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Supplementary Information

A tris(alkyl) yttrium compound containing six β-agostic Si–H interactions

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Experiment details

General Procedures All reactions were performed under a dry argon atmosphere using standard Schlenk techniques, or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane, and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under N_2. Benzene-d_6 and toluene-d_8 were vacuum transferred from Na/K alloy and stored under N_2 in the glovebox. Anhydrous YCl_3 was purchased from Strem and used as received. All organic reagents were purchased from Aldrich. [K(CH_2Ph)][1] and HC($SiHMe_2$)$_3$[2] were prepared as described in literature procedures. ^{1}H and ^{13}C{^{1}H} NMR spectra were collected on Bruker DRX-400 spectrometer. ^{29}Si{^{1}H} NMR spectra were recorded using DEPT experiments, and assigments were verified by ^{1}H COESY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC, and ^{1}H-^{29}Si HMBC experiments. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility.

Tris(dimethylsilyl)methylpotassium. [KC($SiHMe_2$)$_3$] (1)

THF (30 mL) was added to a mixture of HC($SiHMe_2$)$_3$ (1.43 g, 7.4 mmol) and K(CH_2Ph) (0.97 g, 7.4 mmol) in a 100 ml Schlenk flask. The dark red mixture was stirred at room temperature for 12 h, and all volatile materials were removed under reduced pressure. The resulting reddish brown gummy solid was dissolved in minimal amount of toluene

and cooled to -30 °C to afford 1.55 g (6.0 mmol, 90.6%) of [KC(SiHMe$_2$)$_3$] as red needles. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 4.59 (m, 3 H, $^1J_{SiH}$ = 154 Hz, Si*H*Me$_2$), 0.461 (d, 18 H, $^3J_{HH}$ = 3.2 Hz, SiC*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 5.19 (Si*C*H$_3$), 2.61 (K*C*). ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -23.29 (*Si*HMe$_2$). IR (KBr, cm^{-1}): 2950 s, 2892 m, 2108 w (SiH), 1973 m (SiH), 1578 w, 1493 w, 1468 w, 1421 w, 1365 w, 1252 s, 1205 w, 1004 s, 896 s, 826 s, 766 m, 699 w, 673 w. Anal. Calcd for C$_7$H$_{21}$Si$_3$K: C, 36.78; H, 9.26. Found: C, 37.24; H, 8.68.

Tris(tris(dimethylsilyl)methyl)yttrium(III). [Y(C(SiHMe$_2$)$_3$)$_3$] (2)

Anhydrous YCl$_3$ (0.046 g, 0.24 mmol) and **1** (0.163 g, 0.71 mmol) were stirred in 10 ml of benzene at 25 °C for 12 h. The benzene was removed under vacuum, and the resulting brown residue was extracted with pentane (3 × 10 ml). The pentane was allowed to evaporation, affording a sticky yellow solid. This solid was re-recystallized at -30 °C from a minimal amount of pentane to obtain 0.13 g of **2** (0.20 mmol, 82%) as colorless microcrystals. ^{1}H NMR (benzene-d_6, 400 MHz, 25 °C): δ 3.85 (m, 3 H, $^1J_{SiH}$ = 134 Hz, Si*H*Me$_2$), 0.394 (d, 18 H, $^3J_{HH}$ = 3.2 Hz, SiC*H*$_3$). ^{1}H NMR (THF-d_8, 400 MHz, 25 °C): δ 3.70 (m, 3 H, $^1J_{SiH}$ = 137.4 Hz, Si*H*Me$_2$), 0.315 (d, 18 H, $^3J_{HH}$ = 3.2 Hz, SiC*H*$_3$). ^{1}H NMR (toluene-d_8, 400 MHz, -83 °C): δ 4.70 (3 H, $^1J_{SiH}$ = 190 Hz, Si*H*Me$_2$), 3.40 (6 H, $^1J_{SiH}$ = 109 Hz, Si*H*Me$_2$), 0.472 (36 H, SiC*H*$_3$), 0.344 (18 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 100 MHz, 25 °C): δ 3.96 (Si*C*H$_3$), 17.3 (d, $^1J_{YC}$ = 9.8 Hz, Y*C*). ^{13}C{^{1}H} NMR (THF-d_8, 100 MHz, 25 °C): δ 3.67 (Si*C*H$_3$), 17.5 (d, $^1J_{YC}$ = 9.8 Hz, Y*C*). ^{13}C{^{1}H} NMR (toluene-d_8, 100 MHz, -83 °C): δ 16.07 (d, $^1J_{YC}$ = 9.9 Hz, Y*C*), 4.60 (Si*C*H$_3$), 4.39 (Si*C*H$_3$), 2.92 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (benzene-d_6, 79.5 MHz, 25 °C): δ -13.3 (*Si*HMe$_2$). ^{29}Si{^{1}H} NMR (THF-d_8, 79.5 MHz, 25 °C): δ -15.3 (*Si*HMe$_2$).^{29}Si{^{1}H} NMR (toluene-d_8,

