Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile Insertion of Ethylene into a Group 14 Element-Carbon Bond: Effects of the HOMO-LUMO Energy Gap on Reactivity

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Experimental

General Procedures. All operations were carried out under anaerobic and anhydrous conditions using modified Schlenk techniques. All solvents were dried over alumina columns and degassed prior to use. The ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopic data were collected on a Bruker 400MHz spectrometer. ^{119}Sn NMR data were referenced to $Sn^{n}Bu_4$ (−11.7 ppm). Infrared spectroscopy was collected as a Nujol mull using a Bruker Tensor 27 IR spectrometer. UV−visible spectroscopy was carried out as dilute hexane solutions in 3.5 mL quartz cuvettes using an Olis 17 Modernized Cary 14 UV/vis/NIR spectrophotometer. $Sn(Ar^{iPr_4})_2$ and $Sn(Ar^{iPr_6})_2$ were synthesized according to literature methods.[1,2] Ethylene gas was dried via a P_2O_5/Sieves drying column prior to use.

$Ar^{iPr_4}Sn(C_2H_4Ar^{iPr_4})$ (1a) A rapidly stirred solution of $Sn(Ar^{iPr_4})_2$ (1.00 g, 1.09 mmol) in benzene *ca*. 30 mL was treated with an excess of ethylene gas over one hour at 25 °C. The temperature was elevated to 60 °C and stirred for 12h. Upon cooling the solution was filtered using a filter-tipped cannula and concentrated under reduced pressure. Storage of the solution at room temperature afforded **1**. Yield (0.53 g, 51.23%) Mp: 171-176°C, ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.68 (t, 2H, $^{3}J_{H,H}$=9.6Hz $CH_2C\mathbf{H}_2Ar$), 1.04 (d, 12H $^{3}J_{H,H}$=1.6Hz $CH(C\mathbf{H}_3)_2$), 1.05 (d, 12H $^{3}J_{H,H}$=1.6Hz $CH(C\mathbf{H}_3)_2$), 1.08 (d, 12H $^{3}J_{H,H}$=4Hz $CH(C\mathbf{H}_3)_2$), 1.14(d, 12H $^{3}J_{H,H}$=3.6Hz $CH(C\mathbf{H}_3)_2$), 2.17 (t, 2H, $^{3}J_{H,H}$=6.8Hz, $C\mathbf{H}_2CH_2Ar$), 2.71 (m, 4H $^{3}J_{H,H}$=7Hz $C\mathbf{H}(CH_3)_2$), 3.07 (m, 4H $^{3}J_{H,H}$=7Hz $C\mathbf{H}(CH_3)_2$), 7.03-7.28 (m, 18H *m*-C_6H_3, *p*-C_6H_3, *m*-Dipp and *p*-Dipp; Dipp = 2,6-*i*Pr_2-C_6H_3); $^{13}C\{^{1}H\}$ NMR (126 Hz, C_6D_6, 298 K): 22.85, 23.26, 25.49, 25.90, 30.50, 30.58, 122.97, 123.41, 126.08, 128.61, 129.23, 129.50, 135.87, 139.24, 139.50, 143.58, 143.81, 146.39, 146.49 ;$^{119}Sn\{^{1}H\}$ NMR (186.36 Hz, C_6D_6, 298 K): δ=1806 ppm UV-vis: λ_{max} (nm), ϵ (M^{-1} cm^{-1}) = 482nm, 2130. IR (CsI, nujol, mineral oil; selected, cm^{-1}) : 2950, 1480, 1280, 1100, 1040, 820

