FULL PAPER

¹H,⁸⁹Y HMQC and Further NMR Spectroscopic and X-ray Diffraction Investigations on Yttrium-Containing Complexes Exhibiting Various Nuclearities

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Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

Abstract: 2D ¹H,⁸⁹Y heteronuclear shift correlation through scalar coupling has been applied to the chemicalshift determination of a set of yttrium complexes with various nuclearities. This method allowed the determination of ⁸⁹Y NMR data in a short period of time. Multinuclear NMR spectroscopy as function of temperature, PGSE NMR-diffusion experiments, heteronuclear NOE measurements, and X-ray crystallography were applied to determine the structures of $[Y_5(OH)_5(L-Val)_4(Ph_2acac)_6]$ (1) $(Ph_2acac = diben-zoylmethanide, L-Val = L-valine), [Y(2)-(OTf)_3]$ (3), and $[Y_2(4)(OTf)_5]$ (5) (2: $[(S)P\{N(Me)N=C(H)Py\}_3]$, 4: $[B\{N(Me)N=C(H)Py\}_4]^-)$ in solution and in the solid state. The structures

Keywords: cluster compounds • ligand effects • NMR spectroscopy • X-ray diffraction • yttrium found in the solid state are retained in solution, where averaged structures were observed. NMR diffusion measurements helped us to understand the nuclearity of compounds **3** and **5** in solution. ${}^{1}H, {}^{19}F$ HOESY and ${}^{19}F, {}^{19}F$ EXSY data revealed that the anions are specifically located in particular regions of space, which nicely correlated with the geometries found in the X-ray structures.

Introduction

Rare-earth-metal complexes and/or clusters have attracted considerable interest in recent years owing to their utility as highly active catalysts for a variety of processes^[1-7] and as useful compounds in several biological and medical applications.^[8-10] Rare-earth-metal cations are paramagnetic for all configurations from 4f¹ to 4f¹³, and therefore many researchers have chosen to investigate the chemistry of the diamagnetic cations Sc³⁺, Y³⁺, and La³⁺, as they do not possess any 4f electrons. To a lesser extent, Yb²⁺ and Lu³⁺, which exhibit a completely filled 4f shell, have also been investigated. From an NMR spectroscopic point of view, all five nuclei have been directly observed.^[11-14] Metal complexes containing these diamagnetic ions—such as Y³⁺—can be used to model the structures and reactivities of related complexes of

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paramagnetic lanthanides owing to their similar ionic radii and chemical behavior.

As a monoisotopic species with spin I=1/2, the ⁸⁹Y nucleus is attractive for NMR studies. The chemical-shift range of ⁸⁹Y spans about 1300 ppm, and therefore it is quite sensitive to small changes in the coordination sphere of the metal center.^[14,15] However, the rather low receptivity ($D^{C} =$ 0.7) and the long T_1 relaxation times^[14-17] of ⁸⁹Y make conventional pulse-acquisition ⁸⁹Y NMR measurements very time-consuming,^[15,18] thus they are still far away from being used in routine experiments. Valuable coupling information has mainly been extracted from 1D spectra of nuclei to which ⁸⁹Y is scalarly coupled, that is, ¹H-⁸⁹Y,^{[19-24] 13}C- ${}^{89}Y$, ${}^{[20,24]}$ ${}^{15}N$ ${}^{89}Y$, ${}^{[25]}$ ${}^{29}Si$ ${}^{-89}Y$, ${}^{[26]}$ ${}^{31}P$ ${}^{-89}Y$, ${}^{[26-29]}$ and ${}^{77}Se$ ${}^{-9}$ ⁸⁹Y.^[29,30] The alternative procedures proposed for acquiring ⁸⁹Y NMR data under more-convenient conditions include: 1) increasing the amount of substance, 2) using NMR tubes with larger diameters (10-25 mm),^[14,17,30] 3) the addition of paramagnetic reagents,^[28,31,32] 4) the application of polarization-transfer techniques through the nuclear Overhauser effect ($\gamma < 0$, negative NOE),^[17] INEPT,^[33] or DEPT,^[34] and 5) creating hyperpolarized ⁸⁹Y complexes.^[35-37] In case the yttrium cation shows couplings to any protons located in close spatial proximity or at the periphery of the molecule, the alternatives are HMQC or HSQC sequences, which have previously been applied by Anwander and co-workers.^[38-40] Very recently, some of us have reported the indirect ³¹P detection of ⁸⁹Y in the product of the reaction of yttrium nitrate with triphenylphosphine oxide in THF,^[41] and in the

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characterization of 1:1 and 2:1 complexes that were formed between yttrium nitrate and a new class of tridentate ligand that contained two diphenylphosphinic amide side-arms connected through a phenylphosphine oxide moiety.^[42]

Herein, we report the application of indirect ¹H detection of ⁸⁹Y by using 2D HMQC sequences with gradients for coherence selection, thus allowing rapid access to ⁸⁹Y NMR data on a set of yttrium-containing compounds. Moreover, the use of ¹H,¹⁹F PGSE NMR diffusion and ¹H,¹⁹F heteronuclear NOE experiments provided additional information on how cationic complexes interact with their counteranions in solution. These results were compared with those obtained from X-ray diffraction analysis. We studied three compounds that had different numbers of yttrium cations to show the scope of the methods used.

