

bond distances of *anti*-**3** (2.289 (5) Å vs 2.247 (5) Å). All of the Re–S_{bridge} distances are slightly shorter than those in d²–d² *anti*-[Re(μ-S)(η⁵-C₅Me₃O)]₂ (2.343 (2) and 2.329 (1) Å).⁸

The Re–Re single-bond distance in *anti*-**3** is slightly longer than the Re–Re distance in *syn*-**3**, 2.871 (2) Å vs 2.759 (3) Å, respectively, and both distances are significantly longer than those found in *syn*-[Re(μ-O)OR]₂ compounds (R = CH₂CMe₃, 2.606 (1) Å;² R = CH₂CMe₂Ph, 2.6116 (7) Å;⁶ R = Me, 2.593 (1) Å).⁷

Conclusion

We have prepared *syn*-Re₂(μ-S)(μ-O)O₂(CH₂CMe₃)₄ and *syn/anti*-[Re(μ-S)O(CH₂CMe₃)₂]₂ from *syn*-[Re(μ-O)O(CH₂CMe₃)₂]₂ and H₂S. To our knowledge, these are the first examples of dinuclear Re(VI) sulfido compounds. We have also shown that *anti*-[Re(μ-S)O(CH₂CMe₃)₂]₂ is converted to the thermodynamically more stable *syn* form in hydrocarbon and

pyridine solutions, perhaps through a mononuclear Re(O)(S)-(CH₂CMe₃)₂ intermediate. The isomerization is reversible in pyridine. Synthetic efforts to trap the intermediate and redox studies of the [Re(μ-S)O(CH₂CMe₃)₂]₂ compounds, which have shown that reversible reduction reactions are possible, are in progress.

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Supplementary Material Available: Textual details of the X-ray structure determinations, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, and bond angles, an ORTEP plot of *syn*-[Re(μ-S)O(CH₂CMe₃)₂]₂ generated from the other crystallographically independent Re(μ-S)O(CH₂CMe₃)₂ unit, and packing diagrams for *syn*-[Re(μ-S)O(CH₂CMe₃)₂]₂ and *anti*-[Re(μ-S)O(CH₂CMe₃)₂]₂ (26 pages); structure factor tables (26 pages). Ordering information is given on any current masthead page.

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Hydrolytic Polymerization of Rhodium(III). 1. Preparation, Solution Studies, and X-ray Structure of the Doubly Bridged Dimer [(H₂O)₄Rh(μ-OH)₂Rh(OH₂)₄](dmtos)₄·8H₂O

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Several polynuclear Rh(III) species, formed on addition of excess base to solutions of [Rh(OH₂)₆]³⁺, have been separated by ion-exchange chromatography. Solution characterization studies, viz. charge (4+) and charge/Rh (2.1 (±0.1)), have confirmed that the doubly bridged hydrolytic dimer [(H₂O)₄Rh(μ-OH)₂Rh(OH₂)₄]⁴⁺ is one of the species formed. The UV–vis spectrum of the dimer shows an intense peak at 242 nm (ε ~ 1750 M⁻¹ cm⁻¹), which is attributed to an OH⁻ → Rh charge-transfer transition. Addition of dimer solutions to a pyridine buffer yields a fine yellow precipitate of the “active” dimer hydroxide of Rh(III), which consists of discrete dimer units and dissolves rapidly in acid to regenerate solutions of the hydrolytic dimer. Crystalline salts of the hydrolytic dimer of Rh(III) were obtained from concentrated dimer solutions prepared by dissolving the active hydroxide in either mesitylenc-2-sulfonic acid or *p*-toluenesulfonic acid. Electron microprobe and elemental analyses of the mesitylate salt were consistent with the composition [(H₂O)₄Rh(μ-OH)₂Rh(OH₂)₄][(H₃C)₃C₆H₂SO₃]₄·8H₂O. The complex crystallizes in the monoclinic space group *P*2₁/*c* with cell parameters *a* = 17.981 (8) Å, *b* = 9.324 (3) Å, *c* = 17.367 (5) Å, β = 96.40 (3)°, and *Z* = 2. Least-squares refinement of the structure gave a final *R* value of 0.048 for 3151 observed reflections. The structure consists of double layers of the anions with the SO₃⁻ groups pointing toward the complex cation. An extensive H-bonding network links the coordinated ligands, waters of crystallization, and SO₃⁻ groups. The nonbonded Rh...Rh and O...O distances within the bridging moiety are 3.030 and 2.645 Å, respectively, while the O–Rh–O and Rh–O–Rh angles within the bridge are 82.20 and 97.40°, respectively. The Rh–O bridging distances (1.999 (5) and 2.023 (5) Å) are somewhat shorter than the terminal Rh–O distances (2.028 (5)–2.068 (5) Å). The uncertainty in each distance makes it impossible to ascertain whether the OH⁻ bridges exert a significant trans influence.

Introduction

The hydrolytic polymerization of Cr³⁺ has been the subject of numerous investigations.^{1–10} A considerable amount of important, and much needed, information has been obtained about the structure and properties of a series of hydrolytic oligomers, in-

cluding both kinetic and thermodynamic data. The kinetic inertness of Cr(III) has been an important factor in the development of this chemistry, since this has enabled the isolation of a series of Cr(III) oligomers. The success of this work has stimulated our interest in following the hydrolytic behavior of other kinetically inert metal centers and has led us to initiate investigations of Rh³⁺. The diamagnetic nature of this metal center is an attractive feature that offers the opportunity to follow hydrolytic processes by ¹⁰³Rh and ¹⁷O NMR spectroscopy.

