CP/MAS ^{89}Y NMR Spectroscopy: A Facile Method for Characterizing Yttrium-Containing Solids

Jiejun Wu,* Timothy J. Boyle, Julie L. Shreeve, Joseph W. Ziller, and William J. Evans*

Department of Chemistry, University of California at Irvine, Irvine, California 92717

Received November 11, 1992

Solid state CP/MAS ^{89}Y NMR spectroscopy, which had previously been limited to air stable materials containing solvated water, has been extended to a series of air sensitive yttrium complexes with a chemical shift range of over 1000 ppm. The results of this study demonstrate that ^{89}Y CP/MAS spectra can be easily obtained on a broad range of complexes in a short period of time. A convenient method for obtaining the Hartmann–Hahn match is described, and probe ringing is shown to be minimal. The effects of variable power level, contact time, and spinning rate are described. Spectra obtained on mono-, di-, and polymetallic samples which had been characterized by X-ray crystallography show a direct correlation between the number of signals and the number of unique solid state environments. The utility of this method in identifying impurities in yttrium-containing materials difficult to characterize by other methods is demonstrated.

Introduction

Solid state NMR spectroscopy using heteronuclear cross polarization with magic angle spinning (CP/MAS) can provide useful information on solids containing nuclei such as ^{13}C, ^{27}Al, ^{29}Si and ^{31}P.[1] However, the application of CP/MAS to low γ nuclei, i.e. those possessing frequencies lower than ^{15}N (20.26 MHz at 4.7 T), has been rare. For example, for ^{89}Y, which resonates at 9.8 MHz at 4.7 Tesla, solid state MAS NMR spectra traditionally have been obtained by single pulse experiments which suffer significant drawbacks from long relaxation time and low sensitivity.[2-9] Even though yttrium has the favorable NMR characteristic that the natural abundance of the $I = {}^1/_2$ ^{89}Y nucleus is 100%, the extremely long relaxation time makes it difficult to obtain a spectrum in a reasonable time frame. Obtaining data is further hindered by the fact that probe ringing (seen as a rolling baseline) is not negligible with this low frequency nucleus. The probe ringing signal can be reduced by a left shift of the data acquired or by introduction of a delay time before acquisition, but both methods further lower the signal to noise ratio of the ^{89}Y resonance.

Recently it has been shown that solid state NMR spectra can be obtained on low γ nuclei such as ^{89}Y,[10] ^{109}Ag,[11] and ^{183}W [12] by incorporating cross polarization between the metals and proximal protons under the condition of the Hartmann–Hahn match.[13] In the ^{89}Y study published earlier,[10] the protons needed for cross polarization were provided by the water in air stable hydrated compounds, such as $Y(NO_3)_3{\cdot}6H_2O$, $Y_2(SO_4)_3{\cdot}8H_2O$, $YCl_3{\cdot}6H_2O$, $Y(OAc)_3{\cdot}4H_2O$ and $Y(acac)_3{\cdot}3H_2O$. However, a much wider range of yttrium compounds are of interest and most of these are not hydrated. Of particular interest are yttrium compounds related to high temperature superconductors such as $YBa_2Cu_3O_{7-x}$.[14,15] These materials have stimulated research on yttrium containing oxides and on low temperature conversions of yttrium alkoxides to yttrium oxides using sol–gel processes.[16] Although sol–gel processes in general have considerable practical utility in the preparation of oxides, little is known about the specific details of the first steps of these reactions. Recent synthetic and structural studies of yttrium alkoxide and oxoalkoxide complexes suggest that yttrium compounds could provide useful information on sol–gel conversions of alkoxides to oxides.[17] Routine solid state ^{89}Y NMR spectroscopy on hydrate-free systems would be an invaluable tool for studying these yttrium systems.

We now demonstrate that useful CP/MAS ^{89}Y NMR spectra can be obtained quickly on a variety of air sensitive yttrium complexes. As anticipated, protons in ligands other than water can also provide the cross polarization and we find that they are close enough to yttrium to achieve the necessary dipolar interaction. Enhanced sensitivity is obtained via the cross polarization due to the favorable γ_H/γ_Y ratio (theoretical maximum 20.4). More importantly, short relaxation delays can be used in between pulses, because the experimental recycle time is now dependent only on the ^1H relaxation time which is much shorter than that of ^{89}Y. We also report here the spectra of a number of complexes which contain multiple metal environments within a molecule. Since these polymetallic complexes were fully characterized by X-ray crystallography, solution NMR spectroscopy, and other analytical methods, these complexes allowed us to establish that multiple peaks in the solid state ^{89}Y NMR spectra can be correlated with multiple metal environments.

---

(1) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201–208. Frye, J. S. In *NMR, Principles and Applications to Biomedical Research*; Pettegrew, J. W., Ed.; Springer Verlag: New York, 1989; pp 79–98.

(2) Thompson, A. R.; Oldfield, E. *J. Chem. Soc., Chem. Commun.* **1987**, 27–29.

(3) Grey, C. P.; Smith, M. E.; Cheetham, A. K.; Dobson, C. M.; Dupree, R. *J. Am. Chem. Soc.* **1990**, *112*, 4670–4675.

