Prediction of ^{89}Y NMR Chemical Shifts in Organometallic Complexes with Density Functional Theory

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Organometallic and coordination compounds containing yttrium are usefully characterized with ^{89}Y NMR spectroscopy ($I = -^{1}/_{2}$, 100% nat. abund.). Even though the qualitative contributions of various ligand groups to the yttrium NMR chemical shift have been known for some time, attempts to predict the shifts quantitatively have been limited. In the present work, a variety of organoyttrium complexes containing cyclopentadienyl, alkyl, hydride, and aryloxide ligands have been optimized with density functional theory methods. The optimized structures were used with the gauge-including atomic orbital (GIAO) method to calculate the corresponding ^{89}Y NMR magnetic shielding values (σ_{calc}); the latter were linearly scaled to adjust the fit with observed chemical shifts. Agreement between predicted and experimental ^{89}Y NMR shifts is typically within ±70 ppm (∼5% of the ca. 1300 ppm shift range). ^{89}Y NMR calculations were used to provide supporting evidence for the existence of the bulky triallyl complex Y[1,3-$(SiMe_3)_2C_3H_3]_3$.

Introduction

Metal-centered NMR spectroscopy is an increasingly accessible complement to the nonmetal nuclei (^{1}H, ^{13}C, ^{31}P, etc.) routinely used in the NMR characterization of organometallic and coordination complexes.[1] The chemical shifts of metal nuclei are frequently more sensitive to small changes in geometry and coordination number than are those of ligands and can reveal subtle changes in the solution composition of complexes.[2] These benefits are applicable to compounds of yttrium, virtually all of which contain the diamagnetic, tripositive Y^{3+} ion ([Kr]$5s^04d^0$). Yttrium complexes support an extensive range of ligands,[3] a partial list of which includes cyclopentadienyl rings, alkyls, allyls, hydrides, alkoxides and aryloxides,[4] halides,[4] amides, chalcogenides, and even such "nontraditional" species as N_2.[5] This ligand variety has contributed to the use of yttrium compounds as catalysts and in materials chemistry.[6] Yttrium compounds are often structurally similar to those of the late lanthanide elements (the ionic radii of Y^{3+} and Ho^{3+} are virtually identical (ca. 0.90 Å)[7]). Consequently, yttrium complexes are useful in modeling the structures and reactions of related compounds of the paramagnetic heavy lanthanides.

As a monoisotopic species with $I = -^{1}/_{2}$ and a wide chemical shift range (ca. 1300 ppm),[8] the ^{89}Y nucleus should be attractive for NMR study. That it has not been routinely used in the characterization of yttrium complexes is a consequence of several factors, including its low receptivity (0.681 relative to ^{13}C) and resonance frequency (e.g., 24.5 MHz at a magnetic field strength of 11.7 T (^{1}H = 500 MHz)). In addition, the yttrium nucleus' relaxation time (T_1) is long,[8−10] leading to problems with detection and to the necessity for lengthy experiments. There are techniques available that can be used to address some of these problems; for example, spin−echo sequences will minimize probe ringing associated with low-frequency nuclei, and the addition of relaxation agents can shorten T_1.[10,11] It should be noted that solid-state CP/MAS ^{89}Y NMR spectroscopy does not suffer from the problems of long relaxation times and that spectra with good signal-to-noise ratios are obtainable in minutes, as distinct from the several hours or even days often required by solution experiments.[12] However, information obtained in the solid state (particularly the chemical shift) is not directly comparable to that from solution spectra.

Upfield NMR shifts have been observed with higher coordination numbers in beryllium and aluminum complexes,[13,14] but the correlation between ^{89}Y chemical shifts and the metal

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coordination number is unclear. Neutral base adducts can produce both greater shielding[15] and deshielding[16] of the metal nucleus. Over a decade ago, Schaverien used NMR data to estimate the group contribution of various ligands to ^{89}Y chemical shifts and found they moved farther upfield with increased electronegativity and π-donating ability of the ligands.[17] The trend was quantified in values such as +300 ppm for alkyls, +190 ppm for amides, +56 ppm for aryloxides, and −100 ppm for the C_5Me_5 ring. Schaverien excluded from his compilations ^{89}Y NMR data obtained in ethereal solvents (primarily THF) because of the possibility that the formation of adducts or other reaction products would obscure the ligand contributions.

Direct calculation of yttrium chemical shifts would be a valuable tool in the characterization of organometallic yttrium complexes, especially when correlating solid-state and solution structures, distinguishing between homoleptic ML_3 complexes and the heteroleptic ML_nX_{3-n} counterparts, and extending predictions of shifts into new classes of ligands. The compounds of a variety of main-group and transition metals, including ^{9}Be,[13] ^{49}Ti,[18] ^{51}V,[19] ^{55}Mn,[20] ^{57}Fe,[21,22] ^{59}Co,[23] ^{91}Zr,[24] ^{95}Mo,[25] ^{99}Ru,[26] ^{103}Rh,[27] $^{117,119}Sn$,[28] ^{183}W,[29] ^{195}Pt,[30] ^{205}Tl,[30] and ^{235}U,[31] have been studied with DFT methods,[32] although this approach has not yet been applied to complexes of yttrium. We report here the use of density functional theory in combination with the GIAO (gauge-including atomic orbitals)[33] method to predict the ^{89}Y chemical shifts of a variety of organoyttrium species and provide a summary of some of the abilities and current limitations of the approach.

Experimental Section

General Considerations. All operations were performed in an atmosphere of nitrogen using standard glovebox or Schlenk techniques. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-300 spectrometer at 300 and 75.5 MHz, respectively, and were referenced to the residual ^{1}H and ^{13}C resonances of C_6D_6 (δ 7.15 and 128.0) or ^{1}H resonance of THF-d_8 (δ 1.73, 3.58). ^{89}Y NMR spectra were obtained on a Bruker DPX-400 spectrometer at 19.6 MHz and were externally referenced to 2 M YCl_3 in D_2O. The spectra were acquired with a 30° pulse and a 60 s delay, with accumulation times of about 48 h. Postprocessing baseline correction using NUTS (Acorn NMR, Inc., Livermore, CA) was performed with a linear prediction of the first 128 data points of ^{89}Y NMR acquisition. Elemental analysis was performed by the Micro-Mass Facility at the University of California, Berkeley, CA. Transmission electron microscopy (TEM) analysis was conducted using a Phillips CM 20 microscope operating at 200 kV. The sample for TEM study was dissolved in THF, added dropwise to a nickel TEM grid covered with holey carbon film as a substrate (SPI Supplies), and dried. Energy-dispersive X-ray spectrometry (EDS) analysis was obtained using an EDAX DX-4 package integrated onto the TEM. Samples were tilted at 15° for analysis at 200 kV during TEM analysis and were analyzed over a 1 μm area.

Materials. Anhydrous YCl_3 was purchased from Strem Chemicals and used as received. $K[1,3\text{-}(SiMe_3)_2C_3H_3]$[34] and $Y[N(SiMe_3)_2]_3$[35] were prepared as previously reported. Hexanes were distilled under nitrogen from potassium benzophenone ketyl. Anhydrous tetrahydrofuran (THF) was purchased from Aldrich and used as received. Deuterium oxide was purchased from Cambridge Isotope Laboratories and used as received. After vacuum distillation from Na/K (22/78) alloy, C_6D_6 and THF-d_8 were stored over type 4A molecular sieves.