Results and Discussion

Syntheses of the metal complexes: To obtain compounds with various numbers of yttrium cations, we synthesized mono- and dinuclear complexes, as well as a pentanuclear cluster. We recently reported the synthesis of the pentanuclear hydroxy cluster $[Y_5(OH)_5(L-Val)_4(Ph_2acac)_6]$ (1), which features the simultaneous ligation of both an α -amino acid and a β -diketonate ligand.^[43] Compound 1 was obtained from the reaction of yttrium trichloride hexahydrate $[YCl_3-(H_2O)_6]$ with dibenzoylmethane (Ph_2acacH), L-valine (L-ValH), and a base (Scheme 1). The structure of compound



Scheme 1. a) Synthesis of compound 1; b) schematic representation of the solid-state structure of compound 1, which shows the heavy-atom scaffold and the principal coordination of the ligands.

1 was established by X-ray diffraction and by routine ¹H and ¹³C NMR measurements, as well as by PGSE studies.^[43] PGSE studies showed that compound 1 retains its pentanuclear structure when dissolved in CDCl₃. The Y₅ core of compound 1 displays a square-based pyramidal arrangement, that is, the metal atoms occupy the vertices of a square pyramid. In the square base, four yttrium atoms are linked by one μ_4 -O atom, whereas in the four triangular

faces, three metal atoms are linked by one μ_3 -O atom each. All these linking oxygen atoms represent fragments of the hydroxy bridges, which stabilize the pyramidal shape from inside. The amino acids, which were deprotonated under basic conditions at the carboxy group, coordinate through the nitrogen atom of the amino group and through one oxygen atom of the carboxy group in a chelating fashion to one basal metal atom each.^[43] In addition, this carboxy oxygen atom also bridges the chelated basal metal atom with an adjacent metal atom.

Regarding the mono- and dinuclear yttrium complexes, we focused on multifunctional,^[44] chemically robust, and readily accessible N-donor ligands to provide stoichiometrically well-defined 1:1 and 1:2 coordination compounds with yttrium.

Ligand $[(S)P{N(Me)N=C(H)Py}_3]$ (2) was prepared in a two-step synthesis starting from phosphorylsulfide and *N*methylhydrazine according to a modified literature procedure.^[45–47] In the first step, both compounds were reacted at 0°C in dry CHCl₃ to afford tris(methylhydrazido)phosphorylsulfide, followed by condensation with 2-picolinealdehyde in MeOH in the presence of magnesium sulfate to form the product in good yield (80%). The molecular structure of compound **2** (see the Supporting Information, Figure S1) confirmed the expected atomic framework.

The mononuclear complex $[Y(2)(OTf)_3]$ (3; $OTf^-=CF_3SO_3^-)$ was obtained from the reaction of ligand 2 with yttrium triflate, $Y(OTf)_3$, in THF (Scheme 2). The product was insoluble in THF and precipitated only a few minutes after adding a solution of the ligand to a suspension of the metal precursor in THF. Thus, the solid was easily isolated by filtration. Re-crystallization of the crude product from MeCN/Et₂O afforded single crystals of compound 3 that were suitable for X-ray analysis (see below).



Scheme 2. Synthesis of $[(S)P{N(Me)N=C(H)Py}]$ (2) and the mononuclear complex $[Y(2)(OTf)_3]$ (3).

FULL PAPER

To obtain a dinuclear complex, we needed to develop a ligand that is capable of linking several metal centers. The protonated precursor of the boron-containing ligand $[B{N(Me)N=C(H)Py}_{4}]^{-}$ (4) was synthesized according to a modified literature procedure.^[48] H[B{N(Me)N=C(H)Py}] (H-4) was obtained by heating four equivalents of 2-(2methylhydrazono)methylpyridine to reflux in toluene for several hours with one equivalent of tris(dimethylamido)borane. Subsequent washing with n-hexane and MeCN afforded a yellow crude solid, which turned out to be a mixture of the hydrazone and ligand H-4 in a 1:2.4 ratio (Scheme 3). Without further purification, the mixture was reacted in hot toluene with two equivalents (relative to H-4) of Y(OTf)₃ in THF to afford the dinuclear complex $[Y_2(4)(OTf)_5]$ (5). This latter compound was purified by re-crystallization from an MeCN solution that was layered with Et₂O.

NMR investigations and solid-state structures: To confirm the general applicability of the ¹H,⁸⁹Y gHMQC NMR sequence for all three compounds, we first used compound **1** to perform some experiments in addition to the previously reported PGSE studies.^[43]

In the ¹H NMR spectrum of compound **1**, a few diagnostic signals were observed for the Ph₂acac ligands in the aromatic region, plus two well-defined singlets at $\delta_{\rm H}$ =6.22 and 6.44 ppm in a 1:2 ratio, which were due to the methine bridges. As underlined by the X-ray structure of compound **1**, this observation originates from two different coordination environments: the more intense signal was ascribed to those Ph₂acac ligands that coordinate to the basal metal atoms, whereas the other environment was assigned to those Ph₂acac ligands that coordinate to the apical yttrium atom. The NH₂ protons were assigned with the help of two different experiments: 1D gTOCSY NMR measurements re-

vealed an ABCX spin system for the L-valine moiety, in which each of the amino protons showed significantly different chemical shifts (Figure 1). Second, 2D ¹H,¹³C gHMQC spectra showed no scalar interactions for any of the signals at $\delta_{\rm H}$ =1.68 and 5.15 ppm.

