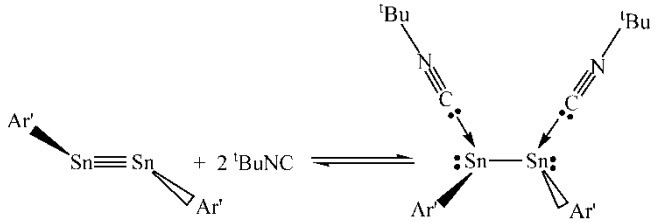
Supplementary Information

Reversible Complexation of Isocyanides by the Distannyne Ar′SnSnAr′ (Ar′ = C_6H_3-2, 6 (C_6H_3-2, 6-$^iPr_2$)$_2$)

Yang Peng, Xinping Wang, James C. Fettinger, and Philip P. Power*

1. Determination of ΔH_{assn} by temperature-dependent NMR spectroscopy

The association enthalpy ΔH_{assn} can be derived from the temperature dependence of the equilibrium constant $K_{eq.}$ (Table S1, Figure S1).



$$(1)\ \ln K_{eq} = \frac{-\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \qquad (2)\ K_{eq} = \frac{[2]}{[1]\ [^tBuNC]^2}$$

Table S1. Variable Temperature ^{1}H NMR and Temperature Data for $\mathbf{1} \rightleftharpoons \mathbf{2} + 2\,^t\mathbf{BuNC}$

Moles	1.40E-05	uncertainty [a] in T	1.0
Vol (L)	0.0060	uncertainty [a] in I	5%

^{1}H NMR Integration Data

Temperature	I_1 (free Ar′SnSnAr′)
295.15	58.08
258.15	23.11
248.15	18.96
238.15	17.86
223.15	14.4

Integration Data for **1**, ^{t}BuNC and **2**

Temperature	I_1 (free Ar′SnSnAr′)	I_2 (^{t}BuNC)	I_3 (complex **2**)
258.15	23.11	46.22	36.71
248.15	18.96	37.92	40.86
238.15	17.86	35.72	41.96
223.15	14.4	28.8	45.42

Temperature	Concentration of **1** (Ar′SnSnAr′)	Concentration of ^{t}BuNC	Concentration of complex **2**
258.15	0.009014	0.018029	0.014319
248.15	0.007396	0.014791	0.015938
238.15	0.006966	0.013933	0.016367
223.15	0.005617	0.011234	0.017716

Temperature	K	□G (J/mol)	□G (kJ/mol)
258.15	4887.242	-18231.1	-18.2311
248.15	9850.599	-18971	-18.971
238.15	12102.37	-18614.1	-18.6141
223.15	24994.18	-19208.1	-19.2081

T (K)	ln K	1/T
258.15	8.494383	0.003874
248.15	9.195287	0.00403
238.15	9.401156	0.004199
223.15	10.1264	0.004383

