

**Figure 6.** Magnetic susceptibility ( $\square$ ) and moment ( $\circ$ ) data for **6**. The solid line is that calculated by using the parameters given in Table V and in the text.

network. A reasonably good fit of the data, shown in Figure 6, was achieved by using matrix diagonalization techniques for a Hamiltonian appropriate to  $S = 2$  pairs which included  $D\hat{S}_z^2$ ,  $-2J\hat{S}_1\hat{S}_2$ , and Zeeman terms,<sup>3</sup> the best-fit parameters being  $g = 2.08$ ,  $J = -0.5 \text{ cm}^{-1}$ , and  $|D| = 2 \text{ cm}^{-1}$ , the latter presumably being negative in sign in view of the axially elongated structure around Mn(III). The moderate agreement between observed and calculated values in the region 10–30 K probably is due to lack of inclusion of a rhombic ( $E$ ) ZFS term or to the binuclear approximation employed.

### Conclusions

The rich series of manganese(III) Schiff-base structures described here complements and extends that recently described by Pecoraro et al.<sup>10</sup> Use of the 2-OH-SALPN ligand, in conjunction with carboxylate or other anionic ligands, and alkali-metal ions can lead to the formation of mono-, bi-, or polynuclear Mn(III) complexes. The particular role of the  $\text{Na}^+$  ion in **5** and **6** is a subtle one and has been emphasized by Pecoraro et al.<sup>10</sup> in relation to the cofactor role that alkali-metal or alkaline-earth-metal ions are known to play in the manganese site of the photosystem II water oxidation center.

As in other recent studies, we have shown that Mn(III)–Mn(III) exchange interactions in these and other related systems are weakly antiferromagnetic in origin and modulated by zero-field splitting effects. We have attempted to briefly summarize, where appropriate, the current state of Mn(III) magnetostructural correlations and find that while it is possible to generally understand the weak net coupling, interpretation of small differences in  $J$  largely depends on the relative orientations of the elongated (or compressed) axial directions on each  $S = 2$  Mn(III) center. To date, the strongest coupling has been observed in  $\mu$ -oxo singly bridged Mn(III)–O–Mn(III)<sup>25</sup> or in doubly bridged Mn<sup>III</sup><sub>2</sub>(O)<sub>2</sub> systems.<sup>27</sup>

**Acknowledgment.** Dr. A. Markiewicz and Mr. K. J. Berry are thanked for their help with the magnetic work. This work was supported by grants from the Australian Research Council and Monash University Research Grants.

**Registry No.** **1**, 120205-66-5; **2**,  $3^{1/2}\text{H}_2\text{O}$ , 135366-41-5; **2**-MeOH, 135366-43-7; **3'**, 135366-42-6; **6**, 135366-45-9; Mn(2-OH-SALPN), 69879-57-8.

**Supplementary Material Available:** For complex **3'**, Table S1 (fractional coordinates and anisotropic thermal parameters for non-hydrogen atoms), Table S2 (hydrogen atom parameters and anisotropic thermal parameters), Table S3 (bond distances), and Table S4 (bond angles), for complex **2**-MeOH, Table S6 (hydrogen atom parameters and anisotropic thermal parameters), Table S7 (bond distances), and Table S8 (bond angles), and for complex **6**, Table S10 (hydrogen atom parameters), Table S11 (bond distances), and Table S12 (bond angles) (14 pages); for all three complexes, Tables S5, S9, and S13 (structure factors) (34 pages). Ordering information is given on any current masthead page.

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### Synthesis and X-ray Structure of a Novel Technetium(IV) Complex with Tris(hydroxymethyl)(trimethylammonio)methane Iodide as a Ligand

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Received July 31, 1990

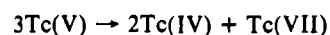
Until recently, the only known complexes of Tc(IV) with organic chelating ligands were dimers built around the characteristic "[Tc( $\mu$ -O)<sub>2</sub>Tc]" core.<sup>1,2</sup> As reported 5 years ago, mononuclear complexes have also been synthesized where the Tc(IV) center is coordinated to the oxygen atoms of an alcohol.<sup>3</sup> Examples of novel complexes of this type are those with ligands such as methanolate, glycolate, and the tridentate 1,2,4-butanetriolate. Glycerol, on the other hand, for steric reasons, cannot coordinate with all three oxygen atoms to the same metal center.<sup>4</sup> A promising group of other tridentate chelating alcoholato ligands are the derivatives of tris(hydroxymethyl)methane, with a "tripod" structure. It has been reported that these alcohols, schematically shown in Figure 1, form stable complexes with metal centers of A type, e.g. Fe(III);<sup>5</sup> thus the formation of Tc(IV) complexes could be expected.