79.5 MHz, -83 °C): -12.3 (*Si*HMe$_2$), -15.2 (*Si*HMe$_2$). IR (KBr): 2954 s, 2899 s, 2105 s (SiH), 1846 s (SiH), 1599 w, 1493 w, 1416 m, 1253 s, 1203 m, 1069 s, 957 s, 887 s, 883 s, 779 s, 690 s cm^{-1}. IR (THF, cm^{-1}): 2980 s, 2682 w, 2102 w (SiH), 1967 w (THF), 1844 w (SiH), 1460 s, 1365 m, 1289 m, 1252 s, 1181 s, 1069 s, 957 s, 837 s, 690 m. Calcd for $C_7H_{21}Si_3Y$: C, 38.37; H, 9.66. Found: C, 38.80; H, 9.21. EI-MS (*m*/*z*, assignment, %): 467 ([M – (C(SiHMe$_2$)$_3$)]$^+$, 8), 276 ([M – (C(SiHMe$_2$)$_3$)$_2$]$^+$, 10), 188 ([C(SiHMe$_2$)$_2$(SiMe$_2$)]$^+$, 100), 129 ([C(SiHMe$_2$)(SiMe$_2$)]$^+$, 18), 174 (68), 72 ([CH(SiHMe$_2$)]$^+$, 16), 59 ([SiHMe$_2$]$^+$, 11). CI-MS (*m*/*z*, %, assignment): 656 ([M]$^+$, 2), 467 ([M – H - (C(SiHMe$_2$)$_3$)]$^+$, 14), 189 ([C(SiHMe$_2$)$_3$ – H]$^+$, 100), 176 (100).

Table 1. Rate constants for agostic and nonagostic SiH exchange obtained from simulation of $^{13}C\{^1H\}$ NMR spectra over the temperature range 190 – 260 K. [3]

T (K)	k (s^{-1})
190	0
200	1.47
210	12.1
220	59.9
230	231
240	785
250	2350
260	7710

