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^{89}Y and ^{29}Si NMR Spectra as Probes of Solution Dynamics: Ligand and Metal Polyhedral Rearrangements in Yttrium Aggregates

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NMR (^1H , ^{89}Y , and ^{29}Si) studies of yttrium alkoxide, siloxide, and acetylacetonate compounds, including aggregates, have been carried out with special attention to solution structure and integrity (compared to solid-state structure) and fluxionality. $\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$ shows Y/Si coupling (8.1 Hz) in the ^{29}Si NMR spectrum only under conditions where exchange of OSiPh_3 ligands with free Ph_3SiOH has been halted. $\text{Y}_{10}(\text{OC}_2\text{H}_4\text{OMe})_{30}$ dissolves in toluene to give only one ^{89}Y signal, consistent with retention of the decameric structure. $\text{Y}_2(\text{OSiPh}_3)_6$ shows two ^{29}Si chemical shifts, consistent with the two bridging and four terminal ligands found in the solid state; only the terminal ligands exhibit detectable Si/Y coupling (7.7 Hz). The fluxionality of inequivalent siloxide ligands in *cis*- $\text{Y}(\text{OSiPh}_3)_4(\text{MeOC}_2\text{H}_4\text{OMe})^-$ was shown to be intramolecular by observation of Si/Y coupling (7 Hz) above the coalescence temperature. Yttrium site exchange in square-pyramidal $\text{Y}_3\text{O}(\text{O}^i\text{Pr})_{13}$ was shown to be promoted by $^i\text{PrOH}$ via an associative mechanism. Features of the structure of the alcohol adduct naturally account for site exchange of the two distinct metal sites. $\text{Y}_3(\text{acac})_4(\text{OC}_2\text{H}_4\text{OMe})_5$ shows no exchange among inequivalent yttrium sites, but ^1H NMR studies show site exchange of the ether ends of the two $\mu_3\text{-}\eta^2\text{-OC}_2\text{H}_4\text{OMe}$ ligands.

Introduction

An active area of research in our groups has been the characterization of metal alkoxides and siloxides.¹⁻⁹ In the course of this work, it has become increasingly clear to us that unambiguous structural information is very difficult to obtain for these complexes in the absence of X-ray crystallographic data. In addition, the physical properties (i.e., soft "plastic" solids) and tendency to disorder the pendant alkyl chains make crystal structure determination an uncertain venture. These difficulties often leave several questions unanswered, including the degree of aggregation of the complex, the coordination number at each metal center, the number of unique ligand environments, and the number of distinct metal environments. As a result, we have investigated both ^{89}Y and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy as a means of answering some of these questions about this class of compounds. Both methods offer potential for the characterization of compounds that do not crystallize easily and, in addition, probe the solution structure of complexes whose solid-state structures are known. Moreover, since sol/gel processing to yield solid oxides proceeds by hydrolysis in solution, these NMR techniques potentially offer very useful information which complements X-ray diffraction results.

Both ^{89}Y and ^{29}Si NMR spectroscopies have been examined previously as methods of characterization. Reports of yttrium NMR spectroscopy are scarce. The bulk of these studies are of yttrium salts in aqueous solution¹⁰⁻¹³ and of organo-yttrium complexes.¹⁴⁻¹⁸ Previously, we reported briefly a ^{89}Y NMR study of a yttrium alkoxide, $\text{Y}_3\text{O}(\text{O}^i\text{Pr})_{13}$.⁹ Conversely, ^{29}Si NMR spectroscopy has been exploited as a method of analysis for a wide variety of silicon-containing compounds, including most importantly siloxane polymers.¹⁹ However, in spite of the vast success of this method for other systems, only very few reports of ^{29}Si NMR studies exist for metal siloxide complexes.^{2-4,20-24}

Since both nuclei have similar properties, they both suffer from the same drawbacks and advantages. The primary advantage is that both nuclei have $I = 1/2$. The resulting lack of quadrupolar coupling indicates that the line widths will be relatively narrow, and this may prove helpful in resolving environments which are very similar. The drawbacks include a negative nuclear Overhauser effect (NOE) due to the negative magnetic moments for both nuclei, very long relaxation times, low sensitivity, and, for ^{29}Si , low abundance.

The negative NOE problems for ^{29}Si have been overcome by employing either inverse gated decoupling routines¹⁹ or one of the spin polarization transfer (SPT) methods (INEPT, DEPT²⁵). The SPT methods also remove the problem of long relaxation times. The use of wide-bore NMR tubes overcomes the problem of poor

sensitivity. These measures have made ^{29}Si NMR spectroscopy relatively routine.

Overcoming the difficulties in observation of ^{89}Y NMR signals is slightly more difficult. Most known yttrium complexes do not require the decoupling of protons for spectral acquisition, so that negative NOE is not a problem. However, since SPT methods require this coupling, they are inapplicable in this instance and the very long relaxation times typical of ^{89}Y nuclei remain a problem.¹⁷

