Supplementary material to "Organotin(IV) Derivatives of some O,C,O-chelating Ligands. Part 2." (Organometallics)

by

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S1. *In silico* generated starting geometries for the geometry optimisations

S2. Further insights into the observed trends in Sn−O distances

S3. Crystallographic data for 5 and 6 and experimental and computed values of selected geometrical parameters of the various L-$SnPh_3$, L-$SnPh_2Cl$, L-$SnPhCl_2$ and L-$SnCl_3$.

S1. *In silico* generated starting geometries for the geometry optimisations

The geometry optimisations of compounds **1**, **2**, **3**, **9**, **10**, **12** and L-$SnCl_3$ (with R=Me) were started from the crystal structures given in the supplementary material to reference 3a.

The geometry optimisations of compounds **5** and **6** were initiated from the crystal structures obtained in this contribution. The starting structures for the geometry optimisations of the compounds **4**, **7**, **8**, **11** and L-$SnCl_3$ (for R = Et and *i*-Pr) were generated in silico and are given in Tables S3-S8. All geometries are supplied as Cartesian coordinates (Å).

Table S1. Starting geometry for the optimisation of compound **4**.

C	1.6248	1.0699	−0.7475
C	−2.9086	1.0550	−0.1523
C	−3.9188	1.8949	−0.6247
C	−3.6380	2.7915	−1.6456
C	−2.3527	2.8509	−2.1854
C	−1.3216	1.9933	−1.7466
C	−3.1846	0.1302	1.0023
C	−1.9480	−1.3212	2.7066
C	−2.4393	−0.8183	4.0507
C	1.0368	0.3297	1.6392
C	1.7068	−0.5402	2.4919
C	2.5489	−0.0281	3.4791
C	2.7126	1.3511	3.6100
C	2.0377	2.2193	2.7528
C	1.1957	1.7067	1.7673
C	0.0353	2.1820	−2.3596
C	2.1241	3.2138	−2.0267
C	3.0360	3.7760	−0.9552
H	0.4574	1.2332	−2.6812
H	−0.0451	2.8005	−3.2631
H	2.5566	4.6134	−0.4378
H	3.9797	4.1195	−1.3880
H	3.2554	3.0155	−0.1994
H	1.9351	3.9763	−2.7902
H	2.5960	2.3454	−2.4985
H	−4.9199	1.8728	−0.1982
H	−4.4120	3.4624	−2.0147
H	−2.1550	3.5909	−2.9617
H	−3.8616	0.6067	1.7193
H	−3.6411	−0.7950	0.6396
H	−0.9503	−1.7477	2.8305
H	−2.6107	−2.1046	2.3268
H	−1.7855	−0.0284	4.4353
H	−2.4570	−1.6344	4.7794
H	−3.4510	−0.4073	3.9750
H	1.5943	−1.6123	2.3941
H	3.0873	−0.7019	4.1430
H	3.3781	1.7499	4.3739
H	2.1800	3.2943	2.8440
H	0.6875	2.3844	1.0878
O	−1.8821	−0.1738	1.7269
O	0.8877	2.8339	−1.4218
C	1.2603	−0.7662	−1.2305
C	−0.8448	−2.4630	−0.0539
Sn	−0.3451	−0.3933	0.1765
C	−1.5475	−5.1373	−0.3641
C	−0.0368	−3.4555	0.4887
C	−1.9861	−2.8008	−0.7788
C	−2.3419	−4.1403	−0.9292
C	−0.3918	−4.7960	0.3385
H	0.8795	−3.2019	1.0062
H	−2.5875	−2.0306	−1.2505

H	−3.2278	−4.4123	−1.4995
H	0.2394	−5.5784	0.7552
H	−1.8176	−6.1846	−0.4889
C	3.2277	−1.3299	−3.1468
C	2.5926	−0.4479	−0.9836
C	0.9183	−1.3553	−2.4529
C	1.8964	−1.6401	−3.4072
C	3.5751	−0.7314	−1.9378
H	2.9056	0.0329	−0.0675
H	−0.1177	−1.5844	−2.6764
H	1.6193	−2.1018	−4.3520
H	4.6146	−0.4816	−1.7365
H	3.9944	−1.5507	−3.8864

Table S2. Starting geometry for the optimisation of compound **7**.

