Impact of a Rigid Backbone on the Structure of an Agostically-Stabilized Dialkylstannylene: Isolation of an Unusual Bridged Stannyl-Stannylene

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SUPPLEMENTARY INFORMATION

Contents:

1.1 Experimental procedures

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Toluene, THF and light petroleum (b.p. 40-60 ºC) were dried prior to use by distillation under nitrogen from sodium, potassium or sodium/potassium alloy, respectively. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF was distilled from potassium and was deoxygenated by three freeze-pump-thaw cycles and stored over activated 4A molecular sieves. 1,2-$C_6H_4\{CH_2P(BH_3)Cy_2\}_2$[S1] and Cp_2Sn[S2] were prepared by previously published procedures; *n*-butyllithium was purchased from Aldrich as a 2.5 M solution in hexanes. All other compounds were used as supplied by the manufacturer.

^{1}H NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 500.16 MHz, respectively and chemical shifts are quoted in ppm relative to tetramethylsilane. $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded on a JEOL ECS400 spectrometer operating at 202.47, 160.47 and 186.51 MHz, respectively; chemical shifts are quoted in ppm relative to external 85% H_3PO_4, $BF_3.Et_2O$, and Me_4Sn, respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

Synthesis of 5: To a solution of 1,2-$C_6H_4\{CH_2PCy_2(BH_3)\}_2$ (0.50 g, 1.17 mmol) in THF (20 ml) was added *n*-BuLi (0.94 ml of a 2.5M solution in hexanes, 2.34 mmol) and this solution was stirred for 30 mins at room temperature. The solvent was removed *in vacuo* to yield a dark orange oil, which was dissolved in toluene (20 ml) and added, dropwise, to a solution of Cp_2Sn (0.29 g, 1.17 mmol) in toluene (20 ml); this mixture was stirred for 45 mins at room temperature. The pale solids were removed by filtration and the filtrate was concentrated to approx. 10 ml and cooled to -20°C. After one week yellow crystals of **5** were isolated and washed with light petroleum (3 x 5ml). Isolated yield: 0.23 g, 28%. The solvent of crystallisation is gradually lost under vacuum and so is diminished in intensity in the ^{1}H NMR spectrum; this solvent was not observed in the elemental analyses of **5**, the sample for which was exposed to vacuum for an extended period. Anal. Calcd. for $C_{64}H_{112}B_4P_4Sn_2$ (1286.1; molecular formula without solvent of crystallisation): C 59.77, H 8.78%. Found: C 59.68, H 8.88%. ^{1}H NMR (d_8-THF): δ ~0.5-2.67 (m, ca. 107H, Cy+BH_3+CHSn+Ph*Me*), 6.58 (m, 1H, ArH), 6.79 (m, 1H, ArH), 7.00 (m, 2H, ArH), 7.07-7.19 (m, ca. 5H, *Ph*Me), 7.28 (m, 2H, ArH), 7.96 (m, 1H, ArH), 8.03 (m, 1H, ArH). $^{11}B\{^1H\}$ NMR (d_8-THF): δ

-43.5, -38.8. $^{31}P\{^1H\}$ NMR (d_8-THF): δ 27.4, 28.6, 30.0, 35.4. $^{119}Sn\{^1H\}$ (d_8-THF): δ -103 (br, FWHM = 770 Hz), 339 (br, FWHM = 480 Hz).

1.2 Crystal Structure determination of 5:

Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer, using MoKα radiation (λ = 0.71073 Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model, while B-bound H atoms were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent C atom. Disorder in the solvent of crystallization was successfully modeled with the aid of restraints and constraints on geometry and displacement parameters. Data were collected and processed using CrysAlisPro and the structure was solved and refined using the Olex2 interface to the SHELXTL suite of programs.[S3]

