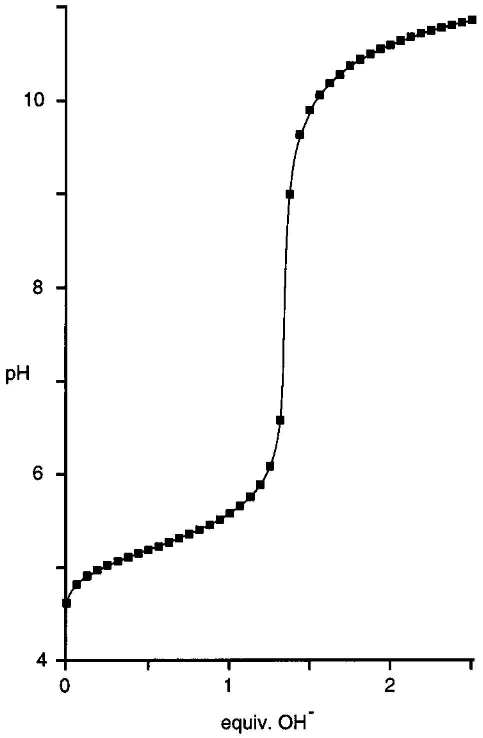

Figure 4. Continuous titration of **2**. Squares represent the measured pH values; the line has been calculated using the evaluated stability constants listed in Table 1.

Further improvement of the fit was obtained by introducing an additional neutral species such as the mononuclear $[Re(CO)_3(H_2O)_2(OH)]$ (**6**) or the dinuclear $[Re_2(CO)_6(OH)_2(H_2O)_2]$ (**5**). On the basis of the continuous titration experiments, it was not possible to determine unambiguously which of the two species was present. However, considering the pK_a value of 7.5 for the aqua ion **2,** as established by the fast titration experiment, substantial amounts of the mononuclear deprotonation product will not form below pH 6 and the mononuclear **6** can therefore be neglected. Neutral species of nuclearity higher than 2 were rejected by SUPERQUAD. For equilibrated solutions, consideration of the mononuclear aqua complex **2**, the hydrolysis products **3** and **4**, and the neutral dinuclear **5** as a minor species is thus sufficient to model the pH-dependent reactivity of the system (Figure 5). The aqua complex exists exclusively in acidic solutions, and the trinuclear complex **3** predominates under neutral conditions, whereas the triply bridged dinuclear complex forms only in strongly alkaline media. The dinuclear complex **5** has a maximal concentration around pH 5, but it never exceeds the 10% level. The formation of **5** in equilibrium is therefore not established with the same reliability as is the case for the major species **2**, **3**, and **4**.

There is, however, some strong evidence that **5** is a predominant intermediate during the hydrolytic polymerization of **2**. This evidence is provided by the fast titration experiment. As shown in Figure 3, the data extrapolated to $t = 0$ showed a continuous increase of the pH for increasing amounts of added base. However, the data which correspond to an intermediate time range (some seconds up to several minutes after base addition) showed a buffer region around pH 6 and a steep pH jump at 1.5 equiv, indicating a rather rapid formation of the dinuclear complex **4** already below pH 7. In the equilibrated system, significant amounts of **4** are not found below pH 9. This observation is only compatible with a rapid formation of a transient species such as **5**. It must, of course, be emphasized that at this stage the system is in a nonequilibrium condition and that the evaluation of formation constants is thus highly questionable. However, the reaction rates of the preliminary deprotonation, the succeeding dimerization, and the final formation of the trimer are obviously sufficiently different to allow a quantitative analysis. In a suitable intermediate time range, the formation of the dimer has almost reached equilibrium, whereas the trinuclear complex has not yet formed to a substantial extent. Close inspection of the curve for $t = 120$ s revealed good agreement with a model comprising the aqua ion **2** and the dinuclear complexes **4** and **5** as the only relevant species (Figure 3). In particular, it should be noted that the formation constants of **4** and **5** obtained from this evaluation are in excellent agreement with the values calculated from the continuous titration, where complete equilibration was ensured (Table 1).

