Supplementary Material (ESI) for Chemical Communications
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Substituent-Dependent Exchange Mechanisms in Highly Fluxional RSn_9^{3-} Anions

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Instrumentation and Materials

All reactions were performed in a nitrogen atmosphere drybox. All NMR samples were prepared from corresponding crystals and washed with toluene and followed by vacuum dried prior to dissolving in dmf solvent and pyridine-d$_5$ for the ^{119}Sn NMR and ^{1}H/^{13}C NMR measurements, respectively. The ^{119}Sn NMR spectra were recorded on a Bruker DRX500 AVANCE spectrometer at 186.5 MHz. In all measurements, to avoid RF heating, a high nitrogen flow rate was used in combination with a temperature controller. The pulse sequence used was the standard Bruker "zgdc" program. A 30 degree pulse strength and 1.0 s relaxation delays were used. A macro automation program was written so that multiple block searches of 300 ppm were used in locating the ^{119}Sn signal. The spectral window -2500 to +3000 ppm was searched by this method. The signals were confirmed and verified by repeating the final measurements with different transmitter offsets. The ^{119}Sn chemical shifts were referenced to Me_4Sn in C_6D_6 (0 ppm) at room temperature. Temperature calibration was done by using methanol for variable temperature ^{119}Sn NMR experiments. Both the ^{1}H and $^{13}C\{^1H\}$ spectra of $[K(2,2,2\text{-crypt})]_3[Sn_9\text{-}Sn(Cy)_3]$.2py were recorded on a Bruker DRX500 AVANCE spectrometer at 500.13 MHz and 125 MHz, respectively, and chemical shifts were referenced to TMS. The ^{1}H spectra of $[K(2,2,2\text{-crypt})]_3[Sn_9\text{-}Sn\text{-}iPr]$.2py were recorded on a Bruker AVIII-600 MHz spectrometer at 600.13 MHz and chemical shifts were referenced to TMS. Integrations of proton signals were not reported for both compounds due to overlapping signals. The percentage yields were calculated by considering the amount of alloy precursor K_4Sn_9 that was used.

Melts of nominal composition K_4Sn_9 were made by fusion of stoichiometric ratios of the elements at high temperature. The chemicals were sealed in evacuated silica tubes and heated carefully with a natural gas/oxygen flame. ***Caution:*** *molten alloy synthesis can result in serious explosion and reactions should be conducted with great caution behind blast shields*. 4,7,13,16,21,24-Hexaoxa-1,10-diazobicyclo[8,8,8]hexacosane (2,2,2-crypt) were purchased from Fisher Scientific. Tricyclohexyl tin chloride was purchased from Aldrich. 2-chloropropane (i-Pr) was purchased from Across Organics and vacuum distilled from $CaCl_2$. Anhydrous ethylenediamine (en) and dimethylformamide (DMF) were purchased from Fisher, vacuum distilled from K_4Sn_9, and stored under dinitrogen. Toluene was distilled from sodium/benzophenone under dinitrogen and stored under dinitrogen. Pyridine was distilled from KOH under dinitrogen and stored under dinitrogen.

General Procedures and Compound data

Synthesis of [K(2,2,2-crypt)]$_3$[Sn$_9$-iPr].2py

In vial 1, K_4Sn_9 (60 mg, 0.049 mmol) and 2,2,2-crypt (110 mg, 0.292 mmol) were dissolved in 3 mL of ethylenediamine. In vial 2, 1ml of ethylenediamine was added to 7 µl of iPrCl (0.011 M, 0.077 mmol). Solution from vial 2 was added dropwise to vial 1, and the reaction mixture was stirred for a half an hour. The ethylenediamine was removed under vacuum. The remaining solid material was redissolved in 2.5 mL of pyridine. After filtration through tightly packed glass wool, solution was layered with 4 mL of toluene. Following day, the black crystals of [K(2,2,2-crypt)]$_3$[Sn$_9$i-Pr].2py (45 mg, %82) were obtained. δ_{119Sn} / ppm (186.4 MHz; dmf; Me_4Sn; 25 °C) -1413 (8 Sn, $J_{119Sn-117Sn}$; 1793 Hz, $J_{119Sn-119Sn}$; 1876 Hz, $J_{119Sn-117Sn}$; 115 Hz, Sn(2-9)). 170 (1 Sn, $J_{119Sn-119/117Sn}$ 1844 Hz, Sn(1)). δ_{1H} / ppm (600 MHz, pyridine-d$_5$, Me_4Si, 25 °C) 3.44 (s, 2,2,2-crypt), 3.37 (t, 2,2,2-crypt), 2.36 (t, 2,2,2-crypt), 2.20 (d, J = 7.19 Hz, -CH_3), 2.41 (septet, J = 7.19 , -CH). δ_{13C} / ppm (500 MHz, pyridine-d$_5$, Me_4Si, 25 °C) 70.7 (2,2,2-crypt), 67.91 (2,2,2-crypt), 54.16 (2,2,2-crypt), 32.16 (-CH_3 of iPr), and 29.79 (-CH of iPr)