C	−0.5100	−1.7726	−0.7462
C	0.4047	−2.6859	−1.3269
C	−0.0559	−3.8020	−2.0276
C	−1.4206	−3.9782	−2.2068
C	−2.3169	−3.0400	−1.6934
C	−1.8799	−1.9208	−0.9533
C	1.8866	−2.4456	−1.1942
C	3.5255	−0.4569	−0.7632
C	−2.9285	−0.9449	−0.5069
C	−4.0650	1.0306	−1.1890
C	0.7406	1.6501	−0.7301
C	1.6077	2.6392	−0.2803
C	1.7610	3.8119	−1.0200
C	1.0482	3.9869	−2.2063
C	0.1789	2.9923	−2.6525
C	0.0270	1.8204	−1.9133
C	4.0348	0.0928	−2.0940
C	4.4933	−1.4978	−0.2154
C	−3.6797	2.4051	−1.7224
C	−5.3005	0.5123	−1.9191
H	0.6337	−4.5288	−2.4528
H	−1.7943	−4.8348	−2.7653
H	−3.3807	−3.1846	−1.8857
H	2.2694	−3.0203	−0.3471
H	2.4076	−2.7466	−2.1091
H	3.4787	0.3726	−0.0523
H	−3.9060	−1.4410	−0.4828
H	−2.7461	−0.6001	0.5057
H	−4.2670	1.1167	−0.1142
H	2.1592	2.5185	0.6431
H	2.4293	4.5964	−0.6700
H	1.1610	4.9067	−2.7781
H	−0.3906	3.1377	−3.5684
H	−0.6677	1.0572	−2.2518
H	4.0975	−0.6959	−2.8520
H	5.0297	0.5356	−1.9791
H	3.3642	0.8672	−2.4812
H	4.1384	−1.9197	0.7282
H	5.4739	−1.0473	−0.0268
H	4.6413	−2.3251	−0.9178
H	−2.8068	2.7903	−1.1864
H	−4.4978	3.1224	−1.6051
H	−3.4035	2.3545	−2.7815
H	−5.0900	0.3616	−2.9837
H	−6.1390	1.2089	−1.8217
H	−5.6187	−0.4566	−1.5225
C	−0.8870	0.6564	1.6894
C	1.6850	−0.7435	2.0303
O	2.1203	−0.9677	−0.9833
O	−2.9556	0.1525	−1.4166
Sn	0.5367	−0.2103	0.3042
C	3.1746	−1.4985	4.2552
C	1.6912	−2.0754	2.4417

C	2.3940	0.2164	2.7421
C	3.1460	−0.1627	3.8541
C	2.4417	−2.4550	3.5535
H	1.0971	−2.8170	1.9174
H	2.3516	1.2602	2.4593
H	3.6987	0.5843	4.4204
H	2.4462	−3.4912	3.8852
H	3.7538	−1.7905	5.1297
C	−2.7362	1.6314	3.5583
C	−1.3695	−0.1669	2.7132
C	−1.3503	1.9659	1.6019
C	−2.2712	2.4537	2.5347
C	−2.2870	0.3173	3.6472
H	−1.0462	−1.1994	2.7810
H	−1.0302	2.6351	0.8158
H	−2.6275	3.4789	2.4600
H	−2.6523	−0.3306	4.4405
H	−3.4510	2.0143	4.2837

Table S3. Starting geometry for the optimisation of compound **8**.