We, therefore, decided to investigate the "tripod" coordination chemistry of technetium and here report the synthesis and the X-ray structure of a stable mononuclear 1:2 Tc(IV) complex with a derivative of tris(hydroxymethyl)methane with  $\text{R} = \text{N}(\text{CH}_3)_3^+$ , i.e. the cation ( $\text{H}_3\text{THMT}$ )<sup>+</sup> that gives the complex [Tc(THMT)<sub>2</sub>].

### Results and Discussion

Among the different derivatives of tris(hydroxymethyl)methane, THMT was chosen as a ligand for Tc(IV) for its coordinating properties. Indeed, the cationic substituent  $\text{R} = \text{N}(\text{CH}_3)_3^+$  strongly reduces the basicity constants, allowing ligand deprotonation, and thus the complex formation may take place at a lower pH value (reducing the tendency for hydrolysis of the central ion in aqueous solution). Furthermore, the bulky substituent forces the ligand into a conformation that favors the tridentate mode of binding. This assumption was confirmed by preliminary results of investigations with the involved derivatives (e.g., the formation of the complex  $\text{TcL}_2^{2-}$  when the ligand has  $\text{R} = \text{H}$  occurs at a much lower rate than with the chosen ligand).

This complex can be prepared in methanol according to the reactions shown in the Scheme I. From the iodide salt of the ligand ( $\text{H}_3\text{THMT}$ )<sup>+</sup> (**3**), compound **4** can be obtained either via the hexamethanolato complex of Tc(IV) (**2**), already described,<sup>3</sup> or by direct reaction of hexabromotechnetate(IV) (**1**) with **3** and subsequent neutralization of the liberated protons. The 1:2 complex [Tc(THMT)<sub>2</sub>] crystallizes only in presence of an excess of the ligand (as an iodide) (**3**) in the form of the double salt **4**. The reaction of [ $\text{H}_3\text{THMT}$ ]<sup>+</sup> salts with Tc(V) compounds such as [ $\text{TcOCl}_4$ ]<sup>-</sup> or [ $\text{TcO}(\text{OCH}_2\text{CH}_2\text{O})_2$ ]<sup>-</sup> yields [Tc(THMT)<sub>2</sub>] (65%) contaminated with small quantities of polymeric compounds (1–2%) and  $\text{TcO}_4^-$  (33%). It seems that "Tc<sup>V</sup>THMT" complexes are very unstable and quickly disproportionate in organic solvents according to the reaction



The obtained Tc(IV) complex shows in methanolic solutions two maxima in the UV region ( $\lambda_{\text{max}}$  295 and 225 nm) instead of one as obtained for other alcoholato complexes at similar wavelengths ( $\lambda_{\text{max}}$  267–274 nm). In the IR spectra the observed band

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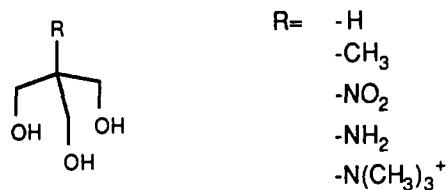


Figure 1. Derivatives of tris(hydroxymethyl)methane.

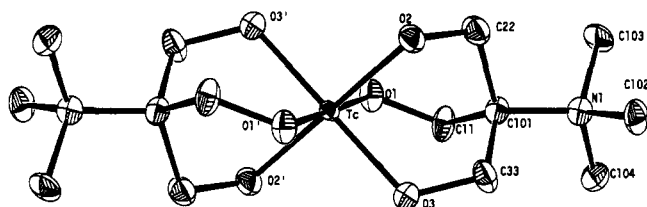
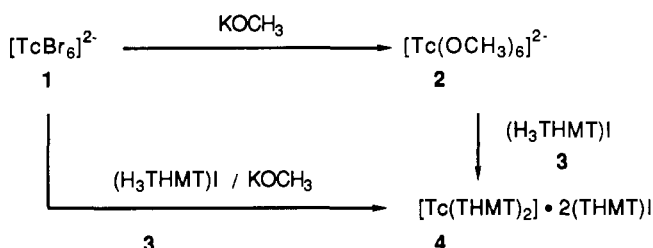


Figure 2. ORTEP plot of  $[\text{Tc}(\text{THMT})_2]$ . Primed atoms are related to those unprimed by the symmetry operation  $\bar{x}, \bar{y}, \bar{z}$ .