(4) Kremer, R. K.; Mattausch, H. J.; Simon, A.; Steuernagel, S.; Smith, M. E. *J. Solid State Chem.* **1992**, *96*, 237–242.

(5) Dupree, R.; Smith, M. E. *Chem. Phys. Lett.* **1988**, *148*, 41–44.

(6) Kramer, G. J.; Grom, H. B.; van den Berg, J.; Kes, P. H.; Iddo, D. J. W. *Solid State Commun.* **1987**, *64*, 705–706.

(7) Market, J. T.; Noh, T. W.; Russek, S. E.; Cotts, R. M. *Solid State Commun.* **1987**, *63*, 847–851.

(8) Han, Z. P.; Dupree, R.; Paul, D. M.; Howes, A. P.; Caves, L. W. *J. Phys. C* **1991**, *81*, 355–362 and references therein.

(9) Corretta, P. *Phys. Rev. B: Condens. Matter* **1992**, *45*, 5760–5763 and references therein.

(10) Merwin, L. H.; Sebald, A. *J. Magn. Reson.* **1990**, *88*, 167–171.

(11) Merwin, L. H.; Sebald, A. *J. Magn. Reson.* **1992**, *97*, 628–631.

(12) Merwin, L. H.; Sebald, A. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 45–47.

(13) Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042–2053. Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *56*, 1776–1777; *J. Chem. Phys.* **1973**, *59*, 569–590.

(14) Bednorz, J. G.; Muller, K. A.; Takashige, M. *Science (Washington, D.C.)* **1987**, *236*, 73. Nelson, D. L.; Whittingham, M. S.; George, T. F. *Chemistry of High-Temperature Superconductors*, *ACS Symp. Ser.* **1987**, *No. 351*; and references therein.

(15) This has prompted many ^{89}Y NMR studies. See refs 7–9 for some leading references.

(16) *Ultrasonic Processing of Ceramics, Glasses and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984; and references therein. Hubert-Pfalzgraf, L. G. *New. J. Chem.* **1987**, *11*, 663–675.

(17) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417–4423.

0020-1669/93/1332-1130$04.00/0

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk, vacuum line and glovebox techniques. All solvents were freshly distilled and dried as previously described.[18] Solution NMR spectra were obtained using Bruker WM-250, General Electric QE-300, Bruker AC-300, General Electric GN-500 and General Electric Ω-500 instruments and referenced against the residual protons in THF-d_8 and benzene-d_6. Elemental analysis was performed at Analytische Laboratorien GMBH, Fritz-Pregl-Strasse, 24 D-5270 Gummersbach, Germany. Complexometric titrations were performed as previously reported.[19] $YCl_3{\cdot}6H_2O$ (Rhône-Poulenc) and YF_3 (Aldrich) were used as received. $Y_3(OCMe_3)_7Cl_2(THF)_2$,[17] $Y_3(OCMe_3)_9(HOCMe_3)_2$,[20] $Y(OCMe_3)_3(AlMe_3)_2(THF)$,[21] $[(C_5H_4SiMe_3)Y(OCMe_3)_2]_2$,[21] $Cp_5Y_5(OMe)_8O$,[22] $[Cp_2YCl]_2$,[23] $Cp_2YCl(THF)$,[23] and $Cp_3Y(THF)$[24] were prepared according to the literature (Cp = C_5H_5). $Cp_2YBr(THF)$ was prepared from YBr_3 following the literature procedure for $Cp_2YCl(THF)$.[23] $YI_3(THF)_3$ and $YCl_3(THF)_3$ were prepared by slurrying YI_3 (Cerac) and freshly dried YCl_3[25] in excess THF, stirring for 30 minutes and removing the solvent in vacuo.

$YBr_3(THF)_3$.[26] In a 250 mL Schlenk flask under N_2, 125 mL of THF and an ingot of freshly polished yttrium metal (8.78 g, 98.8 mmol) were cooled to −15 °C. Bromine (1.0 mL, 19.4 mmol) was added by syringe in two equal portions. After addition of the first portion of bromine the reaction was slowly warmed to room temperature and bubbling occurred. When the effervescence had stopped the reaction mixture was again cooled to −15 °C. The second portion of bromine was added and slowly warmed as before. *Caution: If yttrium chips are used, the reaction is much more exothermic and extreme care should be taken when warming!* After complete addition of the bromine, the reaction mixture was stirred for 24 hours. The solvent was then removed in vacuo yielding an orange-white powder and the remainder of the ingot. The powder was washed with hexanes and diethyl ether and the remaining piece of yttrium metal was removed. The powder was identified as $YBr_3(THF)_3$ by elemental analysis. Anal. Calcd for $YC_{12}H_{24}Br_3O_3$: Y, 16.31; C, 26.43; H, 4.44; Br, 43.98. Found: Y, 16.60; C, 26.36; H, 4.44; Br, 43.76. Complexometric titration. Found: Y, 16.4.