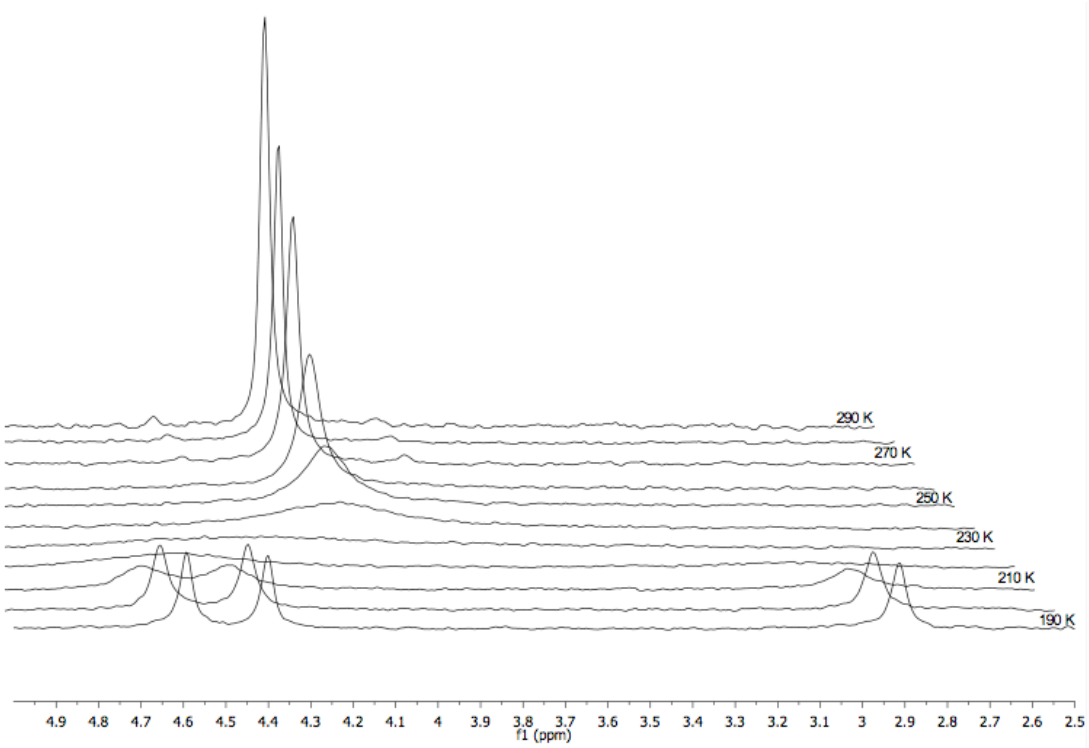

Figure 1. Stack plot of methyl region of $^{13}C\{^{1}H\}$ NMR spectra, acquired from 290 – 190 K.

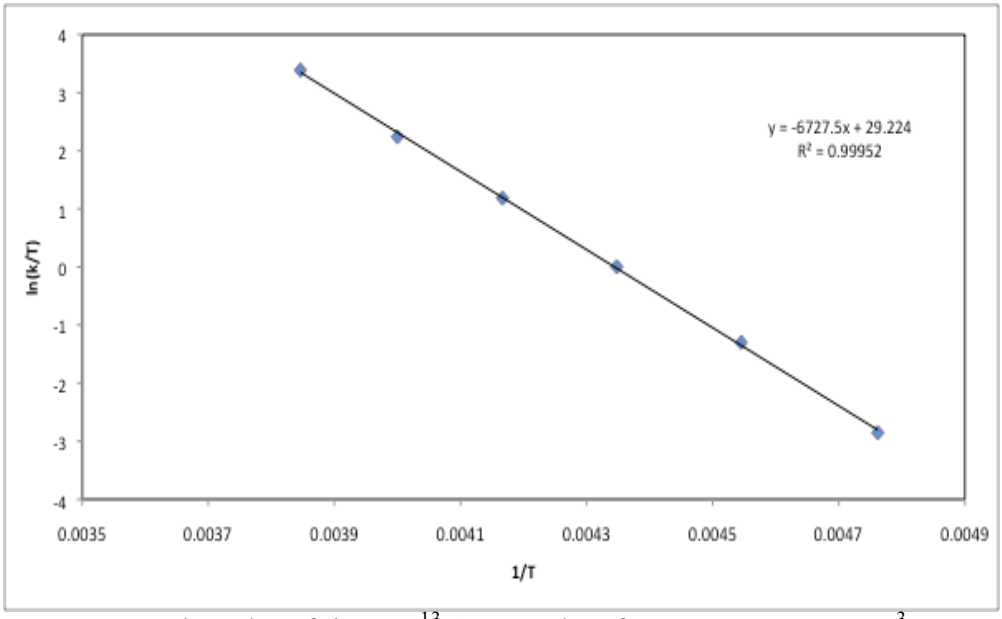

Figure 2. Eyring plot of the VT ^{13}C NMR data from gNMR program.[3]

Determination of Potassium and Chlorine by LA-ICP-MS

ICP-MS was employed to qualitatively determine whether chlorine and potassium were present as part of a stoichiometric compound. Measurements are taken using a Finnigan Element 1 ICP-MS (Table 1). Due to the air sensitivity of **2**, solution phase ICP-MS is not a feasible method, and instead laser ablation (LA-ICP-MS) methods were investigated. A pressed pellet of the sample was ablated with a LSX-500 (CETAC Technologies, Omaha NE) laser ablation system under an argon atmosphere.