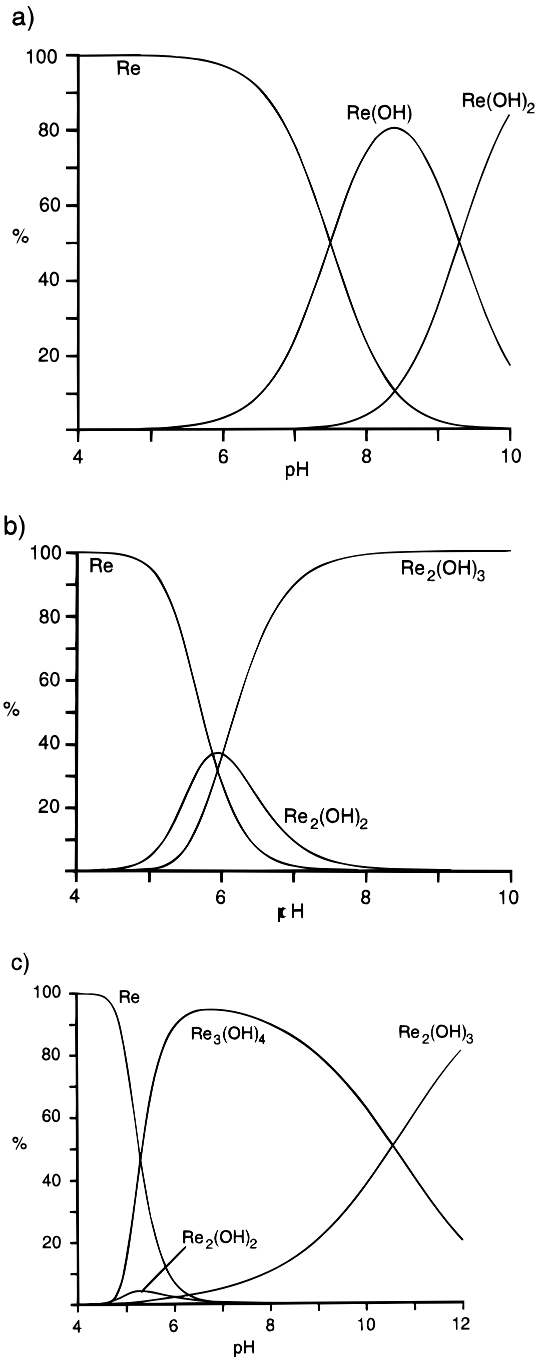

Figure 5. Species distribution plots as a function of pH, (a) considering only the mononuclear species of the fast preequilibrium, (b) for mononuclear and dinuclear species (intermediate time range), and (c) for complete equilibrium. The percentage shown refers to the amount of Re for each component, rather than the species concentration. The distributions were calculated for a total amount of Re of 10^{-3} M using the formation constants, listed in Table 1. In the labels, the CO and H_2O ligands are omitted for clarity.

Mechanism of the Hydrolytic Polymerization of 2. According to the continuous titration experiments, the formation of the trinuclear hydrolysis product **3** had already occurred around pH 5. It is noteworthy that under these conditions the deprotonated aqua ion **6** is present to an extent of less than 1%. However, it is clear from the fast titration experiment that the simple deprotonation must occur as a preliminary step in this reaction. In addition, the fast titration experiment provided evidence that the dinuclear complex **5** is then formed as a further intermediate. We tentatively formulate this intermediate as a di-μ-hydroxo bridged $[Re_2(CO)_6(\mu\text{-}OH)_2(H_2O)_2]$. Obviously two different consecutive reactions are now possible at this stage. Reaction of **5** with OH^- can result in a further deprotonation of one of the two coordinated water molecules, and the resulting hydroxo ligand can substitute the remaining water ligand of the adjacent Re center. This will lead directly to the tri-(μ-OH) dimer **4**:

$$[(CO)_3(H_2O)Re(\mu\text{-}OH)_2Re(H_2O)(CO)_3]\ (\mathbf{5}) \rightarrow [(CO)_3(HO)Re(\mu\text{-}OH)_2Re(H_2O)(CO)_3]^- + H^+ \quad (3a)$$

$$[(CO)_3(HO)Re(\mu\text{-}OH)_2Re(H_2O)(CO)_3]^- \rightarrow [(CO)_3Re(\mu\text{-}OH)_3Re(CO)_3]^- \ (\mathbf{4}) + H_2O \quad (3b)$$