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Table I. ^{89}Y NMR Data

complex	$\delta^{\text{a-c}}$	solvent	refs and notes
$\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$	570.0	CDCl_3	28
$\text{Y}(\text{BHT})_3$	170.8	C_6D_6	d, 29
$\text{Y}[\text{N}(\text{SiMe}_3)_2]_3(\text{OPPh}_3)$	544.4	$\text{C}_6\text{D}_5\text{CD}_3$	30
$\text{Y}(\text{BHT})_3(\text{OPMe}_2\text{Ph})$	148.1	C_6D_6	31
$\text{Y}(\text{OSiPh}_3)_3(\text{OP}^n\text{Bu}_3)_2$	221.6	CDCl_3	doublet, $^2J_{\text{Y-P}} = 14.2$ Hz
$\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$	157.1	THF	1; triplet, $^2J_{\text{Y-P}} = 8.7$ Hz
$[\text{Y}(\text{OSiPh}_3)_4\text{DME}][\text{K}(\text{DME})_4]$	168.1	DME	1
$\text{Y}(\text{OSiMe}_2\text{Bu})_3(\text{THF})_3$	266.6	CDCl_3	1
$\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$	217.7 (4), 214.0 (1)	C_6D_6	9
$\text{Y}(\text{DPM})_3$	168.3	CDCl_3	e, 32
$[\text{Y}(\text{OCH}_2\text{CH}_2\text{OMe})_3]_{10}$	134.5	$\text{C}_6\text{D}_5\text{CD}_3$	8
$\text{Y}_3(\text{OCH}_2\text{CH}_2\text{OMe})_3(\text{acac})_4$	91.4 (2)	$\text{C}_6\text{D}_5\text{CD}_3$	7
	62.7 (1)		

^a Referenced to 3 M YCl_3 in D_2O . ^b All at 23 °C unless noted. ^c Numbers in parentheses indicate integrated intensities. ^d BHT = O-2,6-^tBu₂-4-MeC₆H₂. ^e DPM = 2,2,6,6-tetramethyl-3,5-heptanedionato.

Table II. ^{29}Si NMR Data

complex	$\delta^{\text{a-c}}$	solvent	refs and notes
HOSiPh_3	-12.2	CDCl_3	1
$(\text{Ph}_3\text{Si})_2\text{O}$	-18.2	CDCl_3	
$\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$	-29.2	CDCl_3	1
$\text{Y}(\text{OSiPh}_3)_3(\text{OP}^n\text{Bu}_3)_2$	-32.0	CDCl_3	1
$\text{Y}(\text{OSiPh}_3)_3\text{Py}_3$	-28.3	CDCl_3	1
$[\text{Y}(\text{OSiPh}_3)_4(\text{DME})]^- \text{K}(\text{DME})_4^+$	-34.30	DME	1; $^2J_{\text{Y-Si}} = 7.0$ Hz
$[\text{Y}(\mu\text{-OSiPh}_3)(\text{OSiPh}_3)_2]_2$	-17.9 (1), -26.1 (2)	CDCl_3	3
$[\text{K}(\text{OSiPh}_3)]_n$	-29.7	THF	5
$\text{Ce}(\text{OSiPh}_3)_4(\text{DME})$	-24.2	DME	22
HOSiMe_2Bu	18.8	CDCl_3	1
$[\text{K}(\text{OSiMe}_2\text{Bu})]_n$	-8.9	C_6D_6	5
$\text{K}(18\text{-crown-6})[\text{OSiMe}_2\text{Bu}]$	-8.7	C_6D_6	5
$\text{Y}(\text{OSiMe}_2\text{Bu})_3(\text{THF})_3$	4.8	CDCl_3	1
HOSiMe_2Ph	6.0	C_6D_6	1
$(\text{PhMe}_2\text{Si})_2\text{O}$	-0.87	C_6D_6	4
$[\text{K}(\text{OSiMe}_2\text{Ph})]_4$	-21.4	toluene	4

^a All spectra at 23 °C unless noted. ^b Referenced to $\text{SiMe}_4/\text{C}_6\text{D}_6$ (50:50). ^c Numbers in parentheses indicate integrated intensities.

We report here a number of useful results in yttrium alkoxide and siloxide chemistry which are uniquely obtainable from NMR spectroscopy. One result in particular makes a contribution to the poorly understood topic of multimetal polyhedral rearrangement.^{26a}

Experimental Section

All compounds were prepared by routes published in the literature.²⁷ Hexaphenyldisiloxane was purchased from Petrarch Systems and was used as received. All NMR samples were prepared in a nitrogen-filled glovebox in 10-mm tubes and septum-sealed. All nonchlorinated solvents were dried and deoxygenated by reflux over Na/K alloy. Chlorinated solvents were dried by stirring over P_2O_5 and deoxygenated by repeated freeze-pump-thaw cycles. Samples were prepared in solvents selected to be noncoordinating. Data were recorded on a Bruker AM-500 spec-

Table III. Dependence of ^{89}Y NMR Chemical Shift on Coordination Number (CN)

CN	complex	δ
3	$\text{Y}(\text{O}-2,6\text{-}^t\text{Bu}_2\text{-4-Me-C}_6\text{H}_2)_3$	170.8
4	$\text{Y}(\text{O}-2,6\text{-}^t\text{Bu}_2\text{-4-Me-C}_6\text{H}_2)_3(\text{OPMe}_2\text{Ph})$	148.1
4	$\text{Y}_2(\text{OSiPh}_3)_6^3$	263.2
5	$\text{Y}(\text{OSiPh}_3)_3(\text{OP}^n\text{Bu}_3)_2$	221.6
6	$\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$	157.1
3	$\text{Y}(\text{N}(\text{SiMe}_3)_2)_3$	570.0
4	$\text{Y}(\text{N}(\text{SiMe}_3)_2)_3(\text{OPPh}_3)$	544.4

trometer equipped with a broad-band probe. All spectra were acquired with ^1H lock. ^{29}Si NMR spectra (99.4 MHz) were externally referenced to a tetramethylsilane/benzene-*d*₆ (50:50) mixture and acquired using a 45° pulse and a 5-s pulse delay. ^{89}Y NMR spectra (24.5 MHz) were externally referenced to 3 M YCl_3 in D_2O . Solutions were 0.25 M or saturated solutions, and the spectra were acquired with a 30° pulse and a 50-s delay, for accumulation times of 2–4 h. The “worst case” of a poorly soluble complex required 9 h (625 scans) for an acceptable signal-to-noise ratio. Some ^{29}Si NMR spectra were acquired using an INEPT pulse sequence.²⁵ We found that the addition of a spin relaxation agent ($\text{Cr}(\text{acac})_3$) to a solution of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ is ineffective in shortening the relaxation time of this complex. Relaxation aids were not employed for ^{29}Si NMR spectra.