Ablation was achieved by rastering the sample at 10 Hz with a 100 µm spot size. The material was ablated for 150 seconds at 9 mJ per pulse. Pure argon carrier gas was used at 1.03 L/minute, adjusted for maximum sensitivity. Five separate measurements were taken, each was background corrected and the data was averaged for reporting.

To determine whether chlorine and potassium were present at a high enough content to be part of the molecular structure of the sample, yttrium and silicon were also measured as internal standards. However, since no appropriate matrix-matched external standard exists, a different method of approximating an external standard is necessary. Therefore, an aqueous standard was prepared from stock solutions (Plasmachem Associates Inc, Bradley Beach NJ). The external standard contained 20.0 ppb Y and Si, and 22.8 ppb K and Cl in 1% (v/v) nitric acid. An Apex desolvation system (Elemental Scientific Inc, Omaha NE) was then used to remove solvent and approximate a dry load before entering the plasma. Sample gas rate was 0.80 L/minute during sample uptake with an additional 0.175 L/min added after desolvation, adjusted for maximum sensitivity and elimination of polyatomics.

The atomic ratios in the sample of Y/K, Si/K, Y/Cl and Si/Cl are all sufficiently high to lead to the conclusion that potassium and chlorine are not present in the material in a stoichiometric amount (Table 2). The raw data show that silicon and yttrium were far more abundant in the sample than in the external standard. Likewise the ratio data show chlorine and potassium were far less present in the sample than the primary elements. Five separate trials of each measurement are averaged in the data. The most uncertain ratio found is Y/Cl, which shows chlorine still to be present at 1.1% the abundance of yttrium. Measurements by LA-ICP-MS confirm that potassium and chlorine are only contained in the substance at trace amounts.

Table 1 ICP-MS operating conditions

ICP-MS device	**Finnigan Element 1**
Forward Power	**1200 W**
Reflected Power	**8-9 W**
Cooling Gas	**16.00 L min^{-1}**
Auxiliary Gas	**0.80-0.85 L min^{-1}**
Sample Gas	**0.95 L min^{-1} aqueous, 1.03 L min^{-1} LA**
Resolution	**4000 (medium resolution)**
Isotopes Measured	**^{28}Si, ^{35}Cl, ^{39}K*, ^{89}Y**

Table 1: $^{*\,39}K^{+}$ was integrated only over half the peak to avoid a common interference ion, $^{1}H^{38}Ar^{+}$. The integrated signal was then doubled to readjust the data.

Table 2 Atomic ratios of present and trace elements

2a. Raw Data	Sample (cps)	Ext. Std. (cps)	Sample/Std.	2b. Ratios	Average	St. Dev.	RSD
Si	2.47e6	1.14e4	2.17e2	Y/K	104000	9000	8.71
Cl	2.60e5	1.90e5	1.37e0	Si/K	217000	34000	15.9
K	1.24e6	1.07e9	1.16e-3	Y/Cl	88.1	9.0	10.2
Y	4.74e8	4.52e6	1.05e2	Si/Cl	182	18	9.61

1. P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre, L. C. Henderson, C. Herber, S. T. Liddle, D. L. Gonzalez, A. Parkin, S. Parsons, *Chem. Eur. J.* 2003, **9**, 4820-4828.
2. C. Eaborn, P. Hitchcock, P. Lickiss, *J. Organomet. Chem.* 1983, **252**, 281-288.
3. P.H.M. Budzelaar, gNMR v. 5.0, IvorySoft.