Chemical formula	$C_{64}H_{112}B_4P_4Sn_2 \cdot 1.5C_7H_8$
Formula weight	1424.36
Temperature	150(2) K
Radiation, wavelength	MoKα, 0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell parameters	a = 14.08850(10) Å α = 90°
	b = 26.5770(2) Å β = 95.2730(10)°
	c = 20.0509(2) Å γ = 90°
Cell volume	7475.89(11) Å^3
Z	2
Absorption coefficient μ	0.793 mm^{-1}
Crystal colour and size	yellow, 0.30 × 0.30 × 0.10 mm^3
Reflections collected	108054
Independent reflections	17595 (R_{int} = 0.0359)
Reflections with $F^2>2\sigma$	15111
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.7970 and 0.9250
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17595 / 0 / 767
Final R indices [$F^2>2\sigma$]	R1 = 0.028, wR2 = 0.056
R indices (all data)	R1 = 0.039, wR2 = 0.060
Goodness-of-fit on F^2	1.051
Largest diff. peak and hole	0.67 and –0.55 e Å^{-3}

2.1 DFT calculations:

Geometry optimizations on the gas-phase molecules were performed with the Gaussian09 suite of programs (revision D.01).[S4] Ground state optimizations were performed using the hybrid B3LYP functional;[S5] the 6-31G(2d,p) all-electron basis set[S6] was used for all C, H, B and P atoms, while a LanL2DZ effective core potential basis set[S7] was used for Sn [default parameters were used throughout]. The identity of minima was confirmed by the absence of imaginary vibrational frequencies in each case. The stabilization energy associated with the B-H…Sn interactions was calculated using the NBODel routine, in which the elements affording this interaction were selectively deleted.[S8] Natural Bond Orbital analyses were performed using the NBO 3.1 module of Gaussian09.[S9]

2.2 Final atomic coordinates for 5′:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	50	0	-0.520509	0.044212	0.140892
2	50	0	1.778635	-1.335642	1.395920
3	15	0	-2.682663	0.676651	2.611073
4	15	0	-1.428626	-3.002961	-0.915483
5	15	0	-0.256493	2.772255	-2.128879
6	15	0	4.556608	-1.023596	-0.652267
7	5	0	-2.615688	-1.129347	3.287930
8	1	0	-2.713899	-1.002777	4.488084
9	1	0	-1.533318	-1.575507	2.960268
10	1	0	-3.553028	-1.716677	2.796702
11	5	0	0.479971	-3.347373	-0.802185
12	1	0	0.666699	-4.536606	-0.809680
13	1	0	0.996257	-2.749201	-1.714014
14	1	0	0.870003	-2.925813	0.311827
15	5	0	-1.522167	4.028379	-1.352413
16	1	0	-2.452147	3.364589	-0.952288
17	1	0	-0.984278	4.682433	-0.491583
18	1	0	-1.827146	4.690532	-2.322820
19	5	0	5.658411	-1.561039	0.848354
20	1	0	6.036773	-0.571369	1.429827
21	1	0	4.949005	-2.276686	1.525513
22	1	0	6.564548	-2.168965	0.318811
23	6	0	-2.431772	0.916424	0.801448
24	1	0	-2.383976	1.999026	0.637931
25	6	0	-3.485271	0.325038	-0.131091
26	6	0	-4.778906	0.873122	-0.147257
27	1	0	-5.008935	1.695151	0.520538
28	6	0	-5.761054	0.420637	-1.021383
29	1	0	-6.748713	0.870867	-1.005328
30	6	0	-5.458881	-0.587993	-1.933081
31	1	0	-6.207483	-0.939360	-2.636451
32	6	0	-4.174340	-1.119881	-1.958517
33	1	0	-3.926247	-1.863851	-2.708458
34	6	0	-3.174798	-0.691352	-1.068581
35	6	0	-1.756545	-1.222702	-1.193386
36	1	0	-1.376346	-1.057092	-2.210002