C	−0.1469	−1.9829	−0.1709
C	0.7562	−2.9334	−0.7055
C	0.2823	−4.0569	−1.3828
C	−1.0838	−4.2035	−1.5822
C	−1.9674	−3.2298	−1.1120
C	−1.5157	−2.1011	−0.3974
C	2.2379	−2.7131	−0.5402
C	3.8968	−0.7180	−0.2251
C	−2.5396	−1.0835	0.0120
C	−3.5764	0.9216	−0.7405
C	1.1744	1.4587	−0.1362
C	2.0244	2.4137	0.4145
C	2.2371	3.6136	−0.2613
C	1.5998	3.8476	−1.4809
C	0.7460	2.8858	−2.0234
C	0.5332	1.6848	−1.3490
C	4.3669	−0.1691	−1.5706
C	4.8783	−1.7637	0.2907
C	−3.1272	2.2967	−1.2198
C	−4.7465	0.4300	−1.5879
H	0.9609	−4.8139	−1.7715
H	−1.4687	−5.0680	−2.1210
H	−3.0310	−3.3571	−1.3172
H	2.5809	−3.2380	0.3560
H	2.7815	−3.0747	−1.4189
H	3.8743	0.1106	0.4888
H	−3.5394	−1.5316	−0.0253
H	−2.3937	−0.7645	1.0408
H	−3.8740	0.9979	0.3126
H	2.5082	2.2344	1.3699
H	2.8908	4.3733	0.1631
H	1.7585	4.7894	−2.0041
H	0.2364	3.0819	−2.9649
H	−0.1505	0.9475	−1.7596
H	4.3995	−0.9570	−2.3314
H	5.3680	0.2666	−1.4871
H	3.6899	0.6106	−1.9349
H	4.5497	−2.1900	1.2427
H	5.8648	−1.3156	0.4527
H	5.0048	−2.5881	−0.4193
H	−2.2989	2.6628	−0.6057
H	−3.9427	3.0244	−1.1641
H	−2.7618	2.2550	−2.2518
H	−4.4406	0.2887	−2.6305
H	−5.5806	1.1381	−1.5593
H	−5.1141	−0.5384	−1.2356
C	−0.4775	0.4286	2.2640
Cl	2.2936	−0.9603	2.7535
O	2.4839	−1.2256	−0.4033
O	−2.4619	0.0299	−0.8759
Sn	0.9184	−0.4194	0.8496
C	−2.3165	1.3557	4.1620
C	−0.9240	−0.4101	3.2916
C	−0.9716	1.7270	2.1838
C	−1.8872	2.1915	3.1329
C	−1.8370	0.0511	4.2409
H	−0.5710	−1.4347	3.3483
H	−0.6792	2.4012	1.3906
H	−2.2682	3.2086	3.0676
H	−2.1757	−0.6060	5.0385
H	−3.0278	1.7210	4.9001

Table S4. Starting geometry for the optimisation of compound **11**.

C	6.5940	5.2062	0.9217
C	5.3967	5.2196	1.6500
C	4.3424	5.9844	1.2062
C	4.4318	6.7627	0.0683
C	5.6112	6.7224	−0.6827
C	6.6834	5.9576	−0.2731
C	5.2180	4.3877	2.8789
C	5.3967	2.0395	3.5844
C	7.9343	5.9173	−1.1151
C	9.2031	4.2803	−2.3896
C	8.5403	1.9956	1.0267
H	8.9350	4.1193	−4.4378
H	7.9879	5.2062	−3.8006
H	10.8292	5.3001	−1.6272
H	10.0072	6.1723	−2.6399
H	7.2731	1.2479	3.6299
C	5.3967	2.5226	5.0295
C	4.0029	1.5699	3.1634
C	6.3975	0.9393	3.3909
C	9.7392	2.8983	−2.1620
C	10.3467	5.2867	−2.4579
C	8.3632	4.3206	−3.6868
C	10.0485	4.9927	1.2893
Cl	8.5419	4.1462	3.9144
O	5.8256	3.0996	2.6513
O	8.3453	4.5487	−1.2517
Sn	8.2202	3.9986	1.5703
H	3.5383	5.9844	1.6841
H	3.7170	7.2994	−0.1934
H	5.6648	7.2189	−1.4679
H	5.6469	4.8171	3.6413
H	4.2709	4.2803	3.0837
H	7.7556	6.3065	−1.9913
H	8.6312	6.4406	−0.6941
H	10.2753	2.8983	−1.3655
H	7.6662	3.6765	−3.6299
H	10.9543	5.0452	−3.1634
H	10.2753	2.6299	−2.9130
H	9.0065	2.2811	−2.0596
H	6.2545	2.8983	5.2457
H	5.2359	1.7712	5.6099
H	4.7177	3.1667	5.1547
H	3.3774	2.2945	3.2658
H	3.7170	0.8453	3.7209
H	4.0208	1.2881	2.2417
H	6.3975	0.6575	2.4692
H	6.1473	0.1879	3.9371
C	12.4622	6.3051	0.9183
C	10.6519	5.6473	2.3517
C	10.6519	4.9942	0.0413
C	11.8588	5.6504	−0.1442
C	11.8588	6.3035	2.1662
H	10.1748	5.6461	3.3384
H	10.1748	4.4766	−0.7987
H	12.3359	5.6517	−1.1309
H	12.3359	6.8212	3.0063
H	13.4164	6.8239	0.7716
C	8.9629	−0.6488	0.3091
C	8.6460	1.6489	−0.3112
C	8.6460	1.0201	2.0059
C	8.8573	−0.3021	1.6471
C	8.8573	0.3267	−0.6700
H	8.5624	2.4201	−1.0854
H	8.5624	1.2942	3.0638
H	8.9408	−1.0734	2.4213
H	8.9408	0.0526	−1.7279
H	9.1300	−1.6942	0.0255

Table S5. Starting geometry for the optimisation of compound L-$SnCl_3$ (with R=Et).