The two NH₂ resonances were unambiguously correlated to the ⁸⁹Y NMR resonance at δ_Y =141.5 ppm by ¹H,⁸⁹Y gHMQC NMR experiments (Figure 2). When the preparation delay was optimized for coupling constants below 7 Hz, we observed interactions between the two different Ph₂acac methine protons (at δ_H =6.22 and 6.44 ppm) and the two magnetically different yttrium nuclei, one of which belongs to the aforementioned yttrium resonance at



Figure 1. 1D gTOCSY NMR (500.13 MHz) expansion of pentanuclear cluster **1** in CHCl₃ at ambient temperature (τ_{SL} =120 ms; τ_{SL} : duration of the spin-lock pulse). The asterisks indicate the irradiated signal.



Scheme 3. Syntheses of $[H(B{N(Me)N=C(H)Py}_{4})]$ (H-4) and the dinuclear complex $[Y_{2}(4)(OTf)_{5}]$ (5).

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Figure 2. ¹H,⁸⁹Y gHMQC spectrum (400 MHz) of cluster **1** (60 mM) in CDCl₃ at 292 K. A complete data set was acquired in 2 h 40 min, with a preparation delay optimized for a 7 Hz coupling constant. 1D ¹H NMR and 1D ⁸⁹Y NMR spectra are shown along their respective edges. The references used were TMS and Y(NO₃)₃ for ¹H and ⁸⁹Y, respectively. The gradient ratio was calculated according to the γ values and was set to 60:20:43.9. Note the couplings between the NH₂ protons of the L-Val ligands and the μ_4 -OH group (a sharp singlet of low intensity at δ_H =1.07 ppm, which was not observed for all samples of **1** measured in this study) that was coordinated to the basal Y atoms of the square pyramid, and between the Ph₂acac methine protons coordinated to both the apical and basal yttrium metal atoms.

 $\delta_{\rm Y}$ =141.5 pm and the other represented a new resonance located at $\delta_{\rm Y}$ =59.2 ppm. These two important cross-peaks allowed us to unequivocally assign the two yttrium signals as basal and apical atoms, respectively (Figure 2).

To confirm this assignment, a 1D ⁸⁹Y NMR spectrum was acquired (Figure 2, left axis; also see the Supporting Information, Figure S2), which confirmed the formation of the two expected signals in a 4:1 ratio. In addition, an extra cross-peak was detected in the 2D map (Figure 2), which arises from the coupling between the μ_4 -OH resonance ($\delta_{\rm H}$ =1.07 ppm) and the square-based pyramidal yttrium resonance ($\delta_{\rm Y}$ =141.5 ppm), thus supporting their assignment.

The ¹H,⁸⁹Y gHMQC 2D maps of compounds **3** and **5** showed scalar interactions with the imine protons (Figure 3). In the case of mononuclear complex **3**, only one imine signal correlates with the metal nucleus ($\delta_{\rm Y} = -4.9$ ppm), whereas in complex **5**, the chemically inequivalent imine protons identify the yttrium signal at $\delta_{\rm Y} = 0.4$ ppm.

Pulsed gradient spin-echo (PGSE) NMR-diffusion methods are widely used,^[49–53] in particular when associated with ion-pairing. PGSE measurements, in combination with homo and/or hetero NOE methods, offer a new perspective on the interactions between transition-metal-salt-derived cations and anions in solution.^[54–57] Furthermore, the solvent dependencies of the diffusion constants (*D*) offer a hint as to which extent any solvent promotes ion-pairing. Dissolving a variety of organic and inorganic salts in CHCl₃ often leads to more than 95% ion-pairing, whereas the use of coordinating solvents, such as MeOH or MeCN, affords much-less or no ion-pairing at all.

As demonstrated in previous studies, it is assumed that up to 100% ion pairing occurs, if the cation and the anion reveal approximately identical D values, thereby affording hydrodynamic radii $r_{\rm H}$ (from the Stokes–Einstein equation) that are substantially greater than those estimated by either

crystallography or quantumchemical calculations. The calculated $r_{\rm H}$ values assume spherical shapes; hence, they do not represent the real shape of the molecules. Nevertheless, their use has been well-established for the purposes of comparison because they offer a rapid and facile method to recognize ionpairing. To learn more about how ions interact and to specifically determine whether there might be a preferred structure for the yttrium salts described above, we measured ¹H,¹⁹F PGSE and ¹H,¹⁹F HOESY spectra of the two cationic yttrium complexes. Diffusion data of cluster 1 have been reported previously.^[43] We used solutions

of compounds **3** and **5** in MeCN for these measurements because, as we have previously reported,^[58,59] some dicationic ruthenium species have shown a surprisingly large degree of ion-pairing, which had a significant implication on the catalysis outcome.



Figure 3. ¹H,⁸⁹Y gHMQC spectrum (500 MHz) for a) complex **3** (60 mM) and b) compound **5** (30 mM) in CD₃CN at 294 K. Complete data sets were acquired in 1 h 20 min with a preparation delay optimized for a 12 Hz coupling constant. The internal projections (left edge) and the 1D ¹H NMR spectra (top edges) are both shown. The references signals used were TMS and Y(NO₃)₃ for ¹H and ⁸⁹Y, respectively. The gradient ratio was calculated according to the γ values and was set to 60:20:43.9.

Table 1. D and $r_{\rm H}$ values for vttrium complexes 3 and 5 at ambient temperature in CD₃CN.