Slope/Intercept	3003.6	-3.0748
	□H (kJ/mol)	□S (J/molK)
	-25.0	-25.6

At 298.15K, ΔG = - 17.4 kJmol^{-1}

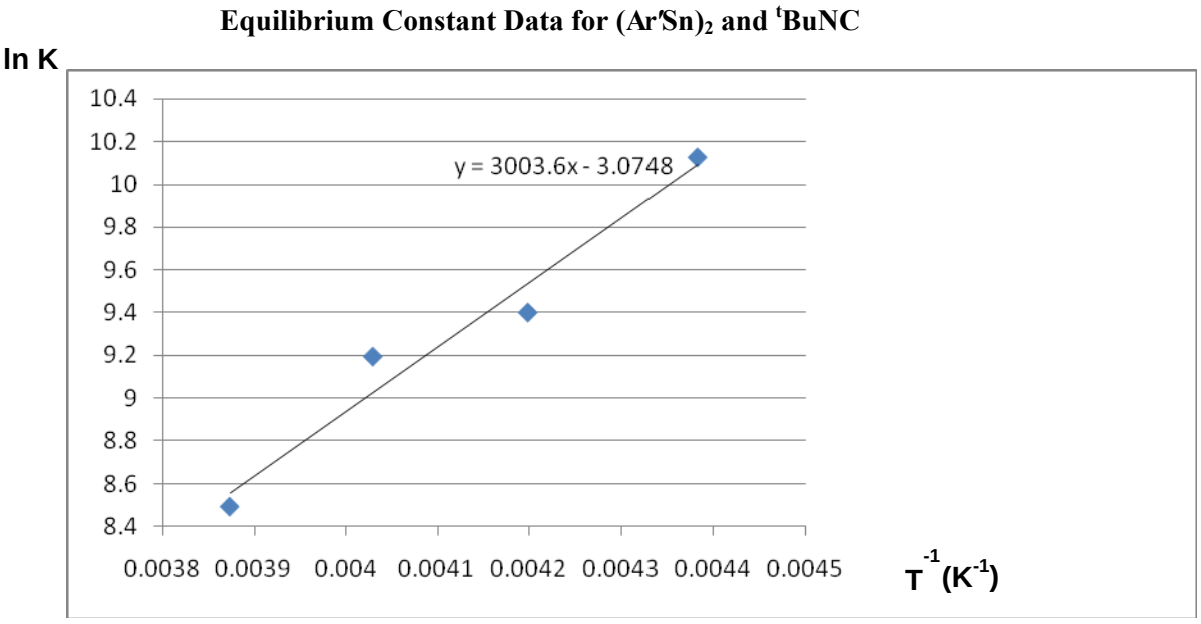
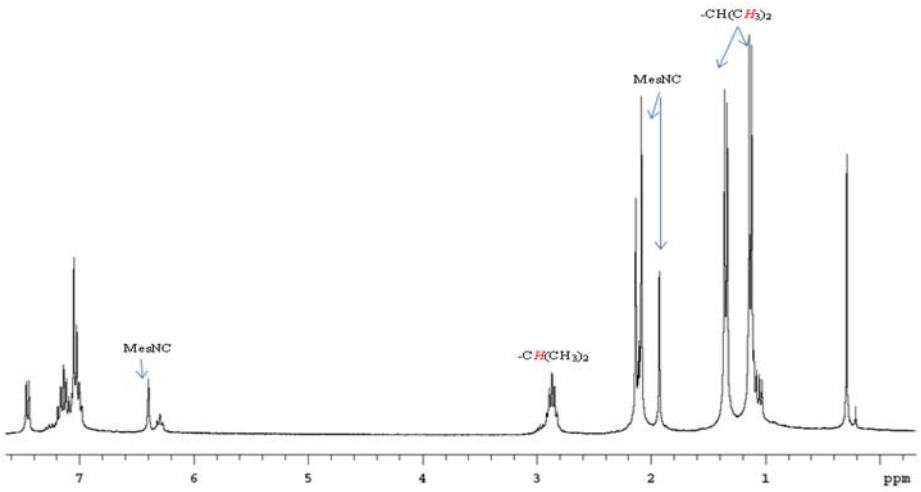


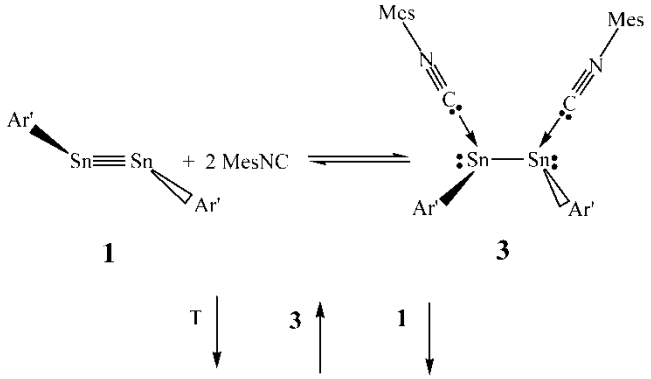
Figure S1. Plot of lnK versus T^{-1} for $\mathbf{1} \rightleftharpoons \mathbf{2} + 2\,^{t}\mathbf{BuNC}$

2. Determination of ΔH_{assn} by temperature-dependent NMR spectroscopy



^{1}H NMR spectrum of complex **3** which completely dissociates to **1** and MesNC at room temperature.

The association enthalpy ΔH_{assn} can be derived from the temperature dependence of the equilibrium constant $K_{eq.}$ (Table S2, Figure S2)



$$(1)\ \ln K_{eq} = \frac{-\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \qquad (2)\ K_{eq} = \frac{[3]}{[1]\ [MesNC]^2}$$

Table S2. Variable Temperature ^{1}H NMR and Temperature Data for $\mathbf{1 \rightleftharpoons 3 + 2\ MesNC}$

moles	1.56E-05	uncertainty [a] in T	1.0
Vol (L)	0.0053	uncertainty [a] in I	5%

^{1}H NMR Integration Data

emperature	I_1 (free Ar′SnSnAr′)
295.15	111.63
290.15	104.81
288.15	102.87
258.15	27.6
253.15	13.5
243.15	10.41