Results

The ^{89}Y and ^{29}Si NMR chemical shifts of the complexes analyzed here are listed in Tables I and II, respectively. The chemical shifts of several complexes reported in the literature are also reported for comparison. The ^{29}Si chemical shifts of terminal ligands on metal siloxide complexes are uniformly upfield from the parent silanol signals. There appear to be too few data to make further correlations among the terminal siloxides. In contrast, the chemical shift range of bridging siloxides is downfield relative to the signals of terminal siloxides. The ^{29}Si NMR signals observed were generally sharp (7-Hz full width at half-maximum, fwhm), with no indication, at room temperature, of coupling to yttrium through the oxygen. The only exception is for $[\text{K}(\text{DME})_4][\text{Y}(\text{OSiPh}_3)_4(\text{DME})]$, where we were able to resolve 7-Hz coupling. Several other complexes exhibit yttrium/silicon coupling at low temperature (see below).

Most of the observed ^{89}Y NMR signals (Table I) are relatively sharp. This allows observation of $^2J(\text{P}-\text{Y})$ for several complexes bearing phosphine oxide ligands. The coupling constants are listed in Table I. The ^{89}Y NMR signals fall into regions depending upon the nature of the ligands (especially the anionic ligands) bound to the metal center. These ranges^{9,14-18} are as follows: oxygen-based ligands, from +270 to +60 ppm; nitrogen-based ligands, from +570 to +100 ppm; carbon-based ligands, from +40 to -371 ppm; halide ligands, from +10 to -30 ppm.

It is premature to make correlations of chemical shift with the type of oxygen ligand bound to yttrium. However, increasing the coordination number at the metal center while keeping the ligand set nearly constant (i.e., making a Lewis base adduct of a complex)

- (26) (a) For a brief review of skeletal isomerization of transition metal clusters, see: Braunstein, P.; de Meric de Bellefon, C.; Bouaoud, S.; Grandjean, D.; Halet, J.-F.; Saillard, J.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 5282. (b) This trend is apparently *not* reflected in the ^{89}Y NMR data reported recently for six-coordinate yttrium in $\text{Y}_3(\text{O}^i\text{Bu})_6(\text{BuOH})_2$ (166.8 ppm), in comparison to several proposed four-coordinate metals in $[\text{Y}(\text{OR})_3]_2$, R = CMe_2Pr , CMeEt^iPr , and CEt^i (36.8–47.8 ppm). See: Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1991**, *10*, 1049.
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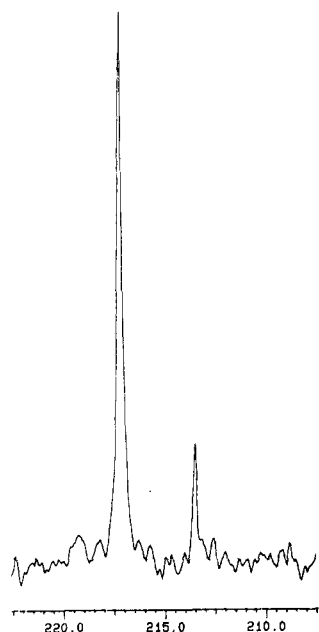
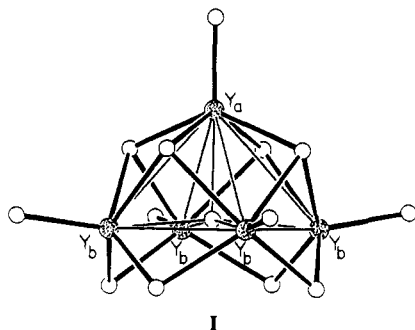


Figure 1. ^{89}Y NMR spectrum of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ in C_6D_6 at 25°C .

results in shielding (upfield shift) of the yttrium nucleus (Table III).^{26b}

Discussion

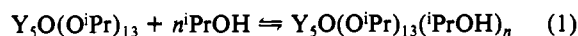
$\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$. An excellent example of the effectiveness of ^{89}Y NMR spectroscopy is the spectrum of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ (Figure 1). This complex (I) has two distinct yttrium sites, b and a, with a



population of 4:1. The spectrum is consistent with the solid-state structure and indicates that the complex retains that structure in solution. It is significant to note that although both sites are very similar (each is coordinated by six oxygens), both can be clearly resolved, even at 25°C . This indicates that ^{89}Y NMR spectroscopy is effective in determining slight structural variations, an ability that will be crucial in elucidating the solution structure of yttrium complexes.