37	6	0	-4.237564	1.516459	3.112296
38	1	0	-4.275848	2.551206	2.760251
39	6	0	-1.398543	1.756123	3.351930
40	1	0	-1.560744	1.795752	4.432264
41	6	0	-2.080225	-3.980190	-2.328043
42	1	0	-3.167817	-3.911094	-2.396690
43	6	0	-2.403736	-3.581097	0.509170
44	1	0	-2.125659	-3.037180	1.414055
45	6	0	0.633678	1.498083	-1.137632
46	1	0	1.050480	0.824859	-1.896838
47	6	0	1.736986	1.978280	-0.219915
48	6	0	1.687015	3.257065	0.356614
49	1	0	0.865113	3.917805	0.103108
50	6	0	2.647274	3.700398	1.263222
51	1	0	2.572077	4.700323	1.679283
52	6	0	3.682360	2.850601	1.637489
53	1	0	4.433371	3.170871	2.352883
54	6	0	3.749240	1.570425	1.095231
55	1	0	4.553856	0.909441	1.401115
56	6	0	2.809185	1.106151	0.152063
57	6	0	2.889715	-0.312474	-0.341827
58	1	0	2.320642	-0.467302	-1.259017
59	6	0	1.061823	3.623185	-3.087044
60	1	0	0.594912	4.322185	-3.785808
61	6	0	-1.124507	1.780307	-3.403123
62	1	0	-1.956183	1.242240	-2.942667
63	6	0	5.404735	0.141659	-1.792988
64	1	0	4.814610	0.316922	-2.696976
65	6	0	4.193885	-2.473487	-1.711248
66	1	0	5.143890	-2.925691	-2.007102
67	1	0	3.625548	-2.195091	-2.602674
68	1	0	3.623147	-3.211778	-1.143674
69	1	0	6.377416	-0.277003	-2.065355
70	1	0	5.566499	1.091935	-1.279298
71	1	0	1.699824	4.186452	-2.403092
72	1	0	1.676594	2.906123	-3.638582
73	1	0	-0.453578	1.074208	-3.901351
74	1	0	-1.538597	2.469291	-4.143691
75	1	0	-1.795892	-5.025921	-2.182881
76	1	0	-1.630247	-3.626212	-3.259285
77	1	0	-2.205018	-4.646430	0.654579
78	1	0	-3.470427	-3.428182	0.327112
79	1	0	-4.283934	1.503245	4.204964
80	1	0	-5.096548	0.962587	2.729377
81	1	0	-0.406140	1.333919	3.175626
82	1	0	-1.438955	2.768302	2.939697

Final energy for **5′**: -2415.14715465 au

NIMAG = 0

2.3 Final atomic coordinates for *rac*-6′:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	50	0	-0.077862	-1.716272	-0.054014
2	15	0	-2.811119	-0.158500	0.173719
3	15	0	2.893682	-0.279771	-0.022148

4	5	0	-2.218990	-0.709244	1.932039
5	1	0	-3.086113	-1.277504	2.541021
6	1	0	-1.707186	0.230234	2.480577
7	1	0	-1.329376	-1.568284	1.666891
8	5	0	3.630942	-2.017556	0.386485
9	1	0	4.733156	-2.015258	-0.117716
10	1	0	3.652333	-2.083529	1.596438
11	1	0	2.883011	-2.827194	-0.122188
12	6	0	-1.311768	0.074087	-0.830069
13	1	0	-1.570530	0.029822	-1.893902
14	6	0	-0.573987	1.347101	-0.465259
15	6	0	-1.045632	2.597042	-0.902343
16	1	0	-1.886399	2.630230	-1.590327
17	6	0	-0.478424	3.786474	-0.456553
18	1	0	-0.864489	4.739194	-0.806250
19	6	0	0.564613	3.741465	0.468438
20	1	0	0.989723	4.659763	0.862198
21	6	0	1.073293	2.510908	0.872188
22	1	0	1.891985	2.483035	1.583660
23	6	0	0.558284	1.299758	0.377961
24	6	0	1.218712	-0.026288	0.694460
25	1	0	1.349348	-0.181664	1.772896
26	6	0	-3.780940	-1.458305	-0.679002
27	1	0	-4.026384	-1.155515	-1.701001
28	6	0	-3.936516	1.288716	0.183341
29	1	0	-4.792362	1.059064	0.825388
30	6	0	4.028796	1.070455	0.492589
31	1	0	3.686043	2.053820	0.165671
32	6	0	2.703346	0.017163	-1.824677
33	1	0	2.114352	-0.789406	-2.272504
34	1	0	5.009292	0.860147	0.055818
35	1	0	4.132645	1.058955	1.580861
36	1	0	3.692624	-0.000818	-2.289366
37	1	0	2.220804	0.976381	-2.028711
38	1	0	-4.704317	-1.637917	-0.122184
39	1	0	-3.209675	-2.389485	-0.709189
40	1	0	-3.410166	2.152319	0.593753
41	1	0	-4.292062	1.523822	-0.823780