$Ar^{iPr_6}Sn(C_2H_4Ar^{iPr_6})$ (1b) A rapidly stirred solution of $Sn(Ar^{iPr_6})_2$ (1.00g,0.924mmol) in benzene *ca*. 30 mL was treated with an excess of ethylene gas over one hour at 25 °C. The temperature was elevated to 60 °C and stirred for 12h. The solution was filtered using a filter-tipped cannula and concentrated under reduced pressure. Storage of the solution at room temperature afforded **1b**. Yield (0.42 g, 40.9%) Mp: 167-175 °C, ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.95 (t, 2H, $^{3}J_{H,H}$=5.8 Hz $CH_2C\mathbf{H}_2Ar$), 1.09 (d, 24H $^{3}J_{H,H}$= 4.8Hz $CH(C\mathbf{H}_3)$), 1.21(d, 12H $^{3}J_{H,H}$=3.6Hz $CH(C\mathbf{H}_3)$), 1.29 (d, 24H $^{3}J_{H,H}$= 4.8Hz $CH(C\mathbf{H}_3)$,, 1.31 (d, 12H $^{3}J_{H,H}$=4Hz $CH(C\mathbf{H}_3)$), 2.60 (t, 2H, $^{3}J_{H,H}$= 4.7Hz, $C\mathbf{H}_2CH_2Ar$), 2.78 (m, 4H $^{3}J_{H,H}$= 4.7Hz $C\mathbf{H}(CH_3)_2$), 2.86 (m, 4H $^{3}J_{H,H}$= 4.8Hz $C\mathbf{H}(CH_3)_2$), 2.97 (m, 2H $^{3}J_{H,H}$= 4.8Hz $C\mathbf{H}(CH_3)_2$), 3.18 (m, 4H $^{3}J_{H,H}$= 4.8Hz $C\mathbf{H}(CH_3)_2$), 7.05-2.25 (m, 14H *m*-C_6H_3, *p*-C_6H_3, and *m*-Trip; Trip = 2,4,6-*i*Pr_2-C_6H_2) $^{13}C\{^{1}H\}$ NMR (126 Hz, C_6D_6, 298 K): 23.21, 23.71, 24.10, 25.50, 25.92, 30.51, 30.59, 34.14, 34.41, 50.10, 120.34, 120.88, 121.03, 124.45, 25.86, 129.85, 130.10, 133.32, 136.95, 139.57, 143.66, 144.32, 146.05, 147.69, 148.42. $^{119}Sn\{^{1}H\}$ NMR (186.36 Hz, C_6D_6, 298 K): δ=1946 ppm. UV-vis: λ_{max} (nm), ϵ (M^{-1} cm^{-1}) = 489nm, 2200 IR (CsI, nujol, mineral oil; selected, cm^{-1}) : 2970, 1470, 1260, 1080, 1040

Figure S1. ^{1}H NMR spectrum for $Ar^{iPr_4}SnC_2H_4Ar^{iPr_4}$ (400 MHz, C_6D_6, 298K, ppm)

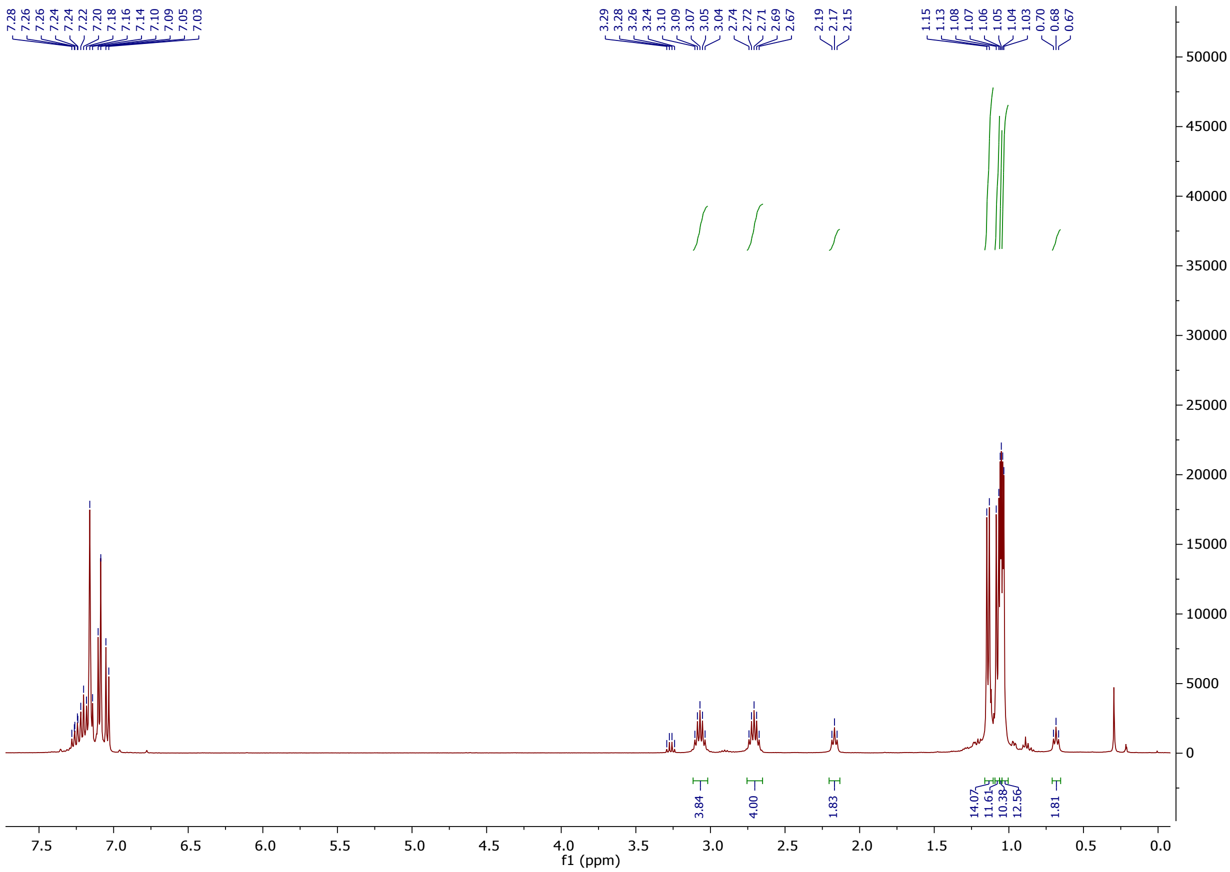


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum for $Ar^{iPr_4}SnC_2H_4Ar^{iPr_4}$ (126 MHz, C_6D_6, 298 K, ppm)