Synthesis of $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$. A 125 mL Schlenk flask was charged with YCl_3 (0.839 g, 4.30 mmol), THF (50 mL), and a stirring bar. An addition funnel was prepared with $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ (1.904 g, 8.49 mmol) in THF (40 mL). After assembly in a glovebox, the apparatus was placed on a Schlenk line, where the YCl_3 solution was cooled to −78 °C. The $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ solution was added dropwise with stirring over 30 min, after which the reaction was allowed to continue stirring as it warmed to room temperature overnight. The orange reaction mixture was then evaporated to dryness, and the residue extracted with hexanes. The extract was filtered, and removal of hexanes under vacuum produced a yellow oil that yielded yellow-orange crystals of $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$ on standing overnight (1.92 g, 70%). Anal. Calc for $C_{27}H_{63}Si_6Y$: C, 50.26; H, 9.84; Cl, 0.00. Found: C, 48.49, H, 9.87; Cl, 0.17. Pure $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_2Cl$ requires C, 43.66; H, 8.55; Cl, 7.16. The somewhat lower than expected carbon analysis and the trace amount of Cl may indicate the presence of unreacted YCl_3 or the formation of a minor amount of $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_2Cl$. ^{1}H NMR (C_6D_6): δ 0.22 (s, 54H, Si*Me*$_3$); 3.58 (d, J = 16.2 Hz, 6H, C*H*CHC*H*); 7.46 (t, J = 16.2 Hz, 3H, CHC*H*CH). The spectrum was invariant from −65 to 45 °C in THF-d_8. ^{13}C NMR (C_6D_6): δ 1.12 (Si*Me*$_3$); 95.29 (*C*HCH*C*H); 163.13 (CH*C*HCH). ^{89}Y NMR (C_6D_6, 0.28 M): δ 470.5. Despite disorder in the allyl ligands, crystallographic data were consistent with the formation of $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$ (details given in the Results and Discussion section).

Variations in the Synthesis of $Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$. To study the effect of changing the order of reagent addition and the temperature of the reaction, the procedure given above was repeated but with all operations at room temperature. In separate reactions

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conducted at −78 °C and at room temperature, the addition order of reagents was reversed (i.e., YCl_3 in THF was added to the K[1,3-$(SiMe_3)_2C_3H_3$] solution). The products from all three of these variations had identical ^{1}H NMR spectra. The unit cell of the crystalline product from the reaction in which YCl_3 was added to K[1,3-$(SiMe_3)_2C_3H_3$] at room temperature was found to be the same as that from the first procedure above (K[1,3-$(SiMe_3)_2C_3H_3$] added to YCl_3, −78 °C).

Computational Methods

Geometry optimization and NMR shielding calculations were performed with the Gaussian 03W suite of programs[36] and the GIAO (gauge-including atomic orbitals) method.[33] For geometry optimizations, the B3PW91 functional, which incorporates Becke's three-parameter exchange functional[37] with the 1991 gradient-corrected correlation functional of Perdew and Wang,[38] was used. This hybrid functional has previously been shown to provide realistic geometries for organometallic species.[39] For yttrium, the DFT-optimized double-ζ basis set of Godbout (DGDZVP; (18s12p9d)/[6s5p3d]) was used; for atoms other than yttrium, the standard 6-311G(d,p) basis sets were employed.

For the shielding calculations, the larger triple-ζ basis set of Ahlrich (TZVPalls2; (19s14p9d)/[8s6p5d])[40] was used for yttrium, and the 6-311+G(2p,d) basis sets were used for other atoms. Typical calculations required at least 24 h on single 3.2 MHz processor machines (≥160 MW memory), although because of the flat potential energy surfaces of the molecules, often considerably more time was required for geometry convergence (e.g., for $Y(CH_2SiMe_3)_3(thf)_3$, geometry optimization required 8 days, 9 h (942 basis functions) and the shielding calculations an additional 2 days, 17 h (1227 basis functions)).

As the optimum functional for calculating transition metal shielding constants can vary depending on the metal,[32] six hybrid and three GGA DFT functionals were evaluated for this study. The hybrids included B3PW91, B3LYP,[41,42] O3LYP,[43] B97-1,[44] the one-parameter mPW1PW91,[45] and the parameter-free PBE1PBE.[46] The GGA functionals included BP86, BPW91,[38,41] and OLYP.[43] Test calculations (described in detail below) performed on the Y^{3+}(aq) ion and with several organometallic molecules led to the selection of O3LYP as the functional of choice, although its superiority over most of the others was small. It provides a strongly linear correlation between calculated and observed chemical shifts, but substantial scaling is still required to provide quantitatively reasonable shift values.

Results and Discussion

Experimental Chemical Shifts. Table 1 provides a compilation of reported ^{89}Y chemical shifts of both organometallic and, for comparative purposes, some coordination compounds in nonaqueous solvents. The lack of correlation between the chemical shift and coordination number mentioned in the Introduction is apparent in the data in Table 1. The linear correlation coefficient (r^2) between the two sets of numbers is 0.25, indicating that there is no significant covariance between them. Organometallic species occupy both extremes of the 1270 ppm range, but as noted earlier,[17,47] cyclopentadienyl species are the most shielded and are found in the range of ca. −370 to 80 ppm; purely σ-bound species are the most deshielded, with the homoleptic alkyl complex $Y[CH(SiMe_3)_2]_3$ possessing the largest reported shift (+895 ppm).

In addition to the group contributions described by Schaverien,[17] some further correlations can now be identified (Table 2). For example, starting with the contribution of +190 ppm from the $N(SiMe_3)_2$ group, the shift of $Y[N(SiMe_3)_2]_3(OPPh_3)$ suggests a contribution of −25 ppm from the $OPPh_3$ group. Similar reasoning using the chemical shifts of $Y(BHT)_3$ and $Y(BHT)_3(OPMe_2Ph)$ indicates a value of −23 ppm for the $OPMe_2Ph$ group. If the average of −24 ppm is used as a starting point for the contribution of a OPR_3 group (R = aryl or alkyl), then the value observed for $Y(OSiPh_3)_3(OP\mathit{n}\text{-}Bu_3)_2$ implies that +90 ppm is an appropriate value for $OSiPh_3$. This value is consistent with the expectation that alkoxides, with an average contribution of +56 ppm, are better σ-donors than are the corresponding aryl silyloxides.[48]

The difficulty in assessing the effects of ethereal solvents (primarily THF) on ^{89}Y NMR data is illustrated by the changes in the chemical shifts of $[Y(C_5H_4Me)_2E]_2$ (in toluene-d_8) and $Y(C_5H_4Me)_2E(thf)$ (in THF-d_8) (Tables 2 and 3). When E = Cl, the shifts of the two compounds differ by only 5 ppm, despite the disruption of the dimer in THF and the coordination of the additional ligand. When E = Me, the shift difference is 55 ppm. In both cases, the shift of the solvated species is upfield, but which of these changes is the more typical of the influence of solvent is unknown. It may be impossible to quantify the effect of coordinated (but rapidly exchanging) THF ligands on the chemical shift when THF is also the solvent. If the group contribution to the chemical shift from THF is arbitrarily set to zero, a second internally consistent set of values can be derived (Table 3). It seems clear that the qualitative trends involving σ-donation and chemical shift that are observed in aromatic solvents persist in THF, although the two scales of values (Tables 2 and 3) are not directly comparable.