**Scheme 1.** Synthesis of  $[\text{Tc}(\text{THMT})_2] \cdot 2(\text{THMT})\text{I}$  in Methanolic Solutions



at  $4466\text{ cm}^{-1}$  is in the expected range for the TcO stretching vibration.<sup>3</sup> Moreover, there is no significant difference with the IR spectrum of the free ligand.

An ORTEP view of the  $[\text{Tc}(\text{THMT})_2]$  molecule is given in Figure 2, while relevant bond lengths and angles are listed in Table I. The six oxygen atoms of two THMT ligands are bound to the Tc atom in an octahedral geometry with idealized  $D_{3d}$  symmetry. The technetium atom lies on a crystallographic inversion center so that only one half of the molecule is crystallographically independent. One uncoordinated  $(\text{H}_3\text{THMT})^+$  and one iodide ion per  $[\text{Tc}(\text{THMT})_2]$  are also present in the asymmetric unit, giving a composition  $[\text{Tc}(\text{THMT})_2] \cdot 2(\text{H}_3\text{THMT})\text{I}$ . The three Tc–O bond lengths are equal within the standard deviations (average  $1.996(9)\text{ \AA}$ ) and are comparable to those found in the complexes with ethylenediaminetetraacetate (EDTA) and with oxalate (ox), i.e.  $[(\text{H}_2\text{EDTA})\text{Tc}(\mu\text{-O})_2\text{Tc}(\text{H}_2\text{EDTA})]$  (average  $2.011(7)\text{ \AA}$ )<sup>4</sup> and  $[(\text{ox})_2\text{Tc}(\mu\text{-O})_2\text{Tc}(\text{ox})_2]^{4-}$  (average  $2.06(4)\text{ \AA}$ ), where strong Tc–O interactions are present.<sup>1,8</sup> In the recently isolated complex  $[\text{AsPh}_4][\text{Tc}^{\text{IV}}(\text{ox})_3]$ , the anion shows a distorted octahedral geometry with a mean Tc–O distance of  $1.991(7)\text{ \AA}$ .<sup>9</sup> These short distances found in the  $[\text{Tc}(\text{THMT})_2]$  complex also rule out the possibility of OH moieties coordinated to the metal center. If we assume that all the oxygens are deprotonated, then the THMT ligand has formally a  $-2$  charge, so that the resulting oxidation state for technetium is  $+4$ , as could have been expected from the use in the synthesis of a Tc(IV) educt. Therefore, the complex

Table I. Selected Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for  $[\text{Tc}(\text{THMT})_2]$  with Esd's in Parentheses

Tc–O1	1.987 (4)	N1–C102	1.526 (8)
Tc–O2	2.005 (4)	N1–C103	1.529 (8)
Tc–O3	1.995 (4)	N1–C104	1.531 (8)
O1–C11	1.399 (7)	C11–C101	1.586 (8)
O2–C22	1.424 (8)	C22–C101	1.562 (8)
O3–C33	1.416 (7)	C33–C101	1.542 (9)
N1–C101	1.539 (7)		
O1–Tc–O2	87.0 (2)	O1–C11–C101	109.7 (5)
O1–Tc–O3	87.4 (2)	O2–C22–C101	109.4 (5)
O2–Tc–O3	86.7 (2)	O3–C33–C101	109.5 (4)
O1–Tc–O2' <sup>a</sup>	93.0 (2)	N1–C101–C11	109.6 (4)
O2–Tc–O3'	93.3 (2)	N1–C101–C22	110.1 (5)
O1'–Tc–O3'	92.6 (2)	N1–C101–C33	109.6 (5)
Tc–O1–C11	117.1 (4)	C11–C101–C22	107.7 (5)
Tc–O2–C22	116.2 (4)	C11–C101–C33	109.0 (5)
Tc–O3–C33	117.9 (4)	C22–C101–C33	110.8 (5)

<sup>a</sup> Primed atoms are related to those unprimed by the symmetry operation  $\bar{x}, \bar{y}, \bar{z}$ .

is zwitterionic with two positive charges on the quaternary ammonium substituent and the negative charges delocalized over the technetium oxygen moiety. We also note that the geometry of the uncoordinated  $[\text{H}_3\text{THMT}]^+$  found in this compound is not significantly different from that coordinated to the Tc center.