C	−0.8216	−0.1157	0.6772
C	−0.3124	−0.1504	1.9953
C	−0.8952	0.6314	2.9908
C	−1.9436	1.4824	2.6585
C	−2.3973	1.5603	1.3382
C	−1.8344	0.7677	0.3206
C	0.8642	−1.0435	2.2968
C	2.7408	−2.3114	1.0965
C	4.0222	−1.6987	1.6282
Cl	1.8747	−0.6897	−2.0947
Cl	0.0477	−3.8351	−0.0673
Sn	0.2409	−1.5030	−0.5642
O	−1.2278	1.3822	−1.8874
O	1.6663	−1.2564	1.0140
Cl	−1.1376	−1.9850	−2.5036
C	−2.3227	0.9432	−1.0863
C	−1.6576	1.7635	−3.1946
C	−0.4389	2.1532	−4.0066
H	−2.7421	0.0072	−1.4642
H	−3.1198	1.6962	−1.1215
H	0.1069	2.9670	−3.5182
H	−0.7265	2.4731	−5.0120
H	0.2538	1.3099	−4.0912
H	−2.3424	2.6154	−3.1218
H	−2.1752	0.9266	−3.6759
H	−0.5427	0.5983	4.0201
H	−2.4045	2.1052	3.4244
H	−3.1993	2.2624	1.1081
H	1.5226	−0.5767	3.0364
H	0.5094	−2.0075	2.6754
H	2.9224	−2.7135	0.0955
H	2.4136	−3.1326	1.7414
H	4.3534	−0.8708	0.9924
H	4.8190	−2.4481	1.6587
H	3.8842	−1.3070	2.6411

Table S6. Starting geometry for the optimisation of compound L-$SnCl_3$ (with R=*i*-Pr).

C	0.2371	−0.4741	1.0495
C	−0.6446	0.0460	2.0267
C	−0.1433	0.5447	3.2280
C	1.2318	0.5736	3.4303
C	2.0998	0.1171	2.4344
C	1.6158	−0.4078	1.2211
C	−2.1282	0.0476	1.7505
C	−3.7508	0.0006	−0.2978
C	2.6040	−0.8196	0.1709
C	3.4784	−0.0902	−1.9238
Cl	−0.9847	0.0924	−2.6147
H	3.6755	0.2867	−4.0583
H	2.5066	1.3472	−3.2338
H	5.0878	0.5106	−0.5869
Cl	−2.2632	−3.1345	−0.3190
O	2.4209	0.0236	−0.9640
C	−4.1436	1.4340	−0.6470
C	−4.7758	−0.6182	0.6442
C	2.9124	0.3302	−3.2752
C	4.6402	0.8198	−1.5362
H	−0.8033	0.9212	4.0075
H	1.6385	0.9686	4.3605
H	3.1733	0.1854	2.6142
H	−2.5752	−0.8395	2.2087
H	−2.5935	0.9531	2.1528
H	−3.7388	−0.5828	−1.2250
H	3.6252	−0.7198	0.5550
H	2.4655	−1.8709	−0.0924
H	3.8156	−1.1317	−1.9925
Sn	−0.8633	−1.2251	−0.6318
H	4.2989	1.8520	−1.4004
Cl	0.5864	−2.7191	−1.8828
O	−2.3436	0.0231	0.2500
H	5.4247	0.8065	−2.2994
H	−4.1595	2.0709	0.2444
H	−5.1368	1.4662	−1.1070
H	−3.4309	1.8744	−1.3525
H	−4.4940	−1.6339	0.9352
H	−5.7571	−0.6722	0.1602
H	−4.8935	−0.0291	1.5601
H	2.0857	−0.3270	−3.5635

S2. Further insights into the observed trends in Sn-O distances

In order to gain further insight into the observed trends in the Sn-O distances in the compounds presented in this paper, we discuss two sets of additional data obtained from ab initio calculations.

In a first part, we have investigated a number of density functional theory based reactivity indices for a series of two model compounds, in order to gain insight into the Lewis acid-Lewis base interaction between the Sn and O atom. All calculations on these model compounds were performed at the B3LYP[1]/6-31G**[2] level of theory, except for the Sn atom for which a LANL2DZ+P[3] basis set was used.