Synthesis of [K(2,2,2-crypt)]$_3$[Sn$_9$-Sn(Cy)$_3$].2py

In vial 1, a solution of K_4Sn_9 (80 mg, 0.065 mmol) and 2,2,2-crypt (98 mg, 0.26 mmol) in 1 mL of ethylenediamine was stirred for half an hour. The ethylenediamine was removed under vacuum. The remaining solid material was redissolved in 2.5 mL of pyridine. In vial 2, the (Cy)$_3$SnCl (39.6 mg, 0.098) was dissolved in 1 ml of toluene. Solution from vial 2 was added dropwise to vial 1, and the reaction mixture was stirred for a half an hour. After filtration through tightly packed glass wool, solution was layered with 2 mL of toluene. After five days, purple-red crystals of the [K(2,2,2-crypt)]$_3$[Sn$_9$-Sn(Cy)$_3$].2py (56 mg, 60%) were formed. δ_{119Sn} / ppm (186.4 MHz; dmf; Me_4Sn; 25 °C) -1172 (9 Sn, $J_{119Sn-117Sn}$; 1272 Hz , $J_{119Sn-119Sn}$; 1331 Hz, $J_{119Sn-117Sn}$; 295 Hz , Sn(1-9)). 155 (1 Sn, $J_{119Sn-117Sn}$; 1272 Hz , $J_{119Sn-119Sn}$; 1331 Hz, Sn(10)). δ_{119Sn} / ppm (186.4 MHz; pyridine;

Me_4Sn; 25 °C) -1167 (9 Sn, $J_{119Sn-119/117Sn}$; 1287 Hz , $J_{119Sn-117Sn}$; 292 Hz , Sn(1-9)). 156 (1 Sn, $J_{119Sn-119/117Sn}$; 1287 Hz, Sn(10)). δ_{1H} / ppm (500 MHz, pyridine-d$_5$, Me_4Si, 25 °C) 4.59 (s, 2,2,2-crypt), 4.52 (t, 2,2,2-crypt), 3.51 (t, 2,2,2-crypt), 3.23 (m, -Cy), 2.97 (m, -Cy), 2.78 (m, -Cy), 2.52 (m, -Cy). δ_{13C} / ppm (500 MHz, pyridine-d$_5$, Me_4Si, 25 °C) 70.70 (2,2,2-crypt), 67.90 (2,2,2-crypt), 54.20 (2,2,2-crypt), 34.43 (-Cy), 30.82 (-Cy), 30.67 (-Cy), 28.40 (-Cy).

X-ray Crystallographic Data

The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoKα fine-focus sealed tube (λ= 0.71073 Å). The detector was placed at a distance of 5.2000 cm from the crystal. The structure was solved and refined using the SHELXS-97 and SHELXL-97 software in the space group *P-1* with *Z* = 2 for the both compound. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS.

Table S1. Selected bond lengths of the [K(2,2,2-crypt)]$_3$[Sn$_9$-iPr].2py in Å.

Sn(1)-Sn(2)	2.8584 (4)	Sn(4)-Sn(7)	2.9531 (4)
Sn(1)-Sn(4)	2.8535 (4)	Sn(4)-Sn(8)	3.0369 (4)
Sn(1)-Sn(5)	2.9547 (4)	Sn(5)-Sn(6)	3.2246 (5)
Sn(1)-Sn(8)	2.9739 (4)	Sn(5)-Sn(8)	3.2302 (5)
Sn(2)-Sn(3)	3.0322 (4)	Sn(5)-Sn(9)	2.9346 (5)
Sn(2)-Sn(5)	3.0716 (5)	Sn(6)-Sn(7)	3.1868 (4)
Sn(2)-Sn(6)	2.9365 (5)	Sn(6)-Sn(9)	2.9642 (5)
Sn(3)-Sn(4)	3.0142 (4)	Sn(7)-Sn(8)	3.1279 (4)
Sn(3)-Sn(6)	2.9671 (4)	Sn(7)-Sn(9)	2.9574 (4)
Sn(3)-Sn(7)	2.9860 (4)	Sn(8)-Sn(9)	2.9674 (5)

Table S2. Selected bond lengths of the [K(2,2,2-crypt)]$_3$[Sn$_9$-Sn(Cy)$_3$].2py in Å.