It should also be noted from the data in Table 1 that charged complexes are shifted substantially from the neutral species. On the basis of the series of $[Y(CH_2SiMe_3)_n(thf)_4]^{(3-n)+}$ complexes and the group contributions in Table 3, a single positive charge is associated with a downfield shift of ca. 75 ppm, and a dipositive charge, with a ca. 115 ppm shift. It is possible that $Y(C_5Me_5)_2(\mu\text{-}Cl)_2K(thf)_2$ exists in solution as the

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Table 1. Yttrium Complexes and Their Corresponding ^{89}Y NMR Chemical Shifts

compound	δ_{exp} (ppm)	CN^a	solvent	ref
$Y(C_5H_4Me)_3(thf)$	−371	10	THF-d_8	47
$Y(C_5Me_5)_2(\mu-Cl)_2K(thf)_2$	−324	8	THF-d_8	47
$Y(C_5Me_5)_2(OAr)$	−129.3 (25 °C)	7	C_6D_6	17
$Y(C_5H_4Me)_2Cl(thf)$	−103 (1.5 M), −101 (1.7M)	8	THF-d_8	47
$[Y(C_5H_4Me)_2Cl]_2$	−97	8	$C_6D_5CD_3$	47
$[Y(C_5H_4Me)_2(\mu-H)(thf)]_2$	−92	9	THF-d_8	47
$[Y(C_5H_4Me)_2(\mu-C\equiv CCMe_3)]_2$	−74	8	THF-d_8	47
$\{Li(thf)_4\}\{[Y(C_5H_5)_2(\mu-H)]_3(\mu_3-H)\}$	−67	9	THF-d_8	47
$[Y(C_5H_4Me)_2(\mu-Me)]_2$	−15	8	$C_6D_5CD_3$	47
$[Y(OH_2)_8]^{3+}$	0.00 (reference)	6	D_2O	
$Y(C_5Me_5)(O-2,6-(t-Bu)_2C_6H_3)_2$	21.0 (25 °C)	5	C_6D_6	17
$Y(OCMe_2i-Pr)_3$	36.8 (37 °C)	4	$C_6D_5CD_3$	16
$Y(C_5H_4Me)_2(Me)(thf)$	40	8	THF-d_8	47
$Y(OCMeEti-Pr)_3$	45.6 (37 °C)	4	$C_6D_5CD_3$	16
$Y(OCEt_3)_3$	47.8 (25 °C)	4	$C_6D_5CD_3$	16
$Y_3(OCH_2CH_2OMe)_5(acac)_4$	62.7 (1), 91.4 (2)	8	$C_6D_5CD_3$	15
$Y(C_5Me_5)_2CH(SiMe_3)_2$	78.9 (25 °C)	4	C_6D_6	17
$Y[H(\mu-H)B(3,5-Me_2Pz)_2]_3$	105.6	9	$CDCl_3$	49
$[Y(OCH_2CH_2OMe)_2]_{10}$	134.5	5,7	$C_6D_5CD_3$	15
$Y(BHT)_3(OPMe_2Ph)$	148.1	4	C_6D_6	15
$Y(OSiPh_3)_3(thf)_3$	157.1	6	THF-d_8	15
$Y_3(Ot-Bu)_9(t-BuOH)_2$	166.8 (37 °C)	6	C_6D_6	16
$[K(dme)_4][Y(OSiPh_3)_4(dme)]$	168.1	6	DME-d_{10}	15
$Y(DPM)_3$	168.3	6	$CDCl_3$	15
$Y[O-2,6-(t-Bu)_2C_6H_3]_3$	168.4 (25 °C)	3	C_6D_6	17
$Y(BHT)_3$	170.8 (23 °C)	3	C_6D_6	15
$Y_3(Ot-Am)_9(t-AmOH)_2$	199.1 (37 °C)	6	C_6D_6	16
$Y_5(\mu_5-O)(\mu_3-Oi-Pr)_4(Oi-Pr)_5$	214.0 (1), 217.7 (4)	5,6	C_6D_6	15
$Y(OSiPh_3)_3(OPn-Bu_3)_2$	221.6	5	$CDCl_3$	15
$Y[H(\mu-H)B(Pz)_2]_3$	238.8 (ambient)	9	CD_2Cl_2	49
$Y[H(\mu-H)B(Pz)_2]_3$	246.0 (−83 °C)	9	CD_2Cl_2	49
$Y(OSiMe_2t-Bu)_3(thf)_3$	266.6	6	$CDCl_3$	15
$[Y(CH_2SiMe_3)(thf)_4][BPh_4]_2$	409.2	5	THF-d_8	50
$[YMe(thf)_6][BPh_4]_2$	433.2	7	pyr-d_5	50
$Y[1,3-(SiMe_3)_2C_3H_3]_3$	470.5	3	C_6D_6	this work
$Y[N(SiMe_3)_2]_3(OPPh_3)$	544.4 (23 °C)	4	$C_6D_5CD_3$	15
$Y[N(SiMe_3)_2]_3$	570.0 (23 °C)	3	$CDCl_3$	15
$[Y(CH_2SiMe_3)_2(thf)_4][BPh_4]$	660.0	6	THF-d_8	50
$[Y(CH_2SiMe_3)_2(thf)_4][BPh_3(CH_2SiMe_3)]$	660.2	6	THF-d_8	50
$[Y(CH_2SiMe_3)_2(thf)_4][Al(CH_2SiMe_3)]$	666.4	6	THF-d_8	50
$Y(CH_2SiMe_3)_3(thf)_2$	882.7	5	THF-d_8	50
$Y[CH(SiMe_3)_2]_3$	895.0 (25 °C)	3	$C_6D_5CD_3$	17

[a] Formal coordination number. All cyclopentadienyl rings are known or assumed to be η^5 and assigned a CN of 3. Abbreviations: acac = acetylacetonate, BHT = $O-2,6-t-Bu_2-4-MeC_6H_2$, dme = dimethoxyethane, DPM = 2,2,6,6-tetramethyl-3,5-heptanedionato, Pz = pyrazolyl ring, *t*-Am = *t*-amyl, thf = tetrahydrofuran.

Table 2. Empirical Group Contributions to ^{89}Y NMR Chemical Shift^a

group	contribution (ppm)	ref
C_5Me_5	−100	51
OPR_3 (R = aryl or alkyl)	−24	this work
$OCMe_2i-Pr$	+12	51
$OCMeEti-Pr$	+15	51
$OCEt_3$	+16	51
$O-2,6-t-Bu_2C_6H_3$	+56	51
$O-2,6-t-Bu_2C_6H_2-4-Me$	+57	51
$OSiPh_3$	+90	this work
$N(SiMe_3)_2$	+190	51
$CH(SiMe_3)_2$	+298	51

[a] Aromatic solvent (benzene or toluene).

Table 3. Empirical Group Contributions to ^{89}Y NMR Chemical Shift in THF-d_8

group	contribution (ppm)
C_5H_4Me	−124
THF	0^a
$OSiPh_3$	+52
Cl	+146
CH_3	+288
$CH_2(SiMe_3)$	+294

[a] Assumed.

solvent-separated ion pair $[K(thf)_n]^+[Y(C_5Me_5)_2Cl_2]^-$ and that the strong upfield shift of the complex (−324 ppm) reflects the negative charge on the yttrium fragment. The limited amount of data currently available makes it impossible to be more definitive about the effects of charge on the ^{89}Y chemical shift.