At present, very little is known about the hydrolytic polymerization of Rh(III), although the formation of polynuclear species has been postulated in the literature.^{11–14} Cola¹¹ and Ayres and Forrester¹² observed changes in the properties of partially neutralized solutions of [Rh(OH₂)₆]³⁺ with time, which they attributed to the formation of polynuclear species. Shukla¹³ in electrophoretic studies of the conversion of Rh(OH)₃·*x*H₂O into [Rh(OH₂)₆]³⁺ obtained evidence for species (possibly polynuclear) that were of

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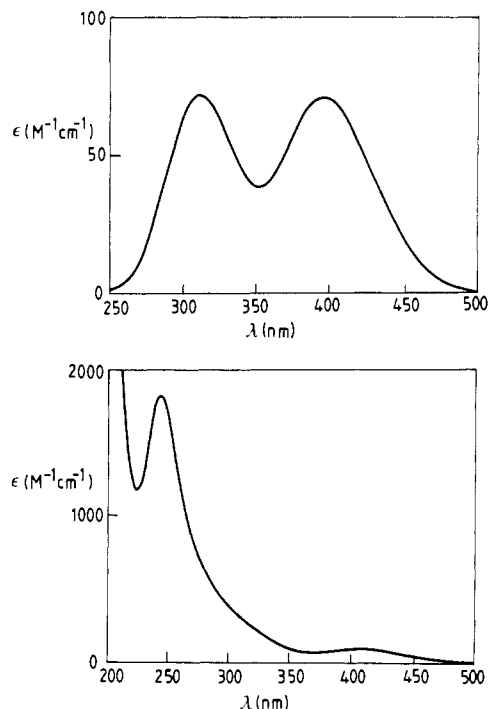


Figure 1. UV-vis spectra of (a) $[Rh(OH_2)_6]^{3+}$ in 0.5 M $NaClO_4$ + 0.02 M $HClO_4$ solution and (b) $[(H_2O)_4Rh(\mu-OH)_2Rh(OH_2)_4]^{4+}$ in 1 M $NaClO_4$ + 0.02 M $HClO_4$ with the same electrolyte as reference, recorded at 25 °C.

higher charge than the aqua ion. Moszner and Ziolkowski¹⁴ found that when solutions of $[(H_2O)_5Rh-Rh(OH_2)_5]^{4+}$ were exposed to air, the color changed from green through violet and finally to yellow. The cation-exchange behavior and UV-vis spectra of the yellow products indicated that they could be dimeric or polynuclear Rh(III) species. However, in none of these studies were the suggested polynuclear species isolated and fully characterized. In contrast, both singly and doubly bridged hydrolytic dimers of Ir(III) have been prepared by electrochemical methods and have been characterized in some detail.¹⁵

We report here initial investigations of the hydrolytic polymerization of Rh(III) that have led to the preparation and structural characterization of the doubly bridged dimer $[(H_2O)_4Rh(\mu-OH)_2Rh(OH_2)_4]^{4+}$. $[Rh(OH_2)_6](ClO_4)_3 \cdot 3H_2O$ has been a convenient starting material for this work because it is monomeric, both in solution¹⁶ and in the solid state.¹⁷ Moreover, its cation-exchange behavior and solution properties have facilitated the detection of polynuclear species.

Results

Preparation and Separation of Rh(III) Oligomers. Addition of excess base to solutions of $[Rh(OH_2)_6]^{3+}$ ($[Rh(III)] \sim 0.08$ M; pH ~ 13) gives a homogeneous solution whose composition changes with time. Chromatographic analysis of the aged solutions on Sephadex SP C25 (after acid had been added to quench the polymerization processes) not only confirmed the generation of new Rh(III) species but also allowed quantitative separation of each species. At the pH of elution (1.5–2.0) solutions of each fraction could be stored for several months below 0 °C and for several days at room temperature without change in composition.

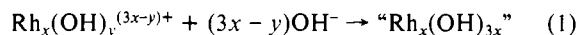
For an aging period in base of 2 min, the dominant fraction (ca. 80% of total Rh) was concluded to be $[Rh(OH_2)_6]^{3+}$ from its elution behavior and a comparison of the UV-vis spectrum with that of a $[Rh(OH_2)_6]^{3+}$ solution (Figure 1). Two other fractions, comprising <20% of total Rh, eluted after $[Rh(OH_2)_6]^{3+}$ and

probably contained polynuclear Rh(III) species with charge ≥ 3 . To increase the proportion of polynuclear species, longer aging periods were used. For a reaction time of 90 min, six fractions containing Rh(III) species and comprising 99% of total Rh were separated. Fraction 1 corresponded to $[Rh(OH_2)_6]^{3+}$ and contained only 9% of total Rh. Fractions 2 and 3 were predominant, comprising 42% and 20% of total Rh, respectively. So, these reactions conditions are attractive for obtaining reasonable yields of these fractions. Fractions 4–6 made up the Rh balance. After an aging period of 1 day, none of the products of the polymerization process could be eluted, even with 4 M $NaClO_4$ and 2 M $Ba(ClO_4)_2$.

Solution Characterization of the Doubly Bridged Hydrolytic Dimer. The Rh(III) species in fraction 2, which eluted after $[Rh(OH_2)_6]^{3+}$, was determined from the following measurements:

(i) **Comparison of the Elution Behavior with That of the Cr(III) Dimer and $[Rh(OH_2)_6]^{3+}$.** The Rh(III) species from fraction 2 was found to elute with the doubly bridged hydrolytic dimer of Cr(III) $(4+)^{2-4,8}$ and well after $[Rh(OH_2)_6]^{3+}$, suggesting an overall charge of 4+. This procedure has been used successfully in the characterization of two Ir(III) dimers,¹⁵ which were prepared by electrochemical methods.

(ii) **Determination of Charge/Rh Ratio.** This is obtained by titrating aliquots of fraction 2, of known $[H^+]$ (pH measurement) and $[Rh(III)]$, with standard NaOH. The titration relies on the quantitative precipitation of rhodium(III) hydroxides (in this case a dimeric hydroxide of rhodium(III); see later), which occurs in the pH range 6–10.¹⁸ The stoichiometry for the process is given by eq 1 (water ligands omitted for clarity). The amount of base



required to precipitate the hydroxide provides a measure of charge on the oligomer from which the charge/Rh can be determined (eq 2). For the Rh(III) species in fraction 2 a charge/Rh ratio

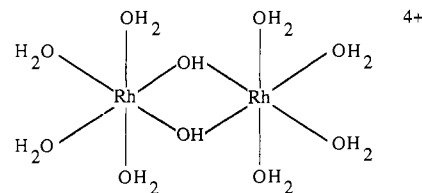
$$\text{charge/Rh} = \frac{3x - y}{x} = \frac{(\text{moles of } H^+)_{\text{titration}} - (\text{moles of } H^+)_{\text{pH}}}{\text{moles of Rh(III)}} \quad (2)$$

of 2.1 (± 0.1) was determined. A similar analysis on $[Rh(OH_2)_6]^{3+}$ gave, as expected, a charge/Rh ratio of 3.0 (± 0.1), confirming the suitability of the procedure. Note that the charge/Rh ratio can be obtained in this way even if polymerization occurs during titration.