Sn(1)-Sn(2)	2.8836 (4)	Sn(5)-Sn(6)	3.2602 (4)
Sn(1)-Sn(4)	2.8988 (5)	Sn(5)-Sn(8)	3.2380 (4)
Sn(1)-Sn(5)	3.0196 (5)	Sn(5)-Sn(9)	2.9172 (5)
Sn(1)-Sn(8)	3.0411 (4)	Sn(6)-Sn(7)	3.0802 (5)
Sn(2)-Sn(3)	3.0093 (5)	Sn(6)-Sn(9)	2.9541 (4)
Sn(2)-Sn(5)	2.9524 (5)	Sn(7)-Sn(8)	3.1936 (4)
Sn(2)-Sn(6)	2.9911 (5)	Sn(7)-Sn(9)	2.9643 (5)
Sn(3)-Sn(4)	2.9970 (5)	Sn(8)-Sn(9)	2.9404 (4)
Sn(3)-Sn(6)	2.9899 (5)	Sn(1)-Sn(10)	2.9112 (4)
Sn(3)-Sn(7)	3.0150 (5)	Sn(10)-C(11)	2.2219 (4)
Sn(4)-Sn(7)	2.9604 (5)	Sn(10)-C(31)	2.2219 (4)
Sn(4)-Sn(8)	2.9600 (4)	Sn(10)-C(21)	2.2222 (4)

1D ge-^{1}H-^{119}Sn HMBC

1D gradient select ^{1}H-^{119}Sn HMBC experiment was carried out with the standard Bruker "inv4gpnd1d" program.[1] The "cnts2" was taken as 54 Hz which is typical for ^2J (^{1}H-^{119}Sn) coupling constant. The frequencies for H-1 and Sn-119 are 500.13 MHz and 186.5 MHz correspondingly. The H-1 FID resolution used was 0.27 Hz per data point. Typically, 1000 scans were used. The Sn-119 offset was sequentially set to the observed ^{119}Sn signals for $[Sn_9Sn(Cy)_3]^{3-}$; 155 ppm and -1172 ppm correspondingly.