Selection of the Density Functional. The initial survey of the functionals in this study focused on the yttrium aquo ion $[Y(OH_2)_8]^{3+}$,[52] which serves as the chemical shift standard for ^{89}Y NMR (typically used in a 1−3 M aqueous solution of YCl_3). It has been established from both EXAFS and X-ray scattering experiments that the ion possesses eight nearly equal Y−O distances at 2.368 ± 0.005 Å.[52,53] The cation is also known in the solid state, and in the $[Y(OH_2)_8]Cl_3\cdot$(15-crown-5) complex, it takes the form of a distorted bicapped trigonal prism with Y−O = 2.31−2.44 Å, averaging to 2.364 Å.[54]

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Table 4. Absolute Shielding Constants (σ_{calc}, ppm) from Various GGA and Hybrid Functionals[a]

functional	$[Y(OH_2)_8]^{3+}$ (0.0 ppm)[b]	$[Y(C_5H_4Me)_2(\mu\text{-}Cl)]_2$ (**4**) (−97 ppm)	$Y(C_5H_4Me)_2(Me)(thf)$ (**2**) (40 ppm)	$Y[CH(SiMe_3)_2]_3$ (**10**) (895.0 ppm)
mPW1PW91	2808.7	2789.8	2623.5	1518.1
PBE1PBE	2807.7	2794.1	2627.0	1522.6
B97−1	2800.9	2797.7	2597.1	1477.9
B3LYP	2784.9	2747.7	2579.8	1451.9
B3PW91	2783.2	2755.1	2587.1	1471.1
O3LYP	2775.4	2702.8	2539.5	1441.4
OLYP	2708.4	2617.3	2454.4	1346.6
BPW91	2661.7	2607.9	2439.4	1299.6
BP86	2653.1	2604.9	2435.6	1281.2

[a] All geometries were calculated at the B3PW91/DGDZVP level. The experimental chemical shifts in ppm from $[Y(OH_2)_8]^{3+}$ are indicated below the compounds. [b] By definition.

The presence of Cl^- in aqueous solutions of YCl_3 has a small but measurable effect (up to ca. 6 ppm) on the chemical shift of the $[Y(OH_2)_8]^{3+}$ ion.[10] In general, it is unknown how changes in concentrations and temperatures affect chemical shifts in ^{89}Y NMR; rarely are experiments run at more than one temperature or concentration, and the latter is frequently not reported in any case. Cooling from ambient temperature to −83 °C causes a 7.2 ppm downfield shift in the resonance for $Y[H(\mu\text{-}H)B(Pz)_2]_3$,[49] for example, but the molecule is fluxional in solution (^{1}H, ^{13}C NMR evidence), so little can be inferred about the temperature change per se on the shift. In addition, the shift of $Y(C_5H_4Me)_2Cl(thf)$ has been reported at two slightly different concentrations (1.5 and 1.7 M), for which there is a shift difference of 2 ppm;[47] in the absence of additional examples, the significance of these changes is unknown.

The $[Y(OH_2)_8]^{3+}$ ion was optimized starting from the coordinates in $[Y(OH_2)_8]Cl_3{\cdot}(15\text{-crown-}5)$, which yielded a square antiprismatic structure with nearly exact S_8 symmetry; the symmetry was made exact in subsequent testing. Table 4 lists the shielding constants calculated with the functionals for the $[Y(OH_2)_8]^{3+}$ ion and three of the organometallic molecules used in this study that together encompass a nearly 1000 ppm shift range. The hybrid functionals lead to consistently more shielded values than the GGA functionals, an effect noted before with calculations on other nuclei.[21] Trial linear fits on the calculated and experimental chemical shifts of the organometallic complexes lead to further testing of O3LYP, mPW1PW91, PBE1PBE, and OLYP as the most promising candidates; additional trials lead to the selection of O3LYP for use in subsequent shielding calculations.

Compounds. The determination of accurate geometries is a key element in the effectiveness of computational NMR as a characterization tool, and comparatively high levels of theory must be used to obtain them.[55] Although hundreds of single-crystal X-ray structures of organometallic and coordination compounds of yttrium are known, there are few for which both ^{89}Y NMR data and solid-state structural data have been reported. Figure 1 contains the geometry-optimized structures and selected bond lengths of the complexes used in this study. In general, the combination of B3PW91/DGDZVP (on Y); 6-311G(d,p) (other atoms) overestimates Y−E bond distances, but not by more than 1.6% (Table 5). The exceptions are neutral oxygen donor ligands, for which the overestimation is larger. The average $Y{-}OH_2$ bond length in the $[Y(OH_2)_8]^{3+}$ standard is overestimated by 0.047 Å (2.0%); discrepancies in the average Y−O(thf) distances range up to 4.6% (in $Y(CH_2SiMe_3)_3(thf)_3$, **14**). Inherent differences between gas-phase (calculated) and condensed-phase structures account for some of the error, but it is specifically the distances to neutral ligands that are less accurately modeled. In the case of **14**, for example, the calculated Y−C(alkyl) distances are within 0.007 Å (0.3%) of experiment.

It might be noted that the description of bonds to neutral oxygen donors is an issue for all the functionals tested. For example, values from 2.405 Å (with PBE1PBE/DGDZVP) to 2.468 Å (OLYP/DGDZVP) are calculated for the $Y{-}OH_2$ bond in the $[Y(OH_2)_8]^{3+}$ ion, which represent overestimates of 1.6 to 4.2%, respectively.

Calculated NMR Chemical Shifts. It is often sufficient to calculate a theoretical shift by subtracting the absolute shielding of a complex from that of a calculated reference. However, if the calculated value of the reference is inaccurate, all the predicted shifts will possess systematic error.[61] For this reason, a scaling method previously developed for ^{13}C NMR chemical shifts[62] was applied to the ^{89}Y NMR data. In this procedure, the predicted chemical shifts (δ_{calc}) were determined by plotting experimental ^{89}Y chemical shifts (δ_{exp}) for the organometallic complexes against theoretical chemical shieldings (σ_{calc}) (Figure 2). The slope (m) and y-intercept (i) of the least-squares correlation line were then used to calculate predicted chemical shifts, as in eq 1.

$$\delta_{calc} = m\sigma_{calc} + i \qquad (1)$$

The values from the geometry-optimized complexes **1**−**13** were used to calculate the line equation. The linear least-squares fit is given in eq 2, from which the δ_{calc} values in Table 6 were derived.

$$\delta_{calc} = -0.8093\sigma_{calc} + 2063.6\ (r^2 = 0.991) \qquad (2)$$

The strong linearity over the large range indicates that the scaled DFT/GIAO combination accounts for most of the contributions to the chemical shift. Nevertheless, the deviation of the gradient from the ideal value of −1.0 indicates that there are still