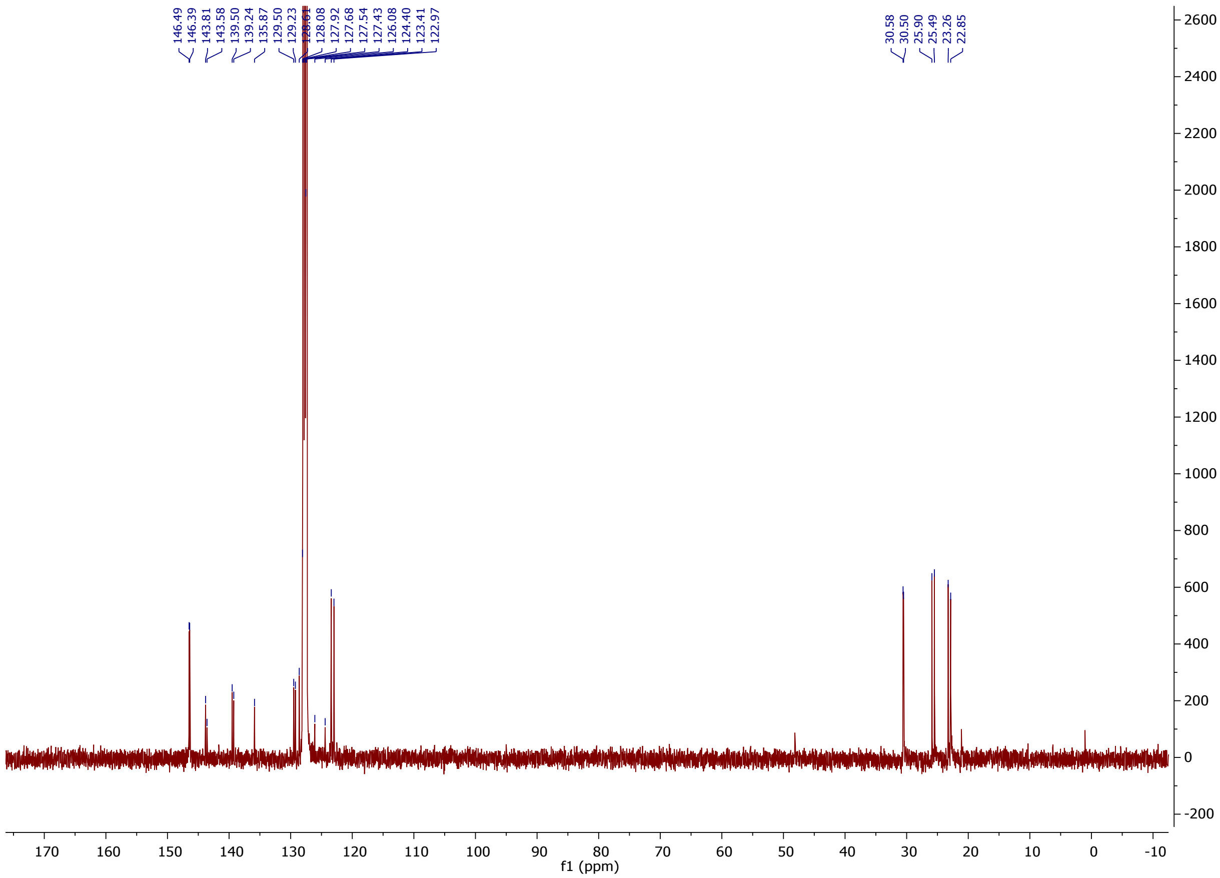


Figure S3. $^{119}Sn\{^{1}H\}$ NMR spectrum for $Ar^{iPr_4}SnC_2H_4Ar^{iPr_4}$ (186.36 MHz, C_6D_6, 298K, ppm)