If the results of the above measurements are combined, it can be concluded that the Rh(III) species in fraction 2 is dimeric (eq 3). The overall charge on this species further indicates that it

$$\text{nuclearity} = \text{charge}/(\text{charge/Rh}) = 1.9 (\pm 0.1) \quad (3)$$

is probably a doubly bridged dimer in which the two Rh centers are linked via two hydroxide bridges **1**, although an oxo-bridged form cannot be discounted at this stage.



(1) Doubly Bridged Rh(III) Dimer

The UV-vis spectra of $[Rh(OH_2)_6]^{3+}$ and the doubly bridged dimer are shown in Figure 1. The latter was recorded in acidified $NaClO_4$ (1 M; $[HClO_4] = 0.02$ M) with the same electrolyte as reference. The spectrum of $[Rh(OH_2)_6]^{3+}$ shows two peaks at 396 nm ($\epsilon = 62 M^{-1} cm^{-1}$) and 308 nm ($\epsilon = 66 M^{-1} cm^{-1}$), which

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(18) More than 99% of total Rh could be recovered as a precipitate by ultrafiltration through millipore membrane filters.

Table I. Crystal Data for $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4](\text{C}_6\text{H}_5\text{SO}_3)_4 \cdot 8\text{H}_2\text{O}$

chem formula $\text{C}_{26}\text{H}_{78}\text{O}_{30}\text{S}_4\text{Rh}_2$	space group $P2_1/c$ (No. 14)
$a = 17.981(8) \text{ \AA}^a$	$T = 20 \text{ }^\circ\text{C}$
$b = 9.324(3) \text{ \AA}^a$	$\lambda = 0.71073 \text{ \AA}$
$c = 17.367(5) \text{ \AA}^a$	$\rho_{\text{calcd}} = 1.52 \text{ g}\cdot\text{cm}^{-3}$
$\beta = 96.40(3)^\circ{}^a$	$\mu = 7.8 \text{ cm}^{-1}$
$V = 2893(2) \text{ \AA}^3$	$R(F_o) = 0.048$
$Z = 2$	$R_w(F_o) = 0.046$
$f_w = 1376$	

^a Cell parameters were derived by least-squares calculations from angular settings of 25 reflections measured between $5^\circ < 2\theta < 22^\circ$.
^b Due to the deliquescent nature of the compound, the density was not measured.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Rh	146 (1)	5368 (1)	5853 (1)	25 (1)
O(1)	233 (3)	4196 (5)	6870 (3)	36 (2)
O(2)	309 (3)	7211 (5)	6495 (3)	38 (2)
O(3)	1 (3)	3615 (5)	5166 (3)	31 (2)
O(4)	-974 (3)	5513 (6)	5900 (3)	32 (2)
O(5)	1274 (3)	5261 (6)	5822 (3)	31 (2)
S(1)	1999 (1)	6471 (3)	2750 (1)	39 (1)
O(6)	1702 (3)	7152 (7)	2021 (3)	61 (3)
O(7)	1961 (3)	7377 (6)	3426 (3)	53 (2)
O(8)	1638 (3)	5089 (6)	2846 (3)	44 (2)
C(1)	2964 (4)	6062 (9)	2707 (5)	36 (3)
C(2)	3339 (5)	6381 (10)	2063 (5)	43 (3)
C(21)	2991 (5)	7277 (13)	1354 (5)	79 (5)
C(3)	4064 (5)	5906 (10)	2038 (6)	56 (4)
C(4)	4434 (5)	5137 (11)	2634 (6)	62 (4)
C(41)	5241 (5)	4592 (13)	2592 (7)	100 (5)
C(5)	4084 (5)	4895 (10)	3282 (6)	61 (4)
C(6)	3350 (5)	5348 (11)	3326 (5)	47 (3)
C(61)	2994 (5)	5036 (11)	4096 (5)	76 (5)
S(2)	2016 (1)	3386 (2)	71 (2)	42 (1)
O(9)	1724 (3)	2989 (7)	-721 (3)	56 (2)
O(10)	1830 (3)	4834 (6)	278 (4)	67 (3)
O(11)	1765 (3)	2348 (6)	615 (3)	53 (2)
C(7)	3020 (5)	3265 (9)	145 (5)	39 (3)
C(8)	3400 (5)	3678 (11)	-478 (6)	53 (4)
C(81)	3020 (6)	4401 (14)	-1199 (6)	112 (6)
C(9)	4155 (5)	3484 (11)	-453 (6)	63 (4)
C(10)	4556 (5)	2915 (11)	188 (6)	56 (4)
C(101)	5399 (5)	2640 (14)	188 (7)	96 (6)
C(11)	4191 (5)	2567 (11)	809 (6)	64 (4)
C(12)	3440 (5)	2741 (10)	805 (5)	50 (4)
C(121)	3115 (5)	2371 (14)	1576 (6)	88 (5)
O(12)	1101 (4)	5078 (7)	8088 (4)	83 (3)
O(13)	879 (3)	3383 (6)	1682 (3)	55 (2)
O(14)	-26 (4)	5325 (7)	799 (4)	77 (3)
O(15)	1416 (3)	7461 (6)	4831 (3)	46 (2)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

correspond well with previous literature reports.¹²⁻¹⁴ For the doubly bridged Rh(III) dimer, peaks were observed at 408 nm ($\epsilon = 96 \pm 3 \text{ M}^{-1} \text{ cm}^{-1}$) and 242 nm ($\epsilon = 1750 \pm 60 \text{ M}^{-1} \text{ cm}^{-1}$).