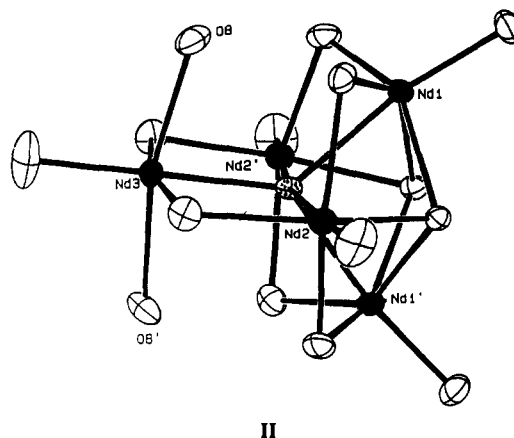
Another advantage of ^{89}Y NMR spectroscopy is that it allows greater insight into chemical-exchange processes occurring in solution. For example, it has been reported³³ that addition of excess 2-propanol to solutions of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ causes broadening of the resonances in the ^1H NMR spectrum. This was attributed to exchange between free alcohol and coordinated alkoxide with the *assumption* of a static metal core. However, observation of the ^{89}Y NMR spectrum of this complex in toluene in the presence of added 2-propanol indicates that a more complex fluxional process is occurring. Addition of 2 mol of 2-propanol to 1 mol of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ causes the signals due to Y_a and Y_b to coalesce to a single broad resonance (fwhm = 18 Hz) at a chemical shift which is the population-weighted (4:1) average of those of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$. Clearly, a fluxional process which exchanges the metal sites within the $\text{Y}_5(\text{O})$ core must exist. Since the single ^{89}Y NMR

signal occurs at the population-weighted average of $\delta(\text{Y}_a)$ and $\delta(\text{Y}_b)$ of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$, we conclude that no significant (>5%) amount of a new species is produced but rather that this is simply an alcohol-promoted site exchange. This is confirmed by the observation that the ^{89}Y NMR spectrum of a 1:1 mixture of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ and $^i\text{PrOH}$ shows no signal due to a new species, but only slight broadening of the Y_a and Y_b signals of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$. The fact that coalescence has not been induced by this lower concentration of added $^i\text{PrOH}$ is consistent with an *associative* mechanism for exchange (eq 1). Since no new signals are seen in the 1:1 experiment, the equilibrium constant is small, but the alcohol adduct is nevertheless kinetically significant.



In order to confirm that a fluxional process was equilibrating the metal sites of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ in the presence of 2 equiv of 2-propanol, a variable-temperature study of such a solution was carried out. To increase solubility of the complex at low temperatures, the solvent system was changed to $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ (80:20). Spectra in this solvent at room temperature were indistinguishable from the spectra obtained in aromatics. Cooling the sample to -40°C caused a further broadening of the resonance (fwhm = 27 Hz). This is consistent with the beginnings of decoalescence. Attempts to more completely freeze out this process are hampered by the small frequency difference (87 Hz) between the two resonances of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ as well as the low solubility of the compound at -40°C .

The question that remains is how adduct formation can effect apical/basal yttrium site exchange. An effective way to accomplish this is to break the 4:1 symmetry of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ in such a way that at least one basal metal becomes symmetry equivalent to the apical metal. This then becomes a question of the structure of the adduct. Here, we benefit from the recent determination of the structure of an alcohol adduct of a neodymium analogue of $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$.⁶ The structure (II; stippled ellipse = oxide; open

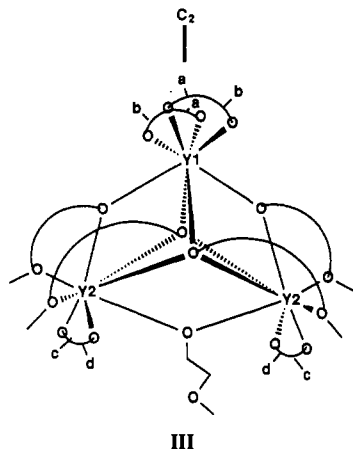


ellipses = OR; O8, O8' = ROH) of $\text{Nd}_5\text{O}(\text{O}^i\text{Pr})_{13}(\text{O}^i\text{PrOH})_2$ has C_{2v} symmetry with the alcohol ligands bound to the unique metal. If this is thought of as being derived by attack of alcohol at one of the basal metals in the $\text{M}_5\text{O}(\text{O}^i\text{Pr})_{13}$ structure observed for $\text{M} = \text{Y}$, the time-average equivalence of the apical and basal metals is achieved. In a like manner, alcohol attack at other basal centers will exchange these with the apical metal. A more detailed view of the alcohol-promoted apical/basal site exchange for $\text{Y}_5\text{O}(\text{O}^i\text{Pr})_{13}$ is shown in Scheme I. While $\text{Nd}_5\text{O}(\text{O}^i\text{Pr})_{13}(\text{O}^i\text{PrOH})_2$ serves as a structural *guide*, it is not required that a bis(alcohol) adduct be involved for yttrium; coordination of one alcohol is sufficient,³⁴ and we remain ignorant of this detail of the mechanism.

$\text{Y}_3(\text{OC}_2\text{H}_4\text{OMe})_5(\text{acac})_4$. Another good example of the effectiveness of ^{89}Y NMR spectroscopy involves $\text{Y}_3(\text{OC}_2\text{H}_4\text{OMe})_5(\text{acac})_4$ (structure III).⁷ In toluene, the ^{89}Y NMR

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(34) If only one alcohol coordinates ($n = 1$ in eq 1), then fast proton transfer between ROH and OR⁻ on M_x is also required for the mechanism in Scheme I.



III

spectrum shows (Figure 2) two signals (intensity 2:1) separated by 28.7 ppm. This is a considerable separation (compare the 3 ppm in $Y_3(O^iPr)_{13}$) of two yttrium types which have identical coordination numbers (8) but different ligand types. The structure has C_2 symmetry, and Y1 differs from Y2 in bearing two acac ligands. The ^{89}Y NMR spectrum thus permits the conclusion that acac ligand migration, if it occurs at all, is slow.