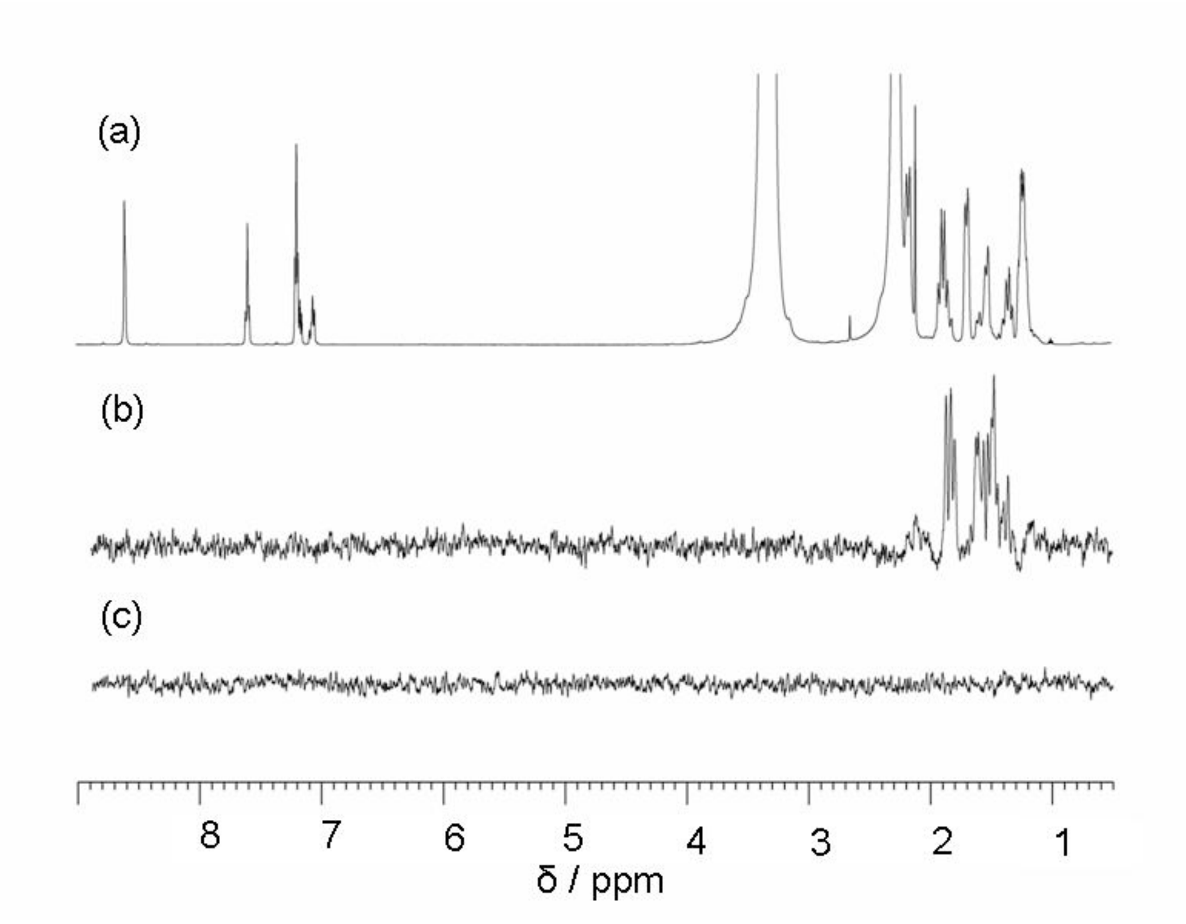

Figure S1. Stack plots of $[K(2,2,2\text{-crypt})]_3[Sn_9\text{-}Sn(Cy)_3]$.2py (a) ^{1}H spectra taken in pyridine-d_5 at room temperature, (b) 1D ge-^{1}H-^{119}Sn HMBC with decoupler offset 155 ppm, (c) 1D ge-^{1}H-^{119}Sn HMBC with decoupler offset -1172 ppm.