Compound	Nucleus	$D \ [10^{-10} \mathrm{m^2 s^{-1}}]^{[a]}$	$r_{ m H} [m \AA]^{[b]}$	r_{X} $[\mathrm{\AA}]^{[\mathrm{c}]}$
3	$^{1}\mathrm{H}$	9.022	6.6	6.4
	¹⁹ F	11.455	5.2	
	¹ H (free CH ₃ CN)	36.15	1.6	
5	$^{1}\mathrm{H}$	8.806	6.8	7.6
	¹⁹ F	n.d. ^[d]	-	
	¹ H (free CH ₃ CN)	35.98	1.6	

[a] Experimental error in the D values was (± 2) %. [b] The viscosity (η) used in the Stokes–Einstein equation was $0.363 \times 10^{-3} \text{ kg m}^{-1} \text{s}^{-1}$. Values of η were taken from http://www.knovel.com. [c] Deduced from the Xray structure by considering the volume of the crystallographic cell divided by Z. This value was only an estimate because both molecular structures contained several solvent molecules in the crystal lattice (See the Experimental Section). [d] Not detected, owing to the broadness of the fluorine signal ($W_{1/2} = 42$ Hz).

Table 1 shows the self-diffusion constants (D) for complexes 3 and 5 in MeCN at concentrations of 60 and 30 mm, respectively. Notably, the D values for the cationic (1 H of the ligand) and anionic (19F of the triflate anions) parts of compound 3 are not identical. The D value for the anion was small and the $r_{\rm H}$ value correspondingly large (the expected value for a solvated triflate group in, for example, MeOH is about 3 Å). As a consequence, the $r_{\rm H}$ value of 5.2 Å (60 mm) was indicative of a relatively large amount of ion-pairing, even in MeCN.

An assessment of the ¹H,¹⁹F HOESY results for compound 3 required a detailed assignment of the most impor-

tant protons (see below) and an understanding of the molecular structure of the cationic complex. The preferred coordination numbers of Ln³⁺ ions, and specifically of Y3+ ions, are in the range 8-12.^[60] The yttrium cation is expected to coordinate to at least two of the three nitrogen atoms of each arm of the tripodal ligand (2); therefore, one may assume that the yttrium atom saturates its coordination sphere by binding to the oxygen atoms of the triflate anions.[61]

These assumptions were supported by X-ray diffraction on single crystals of complex 3, which revealed that six Ndonor atoms of the ligand are coordinated to the central Y³⁺ cation, thus forming a distorted trigonal prismatic coordination polyhedron (Figure 4). Furthermore, all three triflate counteranions are coordinated to the

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5329

metal cation in the solid state: two are lodged between the gaps between the hydrazonyl arms of the ligand, whilst the third is coordinated from underneath. The coordination of the triflate groups is responsible for the different angles between the central yttrium cation and the coordinating pyridyl nitrogen atoms (N7-Y-N8 about 140°, N6-Y-N7 about 125°, and N6-Y-N8 about 74°), and most likely, also for the trigonal twist of the ligand.

The fact that all of the triflate anions coordinate to the central yttrium cation is important for deciding where to place the anion in 3D space. We assigned the only crosspeak detected in the ¹H,¹⁹F HOESY spectrum (Figure 5) to a coupling between the pyridyl alpha proton (H2) with the proximal OTf⁻ anions. This interaction clearly suggested that, in solution, the anion is (on average) located in close proximity to the metal center, most likely on the bottom of the complex. The fact that the D values were found to be different for the cationic and anionic moieties suggested that not all of the triflate molecules are bound to the metal cation in solution, thereby providing an averaged diffusion coefficient. 1D ¹⁹F NMR measurements as a function of temperature supported this statement, as they showed a second fluorine resonance at -40°C, which was assigned to a free triflate anion. Following heteronuclear NOE analysis, we found no contacts to other pyridine protons and no interactions with the NMe group.

Analogous to the investigations on compound 3, a series of 2D experiments (COSY45 and NOESY) helped to assign key protons in complex 5, even though there was not much signal-overlap in the aromatic region. Table 1 summarizes



Figure 4. Molecular structure of compound 3 (left). Ellipsoids set at 30% probability (arbitrary radii for triflate anions). Top right: Local coordination environment around the Y1 atom. Lower right: View along the P-S-Y axis. Selected bond lengths [pm] (also see the Supporting Information, Table S1): Y1-N5 253.9(4), Y1-N8 254.4(4), Y1-N7 254.8(4), Y1-N6 254.9(4), Y1-N4 260.8(4), Y1-N9 267.2(4), Y1-O3 231.1(3), Y1-O8A 232.0(4) (disordered triflate anion), Y1-O1 232.9(4), S1-P1 190.9(2), P1-N3 165.0(4), P1-N1 168.1(4), P1-N2 169.0(4).



Figure 5. The 1 H, 19 F HOESY (300 MHz) spectra of a) complex **3** (60 mM) and b) complex **5** (30 mM) in CD₃CN at ambient temperature, showing the selective interactions. For numbering see Scheme 4.



Figure 6. Molecular structure of compound **5**. Ellipsoids set at 30% probability (arbitrary radii for OTf anions and coordinated MeCN molecules). Right: Local coordination environment around the Y1 atom. Selected yt-trium–nitrogen bond lengths [pm] (also see the Supporting Information, Table S2): Y1–N3 255.7(5), Y1–N4 258.8(5), Y1–N6 254.5(5), Y1–N8 252.4(5), Y1–N11 260.9(5), Y2–N5 259.8(5), Y2–N7 253.5(5), Y2–N12 259.9(5), Y2–N13 255.4(5), Y2–N14 252.8(5), Y2–N15 252.7(6), Y2–N16 247.6(5).

the self-diffusion constants in MeCN for bimetallic triflate salt 5. Unfortunately, the fluorine signal was too broad to be observed under pulse gradient spin echo conditions; hence, no ion-pairing conclusions could be drawn. However, the D value and the calculated hydrodynamic radius suggested a bimetallic structure in solution, which showed a good correlation with the radius deduced by X-ray analysis.

