Electronic Supplementary Material (ESI)

The Nature of π-Hole Spodium Bonds in the $HgLCl_2$ (L = pyrrole, pyrazole, imidazole, pyridine, pyridazine, and pyrimidine) Complexes: from Noncovalent to Covalent

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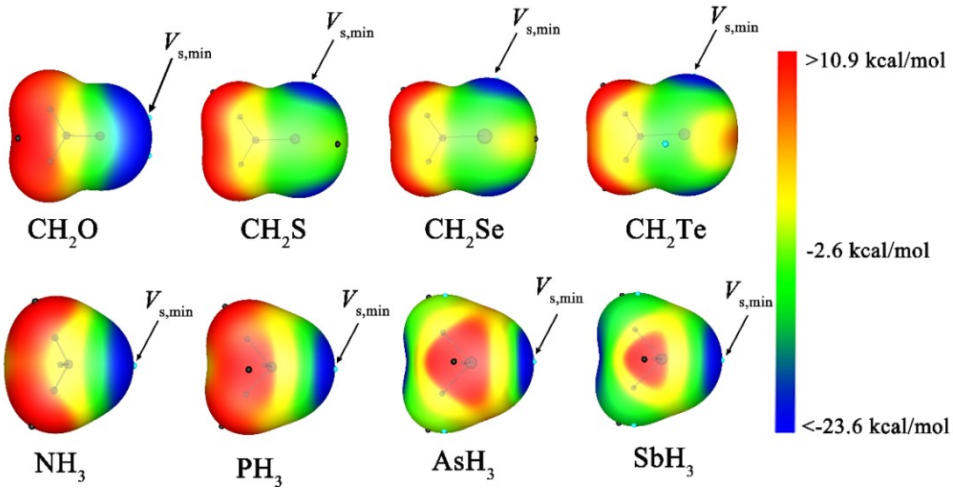

Fig. S1 MEP graphs on the 0.001 a.u. molecular isosurfaces of ZH_3 and CH_2Y (Z = N, P, As, and Sb; Y = O, S, Se, and Te).

Table S1 NOCV orbital energy (E_{tot}, E_{orb}, in kcal/mol) and charge transfer (CT, in e) in the complexes $HgLCl_2\cdots NH_3$.

complex	E_{tot}	NOCV pair	E_{orb}	E_{orb}/E_{tot}	CT
1$\cdots NH_3$	-6.56(α)	1(α)	-5.27	0.80	0.140
		2(α)	-0.43	0.07	0.024
	-6.55(β)	1(β)	-5.27	0.80	0.140
		2(β)	-0.43	0.07	0.024
2$\cdots NH_3$	-14.24	1	-11.41	0.80	0.291
		2	-0.97	0.07	0.050
3$\cdots NH_3$	-13.07	1	-10.49	0.80	0.278
		2	-0.71	0.05	0.049
4$\cdots NH_3$	-12.93	1	-10.41	0.81	0.277
		2	-0.9	0.07	0.047
5$\cdots NH_3$	-18.12	1	-13.08	0.72	0.317
		2	-0.99	0.05	0.051
		3	-2.08	0.11	0.104
6$\cdots NH_3$	-13.04	1	-10.48	0.80	0.280
		2	-0.55	0.04	0.050