$YBr_3{\cdot}6H_2O$. $YBr_3(THF)_3$ was slurried in water with stirring for 24 hours. The solvent was removed by rotary evaporation. The resulting white powder was used without further purification. Anal. Calcd for $YH_{12}O_6Br_3$: Y, 20.54; C, 0.0; H, 2.76; Br, 54.76. Found: Y, 20.60; C, <0.05; H, 2.62; Br, 54.68.

$Y_3(OCMe_3)_7Br_2(THF)_2$. In a glovebox, $NaOCMe_3$ (0.11 g, 1.1 mmol) was added to a slurry of $YBr_3(THF)_3$ (0.20 g, 0.37 mmol) in THF (5 mL). The reaction was stirred for 4 days and a slightly off-white powder formed in the reaction vessel. After the precipitate was removed by centrifugation, the solvent was removed in vacuo. The product was extracted with toluene, and washed with hexanes to yield $Y_3(OCMe_3)_7Br_2(THF)_2$ (246 mg, 66% yield). ^{1}H NMR (THF-d_8): δ 1.95 (9H, s, μ_3-$OCMe_3$), 1.54 (18H, s, μ-$OCMe_3$), 1.46 (9H, s, μ-$OCMe_3$), 1.32 (18H, s, $OCMe_3$), 1.28 (9H, s, $OCMe_3$).

Crystals were grown at room temperature over a two week period from a concentrated THF solution in an H-shaped tube sealed with a greaseless stopcock. Under a nitrogen purge several crystals were selected and placed in Paratone-D oil. The best crystal was mounted onto a Siemens P3 diffractometer equipped with a modified LT-2 low-temperature system. Since the crystal was of poor quality, a limited data set (2θ range 4.0° to 40.0°) was collected at 173 K and only the atomic connectivity of the compound could be unambiguously determined. The observed $Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Br)(\mu\text{-}OCMe_3)_3(OCMe_3)_3Br(THF)_2$ structure (Figure 1) is analogous to that of $Y_3(OCMe_3)_7Cl_2(THF)_2$.[20] The triangle of metals has μ-$OCMe_3$ ligands on each edge and a μ_3-$OCMe_3$ and a μ_3-Br above and below the plane of the metals. One metal is ligated by a terminal $OCMe_3$ and a terminal bromide ligand, whereas the other two metals each are ligated by one terminal $OCMe_3$ ligand and one THF. The compound crystallizes from THF in the space group $P2_1/c$ with a = 17.913(3) Å, b = 15.537(5) Å, c = 20.885(5) Å, β = 104.12(2)°, V = 5637(2) Å^3 and D_{calcd} = 1.445 Mg m^{-3} for Z = 4. Of the 5776 reflections collected, a least squares refinement of the model based on 2341 observed reflections ($|F_o| > 3.0\sigma|F_o|$) converged to a final R_F = 10.3%.

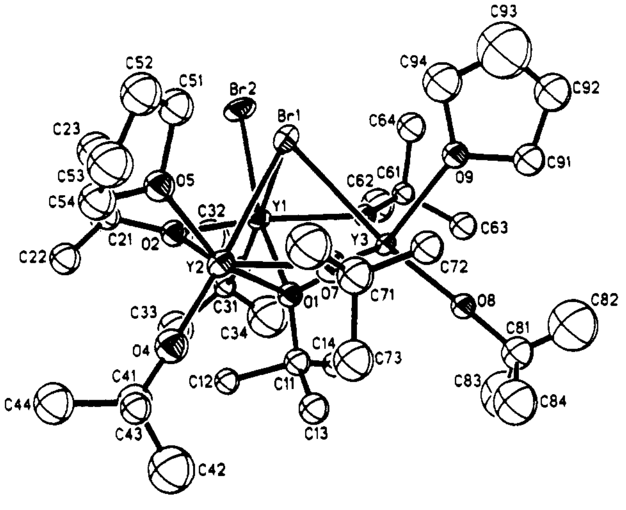

Figure 1. ORTEP diagram of $Y_3(OCMe_3)_7Br_2(THF)_2$, **4**.

CP/MAS Experiments. CP/MAS ^{89}Y NMR spectra were obtained on a Chemagnetics CMX-200 spectrometer equipped with a dedicated MAS ^{89}Y probe. Air sensitive samples (1.0–1.5 grams each) were packed in a glovebox under nitrogen, into 7.5 mm OD MAS rotors with Kel-F caps. Samples were spun at the magic angle at 1.0–3.0 kHz. No other hardware modifications were necessary.

Hartmann-Hahn matching conditions were found on each sample in the following manner. First, the spectrometer was set in the proton observation mode and a single-pulse ^{1}H spectrum of a sample was collected. The 90-degree proton pulse width was calibrated to 10 μs and the corresponding proton channel power was measured on a 400 MHz oscilloscope. The spectrometer was then set to the ^{89}Y CP/MAS observation mode (CP via spin-locking) and the proton channel power level was readjusted to match the original power level. At a contact time of 20 ms, the ^{89}Y channel power was gradually increased until maximum signal intensity was reached. Both ^{1}H and ^{89}Y channels were retuned on each sample and the above calibration process was repeated. In contrast to earlier studies,[10] probe ringing did not cause problems in the CP/MAS experiment. It can easily be eliminated by phase cycling (spin-temperature inversion[1]) and the use of a pre-acquisition delay of 15 μs.