The compound is readily soluble in water and is stable at pH  $>4$  for more than 24 h; indeed, it is more stable toward hydrolysis than the other known alcoholato complexes.<sup>3</sup> Nevertheless, in water the THMT ligand can be substituted by strong amino polycarboxylate ligands such as EDTA or nitrilotriacetate (NTA). The THMT substitution by EDTA in water results in a new mononuclear Tc(IV) complex characterized by Tc–Tc distances of at least  $8\text{ \AA}$ , which will be described in a subsequent communication.

**Experimental Section**

**Cautionary Remark.** The complex was prepared in several small batches to minimize the risk of severe radioactive contamination. The samples of the complex for X-ray analysis, for elemental analysis, and for UV, vis, IR, and paper chromatography characterization were taken from different batches.

$\text{K}_2[\text{TcBr}_6]$  was synthesized from  $\text{NH}_4^{99}\text{TcO}_4$  (Oak Ridge), by known procedures.<sup>5</sup> Several derivatives of tris(hydroxymethyl)methane (Figure 1), with  $\text{R} = \text{CH}_3, \text{NH}_2, \text{and NHCH}_2\text{COOH}$  were obtained from Fluka AG.

The iodide of the tris(hydroxymethyl)(trimethylammonio)methane cation,  $(\text{H}_3\text{THMT})^+$ , was synthesized through methylation of tris(hydroxymethyl)aminomethane<sup>7</sup> and isolated as the iodide salt.

**Preparation of  $[\text{Tc}(\text{THMT})_2] \cdot 2(\text{H}_3\text{THMT})\text{I}$  (4).** A 25-mg sample of the potassium salt of 1 was suspended in 4 mL of methanol. Addition of 110 mg of 3 (0.37 mmol) caused a discoloration which was completed by neutralization with 17.4 mg of  $\text{KOCH}_3$  in methanol ( $\text{Tc}:\text{OCH}_3 = 1:6.7$ ). This procedure led only to a 95% conversion of 1 to the desired product 4 in solution. Reducing the volume to 1 mL by flushing with dry nitrogen forced the precipitation of KBr, which was filtered off. After evaporation to dryness, the remaining white powder was washed with small amounts of hot ethanol to remove excess ligand and  $\text{KOCH}_3$ . The residue dissolved in hot methanol yielded, on standing for about 12 h, 18.9 mg of white crystal needles (yield 50% as referred to Tc). During the synthesis, the ligand excess was about 1:10. The complex was also completely formed in solution by using only a very small excess of THMT (e.g. 1:2.2). Even though the large ligand excess mentioned above was not necessary to obtain the complex, its precipitation did not occur when a stoichiometric reagent ratio was used as the complex crystallized as a double salt. Anal. Calcd for  $[\text{Tc}(\text{THMT})_2] \cdot 2(\text{H}_3\text{THMT})\text{I}$ : Tc, 9.86; C, 33.51; H, 6.63; N, 5.58. Found: Tc, 9.78; C, 33.95; H, 6.75; N, 5.72.

UV-vis ( $\text{CH}_3\text{OH}$ ;  $\lambda_{\text{max}}$ , nm ( $\epsilon, \text{M}^{-1}\text{ cm}^{-1}$ ): 285 ( $4950 \pm 100$ ), 225 ( $21500 \pm 300$ ). IR (CsBr pellet;  $\text{cm}^{-1}$ ): 3410 s, 3023 w, 2902 w, 2861 m, 1487 m, 1445 w, 1425 w, 1414 w, 1264 w, 1240 w, 1180 m, 1109 s, 1053 w, 994 m, 938 m, 874 m, 589 w, 541 s, 465 m, 392 m, 291 w. Paper chromatography with Whatman CF-1 ( $\text{CH}_3\text{CN}:\text{H}_2\text{O} = 5:2\text{ v/v}$ ) gives  $R_f = 0.30 \pm 0.05$  (Chromelec II/Numelec).