Final energy for *rac*-**6′**: -1207.56152326 au

NIMAG = 0

2.4 Final atomic coordinates for *meso*-6′:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	50	0	0.133001	-1.586371	-0.857884
2	15	0	2.575517	-0.262686	0.697966
3	15	0	-2.714362	-0.393344	0.554174
4	5	0	1.394390	-1.110133	1.972582
5	1	0	1.975736	-1.897723	2.670613
6	1	0	0.598503	-1.756954	1.236293
7	1	0	0.786204	-0.250563	2.554343
8	5	0	-3.022821	-2.298514	0.499597
9	1	0	-3.956495	-2.524200	1.236190
10	1	0	-3.259122	-2.540782	-0.666658
11	1	0	-1.984138	-2.803644	0.881623

12	6	0	1.573401	0.212705	-0.736162
13	1	0	2.226353	0.285602	-1.613963
14	6	0	0.742043	1.473271	-0.580745
15	6	0	1.365654	2.732476	-0.589014
16	1	0	2.446298	2.781149	-0.689000
17	6	0	0.637858	3.913765	-0.493254
18	1	0	1.148963	4.871709	-0.502317
19	6	0	-0.750955	3.852373	-0.400889
20	1	0	-1.339454	4.762737	-0.337238
21	6	0	-1.386113	2.614538	-0.417766
22	1	0	-2.469377	2.582470	-0.395301
23	6	0	-0.668013	1.409971	-0.503456
24	6	0	-1.373977	0.070000	-0.613543
25	1	0	-1.877680	0.004736	-1.592163
26	6	0	3.570440	1.099382	1.420766
27	1	0	4.289511	1.496699	0.699050
28	6	0	3.832761	-1.420638	0.039835
29	1	0	4.467298	-1.764613	0.860632
30	6	0	-4.257002	0.518081	0.125761
31	1	0	-4.186900	1.593264	0.304286
32	6	0	-2.276493	0.257955	2.205198
33	1	0	-1.371858	-0.237347	2.561372
34	1	0	-5.064588	0.107853	0.739061
35	1	0	-4.503614	0.337164	-0.923836
36	1	0	-3.097527	0.027206	2.889590
37	1	0	-2.111654	1.337919	2.180816
38	1	0	4.107834	0.713011	2.292251
39	1	0	2.902664	1.899127	1.747234
40	1	0	3.338413	-2.289783	-0.401265
41	1	0	4.451802	-0.936111	-0.720773

Final energy of *meso*-**6′**: -1207.55994283 au

NIMAG = 0

References:

S1 K. Izod, C. M. Dixon, E. McMeekin, L. Rodgers, R. W. Harrington and U. Baisch, *Organometallics*, 2014, **33**, 378.

S2 E. O. Fischer and H. Grubert, *Z. Naturforsch. B*, 1956, **11**, 423.

S3 (a) *CrysAlisPro*; Oxford Diffraction Ltd, Oxford, UK, 2008. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2008, **64**, 112. (c) , O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

S4 Gaussian 09, Revisions B.01, C.01 and D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S5 (a) A. D. Becke *J. Chem. Phys.* 1993, **98**, 5648. (b) P. J. Stephens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623. (c) R. H. Hertwig, W. Koch, *Chem. Phys. Lett.* 1997, **268**, 345.

S6 (a) P.C. Hariharan, J.A. Pople, *Theoret. Chim. Acta* 1973, **28**, 213. (b) M.M. Francl, W.J. Petro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, *J. Chem. Phys.* 1982, **77**, 3654.

S7 (a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270. (b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284. (c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299.

S8 M. W. Wong, *Chem. Phys. Lett.* 1996, **256**, 391.

S9 (a) NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold. (b) J. E. Carpenter, F. Weinhold, *J. Mol. Struct. (Theochem)* 1988, **169**, 41. (c) J. E. Carpenter, PhD thesis, University of Wisconsin, Madison, WI, 1987. (d) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* 1980, **102**, 7211. (e) A. E. Reed, F. Weinhold, *J. Chem. Phys.* 1983, **78**, 4066. (f) A. E. Reed, F. Weinhold, *J. Chem. Phys.* 1983, **81**, 1736. (g) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* 1985, **83**, 735. (h) A. E. Reed, L. A. Curtiss, F. Weinhold*, Chem. Rev.* 1988, **88**, 899.