The spectral width was 10 kHz. From 128 to 1024 complex data points were acquired and zero-filled to 2048 data points before Fourier transformation. The pre-delay was set from 2 to 10 seconds with the pre-acquisition delay set to 15 μs. The chemical shift was referenced to the $YCl_3{\cdot}6H_2O$ signal as 58 ppm, which corresponds to a calibration versus a 1 M solution of YCl_3.[2]

Single-Pulse Experiments. Single-pulse experiments (with proton decoupling during acquisition) were performed on $YX_3(THF)_3$ (X = Cl, Br, I) to obtain the chemical shift values. An YF_3 single-pulse spectrum was also obtained. The spectral width was increased to 20 kHz and 512 complex data points were acquired and zero-filled to 2048 data points before Fourier transformation. Pre-delay was 100 s, pulse width was 3 μs, and the pre-acquisition delay was 15 μs.

Results and Discussion

^{89}Y CP/MAS Spectra. Table I shows the CP/MAS ^{89}Y NMR spectral data on $YI_3(THF)_3$ (**1**), $YBr_3(THF)_3$ (**2**), $YCl_3(THF)_3$ (**3**), $Y_3(OCMe_3)_7Br_2(THF)_2$ (**4**), $Y_3(OCMe_3)_7Cl_2(THF)_2$ (**5**), $Y(OCMe_3)_3(AlMe_3)_2(THF)$ (**6**), $Y_3(OCMe_3)_9(HOCMe_3)_2$ (**7**), $Y_3(OCMe_3)_9(THF)_2$ (**8**), $[(C_5H_4SiMe_3)Y(OCMe_3)_2]_2$ (**9**), $YBr_3{\cdot}6H_2O$ (**10**), $Cp_5Y_5(OMe)_8O$ (**11**), $Cp_2YBr(THF)$ (**12**), YF_3 (**13**), $[Cp_2YCl]_2$ (**14**), $Cp_2YCl(THF)$ (**15**), and $Cp_3Y(THF)$ (**16**) along with some previously reported data. Figures 2–5 show the

---

(18) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

(19) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672–6677.

(20) Bradley, D. C.; Chudzynska, H.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1991**, *10*, 1049–1059.

(21) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.*, in press.

(22) Evans, W. J.; Sollberger, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 6095–6096.

(23) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291–1300.

(24) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383–392.

(25) Carter, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–391.

(26) Clark, D. L.; Francom, T. M.; Miller, M. M.; Watkin, J. G. *Inorg. Chem.* **1992**, *31*, 1628–1633.

Table I. ^{89}Y Solid State NMR Resonances

compd	δ (ppm)	contact time (ms)	ref
$YI_3(THF)_3$ (**1**)	663, 547, 529, 356	20	*a*
$YBr_3(THF)_3$ (**2**)	441	20	*a*
$YCl_3(THF)_3$ (**3**)	370, 361, 253, 218	20	*a*
Y_2O_3	315, 270	single-pulse	3
$Y_3(OCMe_3)_7Br_2(THF)_2$ (**4**)	227, 157	17–20	*a*
$Y_3(OCMe_3)_7Cl_2(THF)_2$ (**5**)	247, 200	20	*a*
$Y(OCMe_3)_3(AlMe_3)_2(THF)$[b] (**6**)	339, 174	17–20	*a*
$Y_3(OCMe_3)_9(HOCMe_3)_2$ (**7**)	161	20	*a*
$Y_3(OCMe_3)_9(THF)_2$ (**8**)	173, 152	20	*a*
$[(C_5H_4SiMe_3)Y(OCMe_3)_2]_2$ (**9**)	158, −11	20	*a*
$Y_2Sn_2O_7$	150	single-pulse	2
$YBr_3{\cdot}6H_2O$ (**10**)	80	20	*a*
$Y_2Ti_2O_7$	65	single-pulse	2
$YCl_3{\cdot}6H_2O$	58	20	10/*a*
$Y(OAc)_3{\cdot}4H_2O$	47	30	10
$Y(acac)_3{\cdot}3H_2O$	27, 22	21.5	10/*a*
$Cp_5Y_5(OMe)_8O$ (**11**)	6, −1	17–20	*a*
$Y_2(SO_4)_3{\cdot}8H_2O$	−46	single-pulse	10
$Y(NO_3)_3{\cdot}6H_2O$	−53	8	10
$Cp_2YBr(THF)$ (**12**)	−90	20	*a*
YF_3 (**13**)	−112	single-pulse	*a*
$[Cp_2YCl]_2$ (**14**)	−122	20	*a*
$Cp_2YCl(THF)$ (**15**)	−200	20	*a*
YCl_3	−230	single-pulse	4
$Cp_3Y(THF)$ (**16**)	−405	20	*a*

[a] This work. [b] This sample was a mixture, containing $Y(\mu\text{-}OCMe_3)_3(AlMe_3)_3$.