The 1H NMR spectrum (in toluene- d_8) is also informative. Although the $-OCH_2CH_2O-$ resonances are too broad and numerous to permit definitive assignment, three sharp singlets of intensity 6:3:6 (3.1–3.5 ppm) are assigned to the three types of OC_2H_4OMe groups detected in the solid state. In particular, the $\mu_2-\eta^1$ group should have half the intensity of the other two types. This indicates that no (facile) site exchange occurs between the different alkoxide types. The acac methine region of the spectrum shows two equally intense singlets. This is consistent with C_2 molecular symmetry and lack of facile acac site exchange.

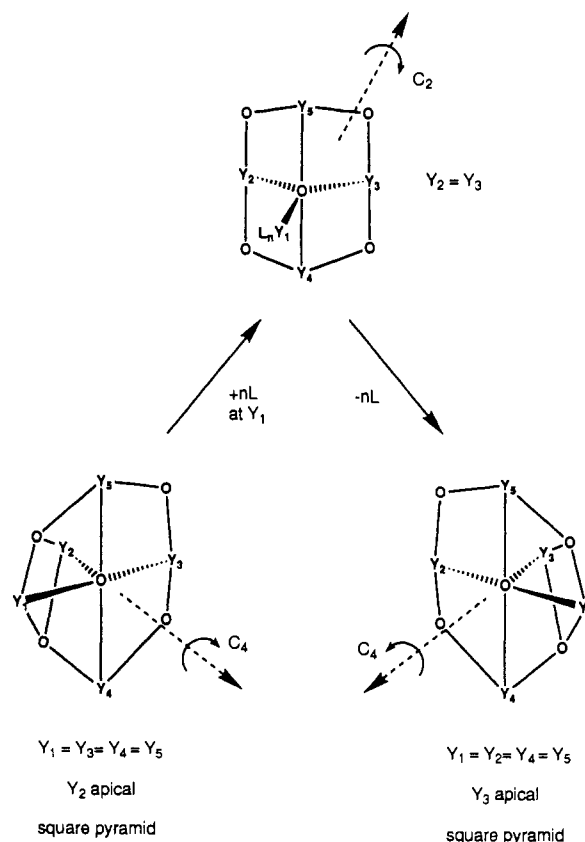
The acac methyl groups exhibit a deceptively simple 1H NMR pattern in toluene- d_8 at 25 °C. While four resonances are expected (a–d in III), only two (intensity 12:12) are observed, due to the ligands on Y1 and the Y2 pair, respectively. On cooling of the sample to –30 °C, the upfield signal splits into two signals of equal intensity, due to the cessation of fluxionality of the acac ligands on Y2. We propose the physical mechanism shown in Scheme II. This process, which also accomplishes racemization of the structure of III, involves migration between the two Y2 sites of those ether linkages (O') on the μ_3 -alkoxide. This migration has the consequence of causing the acac ligand on each Y2 to slide, in its own plane, and thus equalize methyl groups c and d. The remaining intensity 12 acac methyl resonance (which does not decoalesce at –60 °C) we attribute to rapid site exchange of Me_a and Me_b at Y1.

Addition of increasing amounts of $HOCH_2CH_2OMe$ to solutions of $Y_3(OCH_2CH_2OMe)_5(acac)_4$ in aromatic solvent causes the alkoxide resonances in the 1H NMR spectrum to broaden but leaves the resonances of the acac ligands unchanged. This indicates that the alkoxide ligands are exchanging with free alcohol, but because the acac resonances are not affected, the exchange appears to be occurring with the Y_3 framework of the complex remaining unchanged. Since ^{89}Y NMR spectra of solutions of this complex with added alcohol at temperatures from +23 to –40 °C are indistinguishable from those of the pure complex, metal site exchange, if it occurs at all, is much slower than the ^{89}Y NMR time scale.

$[Y(OCH_2CH_2OMe)_3]_{10}$. The cyclic decamer $[Y(OCH_2CH_2OMe)_3]_{10}$ (Figure 3) has only one yttrium environment in the solid state. This large aggregate could perhaps fragment in solution in response to entropic effects. However, the ^{89}Y NMR spectrum in toluene- d_8 at temperatures from +23 to –80 °C shows only one resonance. This indicates that the solid-state structure is maintained in solution or that the smaller aggregates that may form upon dissolution have equivalent yttrium sites.

$Y(OSiPh_3)_3(OPBu_3)_2$. Yttrium/phosphorus coupling constants can be important in determining the aggregation of a complex in solution and can indicate how many Lewis bases are coordinated

Scheme I



Scheme II

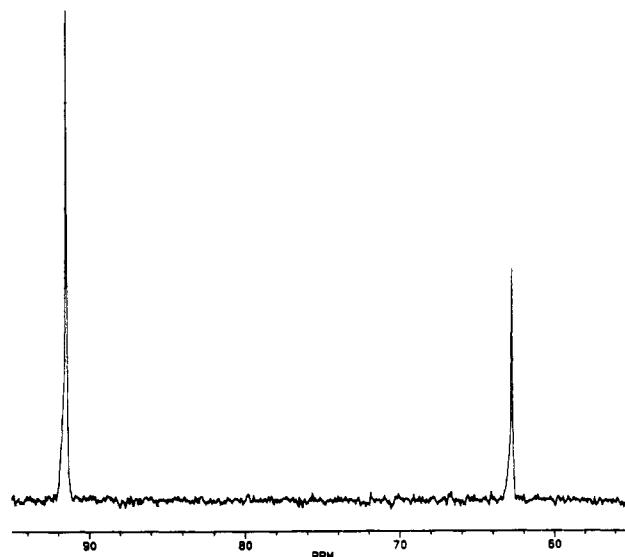
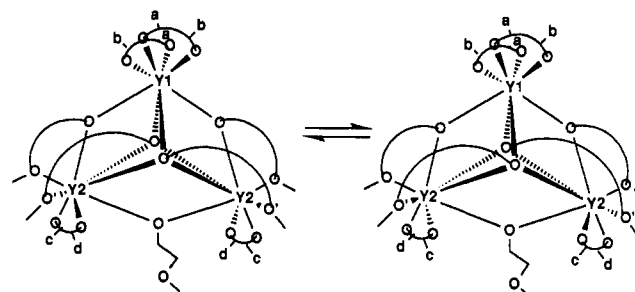