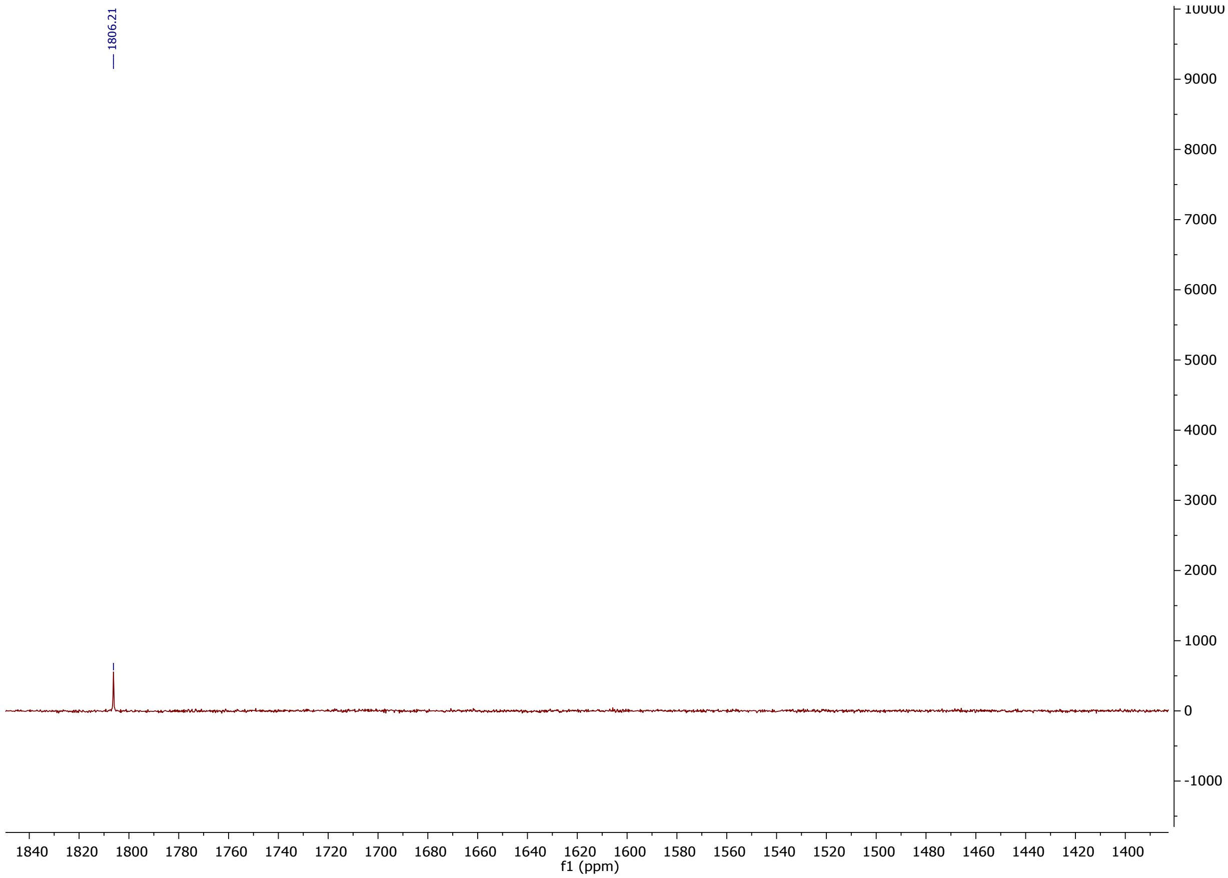
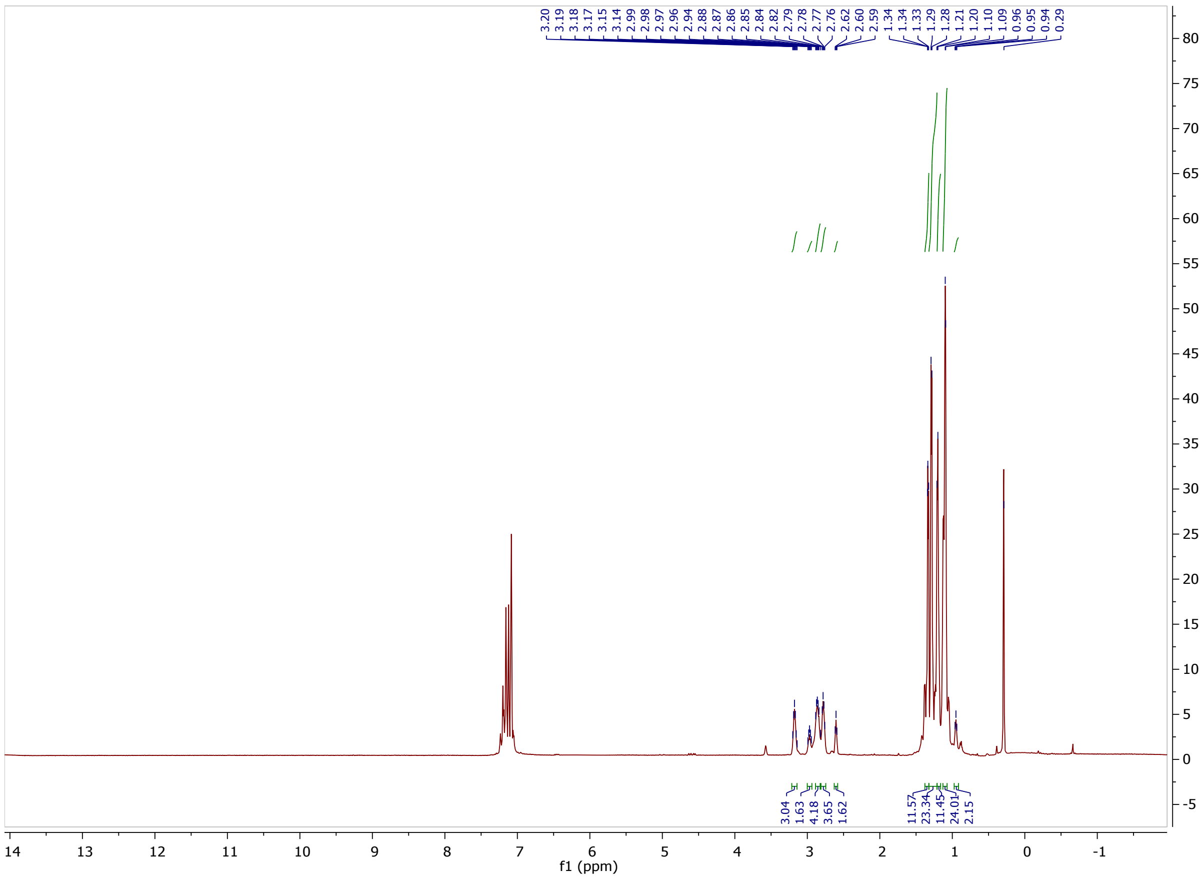