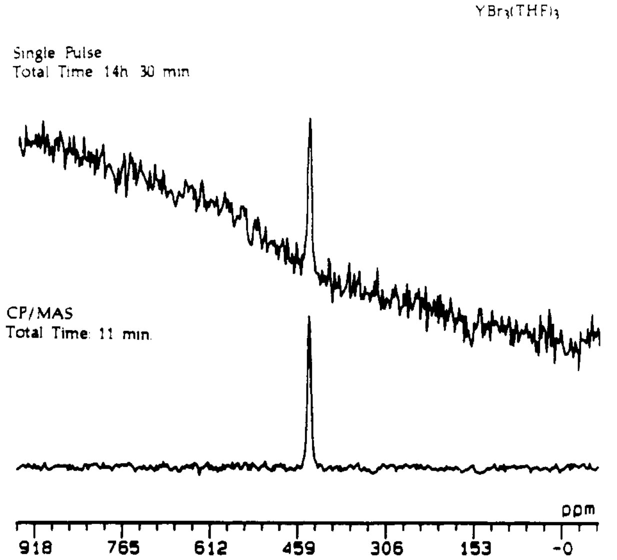

Figure 2. Comparison of single pulse and CP/MAS spectra of $YBr_3(THF)_3$, **2**.

actual spectra of several of the complexes. The spectra were typically obtained using 1.0–1.5 g samples packed into the MAS rotors under nitrogen in a glovebox. Calibration of the Hartmann–Hahn match for each sample typically took 15–20 minutes. A single-pulse MAS ^{1}H spectrum was easily obtained since the proton resonances from most of these compounds are reasonably sharp (10–2000 Hz). No sample change or probe retuning were necessary in the process. In most cases, ^{89}Y spectra with reasonable signal to noise ratios (>40:1) were obtained within 10 minutes. Since the overall time needed to obtain a spectrum was small, decomposition of the air sensitive samples in the rotor was minimal. In most cases, the bulk of the original complex could be recovered in the glovebox after the ^{89}Y experiment was completed.

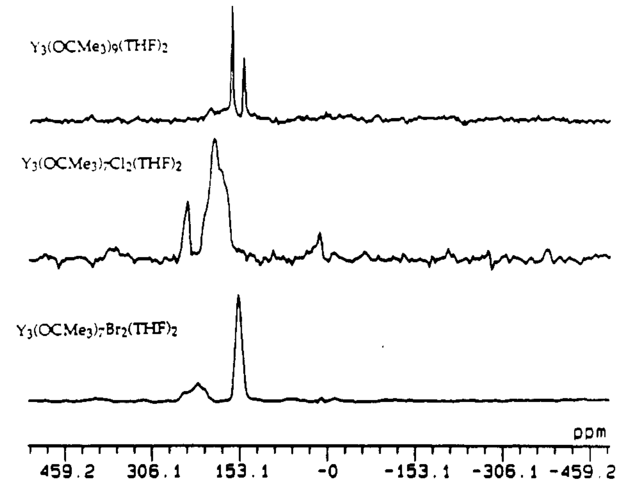

Figure 3. ^{89}Y CP/MAS NMR spectra of compounds with multiple yttrium environments.

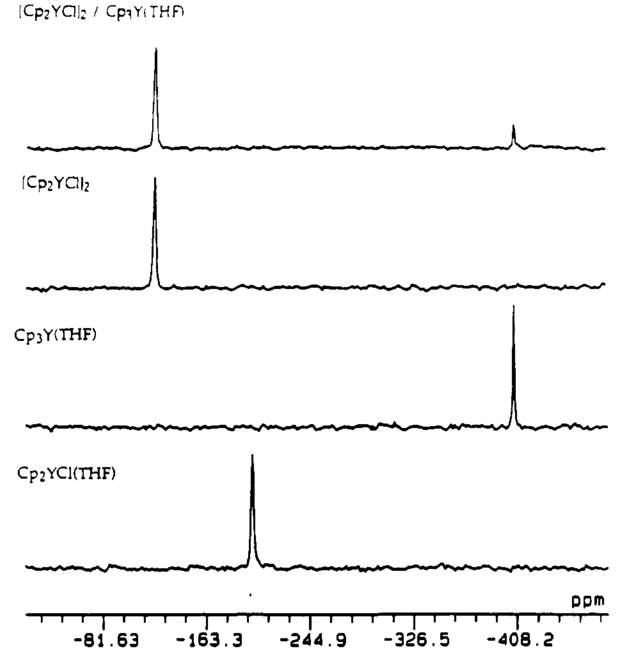

Figure 4. ^{89}Y CP/MAS NMR spectra of compounds with single yttrium environments including a sample which was a mixture of two of these compounds.

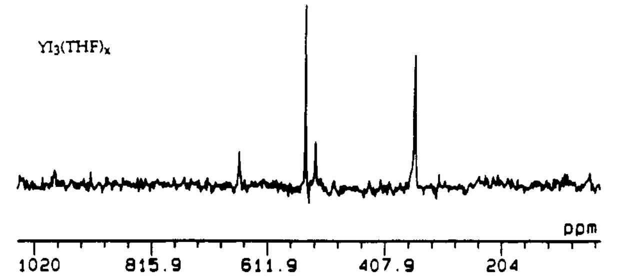

Figure 5. ^{89}Y CP/MAS NMR spectrum of a sample of $YI_3(THF)_3$, illustrating the presence of more than one yttrium environment in the sample.