Density functional theory provides a very convenient framework for the discussion of chemical reactivity. A series of global and local quantities have been introduced to describe the extent of the response of an atomic or molecular system to external perturbations[4]. These quantities are also termed reactivity descriptors, of which an important example is the Fukui function, introduced by Parr and Yang[5] and defined as the initial response of the electron density due to an infinitesimal perturbation in the total number of electrons N, at constant external (i.e. due to the nuclei) potential $v(\boldsymbol{r})$. Due to the discontinuity of the electron density with respect to the number of electrons, three different Fukui functions can be introduced, representing the case of a nucleophilic attack $f^{+}(\boldsymbol{r})$, an electrophilic attack $f^{-}(\boldsymbol{r})$ or a neutral (radical) attack $f^{0}(\boldsymbol{r})$:

$$f^{+}(\boldsymbol{r}) = \left(\check{Z}r(\boldsymbol{r})/\check{Z}N\right)^{+}_{v(\boldsymbol{r})} \;\text{a}\; r_{N+1}(\boldsymbol{r}) - r_{N}(\boldsymbol{r}) \tag{1}$$

$$f^{-}(\boldsymbol{r}) = \left(\check{Z}r(\boldsymbol{r})/\check{Z}N\right)^{-}_{v(\boldsymbol{r})} \;\text{a}\; r_{N}(\boldsymbol{r}) - r_{N-1}(\boldsymbol{r}) \tag{2}$$

$$f^{0}(\boldsymbol{r}) = \frac{1}{2}\left(f^{+}(\boldsymbol{r}) + f^{-}(\boldsymbol{r})\right) \;\text{a}\; \frac{1}{2}\left(r_{N+1}(\boldsymbol{r}) - r_{N-1}(\boldsymbol{r})\right) \tag{3}$$

where $r_{N+1}(\boldsymbol{r})$, $r_{N}(\boldsymbol{r})$ and $r_{N-1}(\boldsymbol{r})$ are the electron densities of the $N+1$, N and $N-1$ electron system respectively, all obtained at the geometry of the N electron system, due to the fact that the derivative is taken at a constant external potential. However, in chemistry it is custom to work with properties associated with atoms or functional groups in a molecule. In this context, a useful approximation to describe the site-reactivity is given by the condensed-to-atom Fukui indices by using an atomic charge-partitioning scheme[6]:

$$f_k^+ \approx N_k(N+1) - N_k(N) \quad (4)$$

$$f_k^- \approx N_k(N) - N_k(N-1) \quad (5)$$

$$f_k^0 \approx \frac{1}{2}\left(N_k(N+1) - N_k(N-1)\right) \quad (6)$$

where $N_k(N+1)$, $N_k(N)$ and $N_k(N-1)$ now represent the electron populations on atom k in the $N+1$, N and $N-1$ electron system. In order to compare the reactivity of atomic sites in different molecules, one has to compute the local softness $s(\mathbf{r})$[7,8] by multiplying the relevant Fukui function (i.e. for a nucleophilic, electrophilic or radical attack) with the global softness S of the compound

$$s(\mathbf{r}) = Sf(\mathbf{r}) \quad (7)$$

This global softness can be approximately computed using the vertical ionization energy (IE) and electron affinity (EA) of the system[7]:

$$S \approx 1/(IE - EA) \quad (8)$$

High values of the local softness on an atomic site imply a high affinity for soft Lewis bases or acids, depending on whether Eq. (7) uses either f^+ or f^- to compute the local softness. Numerous applications in the literature have demonstrated the usefulness of these reactivity indices.[9]

A first series of model compounds consists of the compounds Ph-CH_2-O-R (R = Me, Et, *i*-Pr and *t*-Bu), for which the condensed local softness on the oxygen atom was computed. These compounds, used to model the alkoxy moiety in the structures investigated, are listed in Table S7, together with their softnesses, the atomic charges (obtained using the Natural Population analysis[10]) on the oxygen and tin atoms and the condensed Fukui functions and local softnesses for an electrophilic attack on the oxygen atom. As can be seen, the oxygen atom becomes more negative from R = Me to R = *t*-Bu, indicating its increasing Lewis basicity; the local softness also increases with increasing alkyl group size, but a maximum is encountered for *i*-Pr.