The molecular structure of homobimetallic complex **5** is shown in Figure 6 (space group: $P\overline{1}$). Both yttrium cations are ninefold coordinated by the N-donor atoms of the ligand, one acetonitrile molecule each, and all of the triflate counter anions. Two of the NMe entities of the ligand are located at a bridging position. Furthermore, one triflate anion bridges both yttrium cations, whereas the other four are terminally coordinated. The bond lengths between the pyridyl nitrogen atoms and the cations vary between 251.9 and 256.0 pm, whilst those to the imine nitrogen atoms lie between 253.7 and 258.7 pm. A summary of other relevant bond lengths and angles is given in the Supporting Information, Table S2.

The ¹H,¹⁹F HOESY crosspeaks for the 60 mm and 30 mm solutions (Figure 5) were specific, but they did not differ much between complexes 3 and 5. The key features were: 1) strong interactions between the alpha protons (H2) and both non-equivalent donor arms, and 2) a selective interaction to one of the two donor arms through the H5 proton (Figure 6b, Scheme 4). Again, we did not observe significant cross-peaks owing to either other pyridine protons or to the NMe groups.

Exchange spectroscopy has become the method of choice for studying multisite exchange and slow dynamic processes.^[62-67] For complex **5**, we measured a series of 2D phase-sensitive ¹⁹F EXSY spectra at low temperatures (-10 °C) with different mixing times (τ_m) to investigate the exchange processes between the bridging (**B**) and terminal triflate groups (**T1** and **T2**). It was found that the bridging mode of one tri-



Scheme 4. The structures of compounds **3** and **5** in solution were identified by heteronuclear NOE measurements in acetonitrile solution.

FULL PAPER

flate moiety in solution is quite rigid. At the shortest mixing time (0.1 ms, the instrumental limit), any exchange was too slow to be detected and the spectrum showed only diagonal peaks. For $\tau_m = 25$ ms, cross-peaks between both triflates **T1** and **T2** with **B** were clearly observed (Figure 7). Increasing

plexes (3 and 5). The PGSE data revealed a relatively large amount of ion-pairing for compounds 3 and 5, even in MeCN solution. Close contacts between the anions and the yttrium cations were also detected by X-ray diffraction. By applying HOESY and EXSY techniques, the triflate anions



Figure 7. ¹⁹F, ¹⁹F EXSY at various mixing times (τ_m) for compound 5 at -10 °C shows that the terminal triflate anions (*T1* and *T2*) were in fast exchange with each other. In MeCN, the bridging mode of the third triflate moiety (*B*) was still predominant. The numbers shown on the 2D maps correspond to the relative cross-peak integrals.

the mixing time to 100 ms favored the random exchange among all of the species in solution, although triflates \boldsymbol{B} and T1/T2 were found to be exchanging at a significant slower rate, as deduced from the low intensities of their crosspeaks. These results indicated that terminal triflate counterions T1 and T2 preferably exchange between themselves, that is, they break up and subsequently recombine, whereas the exchange with the bridging triflates is inhibited significantly. The forward (k_1) and reverse rate constants (k_{-1}) associated with the exchange process were calculated from the buildup of the cross-peak intensities on the 2D map, which are directly related to the exchange matrix.^[68] At a mixing time of 100 ms, the k_1 and k_{-1} values between **T1** and **T2** were found to be 20.21 and 11.56 s^{-1} , respectively. The corresponding exchange rates between **B** versus **T1** and **B** versus **T2** are $4.71(k_1)/4.08(k_{-1})$ s⁻¹ and $5.04(k_1)/7.62(k_{-1})$ s⁻¹, respectively.

Based on these data, it was reasonable to assume that the structures shown in Scheme 4 are predominant in solution.

Conclusion

2D ¹H,⁸⁹Y heteronuclear shift correlation through scalar coupling has successfully been applied for the determination of ⁸⁹Y NMR chemical shifts of a series of yttrium complexes in short periods of time. Thus, this technique is a valuable tool for the structural determination of yttrium compounds in solution,^[69] in particular when combined with other NMR methods as well as with solid-state structures obtained by X-ray diffraction. By applying all of these data to three yttrium complexes of various nuclearities, we confirmed previous results (1) and determined the structures of two new com-

were found to be located in particular regions of space and in close proximity to the yttrium cations, which might have a further impact on the overall reactivity of the complexes in solution.

Experimental Section

General considerations: All reactions and manipulations were carried out under an atmosphere of dry argon by using standard Schlenk techniques. Air-sensitive compounds were stored and weighed in a glove box (Braun MB150 G-I and Unilab system). THF was dried over potassium/benzophenone, Et₂O was dried over sodium-potassium alloy/benzophenone, MeCN was dried over CaH₂, and acetone was

dried over $CaSO_4$ and molecular sieves (3 Å). CD_3CN was vacuum transferred from CaH_2 into thoroughly dried glassware equipped with Young teflon valves. Elemental analysis and mass spectrometry were performed in the institutional technical laboratories. Elemental analysis of compounds **3** and **5** could not be obtained owing to the high fluorine content. Melting points were determined in sealed capillary tubes under an argon atmosphere and are uncorrected.