Integration Data for **1**, MesNC and **3**

Temperature	I_1 (free Ar′SnSnAr′)	I_2 (MesNC)	I_3 (complex **3**)
290.15	104.81	209.62	6.82
288.15	102.87	205.74	8.76
258.15	27.6	55.2	84.03
253.15	13.5	27	98.13
243.15	10.41	20.82	101.22

Temperature	Concentration of **1** (Ar′SnSnAr′)	Concentration of MesNC	Concentration of complex **3**
290.15	0.027636	0.055271	0.001798
288.15	0.027124	0.054248	0.00231
258.15	0.007277	0.014555	0.022157
253.15	0.00356	0.007119	0.025874
243.15	0.002745	0.00549	0.026689

Temperature	K	□G (J/mol)	□G (kJ/mol)
290.15	21.30005	-7378.55	-7.37855
288.15	28.93625	-8061.69	-8.06169
258.15	14371.81	-20546.2	-20.5462
253.15	143418.4	-24990.1	-24.9901
243.15	322640.2	-25641.9	-25.6419

T (K)	ln K	1/T
295	3.058709	0.003446
303	3.365095	0.00347
308	9.573024	0.003874
313	11.87352	0.00395
318	12.68429	0.004113

Slope/Intercept	15358	-49.799
	□H (kJ/mol)	□S (J/molK)
	-127.7	-414.0

At 298.15K, ΔG = - 4.3 $kJmol^{-1}$

a. The uncertainty in the integrations was estimated to be a typical 5%. The specifications of the VT apparatus indicated that the uncertainty of the temperature was 1°C. The concentration of **2** and **3** were accurate to ca. 1% to yield overall uncertainty of 8% for the data.

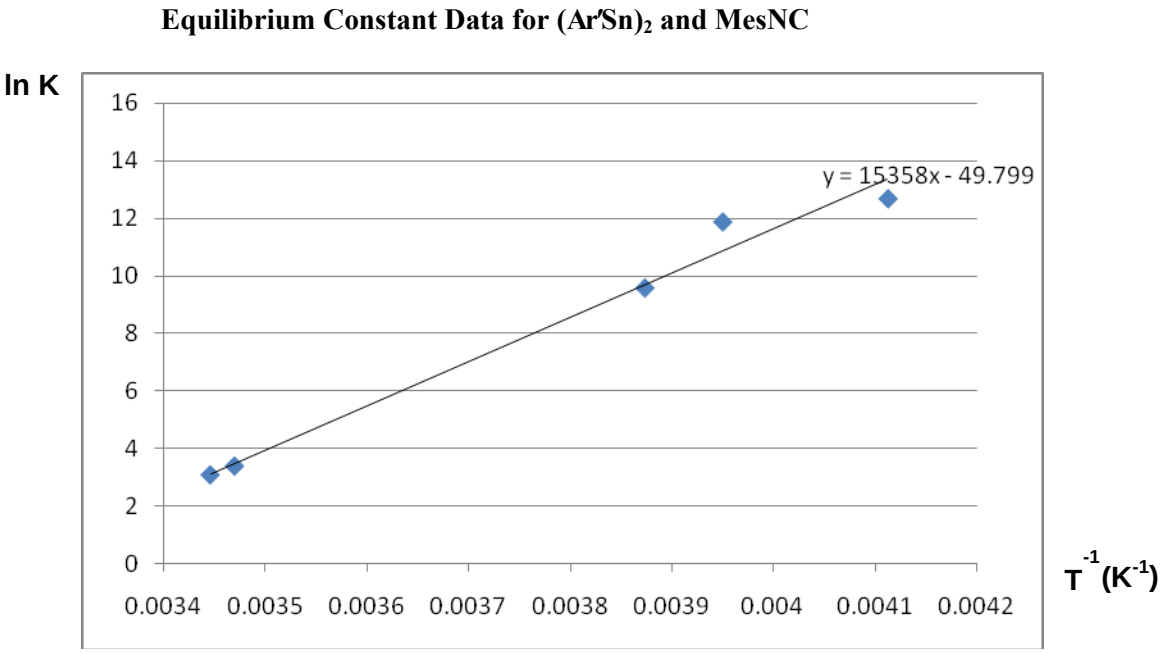


Figure S2. Plot of lnK versus T^{-1} for $\mathbf{1} \rightleftharpoons \mathbf{3} + 2\ \mathbf{MesNC}$

3. Variable temperature behavior of the UV-vis spectrum illustrating the dissociation of **3** to **1** and free MesNC