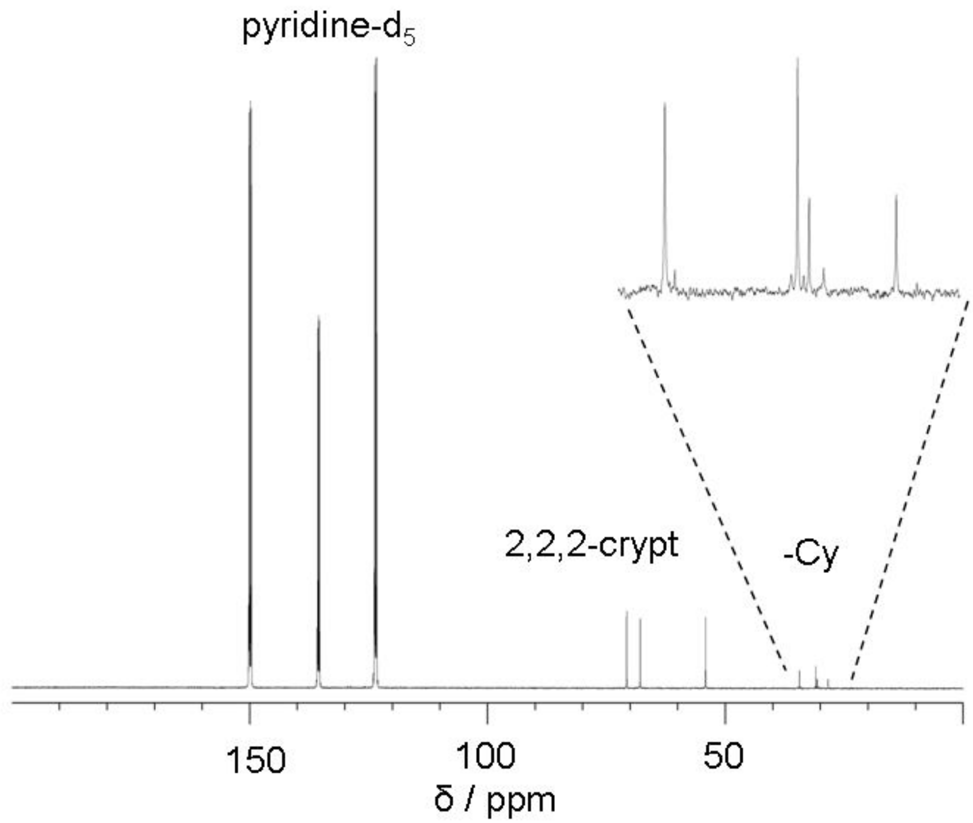

Figure S2. $^{13}C\{^1H\}$ spectrum of [K(2,2,2-crypt)]$_3$[Sn$_9$-Sn(Cy)$_3$].2py was taken in pyridine-d$_5$ at room temperature.

1 D Selective gs-COSY of the [K(2,2,2-crypt)]$_3$[Sn$_9$-iPr].2py

1D gradient selected COSY experiment, using shaped pulse for selective excitation, was carried out with the standard Bruker “selcosygp” program at a 600.13 MHz frequency. The “D4” was taken as 0.0347 s (1/4*J* where *J* (^{1}H(-CH$_3$)-^{1}H(-CH)) is 7.19 Hz). Offset was set to 2.20 ppm and 128 scans were used.

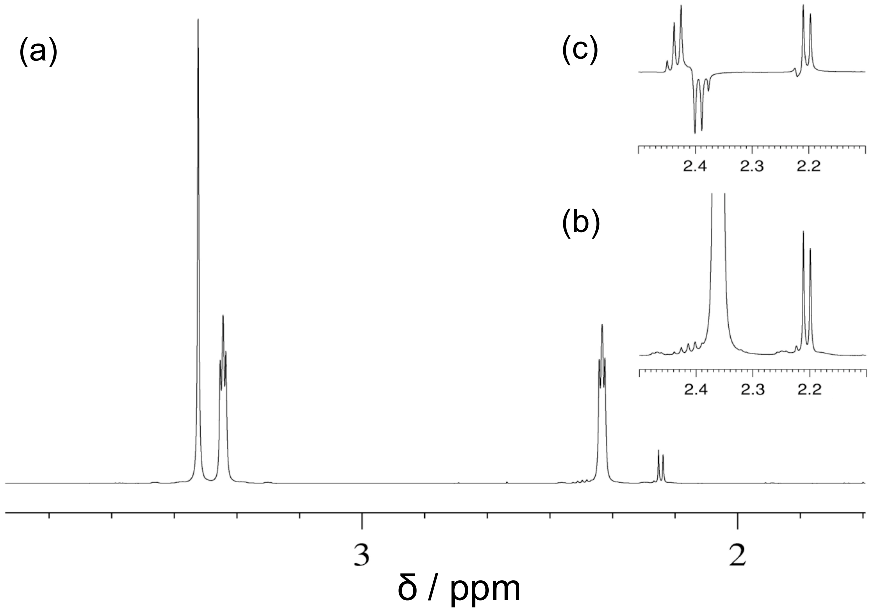

Figure S3. (a) ^{1}H spectra of [K(2,2,2-crypt)]$_3$[Sn$_9$-iPr].2py taken in pyridine-d$_5$ at room temperature at 600.13 MHz. (b) The same spectra is expended in region between 2.5- 2.1 ppm. (c) 1D cosy experiment.