Preparation and Analysis of the "Active" Dimer Hydroxide of Rhodium(III). The addition of a chromatographically pure solution of the doubly bridged dimer of Rh(III) (also containing excess NaClO_4 and some HClO_4) to a pyridine solution results in the quantitative precipitation (>99%) of a finely dispersed yellow solid. Samples of this hydroxide dissolved instantaneously in dilute acid (0.02 M HClO_4). Chromatographic analysis of this solution gave one band comprising >99% of total Rh. The UV-vis spectrum before and after chromatography corresponded to that of doubly bridged dimer (Figure 1). These analyses confirmed that the hydroxide, hereafter called the active dimer hydroxide of Rh(III), consists of discrete dimer units. As in the case of several chromium(III) hydroxides,^{5,7,8} the term active is intended to reflect the ease of dissolution of the material in acid to regenerate the starting oligomer. The greater purity of the active

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

Rh-O(1)	2.068 (5)	Rh-O(2)	2.052 (5)
Rh-O(3)	2.023 (5)	Rh-O(4)	2.028 (5)
Rh-O(5)	2.039 (5)	Rh-O(3A)	1.999 (5)
Rh-Rh(A)	3.030 (2)	O(3)-Rh(A)	1.999 (5)
S(1)-O(6)	1.462 (6)	S(1)-O(7)	1.456 (6)
S(1)-O(8)	1.461 (6)	S(1)-C(1)	1.787 (8)
S(2)-O(9)	1.463 (6)	S(2)-O(10)	1.447 (6)
S(2)-O(11)	1.459 (6)	S(2)-C(7)	1.800 (9)
O(1)-Rh-O(2)	89.2 (2)	O(1)-Rh-O(3)	94.0 (2)
O(2)-Rh-O(3)	176.6 (2)	O(1)-Rh-O(4)	89.0 (2)
O(2)-Rh-O(4)	90.3 (2)	O(3)-Rh-O(4)	90.9 (2)
O(1)-Rh-O(5)	90.9 (2)	O(2)-Rh-O(5)	88.4 (2)
O(3)-Rh-O(5)	90.4 (2)	O(4)-Rh-O(5)	178.7 (2)
O(1)-Rh-O(3A)	175.3 (2)	O(2)-Rh-O(3A)	94.6 (2)
O(3)-Rh-O(3A)	82.2 (2)	O(4)-Rh-O(3A)	88.3 (2)
O(5)-Rh-O(3A)	91.9 (2)	Rh-O(3)-Rh(A)	97.8 (2)
O(6)-S(1)-O(7)	113.7 (4)	O(6)-S(1)-O(8)	111.0 (3)
O(7)-S(1)-O(8)	110.9 (3)	O(6)-S(1)-C(1)	108.7 (4)
O(7)-S(1)-C(1)	106.9 (4)	O(8)-S(1)-C(1)	105.2 (3)
S(1)-C(1)-C(2)	122.9 (6)	S(1)-C(1)-C(6)	118.5 (6)
O(9)-S(2)-O(10)	113.7 (4)	O(9)-S(2)-O(11)	109.7 (4)
O(10)-S(2)-O(11)	111.2 (4)	O(9)-S(2)-C(7)	107.6 (4)
O(10)-S(2)-C(7)	107.4 (4)	O(11)-S(2)-C(7)	107.0 (4)
S(2)-C(7)-C(8)	120.1 (6)	S(2)-C(7)-C(12)	122.0 (7)

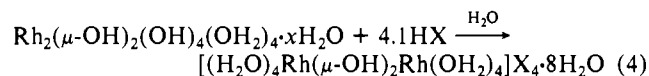
Table IV. Hydrogen Bond Lengths (Å)^a

O(1)···O(12) ⁱ	2.618 (8)	O(2)···O(14) ⁱⁱⁱ	2.634 (8)
O(1)···O(13) ⁱⁱ	2.706 (8)	O(2)···O(6) ⁱⁱⁱ	2.635 (7)
O(3)···O(15) ^{iv}	2.734 (8)	O(4)···O(8) ^{iv}	2.657 (7)
O(5)···O(11) ⁱ	2.626 (8)	O(4)···O(9) ⁱ	2.675 (8)
O(5)···O(15) ⁱⁱ	2.708 (8)	O(13)···O(11) ⁱ	2.749 (9)
O(12)···O(7) ⁱⁱⁱ	2.856 (9)	O(13)···O(14) ^j	2.779 (9)
O(12)···O(14) ^{iv}	2.907 (10)	O(13)···O(14) ^j	2.806 (7)
O(12)···O(9) ^v	2.968 (9)	O(15)···O(10) ⁱⁱⁱ	2.718 (8)
O(14)···O(14) ⁱⁱ	2.852 (13)	O(15)···O(7) ⁱ	2.729 (8)

^a Symmetry key: (i) *x*, *y*, *z*; (ii) *x*, $1/2 - y$, $1/2 + z$; (iii) *x*, $3/2 - y$, $1/2 + z$; (iv) \bar{x} , $1 - y$, $1 - z$; (v) *x*, *y*, $1 + z$.

dimer hydroxide of rhodium(III) (>99%) when compared with the analogous chromium(III) active dimer hydroxide (96%)⁷ is probably a reflection of the greater kinetic inertness of Rh(III).

Preparation and Analysis of $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4](\text{dmtos})_4 \cdot 8\text{H}_2\text{O}$. Crystalline salts of the hydrolytic dimer of Rh(III) were obtained from solutions of the dimer that had been prepared by dissolving the active hydroxide in a slight excess (necessary to avoid polymerization during preparation) of either mesitylene-2-sulfonic acid (Hdmtos) or *p*-toluenesulfonic acid (Htos). The chemistry is summarized in eq 4. The same ap-



X = dmtos, tos

proach was used in the preparation of the analogous Cr(III) dimer,⁸ where it was also found that these salts could not be obtained directly from hydrolytic dimer solutions because of the precipitation of copious amounts of electrolyte, introduced during chromatographic procedures.

Analyses of the dmtos salt, viz. a constant S/Rh ratio of 2/1 (electron microprobe) and a Rh content of 15.6 (± 0.2)%, were consistent with the proposed composition, which was subsequently confirmed by single-crystal X-ray diffraction.

Description of Crystal Structure. The molecular geometry and atomic labeling scheme of $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4](\text{dmtos})_4 \cdot 8\text{H}_2\text{O}$ are shown in Figure 2, and an expanded view of the dimeric cation is shown in Figure 3. Crystal data, atomic coordinates and equivalent isotropic displacement coefficient, bond lengths, bond angles, and significant H-bonding distances ($\text{O}\cdots\text{O}$) < 3 Å are given in Tables I-IV.