Solution NMR spectroscopy: Solution NMR spectra were recorded with Bruker Avance instruments operating at ¹H Larmor frequencies of 300, 400, and 500 MHz. Chemical shifts are given relative to TMS for ¹³C and ¹H nuclei, relative to CFCl₃ for ¹⁹F nuclei, relative to H₃PO₄ for ³¹P nuclei, relative to Y(NO₃)₃ for ⁸⁹Y nuclei, and relative to NH₃ (liquid) for ¹⁵N nuclei. Coupling constants (*J*) are given in Hertz as positive values regardless of their real individual signs. PGSE NMR diffusion measurements were carried out by using the stimulated echo pulse sequence.^[70] A rectangular shape was used for the gradient pulses and their strengths changed automatically during the course of the experiments. The *D* values were determined from the slope of the regression line ln(*I*/ *I*₀) versus *G*², according to Equation 1. *I*/*I*₀=observed spin echo intensity/ intensity without gradients, *D*=diffusion coefficient, δ =gradient length.

$$\ln(\frac{I}{I_0}) = -(\gamma \delta)^2 G^2 (\varDelta - \frac{\delta}{3}) D \tag{1}$$

The measurements were performed without spinning. The calibration of the gradients was carried out by means of a diffusion measurement of HDO in D₂O ($D_{\rm HDO}$ =1.902 10⁹ m²s⁻¹).^[71] The experimental error in *D* values was estimated to be smaller than ±2% (three standard deviations). All of the data that led to the reported *D* values afforded lines with correlation coefficients above 0.999. The gradient strength was incremented in 4% steps from 2% to 98%, so that, depending on the signal/noise ratio, 20–25 points could be used for regression analysis.

EXSY (exchange spectroscopy) ¹⁹F NMR spectra were acquired at 376.5 MHz, by using the phase-sensitive NOESY pulse-program without ¹H-decoupling. EXSY ¹⁹F NMR spectra were collected with 1 K points in t_2 by using a spectral width of 3765 Hz (10 ppm) and a mixing time of 0.1–100 ms. Typically, 256 t_1 experiments were recorded and zero-filled to

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1 K. For each t_1 value, 16 scans were signal-averaged by using a recycle delay of 2 s.

IR spectroscopy: IR spectra were measured by using either the ATR (attenuated total reflection) technique or on NaCl plates (Nujol mull) with a Bruker Vertex 70 spectrometer in the range 4000–400 cm⁻¹ by using a KBr beam splitter. The intensity of the absorption bands is indicated as vw (very weak), w (weak), m (medium), s (strong), vs (very strong), or br (broad).

X-ray diffraction: Crystal-structure determination: Single crystals of compound 3 suitable for X-ray diffraction were obtained by re-crystallization from a concentrated solution of MeCN/iPr2O under ambient conditions; single-crystals of compounds 5 and 2 were obtained from MeCN/Et2O and pure MeCN, respectively. To avoid decomposition during the measurements, the single crystals were covered with perfluoropolyalkyl ether oil and then mounted on top of a glass fiber. Subsequently, they were placed in the cold nitrogen stream of a low-temperature device to achieve solidification of the oil. Data collection was performed with a STOE STADI 4 diffractometer equipped with a CCD area detector, a graphite-monochromated $Mo_{K\alpha}\ (0.71073\ nm)$ radiation source, and a lowtemperature device. All calculations were performed with SHELXTL (v6.12) and SHELXL-97.^[72,73] The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement by using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks.

One triflate counteranion of compound **3** and two counteranions of compound **5** were disordered over two sites. In these cases, the two positions were refined against each other by using one free variable (FVAR) with occupation factors of 35% (**3**) and 45% (**5**) for the disordered position with appropriate restraints (SADI and DFIX instructions within SHELXL). Complex **3** crystallized with two MeCN molecules in the crystal lattice, both of which were refined with 50% occupancy. Compound **5** crystallized with four MeCN molecules in the crystal lattice, two of which were refined with 50% occupancy and the other two with 50 and 25% occupancies, respectively. Repeated measurements of several single crystals (also from other solvents) of compounds **3** and **5** did not lead to improved datasets, in particular regarding the triflate disorder or the number of solvent molecules in the crystal lattice.

Crystallographic data, data-collection, and refinement details are summarized in Table 2. CCDC-841665 (2), CCDC-841666 (3), and CCDC-841667 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Materials and reagents: $Y(OTf)_3$ and $[H(B{N(Me)N=C(H)Py}_4)]$ (H-4) were prepared according to literature procedures (or modified procedures).^[47,74,75] The synthesis of compound 1 has been published previous-ly.^[43] The Ln oxides, (S)PCl₃, *N*-methylhydrazine, 2-pyridinealdehyde, and B(NMe₂)₃ were purchased from Sigma–Aldrich and used without further purification.

Syntheses of H[B{N(Me)N=C(H)Py}₄] (H-4): 2-Pyridinealdehyde (21.4 g, 0.20 mol) was cooled to -78 °C and *N*-methylhydrazine (9.2 g, 0.20 mol) was carefully added. The cooling bath was removed and the mixture was slowly heated to 80 °C and stirred at that temperature for 3 h. 2-(2-meth-ylhydrazono)methylpyridine was received as a yellowish oily liquid by fractional distillation under vacuum (23.0 g, 0.17 mol, 85%).