Figure 2 shows a comparison of a single pulse spectrum and a CP/MAS spectrum for $YBr_3(THF)_3$. As shown, a great improvement in the signal to noise ratio is obtained using the CP/MAS method. To determine the range of Y···H distances needed to effect the cross polarization, the shortest metal to hydrogen distances in the compounds were estimated from the available crystallographic data. Experimentally, we find that cross polarization is successful when hydrogen atoms are within an estimated 2.8–3.5 Å of the yttrium metal center.[27]

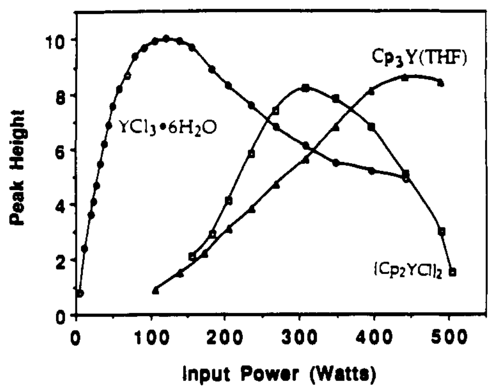

Figure 6. Input power effects.

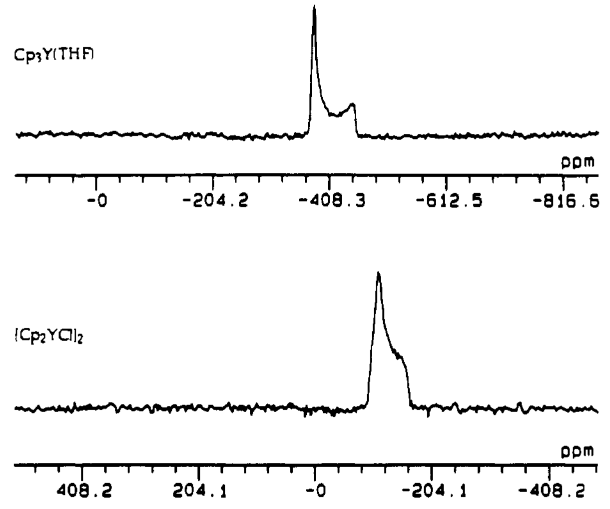

Figure 7. Static CP/MAS spectra of **16** and **14**.

Instrumental Parameters. To show the Hartmann–Hahn match characteristics of ^{89}Y cross polarization, CP/MAS experiments were performed with variable ^{89}Y input power on several samples (Figure 6). The broad power curves in Figure 6 show that, although the optimal Hartmann–Hahn match conditions can change substantially from one sample to another, an exact Hartmann–Hahn match is not strictly required to obtain good CP/MAS ^{89}Y NMR spectra. This agrees with the ^{89}Y NMR results previously reported for hydrated compounds.[10]

Static CP spectra were obtatined on several samples (Figure 7) to show the size of the ^{89}Y chemical shift anisotropy (CSA). Since the ^{89}Y nucleus resonates at a very low frequency, its CSA in frequency units is very small (1–2 kHz at 4.7 Tesla) and high sample spinning rates are not needed. Figure 8 shows that, as long as the spinning rate is sufficient to remove side bands, lower spinning rates actually increase the CP efficiency.[28]

CP/MAS experiments with variable contact time were performed on several samples with the optimized Hartmann–Hahn match conditions (see supplementary material). In all cases, the signal intensities increase with longer contact times (1–20 ms), but there is no change in spectral linewidths. The variable contact time studies showed that ^{1}H $T_{1\rho}$ values in these samples are quite long and the ^{1}H–^{89}Y interactions are weak. This result is consistent with the long Y···H distances in these samples.

Resonance Positions. The samples in Table I display an ^{89}Y resonance range of over 1000 ppm. A comparison of the solution and solid state NMR resonances (Table II) shows that similar shifts are observed in solution and in the solid state, a situation which is typical for other nuclei.[29] However, the solution and solid state resonance positions for a specific complex are not identical.