Figure 2. ^{89}Y NMR spectrum of $Y_3(OC_2H_4OMe)_5(acac)_4$ in toluene- d_8 at 25 °C.

to the metal center. For example, the triplet observed for $Y(OSiPh_3)_3(OPBu_3)_2$ indicates that the solid-state structure is

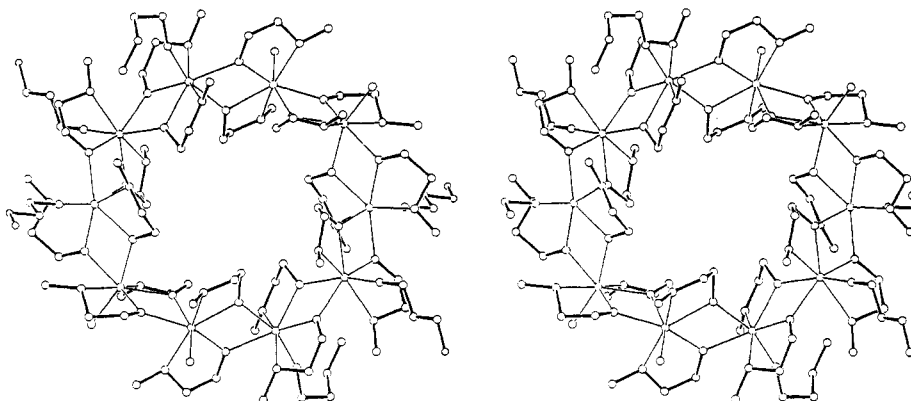
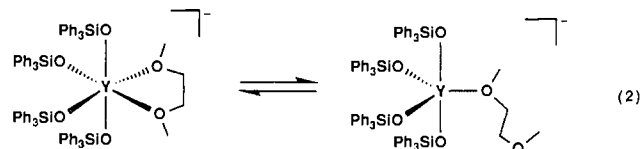


Figure 3. Stereo ORTEP drawing of the non-hydrogen atoms of $[Y(OCH_2CH_2OMe)_3]_{10}$. The molecule has a rigorous center of symmetry, but an idealized S_{10} axis.

retained in solution and the phosphine oxide dissociation is slow, if occurring at all.

Consequences of Observation of Si/Y Coupling. a. $Y(OSiPh_3)_4(DME)^-$. We have reported earlier that the anion $Y(OSiPh_3)_4(DME)^-$, where $DME = MeOC_2H_4OMe$, shows only one type of phenyl ring by both 1H and ^{13}C NMR spectroscopy at $25^\circ C$, but these resolve into two types of equal population at $-90^\circ C$.¹ We postulated siloxide site exchange by a mechanism in which one arm of the DME chelate dissociates (eq 2) followed



by siloxide site exchange in the (fluxional) five-coordinate intermediate. At that time, we could not rigorously exclude a mechanism dissociative in $OSiPh_3^-$. With new NMR data, this becomes possible. Thus, the ^{29}Si NMR spectrum at $25^\circ C$ shows two lines that are separated by 7 Hz at 99.4 MHz. In order to establish the origin of this splitting, the ^{29}Si NMR spectrum was recorded at 49.7 MHz.³⁵ Again two lines were observed, split by 7 Hz. This excludes the possibility that the two signals originate from two distinct silicon environments and confirms that the ^{29}Si NMR pattern is a spin doublet, due to coupling to ^{89}Y . This is the first observation of Y/O/Si coupling. The retention of Si/Y coupling in the fast-exchange regime for silicon site exchange establishes that $OSiPh_3^-$ dissociation is not occurring.

Although the coupling in $[K(DME)_4][Y(OSiPh_3)_4(DME)]$ is small, many of the other siloxides have line widths sufficiently narrow that coupling of a similar magnitude should be observable. That such coupling is not observed indicates that some fluxional process exists which causes loss of spin correlation between yttrium and silicon.

b. $Y(OSiPh_3)_3(THF)_3$. To test this hypothesis, a variable-temperature ^{29}Si NMR study of $Y(OSiPh_3)_3(THF)_3$ was carried out. The ^{29}Si NMR spectrum of $Y(OSiPh_3)_3(THF)_3$ (CH_2Cl_2/C_6D_6 (80:20)) is a sharp singlet at room temperature. At $-20^\circ C$, the resonance is broadened (fwhm = 33 Hz), but no fine structure is observed. Finally, at $-40^\circ C$, the resonance sharpens into a doublet ($^2J_{Y-Si} = 8.1$ Hz) but moves from -29.9 ppm at $23^\circ C$ to -30.9 ppm at $-40^\circ C$. While this change is small, the resonance moves away from the chemical shift of free silanol (-12 ppm). This is consistent with the freezing out of silanol/siloxide exchange. No resonance due to free silanol is observed at any temperature, indicating that its concentration must be very small.