The unsuccessful synthesis of the Tc(V) complex was performed by the following procedure: 15  $\text{cm}^3$  of a solution of 0.1 M  $\text{Bu}_4\text{NOH}$  (1.5 mmol) in 2-propanol was added to 160 mg of  $\text{Bu}_4\text{N}[\text{TcOCl}_4]$  (0.32

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**Table II.** Experimental Data for the X-ray Diffraction Study of [Tc(THMT)<sub>2</sub>]

formula	C <sub>28</sub> H <sub>66</sub> I <sub>2</sub> N <sub>4</sub> O <sub>12</sub> <sup>99</sup> Tc <sub>2</sub>	$\rho_{\text{calcd}}$ , g cm <sup>-3</sup>	3.32
mol wt	1101.64	$\mu$ , cm <sup>-1</sup>	40.96
space group	C2/c (No. 15)	T, °C	22
a, Å	28.334 (5)	$\lambda$ , Å	0.71069 (graphite monochromated, Mo K $\alpha$ )
b, Å	10.199 (2)	transm coeff	0.897-0.999
c, Å	15.196 (2)	R	0.055
$\beta$ , deg	116.74 (1)	R <sub>w</sub>	0.064
Z	4		
V, Å <sup>3</sup>	3921.7		

**Table III.** Final Atomic Coordinates and Equivalent Thermal Parameters with Esd's in Parentheses<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>
I1	0.74611 (3)	-0.0275 (1)	0.36429 (6)	5.12 (3)
TC1	0.000	0.000	0.000	1.67 (2)
O1	0.0727 (2)	0.0680 (7)	0.0411 (4)	3.3 (1)
O2	0.0018 (2)	0.0930 (6)	0.1179 (4)	3.3 (1)
O3	0.0332 (2)	-0.1520 (6)	0.0897 (4)	3.3 (1)
O4 <sup>b</sup>	-0.0728 (2)	0.2711 (7)	0.0831 (5)	4.5 (2)
O5 <sup>b</sup>	-0.1411 (3)	0.6180 (7)	0.1307 (5)	5.3 (2)
O6 <sup>b</sup>	-0.0196 (3)	0.6336 (8)	0.0434 (6)	7.0 (2)
N1	0.1376 (2)	0.0079 (7)	0.3132 (5)	3.0 (2)
N2	-0.1268 (3)	0.5049 (8)	-0.0407 (5)	3.5 (2)
C11	0.1128 (3)	0.020 (1)	0.1295 (6)	3.6 (2)
C22	0.0529 (3)	0.1228 (9)	0.1948 (7)	3.7 (2)
C33	0.0614 (4)	-0.1267 (9)	0.1921 (6)	3.7 (2)
C101	0.0910 (3)	0.0051 (9)	0.2088 (5)	2.8 (2)
C102	0.1200 (4)	-0.037 (1)	0.3897 (6)	3.9 (2)
C103	0.1597 (4)	0.1467 (9)	0.3430 (7)	4.3 (3)
C104	0.1829 (4)	-0.081 (1)	0.3208 (7)	3.9 (2)
C44 <sup>b</sup>	-0.0457 (3)	0.3913 (9)	0.0944 (7)	3.5 (2)
C201 <sup>b</sup>	-0.0845 (3)	0.508 (1)	0.0686 (6)	3.2 (2)
C202 <sup>b</sup>	-0.1499 (5)	0.640 (1)	-0.0796 (9)	6.7 (4)
C203 <sup>b</sup>	-0.1033 (4)	0.452 (1)	-0.1072 (7)	5.9 (3)
C204 <sup>b</sup>	-0.1725 (4)	0.414 (1)	-0.058 (1)	5.9 (3)
C55 <sup>b</sup>	-0.1107 (3)	0.500 (1)	0.1390 (7)	4.1 (2)
C66 <sup>b</sup>	-0.0517 (4)	0.637 (1)	0.0936 (7)	4.6 (2)

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(4/3)[a^2B(1,1) + b^2(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$ .

<sup>b</sup> Atoms of the [H<sub>3</sub>THMT]<sup>+</sup> counterion; for the numbering scheme see the supplementary diagram.

mmol) and 1.02 g of 3 (3.5 mmol) under an argon atmosphere, and the mixture was treated in an ultrasonic vibrator. The color of the solution changed to red brown. After all of the Bu<sub>4</sub>N[TcOCl<sub>4</sub>] had dissolved, the solution was controlled by using paper chromatography (Whatman CF-1; CH<sub>3</sub>CN:H<sub>2</sub>O = 5:2 v/v). This showed the presence of Tc(THMT)<sub>2</sub> (65%, R<sub>f</sub> = 0.3) and TcO<sub>4</sub><sup>-</sup> (33%, R<sub>f</sub> = 1) together with polymeric species (1-2%, R<sub>f</sub> = 0).