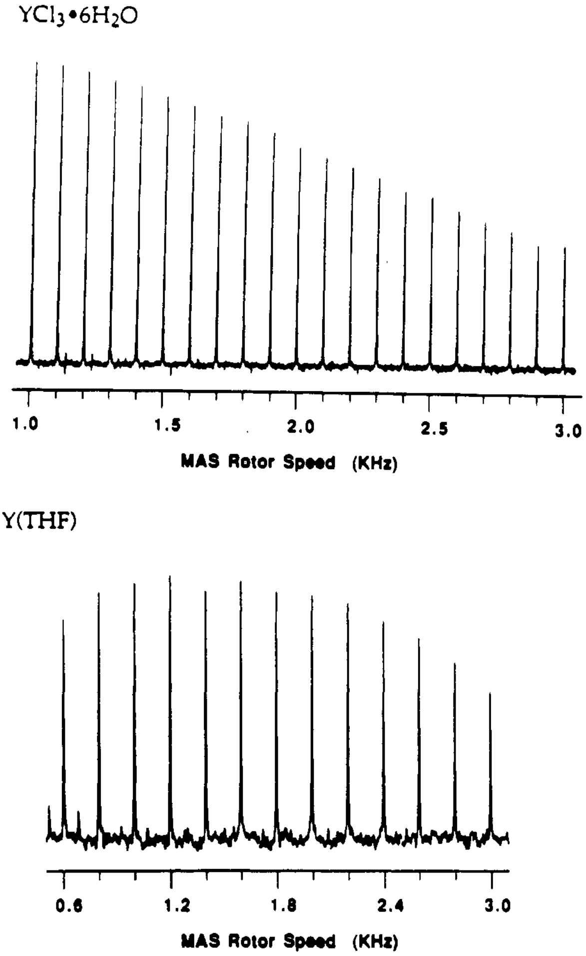

Figure 8. Spinning rate effects.

Table II. Comparison of Solution and Solid State ^{89}Y NMR Shifts (δ (ppm))

compd	solid state	ref	solution	ref
$YBr_3·6H_2O$ (**10**)	80	*a*	6.8	34
$YCl_3·6H_2O$	58	33	8.9	33
$[Cp_2YCl]_2$ (**14**)	−122	*a*	−97.0	34
$Cp_2YCl(THF)$ (**15**)	−200	*a*	−103.0	34
$Cp_3Y(THF)$ (**16**)	−405	*a*		
$(C_5H_4Me)_3Y(THF)$			−371.0	34

[a] This work.

Within a narrow series of complexes, trends in ^{89}Y chemical shift versus the composition of the ligand set of the complex can be observed. However, given the vagaries of heteronuclear NMR shifts,[29,30] the trends observed should not be used to predict resonance positions for complexes of greatly differing composition. From the data in Table I, it appears that cyclopentadienyl ligands cause upfield (negative) shifts. For example, the resonances of $Cp_3Y(THF)$ and $Cp_2YCl(THF)$ occur at −405 and −200 ppm, respectively, whereas $YCl_3(THF)_3$ shows resonances beyond +200 ppm. The polymetallic complexes containing *tert*-butoxide ligands, **4–8**, give low field shifts and in this respect they are similar to Y_2O_3. In the isostructural bromide/chloride pairs, (a) $YBr_3·6H_2O$, **10**, and $YCl_3·6H_2O$ and (b) $Cp_2YBr(THF)$, **12**, and $Cp_2YCl(THF)$, **15**, the bromide complexes have resonances at lower field than the chloride compounds. This same trend is seen for the halogen compounds $YX_3(THF)_n$ [X = Cl, Br, I][31] which

---

[27] Yttrium–hydrogen distances were calculated from crystallographic data in the Cambridge Data Base by using the SHELX program to add hydrogen atoms at fixed positions on the carbon atoms in the molecules.

[28] Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–570.

[29] Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987.

[30] For example, p 72 and p 579 in ref 29 and references therein.

is contrary to the effect observed for carbon nuclei and has been termed an "inverse halogen effect".[29,32] In general, the data available to date show that for the molecular THF solvated halides appear to give the lowest field shifts, followed by alkoxides, followed by organic ligands.

Correlation of the Number of Resonances with the Number of Solid State Environments. Previous solid state ^{89}Y NMR studies have found single resonances for all complexes except Y_2O_3[3] and $Y(acac)_3{\cdot}3H_2O$.[10] In the former case, the crystal structure of the complex has two different yttrium environments. In the latter case, the presence of two solid state peaks was not consistent with the crystal structure of the sample. It was uncertain whether two crystalline forms of this material exist or if an impurity was present in the commercially obtained sample. The sample of $Y(acac)_3{\cdot}3H_2O$ which we obtained commercially also exhibited more than one peak.

In the present study, single yttrium environments are expected in the solid state for complexes **2**, **10**, and **12–16** and single resonances were observed in the corresponding ^{89}Y CP/MAS spectra. For complexes **4**, **5**, and **11**, X-ray crystallographic studies showed that multiple yttrium environments were present in the solid state and multiple peaks were observed in the ^{89}Y CP/MAS spectra. Specifically, for the trimetallic complexes $Y_3(OCMe_3)_7Br_2(THF)_2$, **4**, and $Y_3(OCMe_3)_7Cl_2(THF)_2$, **5**, a 2:1 ratio of unique yttrium environments exists in the molecular species and two peaks are found in the ^{89}Y NMR spectra (Figure 3). $Cp_5Y_5(OMe)_8O$, **11**, also has two types of yttrium environments in its solid state structure and two resonances are observed in the CP/MAS spectrum. Although X-ray crystallographic data are not available on $Y_3(OCMe_3)_9(THF)_2$,[20] the structure is expected to be analogous to those of **4** and **5**. Consistent with this, two resonances are observed for this complex. On the basis of these data, it appears that the number of unique environments observed in X-ray crystallographic studies and the number of resonances seen in ^{89}Y CP/MAS NMR spectra are identical.