2-(2-Methylhydrazono)methylpyridine (3 g, 22 mmol, 4 equiv) was dissolved in toluene (20 mL) and desiccated over molecular sieve (3 Å) overnight. $B(NMe_2)_3$ (0.98 mL, 0.79 mg, 5.6 mmol, 1 equiv) was carefully added whilst stirring the mixture. The solution turned pale yellow. After heating to reflux for 6 h, the solution was allowed to cool to room temperature, then the solvent was removed in vacuo and the orange-brown

Table 2. Crystallographic data	a for compounds 2 , 3 , and 5 .
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Compound	2	3	5
formula	$C_{21}H_{24}N_9PS$	$C_{24}H_{24}F_9N_9O_9PS_4Y\cdot$	$C_{37}H_{38}BF_{15}N_{14}O_{15}S_5Y_2$
		$2 \times 0.5 (C_2 H_3 N)$	$2.75(C_2H_3N)$
$M_{ m r}$	465.52	1042.70	1665.64
crystal system	monoclinic	monoclinic	triclinic
space group ^[76]	$P2_1/n$	$P2_{1}/c$	$P\bar{1}$
a [pm]	892.8(2)	972.4(2)	1425.4(3)
<i>b</i> [pm]	2126.3(4)	1982.0(4)	1565.6(3)
<i>c</i> [pm]	1219.0(2)	2235.0(5)	1838.3(4)
a [°]			75.70(3)
β [°]	93.91(3)	96.22(3)	82.61(3)
γ [°]			64.39(3)
$V \times 10^{6} [\text{pm}^{3}]$	2308.7(8)	4281.9(15)	3583.5(12)
$\mu \text{ [mm^{-1}]}$	0.238	1.691	1.863
$ ho_{ m calcd} [m g cm^{-3}]$	1.339	1.617	1.544
crystal dimensions	$0.15 \times 0.15 \times 0.10$	$0.20 \times 0.20 \times 0.10$	$0.10 \times 0.10 \times 0.05$
[mm]			
Ζ	4	4	2
T [K]	200(2)	200(2)	150(2)
$2\theta_{\rm max}$ [°]	50	50	50
total reflns	15772	29050	24867
unique reflns	4055	7507	12431
parameters/restraints	292/0	646/110	1031/221
$R_1[I \ge 2\sigma(I)]$	0.0829	0.0617	0.0739
wR_2 (all data)	0.2319	0.1638	0.2170
max./min. res. electron density $\times 10^{-6}$ [pm ⁻³]	0.788/-0.391	1.014/-0.715	2.400/-0.706

oily residue was washed with n-hexane (20 mL) and MeCN (10 mL) to remove most of the hydrazone. The off-white residue was subsequently filtrated and dried under a high vacuum. Yield (mixture of hydrazone and H-4): 340 mg; ¹H NMR (CD₃CN, 400.1 MHz): $\delta = 2.94$ (m, 12H; NCH₃), 7.13–7.17 (m, 4H; H_{Ar}), 7.48 (s, 4H; HC=N), 7.64–7.73 (m, 4H; $H_{\rm Ar}$), 7.74–7.77 (m, 4H; $H_{\rm Ar}$), 8.46–8.48 ppm (m, 4H; $H_{\rm Ar}$); ¹³C NMR $(CD_3CN, 100.6 \text{ MHz}): \delta = 32.9, 118.7, 121.6, 132.7, 136.0, 149.0,$ 155.9 ppm; ¹¹B NMR (CD₃CN, 160.5 MHz): $\delta = 0.95$ ppm; IR (ATR): $\tilde{\nu} =$ 1576 (w), 1462 (m), 1386 (s), 1321 (m), 1279 (m), 772 (m), 625 cm⁻¹ (m). [(S)P{N(Me)N=C(H)Py}] (2): A solution of (S)PCl₃ (5.65 g, 33.4 mmol) in CHCl₃ (75 mL) was added dropwise over a period of 1 h to a solution of N-methylhydrazine (9.31 g, 202.0 mmol) in CHCl₃ (75 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature over a period of 1 h and was stirred for a further 10 h at this temperature. The precipitated N-methylhydrazine hydrochloride was filtered and the solvent removed in vacuo to afford a white solid which was dissolved in hot toluene (75 mL) and cooled. n-Hexane (125 mL) was added and the mixture was kept at 5°C to afford (S)P[N(Me)NH2]3 as a colorless crystalline solid.

A solution of 2-pyridinealdehyde (3.242 g, 0.03 mol) in MeOH (20 mL) was added dropwise to a stirring solution of (S)P[N(Me)NH2]3 (2g, 0.01 mol) in MeOH (20 mL) and 1 g of magnesium sulfate at room temperature. After the addition had been completed, the reaction mixture was heated to reflux for 10 h. The mixture was allowed to cool, filtered, and the precipitate was carefully washed with CHCl₃ (3×50 mL). The filtrate and the washings were combined and the solvent was removed in vacuo. The resulting white solid was re-crystallized from hot MeCN and subsequently cooled to 5°C. Yield: 3.77 g (8.1 mmol, 81%); M.p. (sealed tube under an Ar atmosphere): 169°C; ¹H NMR (CDCl₃, 400.1 MHz): $\delta = 3.37$ (d, 9H, ${}^{3}J(H,P) = 9$ Hz; NCH₃), 7.08 (m, 3H; H_{Ar}), 7.29 (m, 3H; *H*_{Ar}), 7.60 (m, 3H; *H*_{Ar}), 7.75 (s, 3H; N=C*H*), 8.55 ppm (m, 3H; *H*_{Ar}); ¹³C NMR (CDCl₃, 100.6 MHz): $\delta = 33$ (NCH₃), 119, 123, 136, 138 (HC= N), 149, 155 ppm; ³¹P NMR (CDCl₃, 121.4 MHz): $\delta = 73.1$ ppm (m, J =9 Hz); MS (EI): m/z (%): 465.16 (75) $[M]^+$, 331 (94) [(S)P(N(Me)N=(64) $[(S)P(NN=C(H)Py)_2]^+$, $C(H)Py_{2}^{+},$ 302.1 198.0 (100) [(S)P(N(Me)N=C(H)Py)]⁺, 134.1 (36) [N(Me)N=C(H)Py]⁺, isotopic distribution: 465.16 (100), 466.16 (27), 467.16 (6), 467.17 (3), 468.16 (1); IR