Figure S4. ^{1}H NMR spectrum for $Ar^{iPr_6}SnC_2H_4Ar^{iPr_6}$ (400 MHz, C_6D_6, 298K, ppm)



0.29= Silicon grease impurity

Figure S5. $^{13}C\{^1H\}$ NMR spectrum for $Ar^{iPr_6}SnC_2H_4Ar^{iPr_6}$ (126 MHz, C_6D_6, 298 K, ppm)

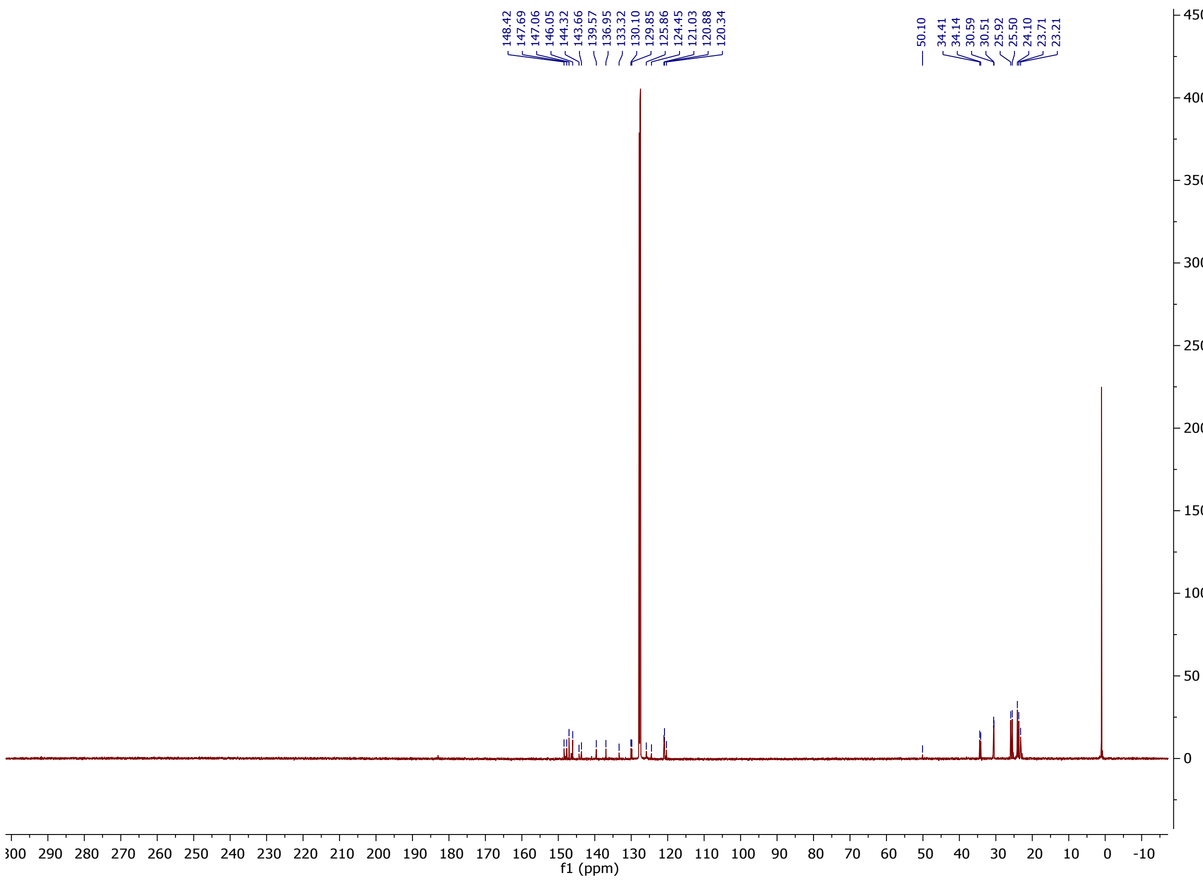


Figure S6. $^{119}Sn\{^1H\}$ NMR spectrum for $Ar^{iPr_6}SnC_2H_4Ar^{iPr_6}$ (186.36 MHz, C_6D_6, 298K, ppm)