The X-ray structure confirms the dimeric nature of the complex cation (Figure 3). The cation consists of two Rh centers linked via two bridging groups, which, from the stoichiometry of the

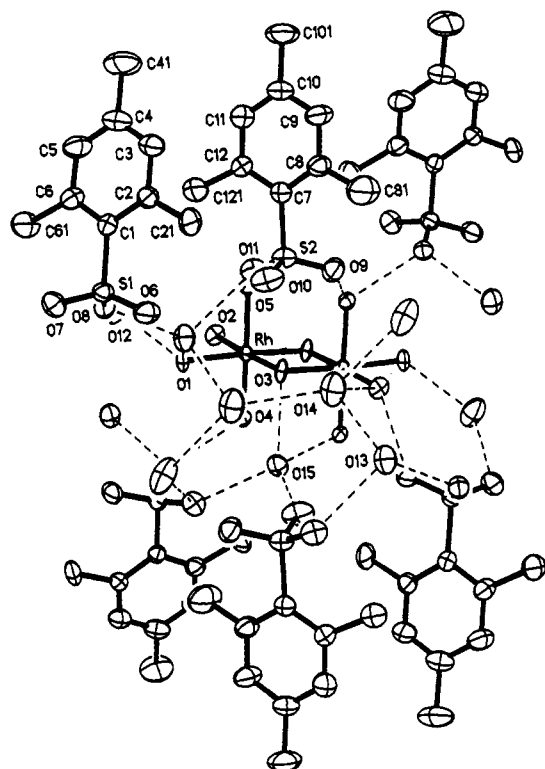


Figure 2. Structure of $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4](\text{dmtos})_4 \cdot 8\text{H}_2\text{O}$, showing the atom-numbering scheme and H-bonding network (dotted lines). Only O...O distances below 3.0 Å were considered to represent H bonds. The ellipsoid probability is 50%.

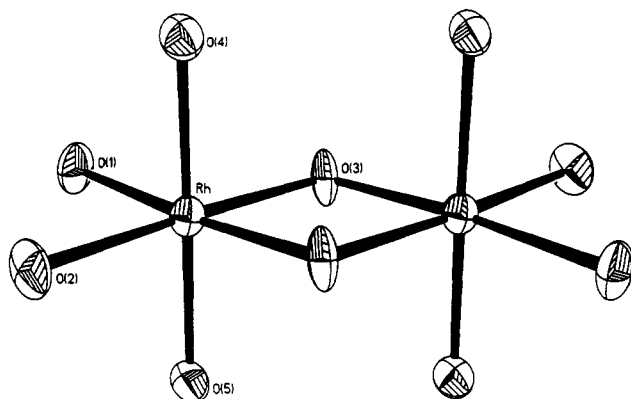


Figure 3. Diagram showing an expanded view of the dimeric cation $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4]^{4+}$.

complex and Rh oxidation state, can be assigned as OH^- groups. In the crystal, the cation and waters of crystallization are arranged in layers parallel to the bc plane and the anions form double layers with the SO_3^- groups being directed toward the cations. An intimate network of H-bonding exists between the SO_3^- groups, waters of crystallization, and coordinated H_2O and OH^- ligands (Figure 2). As can be seen in Table IV, a number of these H-bonds are moderately strong with O...O distances between 2.62 and 2.71 Å. There is no evidence that suggests the presence of intramolecular H-bonding between any of the ligands.

The $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4]^{4+}$ cation has a crystallographic center of symmetry ($\bar{1}$) situated at the midpoint of the Rh_2O_2 bridging unit. As in the case of the Cr(III) dimer,⁷ the bridging moiety gives rise to a distorted octahedral environment about each Rh(III) center. The O(3)-Rh-O(3a) angles within the bridging unit (82.2°) are smaller than expected for an ideal octahedral geometry. To compensate for this, the angles adjacent to the bridging unit O(2)-Rh-O(3a) and O(1)-Rh-O(3) are about 94° , with no change in the angle trans to the bridging unit. As a consequence of this and the planarity of the bridging moiety, the Rh-O(3)-Rh angle (97.4°) is smaller than that found in the

Cr(III) dimer (101.8°).⁷ On average, the Rh-OH distances (1.999 (5) and 2.023 (5) Å) are about 0.04 Å shorter than Rh-OH₂ distances (2.028 (5)-2.068 (5) Å), while the nonbonded Rh...Rh and O...O distances are 3.030 (2) and 2.645 (6) Å, respectively.

Discussion

The transformation of mononuclear Rh(III) species into polynuclear species in alkaline solutions, pH \sim 13, has been followed over a period of 1 day. During this time mononuclear Rh(III) species are converted into polynuclear species, which after acidification cannot be separated by chromatographic methods, and some finely dispersed solid is formed. However, the isolation of several Rh(III) polynuclear species has been possible after intermediate aging periods (0-120 min). The behavior of alkaline Rh(III) solutions parallels that of Cr(III), although polymerization is significantly faster for Cr(III), where almost all Cr(III) (98%) is transformed into polynuclear species during mixing⁸ compared with 20% for Rh(III). The difference in reactivity is attributable to the greater kinetic inertness of Rh(III) compared Cr(III). This is also manifested in acidic solution where preliminary measurements of the conversion of the doubly bridged Rh(III) dimer into the singly bridged form have shown that this process ($t_{1/2} \sim$ 6 weeks in 1 M HClO_4 at 25 °C) is about 3 orders of magnitude slower than for the corresponding Cr(III) dimer ($t_{1/2} \sim$ 1 h).¹⁹ The greater kinetic inertness of Rh(III) provides a clear advantage over Cr(III) in the isolation and characterization of further Rh(III) oligomers, which is currently in progress.