However, an alternative pathway exists in the condensation reaction of the dimer **5** with an additional 1 equiv of the mononuclear complex. Our data do not allow us to decide whether this reaction must be formulated as a condensation of the mononuclear aqua complex with the deprotonated dimer (eq 4) or of the mononuclear hydroxo-complex with the neutral dimer (eq 4′). It is,

$$[(CO)_3(HO)Re(\mu\text{-}OH)_2Re(H_2O)(CO)_3]^- + [(CO)_3Re(H_2O)_3]^+ \ (\mathbf{2}) \rightarrow [(CO)_9(\mu\text{-}HO)_3(\mu_3\text{-}OH)Re_3]^- \ (\mathbf{3}) + H^+ + 3H_2O \quad (4)$$

$$[(CO)_3(H_2O)Re(\mu\text{-}OH)_2Re(H_2O)(CO)_3] \ (\mathbf{5}) + [(CO)_3Re(OH)(H_2O)_2] \ (\mathbf{6}) \rightarrow [(CO)_9(\mu\text{-}HO)_3(\mu_3\text{-}OH)Re_3]^- \ (\mathbf{3}) + H^+ + 3H_2O \quad (4')$$

however, clear that the final formation of the trinuclear **3**, having a μ_3-hydroxo bridge, requires an additional deprotonation and further structural rearrangements as well. In slightly acidic conditions, the formation of complex **3** is thermodynamically favored but slow, whereas the formation of the dinuclear triol **4** is less favored but much faster. This can be understood in terms of a high energy of activation required for the formation of the μ_3-hydroxo bridge.

The rapid addition of base to a solution of **2**, as performed in the fast titration experiment, results thus first in a very fast deprotonation, yielding the mononuclear products **6** and **7**. In an intermediate time range, the dimeric species **4** and **5** are formed, whereas in equilibrated solutions under neutral conditions, the thermodynamically stable trinuclear complex **3** predominates (Figure 5). These considerations are fully compatible with the observation that the trinuclear complex **3** can be isolated almost quantitatively as a crystalline solid from an equilibrated solution at pH 7, whereas rapid addition of at least 1.5 equiv of base to concentrated solutions of **2** resulted in a precipitation of **4** within a few seconds.

A related pH-dependent reactivity as reported here for **2** has been observed for the organometallic aqua complex $[Cp^*Rh(H_2O)_3]^{2+}$ by Fish and co-workers.[4] The first pK_a of this complex was found to be 5.3, indicating that the dipositive RhCp* species is only a slightly stronger acid than the monopositive Re complex **2**. In addition, the authors also provided evidence for the formation of corresponding dinuclear hydrolysis products $[Cp^*(H_2O)Rh(\mu\text{-}OH)_2Rh(H_2O)Cp^*]^{2+}$ and $[Cp^*Rh(\mu\text{-}OH)_3RhCp^*]^+$. It is noteworthy that the pathway of the hydrolytic polymerization of such organometallic species is in close analogy with the well-known hydrolytic behavior of many aqua ions and classical coordination compounds. A particularly interesting example is $[Co^{III}(tach)(H_2O)_3]^{3+}$ (tach = *all-cis*-1,3,5-triaminocyclohexane) investigated by Schwarzenbach and co-workers.[16] This complex, which has a similar arrangement of three facially coordinated water molecules, formed a series of mononuclear deprotonation products upon rapid addition of base. The consecutive formation of the dinuclear $[(tach)(H_2O)Co(\mu\text{-}OH)_2Co(H_2O)(tach)]^{4+}$ and $[(tach)Co(\mu\text{-}OH)_3Co(tach)]^{3+}$ was also established. However, there was no indication of the formation of the corresponding trimer. A significant difference between the reactivity of the $Re(CO)_3^+$ cation and the Co^{III}–tach system is the increased acidity and the much greater inertness of the aqua ligands in the Co complex. Schwarzenbach reported that many hours were needed to reach equilibrium for dimer formation. We note that, for the Re system, the dinuclear species are formed within seconds, whereas equilibration involving the trimer requires hours. It is thus quite possible that Schwarzenbach simply overlooked the formation of the trimer due to its very slow kinetics of formation.