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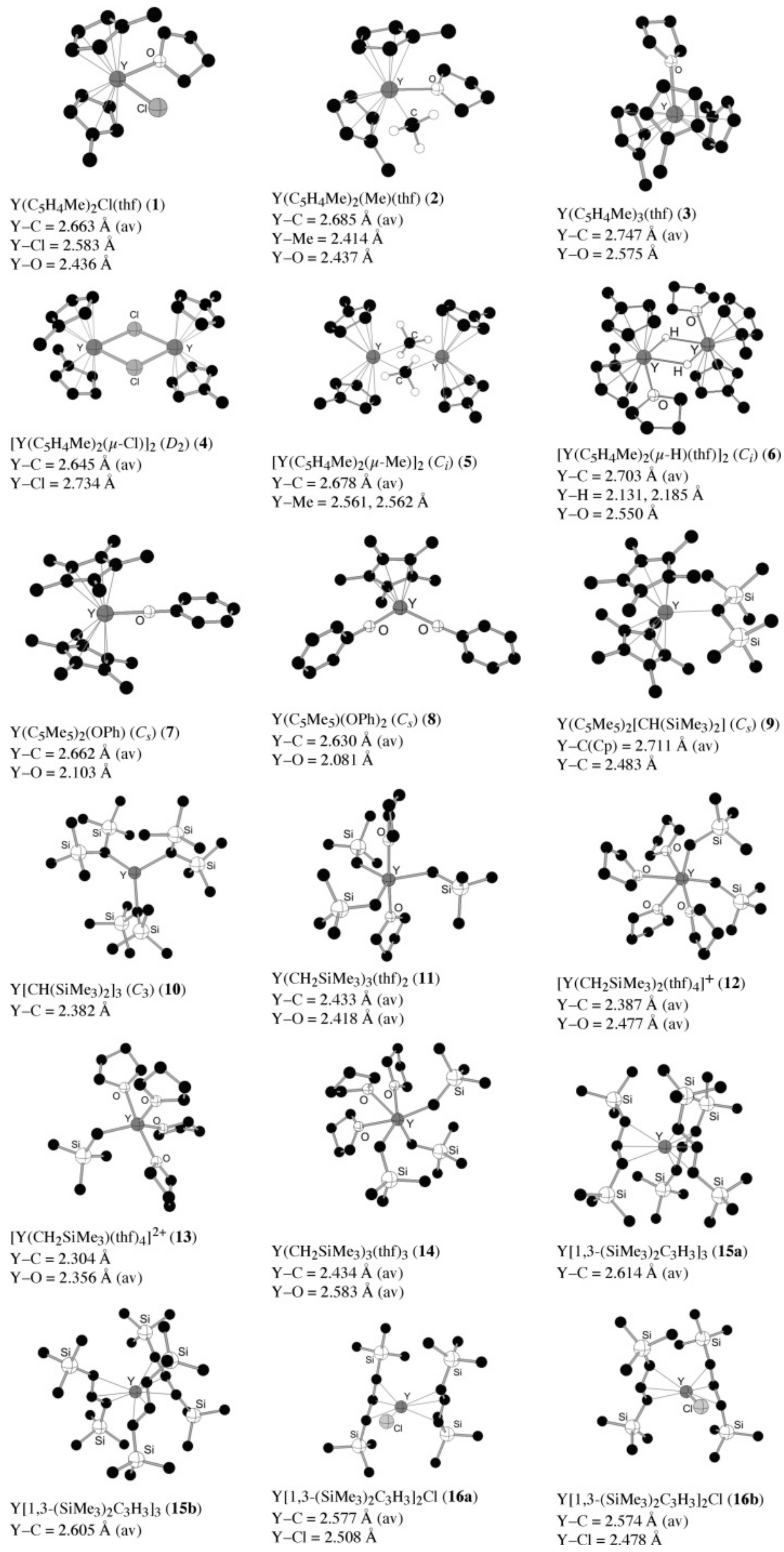

$Y(C_5H_4Me)_2Cl(thf)$ (**1**)
Y–C = 2.663 Å (av)
Y–Cl = 2.583 Å
Y–O = 2.436 Å

$Y(C_5H_4Me)_2(Me)(thf)$ (**2**)
Y–C = 2.685 Å (av)
Y–Me = 2.414 Å
Y–O = 2.437 Å

$Y(C_5H_4Me)_3(thf)$ (**3**)
Y–C = 2.747 Å (av)
Y–O = 2.575 Å

$[Y(C_5H_4Me)_2(\mu\text{-}Cl)]_2$ (D_2) (**4**)
Y–C = 2.645 Å (av)
Y–Cl = 2.734 Å

$[Y(C_5H_4Me)_2(\mu\text{-}Me)]_2$ (C_i) (**5**)
Y–C = 2.678 Å (av)
Y–Me = 2.561, 2.562 Å

$[Y(C_5H_4Me)_2(\mu\text{-}H)(thf)]_2$ (C_i) (**6**)
Y–C = 2.703 Å (av)
Y–H = 2.131, 2.185 Å
Y–O = 2.550 Å

$Y(C_5Me_5)_2(OPh)$ (C_s) (**7**)
Y–C = 2.662 Å (av)
Y–O = 2.103 Å

$Y(C_5Me_5)(OPh)_2$ (C_s) (**8**)
Y–C = 2.630 Å (av)
Y–O = 2.081 Å

$Y(C_5Me_5)_2[CH(SiMe_3)_2]$ (C_s) (**9**)
Y–C(Cp) = 2.711 Å (av)
Y–C = 2.483 Å

$Y[CH(SiMe_3)_2]_3$ (C_3) (**10**)
Y–C = 2.382 Å

$Y(CH_2SiMe_3)_3(thf)_2$ (**11**)
Y–C = 2.433 Å (av)
Y–O = 2.418 Å (av)

$[Y(CH_2SiMe_3)_2(thf)_4]^+$ (**12**)
Y–C = 2.387 Å (av)
Y–O = 2.477 Å (av)

$[Y(CH_2SiMe_3)(thf)_4]^{2+}$ (**13**)
Y–C = 2.304 Å
Y–O = 2.356 Å (av)

$Y(CH_2SiMe_3)_3(thf)_3$ (**14**)
Y–C = 2.434 Å (av)
Y–O = 2.583 Å (av)

$Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$ (**15a**)
Y–C = 2.614 Å (av)

$Y[1,3\text{-}(SiMe_3)_2C_3H_3]_3$ (**15b**)
Y–C = 2.605 Å (av)

$Y[1,3\text{-}(SiMe_3)_2C_3H_3]_2Cl$ (**16a**)
Y–C = 2.577 Å (av)
Y–Cl = 2.508 Å

$Y[1,3\text{-}(SiMe_3)_2C_3H_3]_2Cl$ (**16b**)
Y–C = 2.574 Å (av)
Y–Cl = 2.478 Å

Figure 1. Geometry-optimized structures of complexes **1**−**16** and selected bond lengths. In most cases, hydrogen atoms have been removed for clarity. Symmetry constraints (if any) applied during geometry optimization are listed in parentheses before the compound's number.

Table 5. Calculated and Experimental (X-ray data) Y−X Bond Distances[a]

		[Y(C_5H_4Me)$_2$(μ-H)(thf)]$_2$ (**6**)[56]	Y(C_5Me_5)(OPh)$_2$ (**8**)[57 b]	Y(C_5Me_5)$_2$CH($SiMe_3$)$_2$ (**9**)[58]
Y−C(Cp′)	calc	2.703	2.630	2.711
	expt	2.69(2)	2.652(3)	2.669(4)
Y−O	calc	2.550	2.081	
	expt	2.460(8)	2.059(3), 2.096(4)	
Y−H	calc	2.131, 2.185		
	expt	2.18(8)		
Y−C	calc			2.483
	expt			2.468(7)

		Y[CH($SiMe_3$)$_2$]$_3$(**10**)[59]	Y(CH_2SiMe_3)$_3$(thf)$_3$ (**14**)[60]
Y−C	calc	2.382	2.434 (av)
	expt	2.357(7)	2.427(19)
Y−O	calc		2.583 (av)
	expt	2.451(1), 2.457(1), 2.500(1)	

[a] All values in Å [b] Experimental value is for the Y(C_5Me_5)(O-2,6-t-$Bu_2C_6H_3$)$_2$ complex.