Solution studies have shown that a dimer, viz. charge (4+), charge/Rh (2.1 \pm 0.1), and nuclearity (1.9 \pm 0.1), is one of the early products of hydrolytic polymerization of Rh(III) in alkaline solutions, and this has been confirmed by the molecular structure of $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4](\text{dmtos})_4 \cdot 8\text{H}_2\text{O}$. The structure of this complex closely resembles that of the analogous Cr(III) dimer⁷ particularly with respect to the arrangement of anions and cations, the existence of a strong H-bonding network, and the number of OH^- bridges and terminal H_2O ligands. The M-O distances in the Rh(III) dimer are 0.05-0.25 Å longer than in the Cr(III) dimer⁷ but 0.05-0.25 Å shorter than those found in the Sc(III) dimer, $[(\text{H}_2\text{O})_5\text{Sc}(\mu\text{-OH})_2\text{Sc}(\text{OH}_2)_5]^{4+}$.²⁰ The variation in bond lengths and angles within these dimeric units reflects the difference in ionic radii of the metal centers, viz. 0.665 Å for Rh(III), 0.615 Å for Cr(III), and 0.745 Å for Sc(III),²¹ and the pentagonal bipyramidal geometry adopted by Sc(III). The Rh-O distances, and uncertainty in each distance (esd = 0.005 Å), are such that it is not clear whether the bridging OH^- groups influence the Rh-OH₂ distances directly trans to them. The participation of bridging OH^- and H_2O ligands in H-bonding, is a further complicating factor (Table IV). Nevertheless, the Rh-O distances do vary in a systematic manner. The longest Rh-OH₂ bond (2.068 (5) Å) is trans to the shortest Rh-OH bond (1.999 (5) Å), while that trans to the other Rh-OH bond is 2.052 (5) Å and the two Rh-OH₂ distances trans to each other are 2.028 (5) and 2.039 (5) Å.

In the UV-vis spectrum of the doubly bridged Rh(III) dimer (Figure 1) the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition is observed at lower energy (408 nm) than for $[\text{Rh}(\text{OH}_2)_6]^{3+}$. The shift in position reflects the weaker field strength of OH^- compared to H_2O .²² Another d-d transition ($^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$) is expected at ca. 300 nm but is masked by a stronger transition at 242 nm ($\epsilon = 1750 \text{ M}^{-1} \text{ cm}^{-1}$), which probably corresponds to a L \rightarrow M charge transfer from OH^- to Rh. The spectrum of $[\text{RhCl}_6]^{3-}$ exhibits a $\text{Cl}^- \rightarrow \text{Rh}$ charge-transfer peak of similar intensity at 244 nm.²³ The spectrum of $[\text{Rh}(\text{OH}_2)_6]^{3+}$ was also measured at pH \sim 4, where significant amounts of either $[\text{Rh}(\text{OH})(\text{OH}_2)_5]^{2+}$ or $[\text{Rh}$

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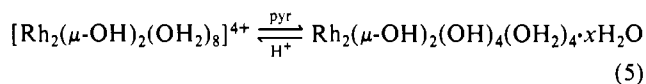
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$(\text{OH})_2(\text{OH}_2)_4]^+$ are likely to be present ($pK_a \sim 3.2^{24}$), and although a clearly defined peak was not observed, an intense absorption developed below 280 nm. This may be due to $L \rightarrow M$ charge transfer that results from the presence of coordinated OH^- .

Neutralization of solutions of the Rh(III) dimer results in the precipitation of the active dimer hydroxide of rhodium(III) (eq 5). The properties of this material indicate that it consists of



uncharged dimer units formed by deprotonation of four terminal H_2O ligands in $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4]^{4+}$. This is not unreasonable, since previous work on the Cr(III) dimer suggests that deprotonation of bridging OH^- groups is more difficult.^{7,25} Addition of acid to the active dimer hydroxide of rhodium(III) results in protonation of terminal OH^- groups and immediate regeneration of solutions of the dimer (eq 5). Thus, this hydroxide has been a convenient precursor for the preparation of crystalline salts. The behavior of the Rh(III) dimer parallels closely that of Cr(III) oligomers, where active hydroxides derived from Cr^{3+} , dimer and trimer, are known.^{5,7,8} We stress, once again, that this is not a common occurrence in the chemistry of freshly precipitated metal hydroxides and that, in general, addition of acid to these types of hydroxides results in quite rapid formation of the aqua ions, $[\text{M}(\text{OH}_2)_6]^{n+}$. The successful isolation of the active hydroxides derived from Rh(III) and Cr(III) oligomers has been possible because of the slow rate of substitution at these centers. Thus, although deprotonation/protonation processes are rapid, subsequent polymerization and acid cleavage processes are slow, allowing the isolation of metastable oligomers (either as solids or in solution) that are intermediates in the polymerization of metal ions.

Experimental Section

Materials. $[\text{Rh}(\text{OH}_2)_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ was prepared from rhodium trichloride (Johnson-Matthey) by the method of Ayres and Forrester.²⁶ All other materials were of laboratory reagent grade or better and were used as received. However, analytical grade reagents were used for quantitative measurements. All solutions were prepared with distilled water and were filtered through 0.22- μm Durapore GVWP membrane filters (Millipore) prior to use.

Instruments and Methods. UV-vis spectra were recorded on either a Varian Superscan 3 or a Hitachi 150-20 double-beam spectrophotometer. The cell compartment in the Superscan 3 instrument was maintained at $25.0 (\pm 0.1)^\circ\text{C}$ by circulating water from a Haake D8 thermostat. Electron microprobe analyses for Rh and S were carried out on a Joel JSM-840A scanning microscope connected through a NEC X-ray detector and pulse-processing system to a Link Systems 860 analyzer. Samples were mounted on aluminum planchettes and coated with carbon by using a Balzers Union CED 010 carbon sputterer. The procedure for pH measurement has been described previously.³

Generation of Rh(III) Oligomers. Solutions of Rh(III) were prepared by dissolving about 1 g of $[\text{Rh}(\text{OH}_2)_6](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ in 20 mL of 1.0 M NaOH, giving $[\text{Rh}(\text{III})] \sim 0.08$ M and $\text{pH} \sim 13$. These homogeneous solutions were then allowed to stand for either 2 or 90 min. The reaction was quenched by acidification to $\text{pH} \sim 1.5$ with HClO_4 (1 M) and stored at -18°C until required for analysis.