The three CO ligands of the Re complex **2** proved to be inert under the conditions of the present investigation. They can thus be regarded as protecting groups which prevent unlimited aggregation and allow the isolation of complexes formed in the early stages of hydrolysis. Clearly, this is not the case for an unprotected aqua ion such as Cr^{3+}. It should, however, be noted that the first steps of Cr^{III} hydrolysis correspond quite closely to the hydrolysis of the Re–tricarbonyl system. A series of mononuclear deprotonation products $[Cr(OH)_x(H_2O)_{6-x}]^{3-x}$ as well as the dinuclear $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ and the trinuclear $[Cr_3(H_2O)_9(\mu\text{-}OH)_3(\mu_3\text{-}OH)]^{5+}$ have been identified in the first stages of hydrolysis.[17] A dinuclear corresponding to **4** has not been observed so far. This is understandable, since this species would require a higher pH, which in the case of Cr^{III} would lead to further aggregation.

Synthesis and Structure of $(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$ (9). Attempts were made to isolate the triaqua complex **2** from aqueous solution as a solid material. For this purpose, the tribromo derivative **1** was dissolved in water and bromide was precipitated by addition of 3 equiv of an appropriate silver salt to the solution. However, at high concentration, the labile water molecules were always substituted by the anion. Even when anions of low nucleophilicity such as trifluoroacetate were used, it was not possible to isolate the triaqua complex **2**. Evaporation of such solutions yielded a compound that was free of water but contained three trifluoroacetate moieties per rhenium, having the composition $(NEt_4)_2[Re(CO)_3(CF_3COO)_3]$. Crystals suitable for X-ray analysis were grown from dichloromethane/hexane. The crystal structure of the complex anion is presented in Figure 6, and structural parameters are summarized in Table 3. The Re center is coordinated by three carbonyl ligands and three O donors of three trifluoroacetate ligands. The Re–O distances are in close agreement with those reported for other Re^I complexes.[18] The other bond lengths also fall into expected ranges. The C–Re–C angles (average: 87.1°) are close 90°, as expected for octahedral coordination, but the O–Re–O angles (average 79.4°) are significantly diminished.

Formation and Isolation of Neutral Species. It would be of particular interest to obtain structural information for the neutral, dinuclear intermediate **5**, identified by the potentiometric titration experiments. Due to its uncharged nature, this complex is expected to be quite soluble in less polar solvents. According to

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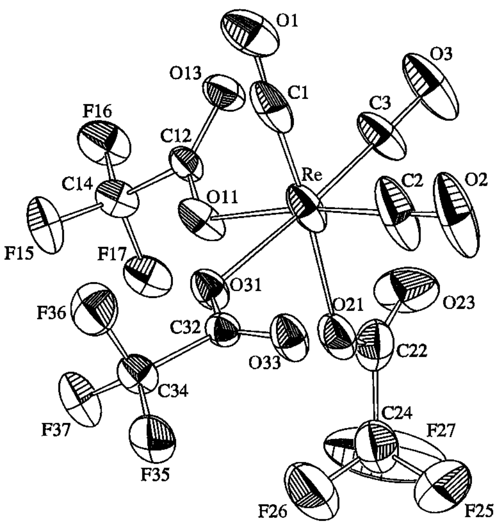

Figure 6. ORTEP drawing of **9** with numbering scheme and vibrational ellipsoids at the 50% probability level.