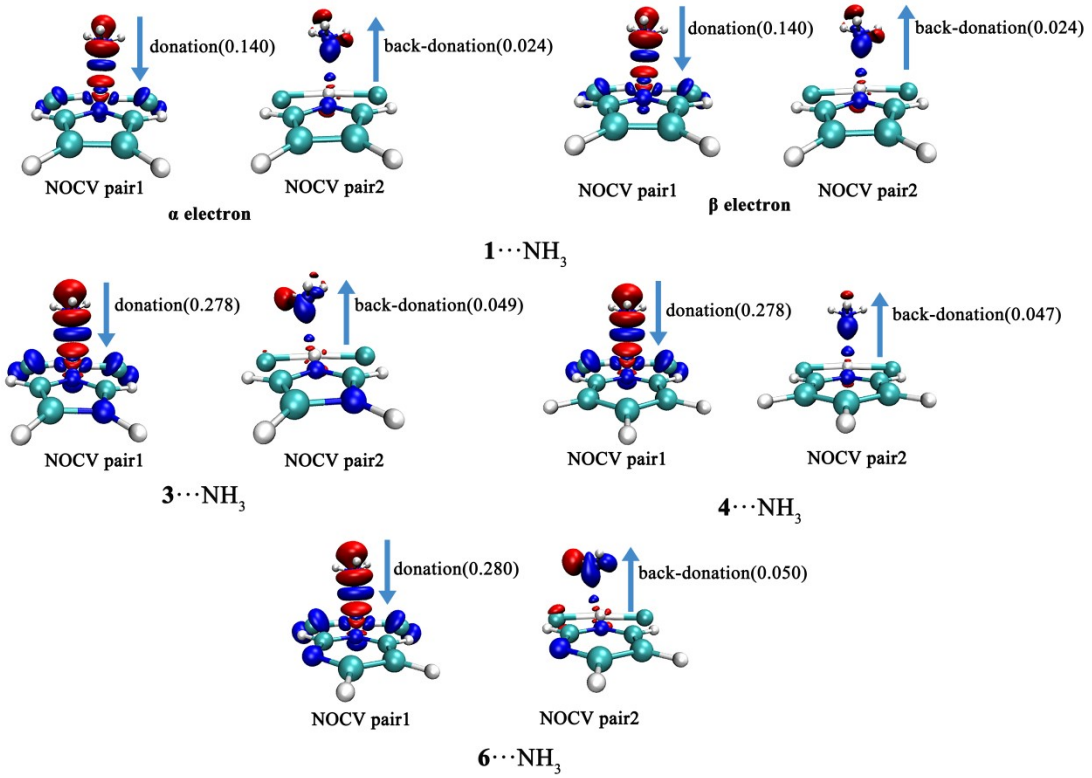

Fig. S2 Isosurface of NOCV pair density map of the complexes $HgLCl_2\cdots NH_3$. (L = pyrrole **1**, imidazole **3**, pyridine **4**, and pyrimidine **6**)