Next, the relevant reactivity indices were computed for a second series of model compounds, $SnPh_nCl_{(4-n)}$ (n = 1–4), in order to model the influence of the gradual substitution of phenyl groups

by chlorine atoms on the Lewis acidity of their tin atom. Table S8 reveals that the condensed local softness (now for the attack of a nucleophile) on the tin atom in these compounds increases upon increasing number of chlorine atoms, thus indicating a higher affinity for soft Lewis bases. This increase of the local softness on the tin atom is accompanied by a decrease of the positive charge on the tin atom, due to the pπ-dπ donor effect from the chlorine atoms toward the tin atom being stronger than that from the phenyl ring, reflecting again the Lewis acidity increase with the number of chlorine atoms.

The highest values of the local softness are thus found on the oxygen atom in the Ph-CH_2-O*i*-Pr compound and the Sn in the $SnPhCl_3$ compound. This is in line with the shortest Sn-O bonds being observed with the bulkier substituents on the oxygen atom and increasing number of chlorine atoms on the tin atoms in the parent compounds studied in this paper.

Table S7. Reactivity descriptors for the Ph-CH_2-OR systems, obtained at the B3LYP/6–31G** level.

Molecule	q_O	S (au)	f^- (au)	s^- (au)
Ph-CH_2-OMe	–0.571	2.578	0.1367	0.3525
Ph-CH_2-OEt	–0.583	2.591	0.1476	0.3824
Ph-CH_2-O*i*Pr	–0.593	2.625	0.1770	0.4648
Ph-CH_2-O*t*Bu	–0.602	2.602	0.1566	0.4075

Table S8. Reactivity descriptors for the $Sn(Ph)_nCl_{4-n}$ (n = 4, 3, 2, 1), obtained at the B3LYP/6−31G** level (LANL2DZ+P on Sn).

Molecule	q_{Sn}	S(au)	f^+ (au)	s^+ (au)
$SnPh_4$	2.003	3.208	0.1063	0.3408
$SnPh_3Cl$	2.000	3.240	0.2092	0.6779
$SnPh_2Cl_2$	1.955	3.004	0.2197	0.6601
$SnPhCl_3$	1.890	2.918	0.4015	1.1716

Next, we have investigated the Mulliken charges[11] on the Sn atoms in the organotin(IV) derivatives that were studied in the paper. Table S9 lists these charges, obtained at the B3LYP/LANL2DZ level.

Table S9. Mulliken charges on the tin atom in the different compounds studied in this work, obtained at the B3LYP/LANL2DZ level of theory.

	L-$SnPh_3$	L-$SnPh_3Cl$	L-$SnPhCl_2$	L-$SnCl_3$
Me	1.322	1.205	1.164	1.144
Et	1.305	1.156	1.122	1.118
i-Pr	1.302	1.199	1.118	1.099
t-Bu	1.255	1.099	1.095	–

As can be seen, the charge on the tin atom in the complexes decreases upon increasing substitution of phenyl rings with chlorine atoms and with increasing alkyl group size on the oxygen atoms. This result also points towards a stronger interaction between O and Sn upon increasing chlorine substitution and increasing alkyl group size attached to the oxygen atoms.

S3. Crystallographic data for 5 and 6 and experimental and computed values of selected geometrical parameters of the various L-$SnPh_3$, L-$SnPh_2Cl$, L-$SnPhCl_2$ and L-$SnCl_3$.

Table S10: Crystallographic data for **5** and **6.**

Compound	**5**	**6**
Formula M.w.	$C_{24}H_{27}ClO_2Sn$ 501.60	$C_{18}H_{22}Cl_2O_2Sn$ 459.95
Crystal system Space group [No.]	Monoclinic *P2₁/c*	Orthorhombic *Pbca*
a [Å]	8.2610(2)	18.0620(2)
b [Å]	9.0570(2)	11.6540(3)
c [Å]	30.3790(9)	18.4450(3)
β [°]	96.7600(10)	
Z	4	8
V *[Å³]*	2257.15(10)	3882.57(13)
D_x [g cm^{-3}]	1.476	1.597
Crystal size [mm]	0.3×0.3×0.25	0.3×0.3×0.15
Crystal shape	Prism	Bar
μ [mm^{-1}]	1.266	1.597
θ_{max} [°]	27.48	27.50
Range of *h*;*k*;*l*	-10,10; -11,11;-39, 39	0,23; -15,15;-23,23
Measured reflections	21248	48295
Independent diffractions (R_{int} [a])	5161 (0.035)	4434 (0.036)
Observed diffract. [I>2σ(I)]	4374	3992
T_{min}, T_{max}	0.681, 0.700	0.689, 0.791
No. of parameters	255	207
w_1, w_2 [b]	0.0045, 1.7442	0.0379, 1.7666
R[c] , *wR* for observed diffract.	0.0225, 0.0458	0.023, 0.062
R; w*R* for all data	0.0315, 0.0489	0.027, 0.064
GOF [d]	1.030	1.030
Residual electron density [e/Å³]	0.451, -0.508	0.542, -0.780

[a] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where P = _[max(F_o^2) + $2F_c^2$]. [c] $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$. [d] GOF = $[\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$.