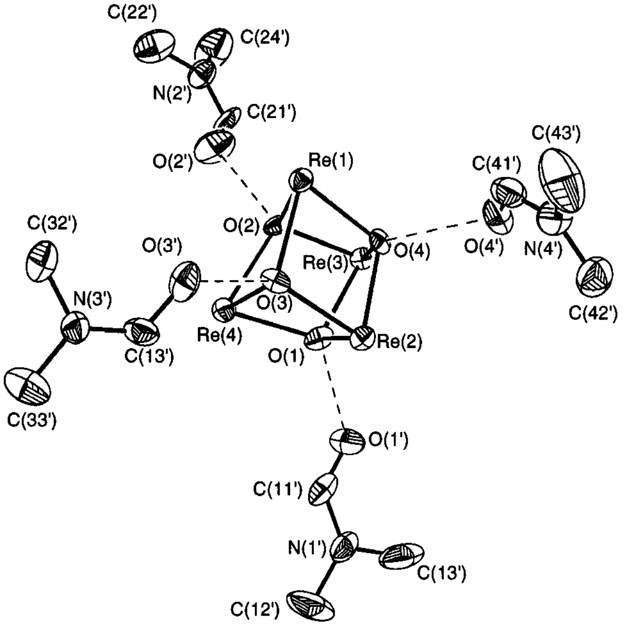

Figure 7. ORTEP drawing and numbering scheme of the $[Re_4(OH)_4]$ core of **8b** and the four DMF molecules which are attached to this core by hydrogen bonds. CO ligands and hydrogen atoms are omitted for clarity. Vibrational ellipsoids are at the 30% probability level.

the potentiometric study, **5** forms rapidly in neutral aqueous solution, whereas the consecutive reaction to the trimer **3** is much slower. We therefore tried to extract **5** from the aqueous reaction mixture to a less polar phase. Addition of diethyl ether together with 1 equiv of base to an aqueous solution of **1** did indeed result in quantitative extraction of a neutral Re complex **8a** of the composition $ReC_3O_5H_3$ into the organic phase. Recrystallization from DMF/H_2O yielded a crystalline material, suitable for single-crystal X-ray diffraction studies. The structure analysis revealed, however, that a tetranuclear complex of the composition $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]\cdot 4DMF$ (**8b**) had formed rather than the expected dinuclear $[Re_2(CO)_6(\mu\text{-}OH)_2(H_2O)_2]$ (**5**). Compound **8b** contains the well-known $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]$ cube (Figure 7), which was first prepared some 20 years ago by photolysis of $Re_2(CO)_{10}$ in the presence of hydroxide.[19] It has been reported that this complex is highly inert.[20] We therefore exclude the possibility that the cubane is already formed in the aqueous medium. It should be noted that the observed composition of the extracted compound **8a** can be formulated as $[Re(CO)_3(OH)(H_2O)]_n$, which is consistent not only with the hydrated cubane but also with the dimer $[Re_2(CO)_6(\mu\text{-}OH)_2(H_2O)_2]$. It is likely that the dimeric **5** is extracted into ether and that final aggregation to form the tetranuclear species **8** occurred in the organic phase. Furthermore, there is evidence that the cubane is formed rather rapidly in the organic medium. We repeated this experiment, adding triphenylphosphine to the ether solution shortly after extraction. If the dinuclear $[Re_2(CO)_6(\mu\text{-}OH)_2(H_2O)_2]$ were present for a sufficiently long time, the terminal water molecules would be expected to be substituted by the phosphines, and further aggregation should be suppressed. However, the crystal structure analysis revealed only the presence of the tetranuclear cubane as a $OPPh_3$ adduct (**8c**). Our results therefore indicate significantly different reaction pathways for the aqueous system and the less polar organic medium. In the ethereal solution, rapid dimerization of the dimer must occur within a few seconds, yielding the inert neutral $[Re_4(CO)_{12}(\mu_3\text{-}OH)_4]$ cube, whereas in aqueous solution the dimer reacts slowly with an additional 1 equiv of the monomer to give the anionic $[Re_3(CO)_9(\mu_2\text{-}OH)_3(\mu_3\text{-}OH)]^-$ (**3**) as the thermodynamically stable product.

Structures of 8b and 8c. Both compounds exhibit the well-known cubane-type structure with vertices that are occupied alternatively by hydroxide and $[Re(CO)_3]^+$ moieties. The hydroxo bridges form strong hydrogen bonds to the incorporated DMF or $OPPh_3$ molecules, respectively.[21] There are no significant structural differences between **8b** and **8c** on the one hand and the previously reported benzene adduct on the other.[19] The CO and the Re−C bond lengths lie all within expected ranges. The $Re-\mu_3\text{-}O-Re$ angles of 103.1(3)−105.8(3)° for **8b** and 102.5(7)° for **8c** indicate a significant distortion of the cube. This can be attributed to a considerable resistance of the oxygen atom to adopt a nontetrahedral geometry. Consequently, the O−Re−O angles are rather small (72.5(3)−74.5(3)° for **8b**, 75.8(9)° for **8c**).