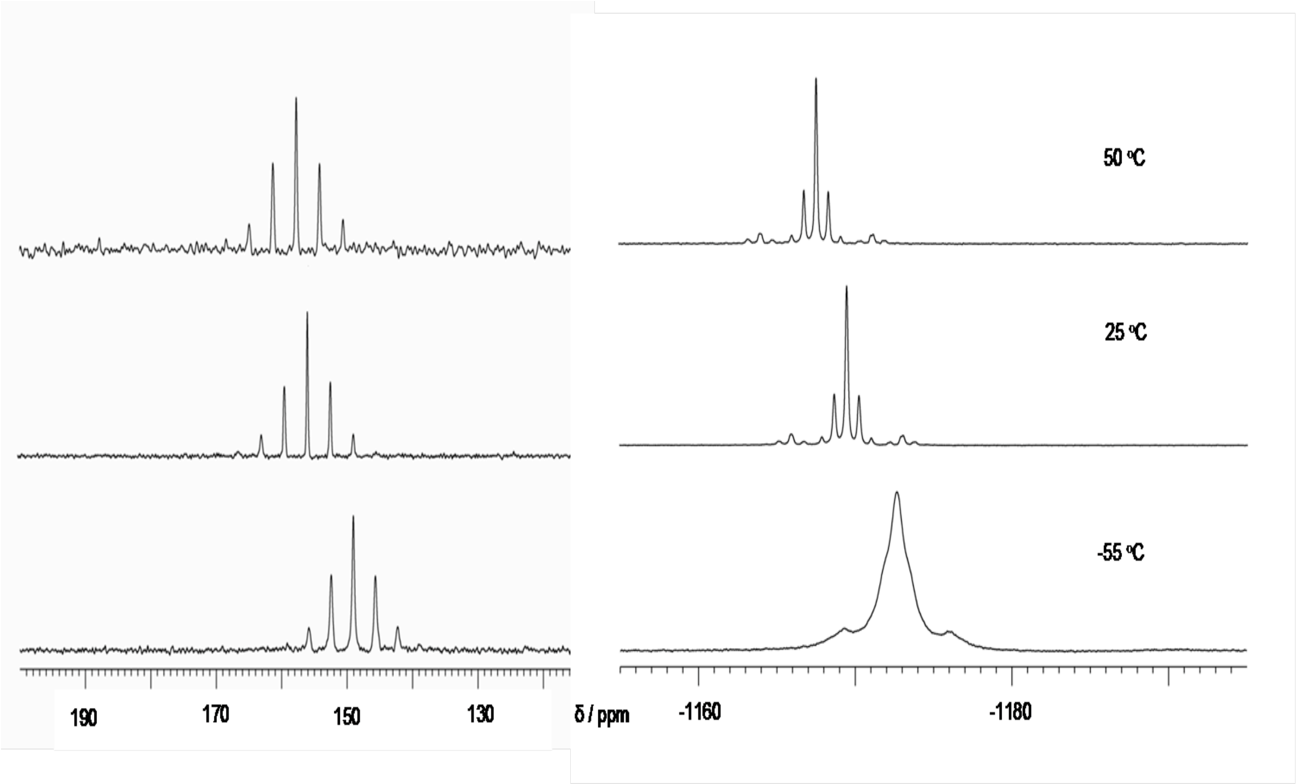

Figure S4. ^{119}Sn NMR spectra of the $[Sn_9\text{-}Sn(Cy)_3]^{3-}$ at variable temperatures