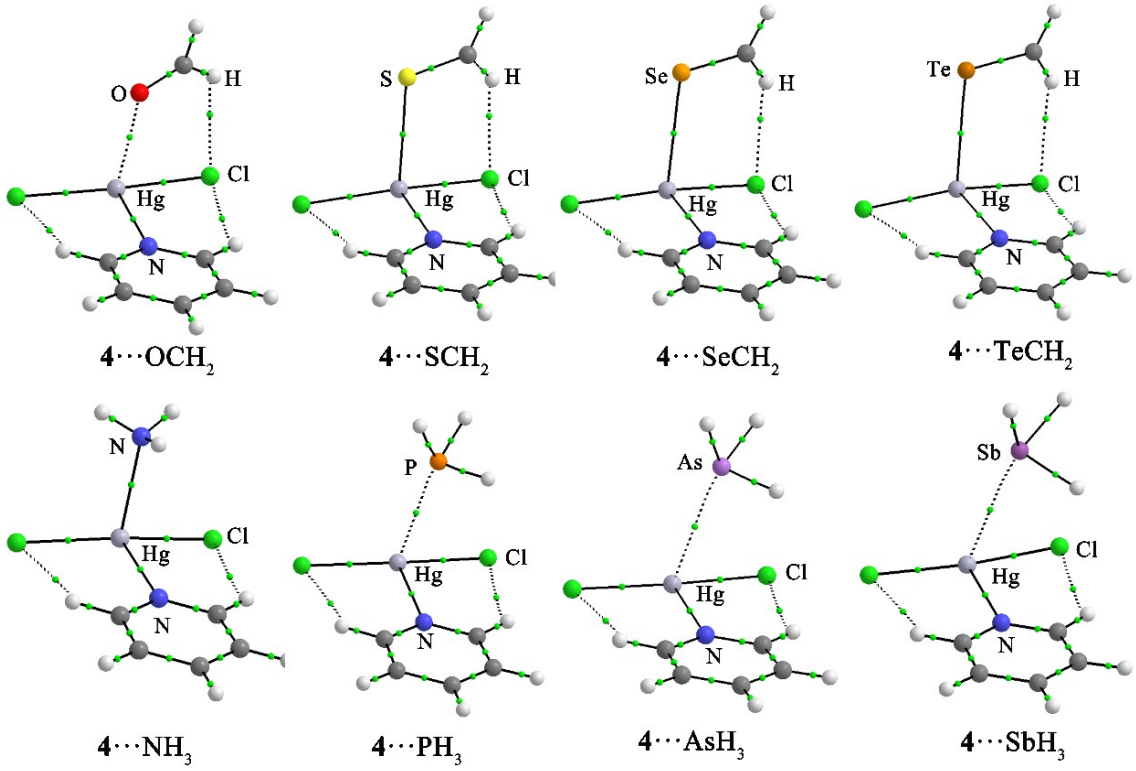

Fig. S3 Molecular graphs of the complexes $\mathbf{4}\cdots YCH_2$ and $\mathbf{4}\cdots ZH_3$.

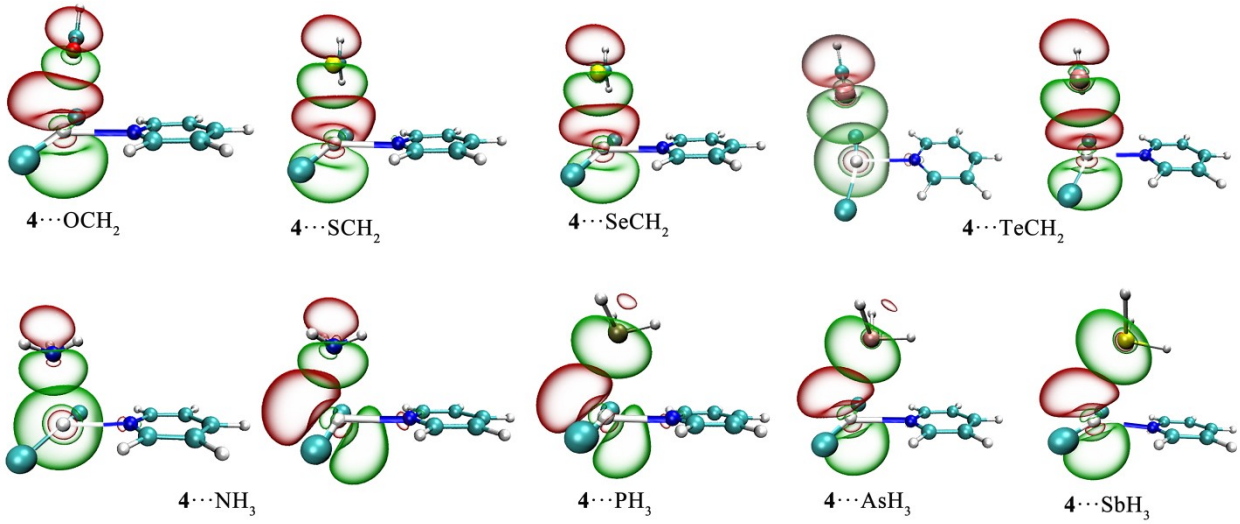

Fig. S4 Schematic diagrams of main orbital interactions for the complexes.

Table S2 Binding energies (in kcal/mol), binding distance (in Å), and topological parameters (in a.u.) at the bond critical points for $HgLCl_2\cdots ZH_3$ complexes (L= pyrrole **1**, pyrazole **2**, imidazole **3**, pyridazine **5**, and pyrimidine **6**; Z = N, P, As, and Sb)