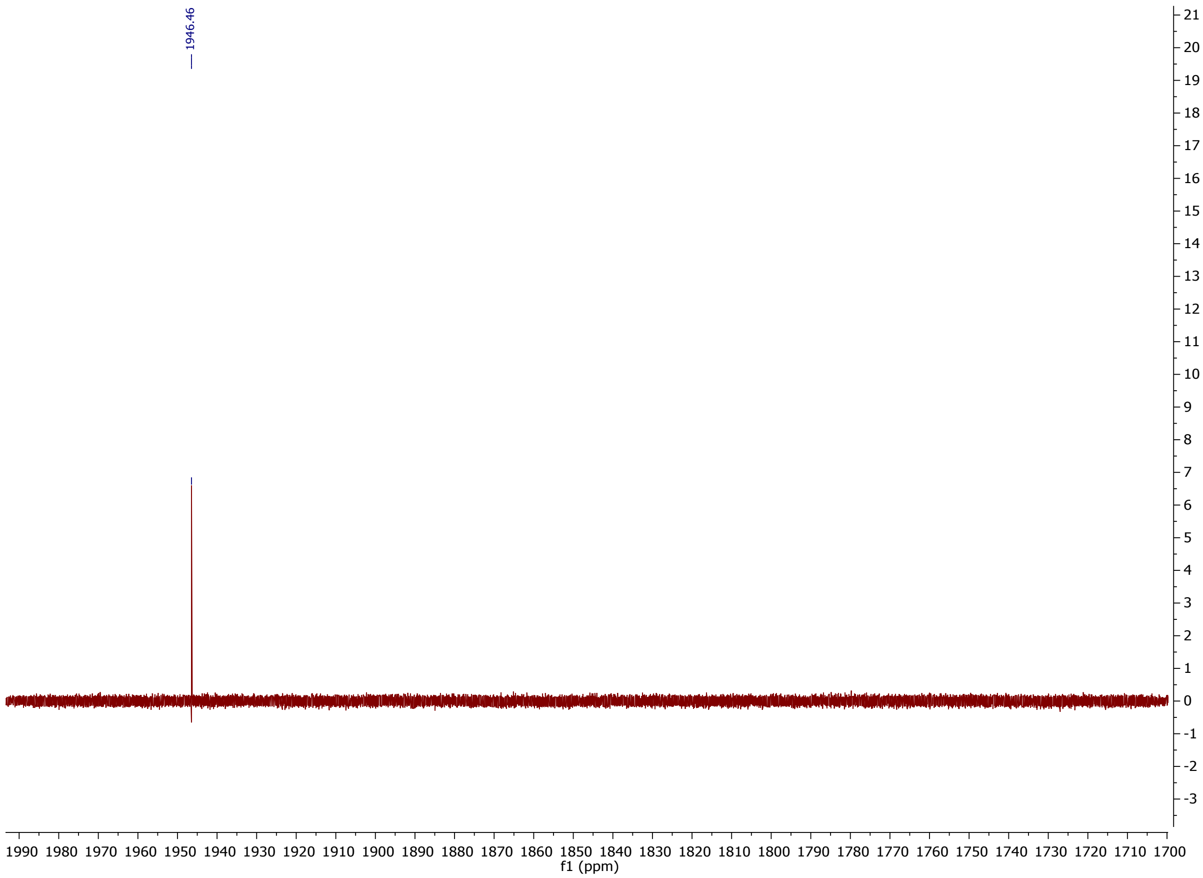


Table S1. Selected X-ray Crystallographic Data for **1a** and **1b**

Compound	**1a**	**1b**
Formula weight, $gmol^{-1}$	C62 H78 Sn	C84 H126 Sn
T (K) / l (Å)	90(2) K / 0.71073 Å	100(2)K/ 0.71073
Crystal system	Orthorhombic	Monoclinic
Space group / Z	$Pna2_1$	P2/n
a, Å	16.2901(9) Å	15.3139(10) Å
b, Å	15.1083(8) Å	12.2886(8) Å
c, Å	21.8016(12) Å	20.4790(14) Å
α, °	90°	90°
β, °	90°	92.374(3)°
γ, °	90°	90°
V, $Å^3$	5365.7(5) $Å^3$	3850.6(4) $Å^3$
ρ, mg m^{-3}	1.166Mg/m^3	1.082 Mg/m^3
Abs. coeff., mm^{-1}	0.512 mm^{-1}	0.372 mm^{-1}
F(000)	2000	1360
Crystal size, mm^3	0.385 x 0.258 x 0.257 mm^3	0.560 x 0.490 x 0.314 mm^3