Table S11. Experimental (first row of each entry) and computed values (second row) of selected geometrical parameters of the various L-$SnPh_3$, L-$SnPh_2Cl$, L-$SnPhCl_2$ and L-$SnCl_3$ compounds studied in this work. The different geometrical parameters are indicated on Figure 1, where Cl1 is substituted for a phenyl ring with atom numberings from C41 to C46 and Figure 4. Theoretical estimates were obtained at the B3LYP/LANL2DZ level. [a] two independent molecules were analyzed.

	L-$SnPh_3$				L-$SnPh_2Cl$				L-$SnPhCl_2$				L-$SnCl_3$		
	R = Me (**1**)	R = Et (**4**)	R = i-Pr (**7**)	R = t-Bu (**10**)	R = Me (**2**)[a]	R = Et (**5**)	R = i-Pr (**8**)	R = t-Bu (**11**)	R = Me (**3**)	R = Et (**6**)	R = i-Pr (**9**)	R = t-Bu (**12**)	R =Me[a]	R = Et	R = i-Pr
Sn1-C11	2.165	-	-	2.165	2.136/2.138	2.150	-	-	2.117	2.123	2.126	2.132	2.103/2.110	-	-
	2.138	2.163	2.164	2.176	2.138	2.141	2.138	2.162	2.116	2.119	2.123	2.125	2.105	2.109	2.115
Sn1-O1	2.908	-	-	4.799	2.567/2.568	2.454	-	-	2.619	2.447	2.475	2.775	2.511/2.513	-	-
	2.911	2.699	2.664	3.251	2.544	2.488	2.956	2.708	2.518	2.457	2.414	2.786	2.450	2.388	3.054
Sn1-O2	2.966	-	-	4.538	2.993/2.981	3.472	-	-	2.655	2.864	2.985	2.882	2.557/2.583	-	-
	3.012	3.294	3.466	3.334	2.772	3.104	2.626	3.952	2.516	2.803	2.987	2.787	2.449	2.736	2.317
Sn1-C21	2.168	-	-	2.150	2.457/2.440	2.437	-	-	2.395	2.414	2.401	2.388	2.383/2.383	-	-
	2.172	2.172	2.156	2.155	2.515	2.510	2.498	2.500	2.486	2.482	2.469	2.466	2.465	2.456	2.450
Sn1-C31	2.153	-	-	2.148	2.137/2.148	2.144	-	-	2.398	2.392	2.378	2.376	2.391/2.365	-	-
	2.159	2.157	2.175	2.164	2.148	2.143	2.152	2.140	2.486	2.480	2.484	2.466	2.465	2.460	2.451
Sn1-C41	2.144	-	-	2.156	2.125/2.130	2.120	-	-	2.121	2.116	2.142	2.112	2.340/2.337	-	-
	2.138	2.135	2.136	2.134	2.123	2.123	2.124	2.117	2.112	2.112	2.113	2.107	2.410	2.410	2.414
C11-Sn1-C21	112.9	-	-	108.0	106.0/104.5	107.9	-	-	110.5	111.0	112.3	100.8	111.8/109.9	-	-
	112.2	111.1	108.6	110.8	106.7	106.6	106.1	103.1	108.0	108.3	108.4	109.5	110.2	111.1	111.1
C11-Sn1-C31	109.4	-	-	109.7	114.9/113.4	109.6	-	-	105.3	107.6	106.5	111.6	110.5/117.0	-	-
	108.3	106.6	110.2	113.6	111.2	111.1	111.4	117.4	107.6	107.1	107.9	109.6	110.2	109.3	110.4
C11-Sn1-C41	117.0	-	-	118.6	121.9/123.9	126.7	-	-	131.3	131.6	129.1	125.4	132.6/128.0	-	-
	118.8	121.2	120.1	115.7	126.1	126.1	126.5	119.8	132.4	132.3	131.5	127.1	130.3	130.7	128.6
C11-Sn1-O1	65.6	-	-	47.5	71.1/70.3	72.8	-	-	70.1	72.9	72.4	69.1	70.1/69.9	-	-
	66.3	69.4	59.8	66.3	70.9	72.5	66.6	72.7	70.5	72.5	73.3	69.6	71.3	73.3	64.2
C11-Sn1-O2	66.8	-	-	51.8	64.2/64.9	60.1	-	-	68.3	65.5	64.8	68.0	68.8/69.0	-	-