Complex	ΔE	d	BCP	ρ_b	$\nabla^2\rho$	G_b	V_b	H_b	$-G_b/V_b$
1$\cdots NH_3$	-8.30	2.563	Hg···N	0.0420	0.1321	0.0361	-0.0392	-0.0031	0.9210
1$\cdots PH_3$	-3.88	3.165	Hg···P	0.0215	0.0472	0.0123	-0.0128	-0.0005	0.9604
1$\cdots AsH_3$	-3.81	3.448	Hg···As	0.0133	0.0307	0.0071	-0.0066	0.0005	1.0812
1$\cdots SbH_3$	-3.90	3.758	Hg···Sb	0.0092	0.0198	0.0044	-0.0039	0.0005	1.1396
2$\cdots NH_3$	-9.23	2.543	Hg···N	0.0437	0.1379	0.0380	-0.0415	-0.0035	0.9158
2$\cdots PH_3$	-4.39	3.083	Hg···P	0.0252	0.0543	0.0147	-0.0158	-0.0011	0.9291
2$\cdots AsH_3$	-4.24	3.391	Hg···As	0.0149	0.0340	0.0081	-0.0077	0.0004	1.0514
2$\cdots SbH_3$	-4.23	3.641	Hg···Sb	0.0115	0.0240	0.0056	-0.0052	0.0004	1.0768
3$\cdots NH_3$	-8.14	2.561	Hg···N	0.0421	0.1325	0.0362	-0.0394	-0.0031	0.9208
3$\cdots PH_3$	-3.81	3.176	Hg···P	0.0209	0.0461	0.0119	-0.0124	-0.0004	0.9657
3$\cdots AsH_3$	-3.78	3.445	Hg···As	0.0133	0.0308	0.0072	-0.0066	0.0005	1.0814
3$\cdots SbH_3$	-4.05	3.708	Hg···Sb	0.0099	0.0214	0.0048	-0.0043	0.0005	1.1201
5$\cdots NH_3$	-9.76	2.518	Hg···N	0.0461	0.1445	0.0402	-0.0443	-0.0041	0.9075
		2.238	N···H	0.0151	0.0537	0.0111	-0.0087	0.0024	1.2721
5$\cdots PH_3$	-4.32	3.072	Hg···P	0.0255	0.0540	0.0147	-0.0160	-0.0012	0.9228
		3.036	N···H	0.0043	0.0151	0.0029	-0.0020	0.0009	1.4672
5$\cdots AsH_3$	-4.14	3.369	Hg···As	0.0154	0.0348	0.0084	-0.0080	0.0003	1.0427
		3.184	N···H	0.0035	0.0119	0.0022	-0.0014	0.0008	1.5365
5$\cdots SbH_3$	-4.15	3.675	Hg···Sb	0.0110	0.0228	0.0053	-0.0048	0.0004	1.0909
6$\cdots NH_3$	-8.77	2.571	Hg···N	0.0413	0.1293	0.0353	-0.0383	-0.0030	0.9222
6$\cdots PH_3$	-4.21	3.159	Hg···P	0.0220	0.0481	0.0126	-0.0132	-0.0006	0.9566
6$\cdots AsH_3$	-4.15	3.401	Hg···As	0.0148	0.0337	0.0080	-0.0076	0.0004	1.0547
6$\cdots SbH_3$	-3.99	3.680	Hg···Sb	0.0108	0.0226	0.0052	-0.0048	0.0004	1.0934

Table S3 Binding energies (in kcal/mol), binding distance (in Å), and topological parameters (in a.u.) at the bond critical points for $HgLCl_2\cdots YCH_2$ complexes (L= pyrrole **1**, pyrazole **2**, imidazole **3**, pyridazine **5**, and pyrimidine **6**; Y = O, S, Se, and Te)