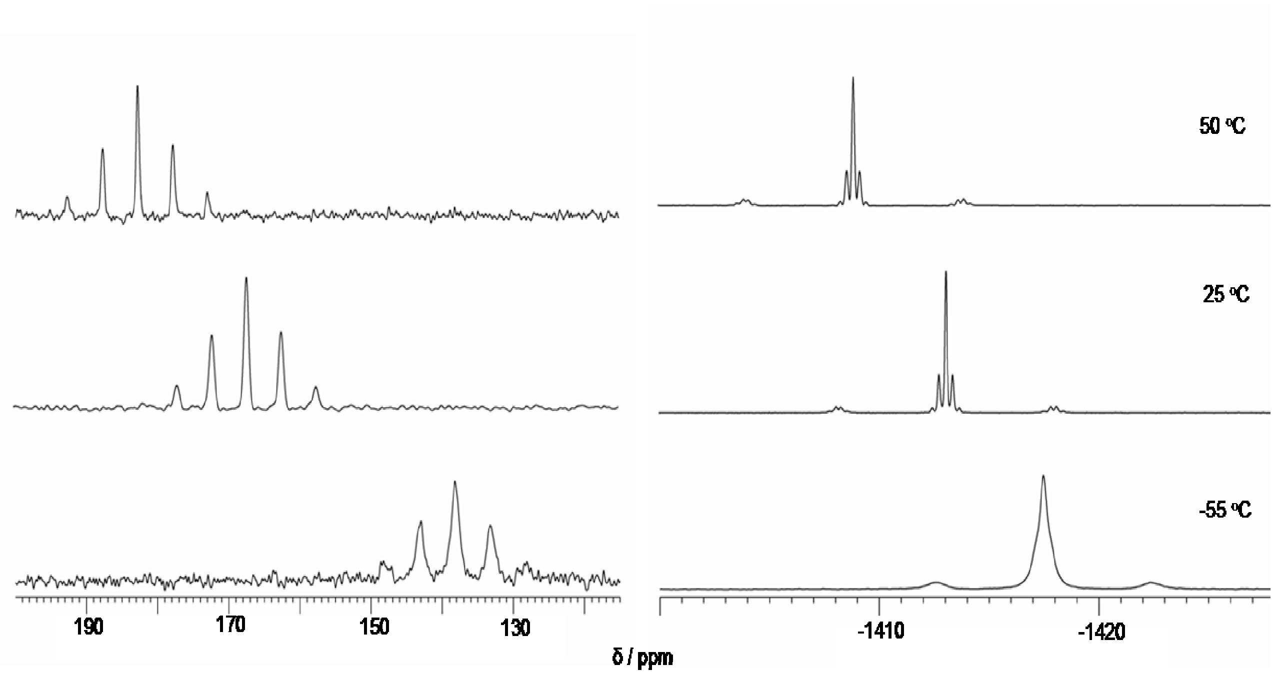

Figure S5. ^{119}Sn NMR spectra of $[Sn_9\text{-iPr}]^{3-}$ at variable temperatures

Calculations of the ^{119}Sn NMR Peak Integrations

The resonances show complicated satellite structures arising from various isotopomers that contain statistical mixtures of naturally-abundant ^{119}Sn nuclei (I = ½, 8.58 % abundance) and ^{117}Sn nuclei (I = ½, 7.61 % abundance). The overall multiplet pattern is obtained by super positioning the binomial probability weighted intensity multiplets for the collections of isotopes as described in the reference.[2]