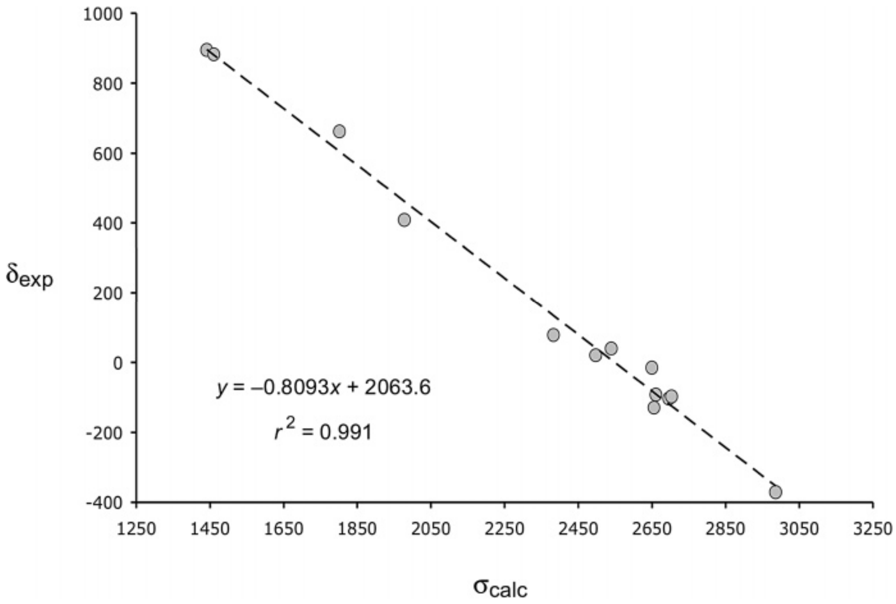

Figure 2. Plot of experimental chemical shifts (δ_{exp}) versus calculated chemical shieldings (σ_{calc}) for geometry-optimized organometallic complexes.

Table 6. Predicted Shielding Constants (σ_{calc}) and Chemical Shifts (δ_{calc}) in ppm

complex	σ_{calc}	δ_{calc}	δ_{exp} (solvent)	$\Delta\delta$[a]	C.N[b]
Y(C_5H_4Me)$_2$Cl(thf) (**1**)	2696.1	−118.4	−103 (THF-d_8)[47]	−15.4	8
Y(C_5H_4Me)$_2$(Me)(thf) (**2**)	2539.5	8.4	40 (THF-d_8)[47]	−31.6	8
Y(C_5H_4Me)$_3$(thf) (**3**)	2985.8	−352.8	−371 (THF-d_8)[47]	18.2	10
[Y(C_5H_4Me)$_2$(μ-Cl)]$_2$ (**4**)	2702.8	−123.8	−97 ($C_6D_5CD_3$)[47]	−26.8	8
[Y(C_5H_4Me)$_2$(μ-Me)]$_2$ (**5**)	2649.9	−81.0	−15 ($C_6D_5CD_3$)[47]	−66.0	8
[Y(C_5H_4Me)$_2$(μ-H)(thf)]$_2$ (**6**)	2660.4	−89.5	−92 (THF−d_8)[47]	2.5	9
Y(C_5Me_5)$_2$(OPh) (**7**)	2655.1	−85.2	−129.3[c] (C_6D_6)[17]	44.1	7
Y(C_5Me_5)(OPh)$_2$ (**8**)	2497.1	42.7	21[c] (C_6D_6)[17]	21.7	5
Y(C_5Me_5)$_2$CH($SiMe_3$)$_2$ (**9**)[58 d]	2382.7	135.3	78.9 (C_6D_6)[17]	56.4	7
Y(C_5Me_5)$_2$CH($SiMe_3$)$_2$ (**9**)[e]	2520.1	24.1	78.9 (C_6D_6)[17]	−54.8	7
Y[CH($SiMe_3$)$_2$]$_3$ (**10**)[59, d]	1441.4	897.1	895.0 ($C_6D_5CD_3$)[17]	2.1	3
Y[CH($SiMe_3$)$_2$]$_3$ (**10**)[e]	1431.6	905.0	895.0 ($C_6D_5CD_3$)[17]	10.0	3
Y(CH_2SiMe_3)$_3$(thf)$_2$ (**11**)	1460.2	881.9	882.7 (THF-d_8)[50]	−0.8	5
[Y(CH_2SiMe_3)$_2$(thf)$_4$]$^+$ (**12**)	1801.5	605.6	662.2[f] (THF-d_8)[50]	−56.6	6
[Y(CH_2SiMe_3)(thf)$_4$]$^{2+}$ (**13**)	1977.6	463.1	409.2 (THF-d_8)[50]	53.9	5
Y(CH_2SiMe_3)$_3$(thf)$_3$ (**14**)	1613.6	757.7	(882.7[g] (THF-d_8)[50])	(−125.0)	6

[a] $\Delta\delta = \delta_{calc} - \delta_{exp}$. [b] Formal coordination number. All cyclopentadienyl rings are known or assumed to be η^5 and assigned a CN of 3. [c] This value is for OPh = O-2,6-t-$Bu_2C_6H_3$. [d] Calculation with geometry-optimized structure. [e] Single-point calculation. [f] This value was derived from averaging ^{89}Y NMR shifts of **12** with various counterions.[50] [g] This value is for complex **11**, but is listed for **14** for comparison.

deficiencies in the approach, possibility involving the functionals or basis sets (especially for Y, for which there are few all-electron options for the Gaussian program) or both. It should be stressed, however, that the linear relationship between the calculated and experimental chemical shifts means that the error is systematic, and hence the results are still useful for discussing ligand effects on chemical shifts.

Comparisons of Calculated and Experimental Shifts. Experimental and predicted ^{89}Y NMR shifts of the complexes studied are listed in Table 6. For complexes **9** and **10**, the ^{89}Y

NMR shift was calculated both from a single-point calculation using the crystallographic data and from the geometry-optimized structure.

(a) Complexes 1−6:[47] $Y(C_5H_4Me)_2Cl(thf)$ (**1**), $Y(C_5H_4Me)_2(Me)(thf)$ (**2**), $Y(C_5H_4Me)_3(thf)$ (**3**), $[Y(C_5H_4Me)_2(\mu\text{-}Cl)]_2$ (**4**), $[Y(C_5H_4Me)_2(\mu\text{-}Me)]_2$ (**5**), $[Y(C_5H_4Me)_2(\mu\text{-}H)(thf)]_2$ (**6**). With the exception of **5**, the predicted ^{89}Y NMR shifts for these methylcyclopentadienyl complexes are within 35 ppm of the experimental shifts (Table 6). Compared to the large window of ^{89}Y NMR shifts (ca. 1300 ppm), these values represent errors of less than 3%. The use of THF as a solvent does not appear to affect the calculations in a systematic fashion; both under- and overestimations of the chemical shifts are found for samples measured in THF-d_8 (e.g., $\Delta\delta = -31.6$ ppm for **2**, and $\Delta\delta = 18.2$ ppm for **3**). In agreement with trends reported for cyclopentadienyl complexes of other metals, the ^{89}Y resonances for these complexes are shifted upfield compared to the σ-bound complexes.[13,14] The discrepancy between the observed and calculated values for the dimeric **5** is roughly twice that of the other cyclopentadienyl complexes. A trial calculation on the monomeric $Y(C_5H_4Me)_2Me$ produced an even larger error, so partial dissociation in solution is not part of the reason for the difference.