5332

[Y(2)(OTf)₃] (3): A solution of ligand 2 (0.58 mmol, 270.35 mg) in THF (10 mL) was added dropwise to a turbid suspension of Y(OTf)3 (0.58 mmol, 310.9 mg) in THF (10 mL) over several minutes at room temperature. After the addition, the turbid solution slowly cleared and the product precipitated. After filtering the solid, it was dissolved in MeCN (5 mL) and layered with 15 to 18 mL of iPr₂O. After one day, colorless single crystals suitable for X-ray diffraction had formed. Yield: 481 mg (0.48 mmol, 82%); M.p. (sealed tube under an Ar atmosphere): 197°C; ¹H NMR (CD₃CN, 400.1 MHz): $\delta = 3.51$ (d, 9H, ³J(H,P) = 10.5 Hz; NCH₃), 7.65 (m, 3H; H_{Ar}), 7.80 (m, 3H; H_{Ar}), 8.13 (m, 3H; $H_{\rm Ar}$), 8.35 (s, 3H; *HC*=N), 8.90 ppm (d, 3H; $H_{\rm Ar}$); ¹³C NMR (CD₃CN, 100.6 MHz): $\delta = 36$ (NCH₃), 117, 126, 127, 140 (HC=N), 149, 150 ppm; ³¹P NMR (CD₃CN, 121.4 MHz): $\delta = 65.4$ ppm (m, J = 10.5 Hz); ¹⁹F NMR (CD₃CN, 282.4 MHz): $\delta = -79.1$ ppm; ¹⁵N NMR (CD₃CN, 50.7 MHz): $\delta = 128.1$ (N_{hvdr}), 306.6 (N_{pvr}), 273.6 (N_{imine}); MS (ESI): m/z (%): 852 (100), 853 (30), 854 (13); calcd for [(S)P[N(Me)N=C(H)Py]₃Y(OTf)₂]+: m/z (%): 852 (100), 853 (31), 854 (20), 855 (5), 856 (2), 857 (<1), 858 (< 1); IR (ATR): \tilde{v} =3031 (vw), 1568 (w), 1441 (w), 1152 (s), 632 cm⁻¹ (m). [Y₂(4)(OTf)₅] (5): A hot solution of compound H-4 (110 mg, 0.19 mmol of the ligand, 0.07 mmol of hydrazone) in toluene (10 mL) was added dropwise to a turbid suspension of $Y(OTf)_3$ (200 mg, 0.37 mmol) in MeCN (10 mL) under vigorous stirring. The clear solution was allowed to cool to room temperature. After removing the solvent in vacuo, the pale yellow residue was washed with n-hexane (10 mL) to remove any residual hydrazone, filtered, and dissolved in MeCN (8 mL) and layered with Et_2O (20 mL). After several weeks, yellow single-crystals suitable for X-ray diffraction had formed. Yield: 102 mg (0.07 mmol, 19%); M.p. (sealed tube under an Ar atmosphere): 232°C; ¹H NMR (CD₃CN, 400.1 MHz): $\delta = 3.09$ (s, 6H; NCH₃), 3.22 (s, 6H; NCH₃), 7.31 (m, 2H; $H_{\rm Ar}$), 7.43 (d, 2H, J(H,H)=7.8 Hz; $H_{\rm Ar}$), 7.56 (s, 2H; HC=N), 7.57 (m, 2H; H_{Ar}), 7.73 (d, 2H, J(H,H) = 7.7 Hz; H_{Ar}), 7.87 (m, 2H; H_{Ar}), 8.05 (m, 2H; H_{Ar}), 8.47 (s, 2H; HC=N), 9.00 (d, 2H, J(H,H) = 5.2 Hz; H_{Ar}), 9.12 ppm (d, 2 H, J(H,H) = 4.9 Hz; H_{Ar}); ¹³C NMR (CD₃CN, 100.6 MHz): $\delta = 38.3, 40.3, 123.4, 126.7, 133.4, 140.0, 140.9, 149.0, 149.6, 150.1, 152.7,$ 153.9, 153.9 ppm; ¹¹B NMR (CD₃CN, 160.5 MHz): $\delta = 5.55$ ppm; ¹⁹F NMR (CD₃CN, 282.4 MHz): $\delta = -79.01$ ppm; ¹⁵N NMR (CD₃CN, 50.7 MHz): δ=135.4, 267.6, 272.5, 323.5, 322.7 ppm; MS (ESI): *m/z* (%): 1320 (21), 1321 (100), 1322 (43), 1323 (26), 1324 (9), 1325 (2), 1326 (1); MS: m/z (%) calcd for [B{N(Me)N=C(H)Py}_4Y_2(CF_3SO_3)_4]^+: 1320 (22.4), 1321 (100), 1322 (46), 1323 (29), 1324 (10), 1325 (4), 1326 (1), 1327 (<1), 1328 (<1); IR (ATR): $\tilde{\nu} = 1605$ (w), 1309 (m), 1153 (m), 773 (m), 630 cm^{-1} (s).

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5334