Separation of Rh(III) Oligomers. The procedure described here refers to solutions aged for 90 min, since this reaction time produced a wider range of oligomers. Typically, the Rh(III) solution (20 mL) obtained as described above was diluted to 200 mL with 0.02 M HClO_4 and absorbed onto a Sephadex SP C25 cation-exchange column (H^+ form, 10×2 cm) and the column washed thoroughly with water. On addition of 25 mL of 0.5 M NaClO_4 (all electrolytes contained 0.02 M HClO_4 to suppress the possible polymerization of Rh(III) oligomers) the first fraction separated from other Rh(III) species and was collected. Two further fractions were eluted separately on addition of 30 mL of 1 M NaClO_4 followed by 30 mL of 2 M NaClO_4 . Three further fractions were obtained on elution with 4 M NaClO_4 . Small amounts of other Rh(III) species remained on the column and could not be eluted even with 2 M $\text{Ba}(\text{ClO}_4)_2$.

A small-scale experiment was carried out to determine the yield of each fraction. The same Rh(III) solution (1 mL) was diluted with 0.02 M HClO_4 (20 mL) and absorbed onto a Sephadex SP C25 column (5×1 cm). The Rh(III) species were then eluted as before, except that fractions 5 and 6 were collected together. The rhodium content of each fraction was determined spectrophotometrically at 470 nm ($\epsilon = 4.24 (\pm 0.04) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) following treatment of the Rh(III) solutions with a solution of SnCl_2 in hydrochloric acid (2 M).²⁷ The percentage of total Rh present in each fraction is as follows: (1) 9%; (2) 42%; (3) 29%; (4) 12%; (5 and 6) 7%; 1% for higher oligomers.

Chromatographic analysis of solutions that had been aged in base for 2 min gave three fractions on elution with increasing concentrations of NaClO_4 (0.5–2 M), of which fraction 1 comprised 80% of total Rh.

Characterization of Fraction 2. Solutions of fraction 2 were purified and concentrated by ion-exchange chromatography prior to use in characterization studies.

(i) Elution Behavior. The elution behavior of fraction 2 was compared to that of the doubly bridged hydrolytic dimer of Cr(III),⁸ $[\text{Cr}_2(\mu\text{-OH})_2(\text{OH}_2)_8]^{4+}$. A mixture of fraction 2 (2 mL, 0.05 M), the Cr(III) dimer (0.2 mL, 0.05 M), and $[\text{Rh}(\text{OH}_2)_6]^{3+}$ (0.5 mL, 0.05 M) was diluted to 100 mL (0.02 M HClO_4) and absorbed onto Sephadex SP C25 (H^+ form, 3×1 cm). A light yellow band separated from the other species on elution with 0.5 M NaClO_4 . It was collected and identified as $[\text{Rh}(\text{OH}_2)_6]^{3+}$ from its UV-vis spectrum.^{12,13,19} The yellow Rh(III) and blue Cr(III) dimer fractions that remained on the column eluted together on addition of 1 M NaClO_4 .

(ii) Charge/Rh Determination. Solutions of fraction 2 and $[\text{Rh}(\text{OH}_2)_6]^{3+}$ (analyzed to check the suitability of the procedure) were diluted to give solutions with $\text{pH} \sim 2.0$ – 2.2 and $I = 1.0$ M. The pH and $[\text{Rh}(\text{III})]$ were determined for each solution. Aliquots of each solution were then titrated with standardized NaOH, by using phenolphthalein as the indicator while the solution was maintained at 0°C in an ice bath. This indicator was chosen because it undergoes a color change in the pH region where these rhodium(III) hydroxides are most insoluble. From this titration the sum of the free acid present in solution and the acid generated by deprotonation of the Rh(III) species to give the active hydroxides was determined and used to calculate the charge/Rh ratio (see Results).

Preparation of the Active Dimer Hydroxide. The active hydroxide derived from fraction 2, proposed to be a doubly bridged Rh(III) dimer (see Results), was prepared by slow addition of an ice-cold solution of fraction 2, $[\text{Rh}(\text{III})] \sim 0.05$ M, to an ice-cold pyridine solution (0.25 M). The final suspension pH was 6. As in the case of the active chromium(III) hydroxides,^{7,8} low temperatures were used to reduce contamination of the product with higher oligomers. The precipitate was separated by centrifugation, resuspended twice in cold water and once in acetonitrile, and each time separated by centrifugation. Finally, it was suspended in acetonitrile, filtered through millipore membrane filters, dried in a stream of air, and then stored at -18°C until required.

The purity of the active hydroxide was checked by ion-exchange chromatography.⁸ The active hydroxide (0.02 g) was dissolved in 0.02 M HClO_4 (10 mL), and the solution was absorbed onto a Sephadex SP C25 column (H^+ form, 3×0.5 cm) and then eluted with NaClO_4 (0.5–2.0 M). The Rh on the column eluted as one band, no other Rh(III) species were present, and the UV-vis spectrum of the solution before and after chromatography was identical with that of fraction 2. The IR spectrum of the active hydroxide showed the presence of traces of ClO_4^- .

Preparation of $[(\text{H}_2\text{O})_4\text{Rh}(\mu\text{-OH})_2\text{Rh}(\text{OH}_2)_4(\text{dmtos})_4] \cdot 8\text{H}_2\text{O}$. The active dimer hydroxide (ca. 0.065 g, 0.17 mmol) was dissolved in an aqueous solution containing 0.17 g (0.7 mmol) of mesitylene-2-sulfonic acid dihydrate, at ambient temperature. After dissolution was complete the resulting solution was filtered, evaporated to ca. 3 mL under reduced pressure (Rotavap), and then stored at 2°C . Small yellow plates formed within 2 days. These were collected and washed once with ice-cold dilute mesitylene-2-sulfonic acid (0.01 M). Yield: 0.12 g (53%).

Analyses. The Rh content of the complex, 15.6 (± 0.2)%, compared well with a calculated value of 15.56% for $\text{C}_{36}\text{H}_{78}\text{O}_{30}\text{S}_4\text{Rh}_2$. Electron microprobe analysis indicated that the product was of constant composition with a S/Rh ratio of 2. The UV-vis spectrum recorded after chromatographic exchange of the sulfonate (absorbs strongly in the UV region) by ClO_4^- was identical with that of pure dimer solutions (Figure 1).