(b) Complexes 7 and 8:[51] $Y(C_5Me_5)_2(OAr)$ (**7**), $Y(C_5Me_5)(OAr)_2$ (**8**). Complexes **7** and **8** both contain bulky substituted cyclopentadienyl (C_5Me_5) and aryloxide (O-2,6-*t*-$Bu_2C_6H_3$) ligands. To explore the effect on the predicted ^{89}Y chemical shift of substitution of the cyclopentadienyl and aryloxide rings, the geometry of a simplified version of **7** (i.e., $Y(C_5H_5)_2(OC_6H_5)$) was optimized and its ^{89}Y NMR shift was calculated. Given the changes in the model, it is not surprising that the error ($\Delta\delta$) of −161.0 ppm from the fully substituted **7** is considerably larger than that observed with the methylcyclopentadienyl complexes **1**−**6**. The geometry and chemical shift for a model of **7** with an unsubstituted phenoxide ligand and fully methylated cyclopentadienyl ligands (i.e., $Y(C_5Me_5)_2(OC_6H_5)$) were then calculated; the predicted chemical shift is now −85.2 ppm ($\Delta\delta = 44.1$ ppm), a substantial improvement over the unsubstituted cyclopentadienyl model.

When a similar modification was made for **8**, i.e., using a model with a methylated cyclopentadienyl ligand and an unsubstituted phenoxide ligand ($Y(C_5Me_5)(OC_6H_5)_2$), there was relatively good agreement between the predicted and experimental shifts ($\Delta\delta = -21.7$ ppm). The results for **7** and **8** indicate that the presence of the methyl groups on the cyclopentadienyl ligand is crucial to the accurate prediction of chemical shifts for complexes with such cyclopentadienyl rings. However, the absence of the more distant *tert*-butyl groups on the phenoxide ligands (three bonds from the yttrium center) does not seem to have detrimental effects on ^{89}Y shift prediction.

(c) Complexes 9 and 10:[51] $Y(C_5Me_5)_2[CH(SiMe_3)_2]$ (**9**), $Y[CH(SiMe_3)_2]_3$ (**10**). In the case of complex **9**, the calculated ^{89}Y NMR shift differs by 56.4 ppm from the experimental value. Using the coordinates from the crystal structure, a single-point calculation was also performed and resulted in a predicted shift of 24.1 ppm ($\Delta\delta = -54.8$ ppm). It seems that the use of neither the geometry-optimized or the crystal structure coordinates for **9** leads to highly accurate predictions of the experimental chemical shift.

For the trialkyl complex **10**, the ^{89}Y NMR shift of 897.1 ppm for the geometry-optimized structure differs by only 2.1 ppm from the experimental value ($\delta_{exp} = 895.0$ ppm).[51] The ^{89}Y NMR shift was also calculated directly from the crystal structure coordinates;[59] the value (905.0 ppm) is only 10.0 ppm from the literature value (Table 6). It is surprising that the predicted chemical shift from the crystal coordinates and the geometry-optimized structure of **10** differ by only ∼8 ppm, while the analogous difference for **9** is ∼110 ppm. For **9**, the average Y−C bond length to the cyclopentadienyl and alkyl ligands in the optimized structure differs from the experimental values by 0.042 and 0.015 Å, respectively (Table 5). The Y−C length in **10** was overestimated by 0.025 Å in the optimized structure. As the Y−C bonds to the alkyl ligand are estimated more accurately in **9** than in **10**, the discrepancy in the bond length to the cyclopentadienyl ligand must have a large influence on the chemical shift for **9**. This discrepancy evidently leads to the difference in the predicted shifts for the optimized and single-point structures of **9**.

(d) Complexes 11−14:[50,60] $Y(CH_2SiMe_3)_3(thf)_2$ (**11**), $[Y(CH_2SiMe_3)_2(thf)_4]^+$ (**12**), $[Y(CH_2SiMe_3)Y(thf)_4]^{2+}$ (**13**), $Y(CH_2SiMe_3)_3(thf)_3$ (**14**). The predicted ^{89}Y NMR shifts for the alkyl complexes **11**−**13** differed by up to 60 ppm from the experimental values (Table 6). Of the three complexes, the shift for the neutral complex **11** is the closest to its experimental value ($\Delta\delta$ for **11** = −0.8 ppm). It is certainly possible that discrepancies in the predicted shifts for **12** and **13** are due to the influence of counterions in solution. Such effects are not accounted for in these gas-phase calculations.

The coordination environment of the neutral **11** is variable; two coordinated THF molecules are observed in solution (^1H NMR),[63] but three THFs are coordinated in the crystal structure.[60] For this reason, we wanted to see whether the addition of the third THF molecule (**14**) would result in a predicted chemical shift close to that of the literature value for **11**. The addition of a third THF molecule to the structure of **11** to form **14** moves the calculated shift upfield by approximately 120 ppm and ends up far from the experimental value ($\Delta\delta = 125.0$ ppm). The inaccuracy of this value coupled with the highly accurate prediction for **11** indicates that three coordinated THF molecules are primarily a result of solid-state forces and that only two solvent molecules are closely associated with the yttrium center in solution.

Case Study. Our own interest in ^{89}Y NMR spectroscopy stems from experiments with metal complexes containing bulky allyl ligands, particularly 1,3-$(SiMe_3)_2C_3H_3$.[34,64−66] Unlike cyclopentadienyl ligands, for which it is usually possible to predict the preferred products of reactions involving electropositive metals from the molar ratio of reactants, reactions with bulky allyl ligands do not always give the stoichiometrically expected products.[64,67] For example, in an attempt to synthesize La[1,3-$(SiMe_3)_2C_3H_3]_3$, Bochmann and co-workers treated 3 equiv of K[1,3-$(SiMe_3)_2C_3H_3$] with $LaCl_3$.[67] Instead of obtaining the expected triallyllanthanum product, La[1,3-$(SiMe_3)_2C_3H_3]_2Cl(thf)$ was produced, even with excess K[1,3-$(SiMe_3)_2C_3H_3$].[67] Given that four of the bulky allyl ligands can fit around the smaller Th^{4+} ion,[65] steric crowding around the lanthanum center would not prevent the coordination of a third allyl ligand. An unexpected kinetic stability of the bis(allyl′)-lanthanum chloride is possibly responsible for its resistance to further substitution.

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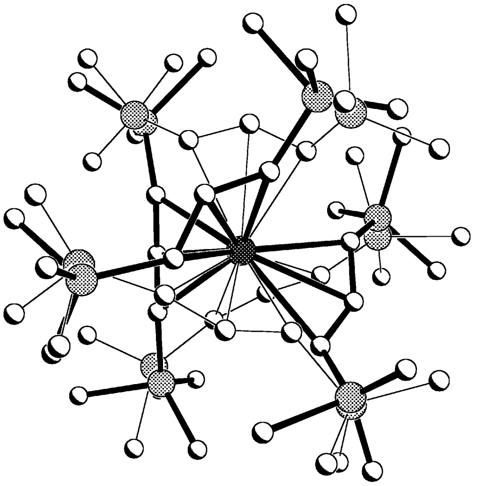

Figure 3. Structure of Y[1,3-$(SiMe_3)_2C_3H_3]_3$ (**15**), with two disordered parts (bolded and nonbolded) shown.