	66.6	61.8	60.9	63.9	66.7	63.4	69.5	55.1	70.5	67.5	65.6	69.6	71.3	68.0	75.3
O1-Sn-O2	112.0	-	-	98.7	114.4/113.1	113.6	-	-	117.0	118.5	118.4	118.8	113.8/114.9	-	-
	111.3	110.5	109.2	111.4	115.1	114.8	115.9	108.1	118.1	119.2	119.5	121.9	118.1	119.1	119.8
O1-Sn1-C21	172.6	-	-	128.9	166.8/166.4	179.0	-	-	165.1	167.7	168.7	162.9	162.9/168.4	-	-
	170.9	175.6	160.0	171.2	168.1	172.1	160.4	168.9	162.6	165.1	154.8	160.3	164.1	166.8	155.3
O1-Sn1-C31	74.7	-	-	121.2	78.4/77.6	85.7	-	-	76.7	79.0	79.7	75.6	79.1/78.2	-	-
	74.2	77.6	74.1	74.9	79.5	81.3	76.1	117.4	75.9	76.9	71.3	73.7	76.3	77.5	70.6
O1-Sn1-C41	79.7	-	-	71.3	89.2/89.3	83.6	-	-	87.1	84.0	83.6	85.8	85.5/86.3	-	-
	81.0	79.4	85.1	79.5	87.2	86.1	91.0	119.8	86.4	86.0	90.0	86.5	84.3	83.1	88.7
O2-Sn1-C21	72.8	-	-	82.6	74.0/74.0	67.3	-	-	75.7	73.1	72.4	74.9	76.9/76.9	-	-
	75.1	73.1	78.6	73.0	73.1	70.7	75.5	76.4	75.9	73.4	78.9	73.7	76.3	73.6	79.4
O2-Sn1-C31	168.1	-	-	78.8	164.1/166.2	150.7	-	-	159.2	155.1	152.9	162.0	164.7/166.9	-	-
	168.5	159.6	175.6	82.5	161.7	157.8	165.7	165.2	162.4	157.7	167.2	160.3	164.1	159.5	169.6
O2-Sn1-C41	81.8	-	-	169.5	77.4/78.1	89.3	-	-	86.8	91.3	90.8	85.7	86.4/81.7	-	-
	80.9	86.5	80.1	169.7	80.9	83.8	79.8	78.6	86.4	88.9	85.6	86.5	84.3	88.3	83.5
C21-Sn1-C31	99.6	-	-	105.9	91.7/93.8	93.4	-	-	89.0	88.7	89.1	89.2	89.7/90.0	-	-
	98.4	98.2	97.3	108.9	90.9	91.9	90.8	94.5	88.5	88.9	88.7	88.7	88.6	89.4	90.3
C21-Sn1-C41	107.0	-	-	105.9	102.9/103.8	96.4	-	-	102.1	100.6	100.0	106.4	100.1/103.7	-	-
	106.9	103.6	114.6	99.6	103.1	100.4	107.3	100.2	105.6	103.0	109.6	107.6	104.8	101.7	110.0
C31-Sn1-C41	109.6	-	-	105.4	113.4/111.8	115.6	-	-	110.6	108.9	112.4	107.1	103.5/101.2	-	-
	110.4	113.7	103.4	107.0	112.1	113.7	108.8	115.0	106.0	108.6	102.0	107.6	104.8	106.7	98.7
C14-C13-C12-O1	142.7	-	-	161.2	140.7/145.0	-147.4	-	-	144.3	145.4	151.8	142.3	141.56/136.54	-	-
	142.4	146.7	134.5	142.1	141.8	146.1	139.8	142.6	138.7	144.7	139.0	144.8	137.3	144.2	136.6
C14-C15-C16-O2	141.4	-	-	179.2	-140.7/-135.6	139.0	-	-	138.2	131.8	137.9	140.7	137.1/135.57	-	-
	139.6	135.6	148.2	143.5	~137.1	~136.7	~144.9	~138.7	138.5	138.2	147.9	144.8	-137.3	-137.0	-151.3

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