**Determination and Refinement of the Structure.** Crystals suitable for X-ray diffraction of [Tc(THMT)<sub>2</sub>]-2(H<sub>3</sub>THMT)I were obtained as described above and are air stable. A prismatic white crystal mounted on a glass fiber at a random orientation on an Enraf-Nonius CAD4 diffractometer was used for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by a least-squares fit of the 2 $\theta$  values of 25 high-order reflections (9.5 <  $\theta$  < 17.0°) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table II; an extended list of structural and data collection parameters is given in supplementary Table S1. Data were measured with a variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and were measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections every 300 reflections. Data were corrected for Lorentz and polarization effects and for decay, by using the data reduction programs of the CAD4-SDP package.<sup>10</sup> An empirical absorption correction was also applied by using azimuthal ( $\psi$ ) scans of three reflections at a high  $\chi$  angle ( $\chi \geq 84^\circ$ ). Transmission factors were in the range 0.897-0.999. Intensities were considered as observed if  $|F_o|^2 \geq 2.5\sigma|F|^2$ . A  $F_o = 0$  was assigned to those reflections having negative net intensities. The structure was

solved by a combination of Patterson and Fourier methods and refined by full-matrix least squares<sup>10</sup> (the function minimized was  $\sum[w(|F_o| - (1/k)|F_c|)^2]$  with  $w = (\sigma^2|F_o|)^{-1}$ ). No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from ref 11. Anisotropic temperature factors were used for all non-hydrogen atoms. Upon convergence (no parameter shift > 0.2 $\sigma(p)$ ), the final Fourier difference map showed no significant features. Final atomic coordinates and equivalent thermal factors are given in Table III.

**Acknowledgment.** Financial support from the Schweizerischer Nationalfond and Paul Scherrer Institut, Würenlingen (R.A and G.H), is gratefully acknowledged.

**Registry No.** K<sub>2</sub>I, 98479-41-5; 4, 135366-82-4; Bu<sub>4</sub>N[<sup>99</sup>TcOCl<sub>4</sub>], 92622-25-8.

**Supplementary Material Available:** A diagram showing the atom numbering of the [H<sub>3</sub>THMT]<sup>+</sup> cation, a complete list of crystal data and experimental parameters (Table S1), a table of anisotropic displacement parameters (Table S2), and extended lists of bond lengths and bond angles (Tables S3 and S4) (6 pages); a list of observed and calculated structure factors (Table S5) (20 pages). Ordering information is given on any current masthead page.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

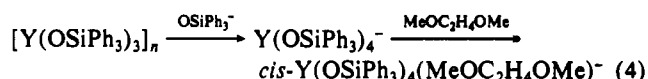
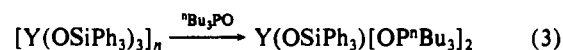
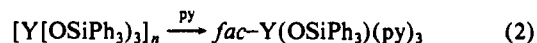
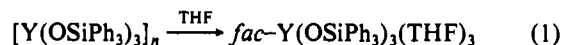
Contribution from the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

### Low-Coordinate Yttrium in an Oxygen Ligand Environment. Solid-State and Solution Characterization of Y<sub>2</sub>(OSiPh<sub>3</sub>)<sub>6</sub>

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Received February 13, 1991

We have reported<sup>1</sup> that treatment of Y[N(SiMe<sub>2</sub>)<sub>2</sub>]<sub>3</sub> with Ph<sub>3</sub>SiOH in toluene gives a high yield of a material of empirical formula Y(OSiPh<sub>3</sub>)<sub>3</sub>. On the basis of its low solubility and its complex <sup>1</sup>H and <sup>13</sup>C NMR spectra, we have concluded that this is an aggregate. However, establishing the exact degree of aggregation was not possible, in part because we were only able to produce featherlike solids unsuitable for an X-ray structure determination. While this compound was shown to react with a variety of ligands to yield adducts of varying coordination numbers (eq 1-4), the detailed composition and structure of the reagent remained unknown.



We report here the resolution of this uncertainty as well as an application of <sup>29</sup>Si NMR spectroscopy to evaluate solution structure. This NMR technique convincingly resolves bridging and terminal siloxide environments.

(10) Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, The Netherlands, 1980.

(1) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.*, in press.