In an attempt to remake the previously reported[67] complex Y[1,3-$(SiMe_3)_2C_3H_3]_2Cl$, 2 equiv of K[1,3-$(SiMe_3)_2C_3H_3$] was allowed to react with YCl_3 in THF at −78 °C (eq 3):

$$2\ \mathrm{K[1,3\text{-}(SiMe_3)_2C_3H_3]} + \mathrm{YCl_3} \rightarrow \mathrm{Y[1,3\text{-}(SiMe_3)_2C_3H_3]_2Cl} + 2\ \mathrm{KCl}\downarrow \quad (3)$$

A hexanes extract of the filtered reaction mixture yielded a yellow oil that crystallized overnight. Elemental analysis (0.17% Cl), X-ray EDS (mass ratio of Y:Cl = 42.1:1), and an aqueous $AgNO_3$ test (only a slight haze was observed) all suggested that substantially less than the 7.2% Cl required by Y[1,3-$(SiMe_3)_2C_3H_3]_2Cl$ was present.

Variations in the temperature or the order of addition of reagents, as described in the Experimental Section, produced in every case yellow oils that had identical ^{1}H NMR spectra. When YCl_3 was treated with 3 equiv of K[1,3-$(SiMe_3)_2C_3H_3$], the yellow oil produced had an ^{1}H NMR spectrum identical to those from the 1:2 reactions.

Crystals of the product from the reaction with the allyl reagent added to the yttrium chloride at low temperature (eq 3) and those from the reaction following the literature report exactly (yttrium chloride added to the allyl reagent at room temperature) were examined with X-ray crystallography. Both had the same unit cell dimensions and space group.[68] Unfortunately, the structure is afflicted by substantial, and not completely resolvable, disorder; the silicon atoms are arranged in a roughly octahedral manner around the yttrium center (Figure 3). The crystallographic data, although not definitive, are consistent with the chloride tests for the formation of Y[1,3-$(SiMe_3)_2C_3H_3]_3$. The ^{89}Y NMR spectrum of the isolated complex was obtained in toluene-d_8 and contained a single peak at 470.5 ppm.[69]

Geometries of several different bis(1,3-trimethylsilyl)-substituted triallylyttrium (**15**) and diallylyttrium chloride (**16**) complexes were first minimized with molecular mechanics and then optimized with the DFT methods described above. A model for **15** (**15a**) was constructed in which one of the allyl ligands was oriented antiparallel to the other two (Figure 1). This was the arrangement reached when the major peaks in the disorder model of the X-ray structure were used as starting coordinates. It is also the arrangement found in the structure of Tm[1,3-$(SiMe_3)_2C_3H_3]_3$, which is disordered as well, but resolvably so (R_1 = 0.034).[70] The predicted ^{89}Y shift was found to be 402.0 ppm ($\Delta\delta = -68.5$ ppm). For comparison, the alternate model **15b** was constructed, in which the allyl ligands point in the same direction around the metal center (approximate C_3 symmetry, although none was imposed). The predicted shift for this conformation was 362.2 ppm, $\Delta\delta = -108.3$ ppm from the experimental value. On the basis of the X-ray data, we believe it likely that **15a** represents the actual structure more closely than does **15b**, although frequency calculations indicated that both structures were minima on the potential energy surface ($N_{imag} = 0$) and differed negligibly in total energy (2.2 kcal mol^{-1}).

It is possible that **16** could occur in monomeric or dimeric forms. In the latter case, the two yttrium centers would be expected to be within ca. 4.5 Å of each other, on the basis of known $[YCp'_2(\mu\text{-}Cl)]_2$ examples.[71] In the only known organoyttrium complex with a single chloride bridge, $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$, the metals are separated by 5.35 Å.[72] Despite the disorder in the ligands, the metal centers in the crystal structure (Figure 3) are well located and have a closest approach of 8.63 Å. A dinuclear structure for the complex would appear to be ruled out.

For **16**, calculations with the ligands pointing in eclipsed (**16a**) and staggered (**16b**) conformations around the yttrium center were completed. The predicted ^{89}Y NMR shifts for these complexes are 645.4 ($\Delta\delta = 174.9$ ppm) and 637.2 ppm ($\Delta\delta = 166.7$ ppm), respectively. The discrepancy between either of these values and the experimental shift is up to 100 ppm larger than that of the predicted shifts for **15a** and **15b**. The NMR results support the formation of the triallylyttrium complex from the experimental work described above, although the agreement between predicted and measured shifts, even in the best case (**15a**), is not as strong as with, for example, cyclopentadienyl complexes.

Conclusions

Calculation of ^{89}Y NMR shifts with DFT/GIAO methods is feasible for a variety of organometallic molecules. Despite systematic error in the absolute values of the shielding constants, a highly linear fit between calculated and observed shifts exists across a nearly 1300 ppm range. For most complexes, agreement within ±70 ppm between calculated and experimental shifts is found; for some classes of complexes, such as methylcyclopentadienyl species, the maximum discrepancy is usually half this. It is encouraging that solvent effects (apart from the possibility of actual coordination) do not appear to introduce systematic error into the predictions and that the shift of well-defined cationic complexes can also be estimated satisfactorily. The previously observed contributions to the chemical shifts (e.g., upfield values associated with cyclopentadienyl complexes,

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(68) Crystals of $C_{27}H_{63}Si_6Y$ are orthorhombic, space group $Pna2_1$, with $a = 20.658(5)$ Å, $b = 10.580(5)$ Å, $c = 18.999(5)$ Å, $V = 4152(2)$ Å^3, and $\rho_{calc} = 1.032$ Mg/m^3 for $Z = 4$. Refinement of 7322 reflections collected at the University of Minnesota at 173(2) K led to residuals of $R(F^2) = 0.0968$ and $R_w(F^2) = 0.2098$ (for $I > 2.0\sigma(I)$).

(69) To test the accuracy of our experimental ^{89}Y NMR method, Y[N$(SiMe_3)_2]_3$ was synthesized according to the method given in ref 35, and its ^{89}Y NMR spectrum obtained as described in the Experimental Section. The observed shift of 566.7 ppm (0.27 M) can be compared to the literature value of 570 ppm (no concentration given) (ref 15).

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downfield with alkyl groups[17]), are still reflected in the calculated results, but attempts at quantitative partitioning of the contribution of various ligands to the chemical shift have not been successful.

Simplification of the computational models of organoyttrium complexes must be done with care, but the results obtained here indicate that retention of substituents α and β to the metal is sufficient to avoid large changes in chemical shifts. This will be important if the method is extended to the study of larger molecules than those examined here, in particular, polymetallic aggregates.[16,73]

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Supporting Information Available: Coordinates for the geometry-optimized structures of complexes **1**−**16** and the experimental ^{89}Y NMR spectrum of Y[1,3-$(SiMe_3)_2C_3H_3$] (**15**). This material is available free of charge via the Internet at http://pubs.acs.org.

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