θ range, °	2.248 to 30.628°	2.324 to 27.524°
Reflns collected	63919	32439
Ind. reflns	16425	8853
R(int)	0.0249	0.0207
Obs. reflns [$I > 2\sigma(I)$]	15193	8015
Completeness to 2θ	99.9%	99.9%
Goodness-of-fit F^2	1.122	1.034
Final R [$I > 2\sigma(I)$]	R1 = 0.0419 wR2 = 0.0928	R1 = 0.0326 wR2 = 0.0799
R (all data)	R1 = 0.0458 wR2 = 0.0942	R1 = 0.0370, wR2 = 0.0824

Figure S7. Calculation Details of the Reaction of Sn(Ar^{iPr6})$_2$ and Ethylene

Optimization/freq: TPSSTPSS-D3(BJ)/Lanl2dz+d(Sn)/6-31G(d) (others)
Single point calc.: TPSSTPSS-D3(BJ)/[4333111/433111/43]+2d (Sn)/6-311G(d,p) (others)

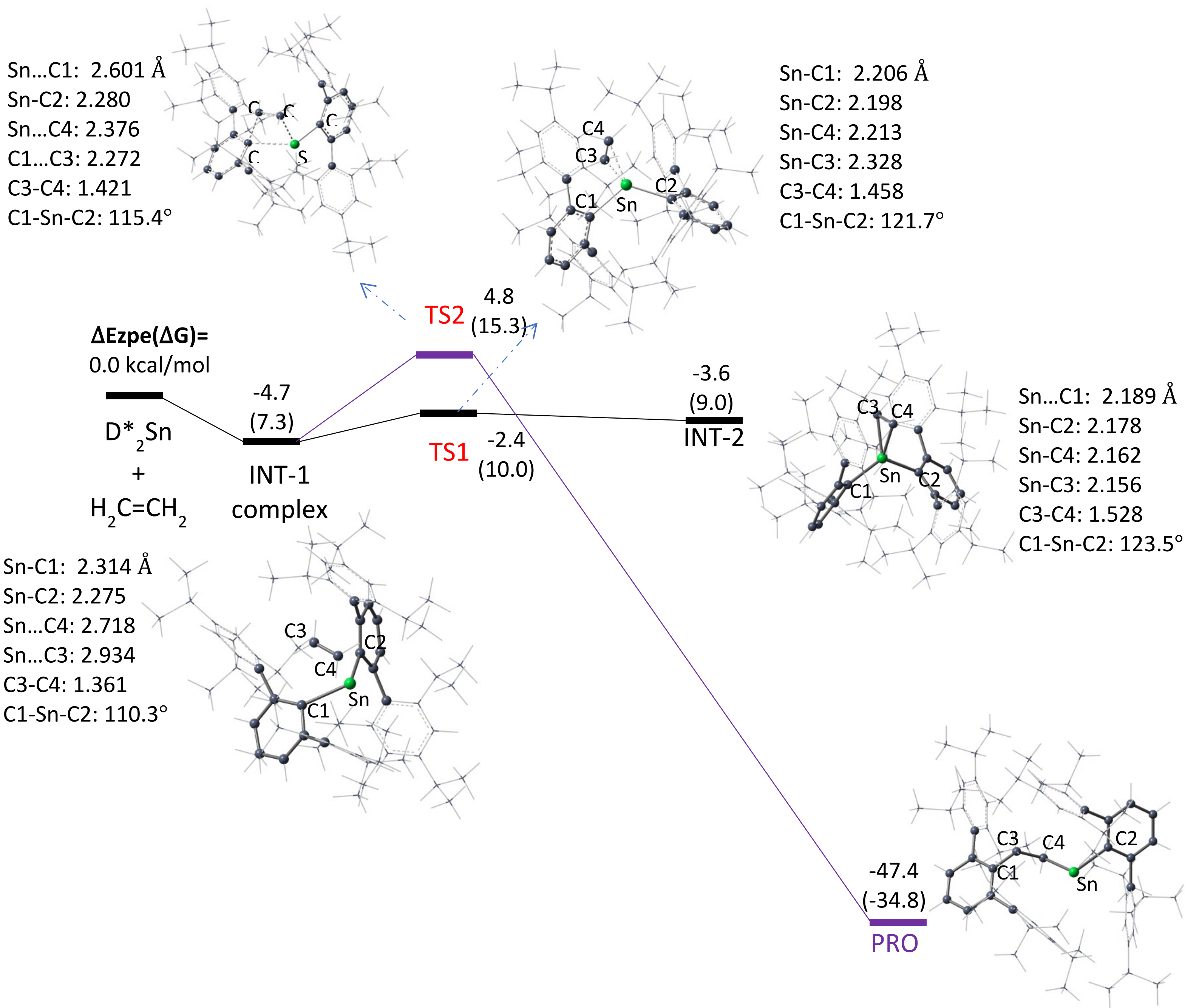
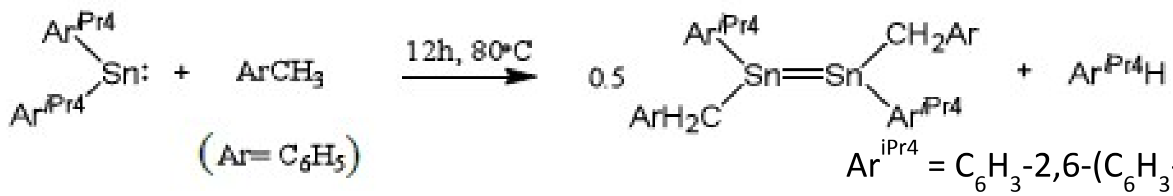