However, in some cases the number of resonances did not match the expected solid state structure. $YI_3(THF)_3$ and $YCl_3(THF)_3$ each exhibited four resonances, although a single signal was expected. We cannot determine if this is due to multiple solid state environments, variable solvation by THF, or impurities. However, since the sample of $YBr_3(THF)_3$ freshly prepared directly from the metal and bromine exhibited a single resonance, the latter two reasons seem more likely. The spectrum of $YI_3(THF)_3$, Figure 5, shows how valuable the CP/MAS ^{89}Y NMR technique is in demonstrating non-uniform samples. A spectrum obtainable in 10 minutes showed that more than one yttrium environment was present whereas it would be difficult to get the same information in a comparable amount of time by other analytical means.

The spectra of $Y(OCMe_3)_3(AlMe_3)_2THF$, **6**, and $[(C_5H_4SiMe_3)Y(OCMe_3)_2]_2$, **9**, also exhibit one more resonance than expected. For this first case, we know that this sample was a mixture of two complexes, since two different crystallographically characterized compounds have been crystallized from this system. For **9**, we suspect that there are two accessible crystalline forms in the solid state. It has proven much more difficult to crystallize **9** than analogs with other cyclopentadienyl groups and this may be due to the availability of more than one solid state structure. Hence, it is possible that CP/MAS ^{89}Y NMR may be useful in identifying which yttrium complexes are optimum for obtaining good single crystalline samples. $Y_3(OCMe_3)_9(HOCMe_3)_2$, **7**, which is formally analogous to $Y_3(OCMe_3)_7Br_2(THF)_2$, **4**, $Y_3(OCMe_3)_7Cl_2(THF)_2$, **5**, and $Y_3(OCMe_3)_9(THF)_2$, **8**, is also anomalous in that a single resonance was observed in contrast to two signals for the analogs. No crystal data are available on **7**, but its lanthanum analog has been found to have a disordered structure in the solid state.[20] The linewidth of the signal for **7**, 238 Hz, is much greater than linewidths observed for **4**, 127 Hz.

Integrated Intensity. Although the integrals of the resonances for $Y_3(OCMe_3)_7Br_2(THF)_2$, **4**, $Y_3(OCMe_3)_7Cl_2(THF)_2$, **5**, and $Y_3(OCMe_3)_9(THF)_2$, **9**, match the ratio of unique solid state environments, this is not the case for $Cp_5Y_5(OMe)_8O$, **11**. To probe the validity of the integrals of the ^{89}Y CP/MAS spectra, the spectrum of a mixture of $[Cp_2YCl]_2$ and $Cp_3Y(THF)$ of known composition (2:1 molar ratio, Figure 4) was obtained at contact times of 5, 10, 15, and 20 msec. The observed ratio of integrals varied from 100:15 to 100:28 when approximately a 2:1 ratio was expected. Even in these somewhat similar complexes, the difference in CP efficiency between the two ^{89}Y sites appears to be large enough to make the integrals unreliable.

YF_3. To obtain an ^{89}Y spectrum on YF_3, a single pulse spectrum was taken. A higher sample spinning rate, 3.0 kHz, was used and the total acquisition time was more than 24 h. Attempts to generate a solvated sample of YF_3 containing either H_2O or THF were unsuccessful, since the samples displayed no CP/MAS spectra. In this case, the CP/MAS method proved to be a very useful, quick method for demonstrating that no solvated adduct was formed.

Conclusion

Using CP/MAS techniques, solid state ^{89}Y NMR spectroscopy is conveniently applicable to a wide variety of solids containing yttrium. The technique can be extended beyond air stable hydrated samples and can easily provide quality spectra in minutes with a minimum of instrumental setup and adjustment. The solid state ^{89}Y resonances span a broad range and provide characteristic "fingerprint" data for a given ligand environment around the metal. The number of resonances observed in a spectrum correlates well with the number of solid state environments present. This technique provides an easy method to quickly determine the purity of a bulk sample not tractable by other standard methods.

Acknowledgment. We thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy for support of this research. Funds for the purchase of the solid state NMR spectrometer were from Grant NSF CHE-9008508. We thank Dr. Jim Frye of Chemagnetics Inc. for assistance with the initial set up of the solid state spectrometer and Professor F. J. Feher for helpful discussions.

Supplementary Material Available: Figures showing CP/MAS, static, and single pulse solid state NMR spectra and an ORTEP diagram and tables listing crystal data, positional parameters, bond distances and angles, and thermal parameters for $Y_3(OCMe_3)_7Br_2(THF)_2$, **4** (38 pages). Ordering information is given on any current masthead page.

---

(31) The bromide/chloride pair **4** and **5** may show the opposite trend. However, since each of these complexes has two types of yttrium environments and since the pairs of resonances overlap, a trend cannot be definitively assigned.

(32) (a) Kidd, R. G. *Ann. Rep. NMR Spectrosc.* **1980**, *10A*, 1–79. (b) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; Chapter 8, pp 195–278.

(33) Adam, R. M.; Fazakerleye, B. V.; Reid, D. G. *J. Magn. Reson.* **1979**, *33*, 655–657.

(34) Evans, W. J.; Meadows, J. H.; Kostka, A. G.; Closs, G. L. *Organometallics* **1985**, *4*, 324–326.