Substitution of *p*-toluenesulfonic acid hydrate (ca. 0.12 g, 0.7 mmol) in the above synthesis gave the corresponding "dimer tosylate" in a yield of 0.10 g.

Crystal Structure Determination. A representative light yellow tabular crystal mounted in a Lindemann glass capillary was used for data col-

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lection. Intensity measurements were made on a Nicolet R3m/V diffractometer using graphite-monochromated Mo K α radiation with $3.5^\circ < 2\theta < 50^\circ$, operating in an ω -scan mode with a scan range of 1.20° , at a scan rate between 3.00 and $15.00^\circ \text{ min}^{-1}$. A total of 5091 unique data were collected ($\pm h, +k, +l$), 3151 of which were considered to be observed [$F \geq 6\sigma(F)$]. Three standard reflections monitored every 197 reflections showed no significant variation in intensity over the data collection period. No absorption correction was applied because the faces of the crystal were poorly defined and difficult to identify. Intensity data were corrected for Lorentz and polarization effects. The atomic scattering factors for neutral atoms were taken from ref 28 and were corrected for anomalous dispersion. All calculations were performed on a MicroVAX 2000 computer. The program used for least-squares refinement was that due to Sheldrick.²⁹

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The structure was solved by Patterson methods. Full-matrix least-squares refinement employing anisotropic thermal parameters for all non-hydrogen atoms and a single-variable isotropic thermal parameter for hydrogen that refined to $0.17 (1) \text{ \AA}^2$, located in geometrically idealized positions (C–H = 0.96 \AA), reduced R to 0.048 and R_w to 0.046 , respectively, at convergence, where $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w(|F_o|)^2)^{1/2}$ and $w = [\sigma^2(F_o)]^{-1}$. The goodness of fit value $(\sum w(|F_o| - |F_c|)^2 / (N_{\text{observs}} - N_{\text{params}}))^{1/2}$ was 2.22 . The largest peak in the difference Fourier synthesis was 0.80 e \AA^{-3} .

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Supplementary Material Available: Tables of all bond lengths (Table S1) and bond angles (Table S2), anisotropic displacement coefficients (Table S3), and hydrogen atom coordinates (Table S4) and a unit cell and crystal packing diagram of the Rh(III) dimer (Figure S1) (5 pages); a listing of observed and calculated structure factors (Table S5) (18 pages). Ordering information is given on any current masthead page.

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Photochemical Generation of Reactive Transition-Metal Intermediates from Air-Stable Precursors. Carbon–Hydrogen Bond Activation via Near-Ultraviolet Photolysis of Cp*Ir(L)(oxalate) and Cp*Ir(L)(N₃)₂ Complexes

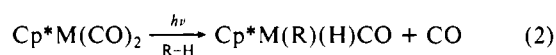
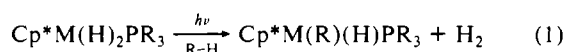
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We have synthesized several new oxalate and azide complexes of the form Cp*Ir(Ox)L (Cp* = pentamethylcyclopentadienyl, Ox = oxalate and L = P(Me)₃, P(Cy)₃) and Cp*Ir(N₃)₂L (L = P(Me)₃, P(Ph)₃, P(Cy)₃, and *t*-BuNC) respectively. Upon photolysis, these complexes undergo reactions that result in the elimination of CO₂ or N₂ to give reactive intermediates that undergo net oxidative-addition reactions with C–H and C–Cl bonds. We have observed either intermolecular (reaction with solvent) or intramolecular (reaction with a ligand bond) oxidative addition to the Ir center. For photolysis of the azide complexes in benzene solutions, the mode of reaction is determined by L. An exclusively intermolecular reaction is observed when L = P(Me)₃, while products indicative of inter- and intramolecular reactivity are observed with P(Ph)₃. The P(Cy)₃ complexes produce two different orthometalated complexes we identify as the *cis* and *trans* isomers, which arise from activation of either the axial or equatorial hydrogen on the α carbon of a cyclohexyl ring. Photolysis of the oxalate complexes in CCl₄, CHCl₃, or CH₂Cl₂ produces the corresponding dichloride. For the photolysis of Cp*Ir(Ox)(P(Me)₃) in CHCl₃ and CH₂Cl₂, intermediates are observed. These intermediates result from the initial oxidative addition of C–Cl bonds of the solvent. The quantum yields for the oxalate photochemical reactions with halocarbons are in the range 0.02 – 0.28 . For the azide complexes, the identity of L has little effect on the quantum yield. Similar quantum yields are observed for reaction in C₆H₆, CHCl₃, and CH₂Cl₂; substantially larger quantum yields are observed for CCl₄ solutions. In the case of the oxalate complexes, the quantum yield correlates inversely with the hydrogen-bonding ability of the solvent, resulting in the curious quantum yield ordering CHCl₃ \approx CH₂Cl₂ $<$ C₆H₆. IR spectral data indicate significant shifts for the $\nu(\text{CO})$ frequencies of the oxalate bands in solvents of even moderate H-bonding ability. We suggest that H-bonding enhances nonradiative excited-state decay, which controls the quantum yields of the oxalate complexes. The enhanced reactivity observed for the azide and oxalate complexes in CCl₄ is due to an electron-transfer mechanism from the photogenerated excited state to the solvent.

Introduction

Carbon–hydrogen bond activation has received a great deal of attention in recent years. Of particular interest are the photochemical systems developed by the Bergman^{1–4} and Graham^{5–7} groups:



M = Rh, Ir; Cp* = pentamethylcyclopentadienyl; PR₃ = trimethylphosphine; R–H = aromatic, aliphatic

Photochemical extrusion of CO or H₂ results in oxidative addition of C–H bonds. The proposed photogenerated intermediates in both of these systems react with a wide variety of substrates that include unactivated hydrocarbons (e.g. methane).^{4,5} It is becoming

increasingly clear as illustrated through studies of reaction 2 by several groups that photolysis of the bis(carbonyl) complex in inert-gas matrices or in liquified inert gases^{8–10} results in the loss of CO in the primary photochemical reaction to form the coordinatively unsaturated CpM(CO) complex.¹¹ A similar, but even more reactive, intermediate is generated via reaction 1 from the

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- (11) Evidence suggests that in liquid xenon solutions the open coordination site is occupied by a solvent molecule.

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