Figure S8. Calculation Details of the Reaction of Sn(Ar^{iPr4})$_2$ and Toluene

Reaction of stannylene with toluene



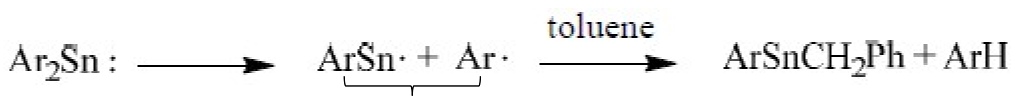
Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)$_2$

Reaction mechanisms

Optimization/Freq.: B3PW91-D3(BJ)//Lanl2dz+d (Sn)/3-21G(others)

Single point calc. B3PW91-D3(BJ)//[4333111/433111/43]+2d (Sn)/6-311G(d,p) (others)

1. Radical reaction



ΔEzpe=0.0 kcal/mol — 67.2(R.T.), for Ar= Ar^{iPr4}

ΔG=0.0 kcal/mol — 44.8(R.T.)/40.6 (80°C), for Ar= Ar^{iPr4}

2. SnAr$_2^{iPr4}$: [singlet state] ⟷ [triplet state]

ΔEzpe=0.0 kcal/mol — 21.8 (R.T.)

ΔG=0.0 kcal/mol — 20.6 (R.T.)/21.1 (80°C)

Ar$_2$Sn: + PhCH$_3$

ΔEzpe=0.0 kcal/mol

ΔG=0.0 kcal/mol

TS_concerted_singlet

37.4 (R.T.)

49.3 (R.T.)/51.4 (80°C)

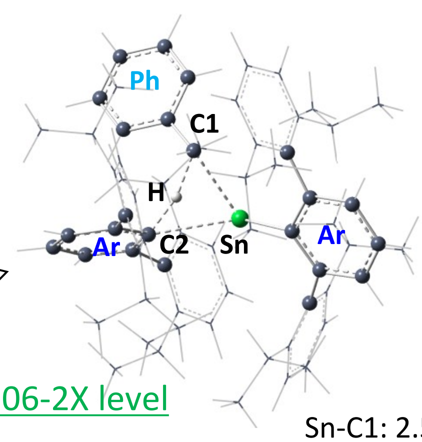
50.4 (R.T.)

64.8 (R.T.)/67.6 (80°C)

M06-2X level

TS_concerted_triplet

> 70 (R.T.)



Sn-C1: 2.591 Å

Sn-C2: 2.765

C1-H: 1.468

C2-H: 1.371

References:

1. G.H. Spikes; Y. Peng; J.C. Fettinger; P.P. Power, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1005−1010

2. M. McCrea-Hendrick; M. Bursch; K.L. Gullett; L.R. Maurer; J.C. Fettinger; S. Grimme; and P.P. Power, *Organometallics*, **2018**, *37*, 2075-2085