The room-temperature ^{29}Si NMR spectrum of $Y(OSiPh_3)_3(THF)_3$ in THF/C_6D_6 (80:20) shows only a sharp singlet. Since this solvent should suppress any loss of coordinated THF, this observation indicates that a mechanism involving only dissociation

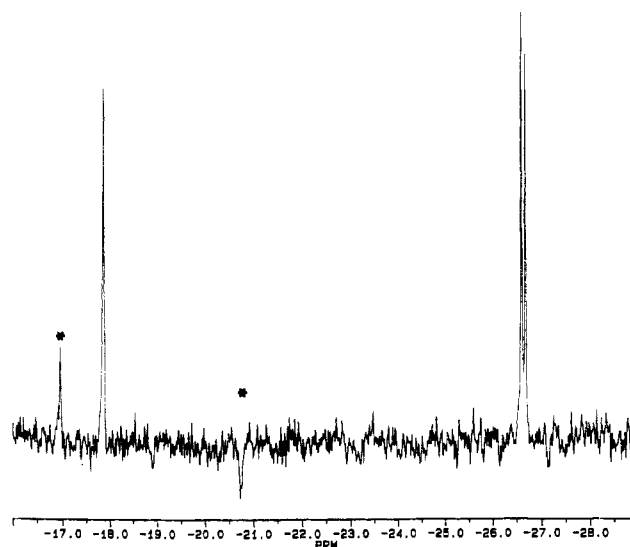
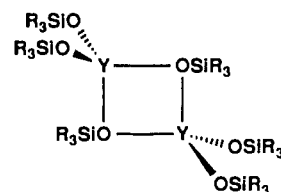


Figure 4. INEPT ^{29}Si NMR spectrum of $[Y(OSiPh_3)_3]_2$ at $-40^\circ C$ in CD_2Cl_2/C_6D_6 (80:20). Asterisks denote probe artifacts.

of THF is not sufficient to account for loss of spin correlation.

^{29}Si NMR spectra of $Y(OSiPh_3)_3(THF)_3$ were recorded (in CD_2Cl_2/C_6D_6 (80:20)) with varying amounts (0.2 and 1.0 equiv) of added silanol. At room temperature, only one resonance is observed, but increasing the amount of silanol broadens this resonance and shifts it toward the chemical shift of free silanol. At $-20^\circ C$, this resonance is split into two new broad peaks. The low-field peak corresponds to free silanol. At $-40^\circ C$, both resonances are sharp, and the upfield one (corresponding to $Y(OSiPh_3)_3(THF)_3$) appears as a doublet with $J_{Y-Si} = 8$ Hz. These results indicate that, at $23^\circ C$, silanol/siloxide exchange is rapid on the ^{29}Si NMR time scale. The very small amount of silanol available from adventitious hydrolysis is sufficient to initiate this exchange. This results in a loss of spin correlation between yttrium and silicon. At $-20^\circ C$, this exchange has slowed considerably, and at $-40^\circ C$, it is slower than the ^{29}Si NMR time scale.

c. $[Y(\mu-OSiPh_3)(OSiPh_3)_2]_2$. We have previously reported the ^{29}Si NMR spectra of $[Y(\mu-OSiPh_3)(OSiPh_3)_2]_2$ in $CDCl_3$ as two broad resonances (-17.1 and -26.1 ppm) in a 1:2, ratio consistent with the solid-state structure.³



The low solubility of this complex precluded the recording of

(35) Spectrum acquired by Frank J. Feher, University of California, Irvine.

low-temperature spectra using our standard technique. However, with the INEPT pulse sequence, we have acquired spectra (Figure 4) at $-40\text{ }^{\circ}\text{C}$ in $\text{CD}_2\text{Cl}_2/\text{C}_6\text{D}_6$ (80:20). At this temperature, both resonances sharpened considerably and the intensity 2 resonance split into a doublet ($J_{\text{Y-Si}} = 7.7\text{ Hz}$). The other resonance showed no sign of coupling. This unambiguously identifies the upfield resonance as resulting from the terminal siloxides, as the large Y-O-Si angles should favor a large Y/Si coupling constant. The bridging siloxides have relatively small Y-O-Si angles (142 and 111°), and a correspondingly small Y/Si coupling is expected.

Conclusions

The results presented here are perhaps the most interesting when they involve aggregated species containing inequivalent yttrium (or silicon) sites. This is because detection of rearrangement of metal polyhedra almost demands direct observation of metal NMR spectra. However, the detection of intra- and intermolecular

exchange of siloxide ligands has also been demonstrated by ^{29}Si NMR spectroscopy. Chemical-shift-based discrimination between bridging and terminal siloxide groups appears promising. In addition, studies of complexes that contain $\mu_3\text{-OSiR}_3$ groups² indicate that these ligands may also be uniquely identified via ^{29}Si NMR spectroscopy.

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Registry No. I, 118458-20-1; III, 128683-45-4; $^i\text{PrOH}$, 67-63-0; CH_2Cl_2 , 75-09-2; C_6D_6 , 1076-43-3; $\text{HOCH}_2\text{CH}_2\text{OMe}$, 109-86-4; $[\text{Y}(\text{OCH}_2\text{CH}_2\text{OMe})_3]_{10}$, 126939-63-7; $\text{Y}(\text{OSiPh}_3)_3(\text{OPBu}_3)_2$, 133270-51-6; $\text{Y}(\text{OSiPh}_3)_4(\text{DME})^-$, 133270-54-9; $\text{Y}(\text{OSiPh}_3)_3(\text{THF})_3$, 122020-72-8; HOSiPh_3 , 791-31-1; $[\text{Y}(\mu\text{-OSiPh}_3)(\text{OSiPh}_3)_2]_2$, 135658-43-4; toluene, 108-88-3.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