Conclusions

The principal implications of our present work can be summarized as follows:

(1) We present for the first time a quantitative analysis of the entire hydrolytic reaction scheme (Scheme 1) of an organometallic aqua ion. On the basis of the experimentally determined formation constants, an exact calculation of the species distribution in aqueous solution as a function of the pH could be performed. Our investigation demonstrates that, although the formation of mononuclear deprotonation products occurred in a preliminary step, the polynuclear hydrolysis products **3** and **4** are of much higher stability and predominate in equilibrated complex solutions. This might be of

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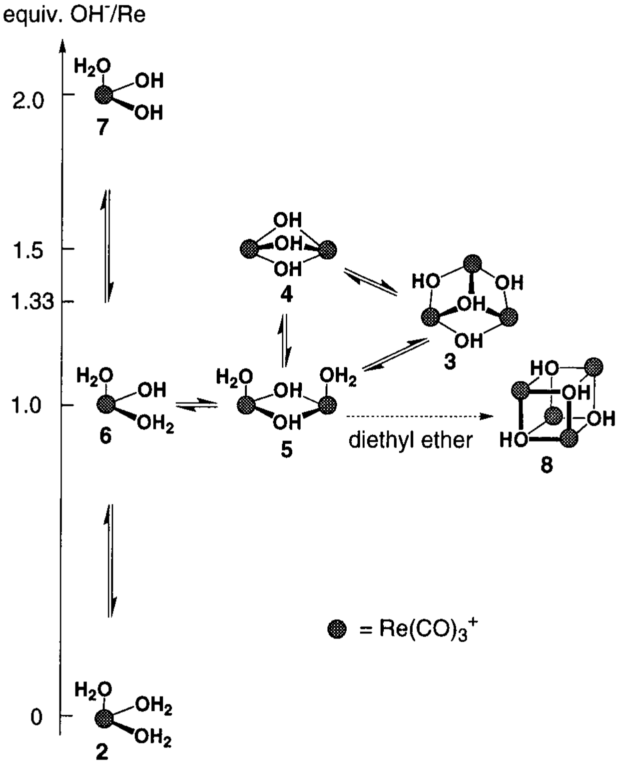
Scheme 1



importance, since such compounds are of considerable interest in materials science as precursors for mixed oxides of defined stoichiometry.[22]

(2) The elucidation of the hydrolytic pathway of **2** indicated a close analogy with the well-known hydrolysis of simple aqua ions and of other classical "Werner-type" complexes. It is unquestionable that many organometallic compounds are vulnerable toward oxidation and hydrolytic decomposition, and thus most protocols exclude oxygen and water. This fact has separated organometallic from aqueous chemistry for a long time. It is thus of interest to note that significant differences of hydrolytic polymerization can be observed in aqueous and nonaqueous media. This is clearly indicated by the hydrolysis of **2**, yielding anionic, dinuclear and trinuclear species in water, but the uncharged tetranuclear cubane in diethyl ether. We regard the rapid formation of the cubane as a dimerization of the neutral dinuclear intermediate, a process which was not observed at all in aqueous solution.

3) The coordination properties of the $Re(CO)_3^+$ moiety are remarkable and do not fit into the conventional HSAB classification. Due to the low oxidation state, the $5d^6$ electron configuration, and the presence of three carbonyl ligands, a soft behavior would be expected for this cation. The formation of stable complexes with soft donors like thioethers and phosphines is in fact well established.[23] However, compared with a typical soft, monopositive cation like Ag^+, we note a remarkably high affinity of $Re(CO)_3^+$ for the hard hydroxide ion (the equilibrium constant for the reaction $M^+ + OH^- \rightarrow MOH$ is 10^2 for Ag^+, but 2×10^6 for $Re(CO)_3^+$), whereas the soft Br^- showed no significant interaction with $Re(CO)_3^+$ ($K < 10$) in dilute aqueous solution (to be compared with a value of 2×10^4 for the corresponding equilibrium $Ag^+ + Br^- \rightarrow AgBr$).[24]

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Supporting Information Available: Listings of crystallographic data, atomic coordinates, anisotropic displacement parameters, positional parameters of hydrogen atoms, bond distances, and bond angles for **8b**,**c** and **9** (11 pages). Ordering information is given on any current masthead page. A table of calculated and observed structure factors is available from the authors upon request.

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