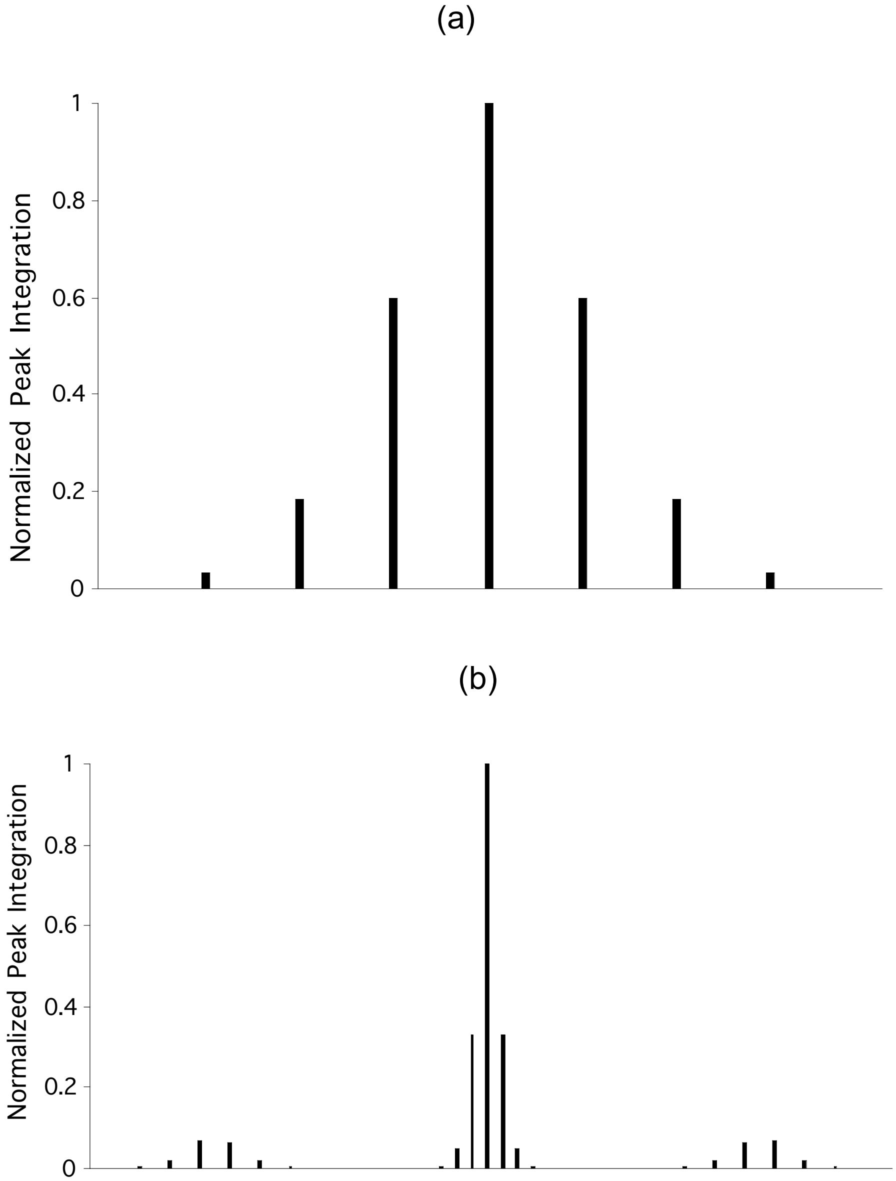

Figure S6. Calculated peak integrations: (a) ^{119}Sn nuclei coupled to 8 equivalent Sn nuclei, (b) 8 equivalent ^{119}Sn nuclei coupled to 1 Sn nucleus.

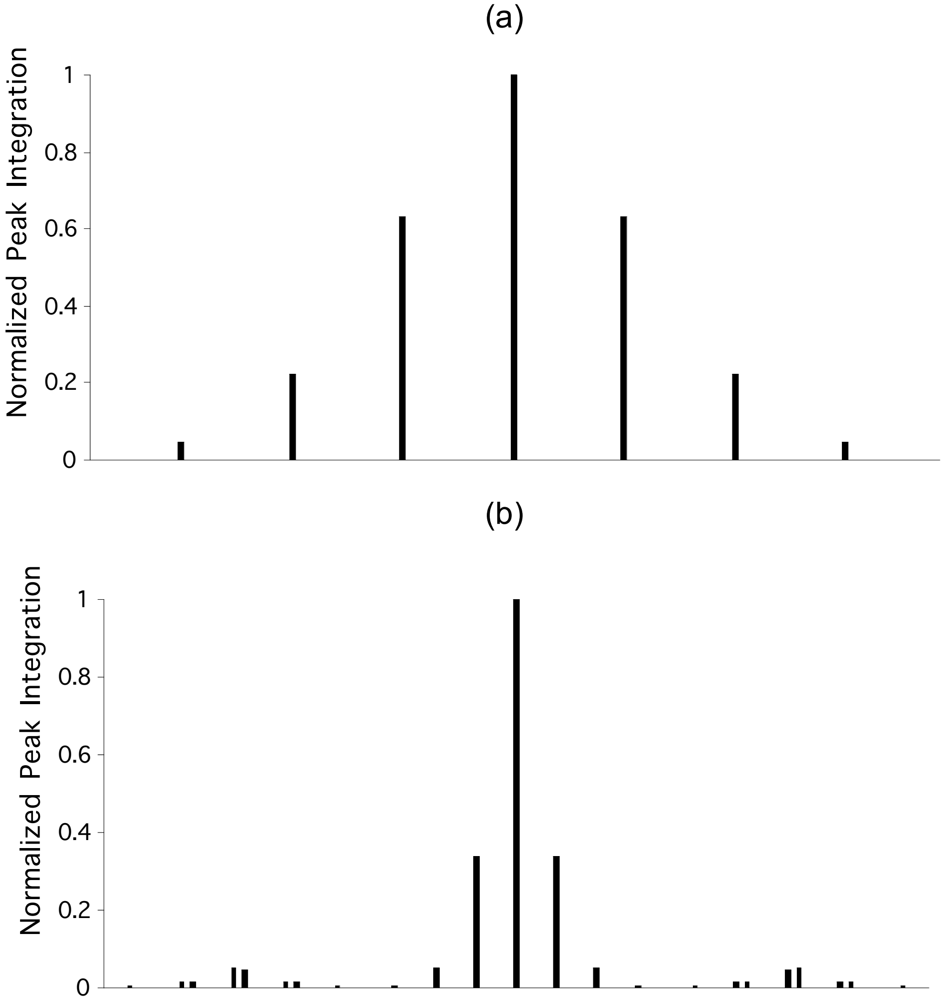

Figure S7. Calculated peak integrations: (a) ^{119}Sn nuclei coupled to 9 equivalent Sn nuclei, (b) 9 equivalent ^{119}Sn nuclei coupled to 1 Sn nucleus.

References

1 J.C.Martins, Biesemans M., Willem R.; *Prog. in Nucl. Magn Reson. Spect.* **2000**, 36, 271–322.

2 W.L. Wilson, PhD. Dissertation, *University of Michigan,* **1982**.