New Halogen-Bridged Dinuclear Edge-Sharing and Face-Sharing Bicoctahedral Tungsten(III) Complexes, $\text{W}_2\text{X}_6(\text{PR}_3)_m$ Where X = Cl or Br, $\text{PR}_3 = \text{PMe}_3, \text{PMe}_2\text{Ph}$, or PBu_3 , and $n = 4$ or 3 : Crystal Structures of $\text{W}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_4$, $\text{W}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_3$, and $\text{W}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$

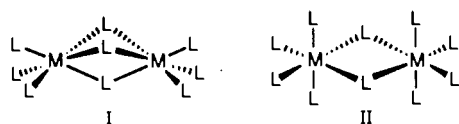
F. Albert Cotton* and Sanjay K. Mandal

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The reduction of WCl_4 by 1 equiv of reducing agent, either Na/Hg or $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$, in toluene followed by the addition of 2 equiv (or an excess) of phosphine ligand produced the edge-sharing compound $\text{W}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_4$ (**1**) in high yield. The face-sharing compounds $\text{W}_2\text{Cl}_6(\text{PMe}_2\text{Ph})_3$ (**2**) and $\text{W}_2\text{Cl}_6(\text{PBu}_3)_3$ (**3**) were prepared by reacting WCl_4 with 1 equiv of reducing agent (Na/Hg for **2** and $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ in THF for **3**) in toluene followed by the addition of 1.5 equiv of the appropriate phosphine ligand. The first bromo-bridged dinuclear complexes $\text{W}_2\text{Br}_6(\text{PMe}_2\text{Ph})_3$ (**4a**) and $\text{W}_2\text{Br}_6(\text{PMe}_3)_3$ (**5**) were synthesized by reducing WBr_5 with 2 equiv of reducing agent (Na/Hg for **4a** and $\text{NaB}(\text{C}_2\text{H}_5)_3\text{H}$ in toluene for **5**) in toluene followed by the addition of 1.5 equiv of PMe_2Ph and PMe_3 , respectively. Compounds **1**, **2**, and **4a,b** have been structurally characterized by X-ray diffraction studies. Compound **4** (**4a,b**) exists in two different crystalline forms. Crystal data: for **1**, space group $C2/c$, $a = 17.577$ (2) Å, $b = 11.200$ (1) Å, $c = 21.001$ (3) Å, $\beta = 108.25$ (2) $^{\circ}$, $V = 3934$ (2) Å³, and $Z = 4$; for **2**, space group $P\bar{1}$, $a = 9.796$ (2) Å, $b = 12.603$ (2) Å, $c = 13.856$ (3) Å, $\alpha = 76.51$ (2) $^{\circ}$, $\beta = 82.66$ (2) $^{\circ}$, $\gamma = 73.47$ (1) $^{\circ}$, $V = 1591$ (1) Å³, and $Z = 2$; for **4a**, space group $P\bar{1}$, $a = 9.896$ (3) Å, $b = 12.866$ (4) Å, $c = 14.246$ (3) Å, $\alpha = 75.62$ (2) $^{\circ}$, $\beta = 82.95$ (2) $^{\circ}$, $\gamma = 74.07$ (2) $^{\circ}$, $V = 1687$ (1) Å³, and $Z = 2$; for **4b**, space group $P\bar{1}$, $a = 10.665$ (2) Å, $b = 16.009$ (5) Å, $c = 10.154$ (3) Å, $\alpha = 98.12$ (2) $^{\circ}$, $\beta = 101.92$ (2) $^{\circ}$, $\gamma = 79.95$ (2) $^{\circ}$, $V = 1660$ (1) Å³, and $Z = 2$. In all these complexes, the W-W bond distances 2.6950 (3) (1), 2.4433 (4) (2), 2.4768 (9) (4a), and 2.4496 (6) Å (4b) indicate strong metal-metal bonding. The face-sharing compounds **2** and **4b** have the shortest W-W bond distances in any neutral halogen-bridged dinuclear tungsten(III) complexes so far reported. The average W-X_n-W bond angle in the edge-sharing compound **1** is 68.98 (3) $^{\circ}$ and those in the face-sharing compounds are 58.45 [4], 56.28 [3], and 55.32 [2] $^{\circ}$ for **2**, **4a**, and **4b** respectively. Compounds **3** and **5** have been characterized by a $^{31}\text{P}\{\text{H}\}$ NMR spectrum and an electronic spectrum (similar to that of **4**), respectively.

Introduction

The chemistry of dinuclear transition metal complexes containing direct metal-metal bonds has been of great interest for over 3 decades.¹ One of the most interesting subsets of this family is the one having the general formula M_2L_n^m , where M = transition metal, L_n represents an assembly of halogen atoms and monodentate neutral ligands, $n = 9$ or 10 , and the value of m depends on the transition metal as well as its oxidation state and the number of neutral ligand present in the molecule. When $n = 9$, these complexes adopt the face-sharing bicoctahedral geometry (type I) while complexes with $n = 10$ have the edge-sharing bicoctahedral geometry (type II). Type I complexes with three



and type II complexes with four monodentate phosphine ligands in the terminal positions may have different ligand arrangements among the terminal halogen and phosphorus atoms for different transition metals.² Such complexes of group 6 metals have attracted much attention recently due to their interesting structural features and chemical properties. Studies on chromium compounds³ show that there is never any direct metal-metal bonding in these complexes. Extensive studies on molybdenum compounds⁴⁻⁶ have been reported in the literature, and it is found that a direct metal-metal bond is present in all complexes except

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