Complex	ΔE	d	BCP	ρ_b	$\nabla^2\rho$	G_b	V_b	H_b	$-G_b/V_b$
1$\cdots OCH_2$	-5.06	2.846	Hg$\cdots$O	0.0194	0.0723	0.0168	-0.0156	0.0013	1.0809
		2.760	Cl$\cdots$H	0.0094	0.0302	0.0062	-0.0048	0.0014	1.2802
1$\cdots SCH_2$	-7.08	3.024	Hg$\cdots$S	0.0276	0.0653	0.0177	-0.0190	-0.0013	0.9293
		2.609	Cl$\cdots$H	0.0119	0.0379	0.0078	-0.0060	0.0017	1.2840
1$\cdots SeCH_2$	-7.81	3.085	Hg$\cdots$Se	0.0282	0.0585	0.0164	-0.0182	-0.0018	0.9017
		2.603	Cl$\cdots$H	0.0119	0.0380	0.0078	-0.0060	0.0017	1.2908
1$\cdots TeCH_2$	-8.44	3.152	Hg$\cdots$Te	0.0309	0.0527	0.0160	-0.0189	-0.0028	0.8494
		2.618	Cl$\cdots$H	0.0115	0.0367	0.0074	-0.0057	0.0017	1.2999
2$\cdots OCH_2$	-5.62	2.809	Hg$\cdots$O	0.0210	0.0785	0.0185	-0.0173	0.0012	1.0666
		2.759	Cl$\cdots$H	0.0094	0.0299	0.0061	-0.0048	0.0014	1.2840
2$\cdots SCH_2$	-7.19	2.985	Hg$\cdots$S	0.0296	0.0699	0.0192	-0.0210	-0.0017	0.9170
		2.634	Cl$\cdots$H	0.0114	0.0364	0.0074	-0.0058	0.0017	1.2880
2$\cdots SeCH_2$	-8.03	3.046	Hg$\cdots$Se	0.0303	0.0626	0.0178	-0.0200	-0.0022	0.8910
		2.630	Cl$\cdots$H	0.0113	0.0363	0.0074	-0.0057	0.0017	1.2952
2$\cdots TeCH_2$	-8.89	3.109	Hg$\cdots$Te	0.0333	0.0560	0.0174	-0.0209	-0.0034	0.8360
		2.644	Cl$\cdots$H	0.0110	0.0351	0.0071	-0.0055	0.0017	1.3038
3$\cdots OCH_2$	-4.72	2.845	Hg$\cdots$O	0.0194	0.0724	0.0168	-0.0156	0.0013	1.0812
		2.752	Cl$\cdots$H	0.0096	0.0306	0.0063	-0.0049	0.0014	1.2770
3$\cdots SCH_2$	-6.86	3.025	Hg$\cdots$S	0.0274	0.0652	0.0176	-0.0189	-0.0013	0.9310
		2.611	Cl$\cdots$H	0.0119	0.0378	0.0077	-0.0060	0.0017	1.2833
3$\cdots SeCH_2$	-7.59	3.088	Hg$\cdots$Se	0.0280	0.0583	0.0163	-0.0180	-0.0017	0.9040
		2.605	Cl$\cdots$H	0.0119	0.0379	0.0077	-0.0060	0.0017	1.2901
3$\cdots TeCH_2$	-8.23	3.161	Hg$\cdots$Te	0.0304	0.0523	0.0158	-0.0185	-0.0027	0.8542
		2.624	Cl$\cdots$H	0.0114	0.0362	0.0074	-0.0057	0.0017	1.3004
5$\cdots OCH_2$	-4.72	2.875	Hg$\cdots$O	0.0183	0.0679	0.0157	-0.0144	0.0013	1.0910
		2.792	Cl$\cdots$H	0.0090	0.0292	0.0060	-0.0047	0.0013	1.2830
5$\cdots SCH_2$	-7.04	2.994	Hg$\cdots$S	0.0291	0.0687	0.0188	-0.0204	-0.0016	0.9203
		2.626	Cl$\cdots$H	0.0115	0.0366	0.0075	-0.0058	0.0017	1.2882
5$\cdots SeCH_2$	-7.97	3.045	Hg$\cdots$Se	0.0303	0.0624	0.0178	-0.0200	-0.0022	0.8911
		2.639	Cl$\cdots$H	0.0111	0.0354	0.0072	-0.0055	0.0017	1.2997
5$\cdots TeCH_2$	-9.14	3.097	Hg$\cdots$Te	0.0340	0.0565	0.0177	-0.0214	-0.0036	0.8304
		2.695	Cl$\cdots$H	0.0099	0.0316	0.0064	-0.0049	0.0015	1.3148
		3.384	N$\cdots$Te	0.0096	0.0258	0.0055	-0.0045	0.0010	1.2106
6$\cdots OCH_2$	-5.28	2.833	Hg$\cdots$O	0.0199	0.0743	0.0174	-0.0161	0.0012	1.0761

		2.782	Cl···H	0.0091	0.0292	0.0060	-0.0047	0.0013	1.2847
6···SCH_2	-7.32	3.025	Hg···S	0.0276	0.0651	0.0176	-0.0190	-0.0014	0.9284
		2.622	Cl···H	0.0116	0.0371	0.0076	-0.0059	0.0017	1.2876
6···$SeCH_2$	-8.09	3.087	Hg···Se	0.0282	0.0582	0.0164	-0.0182	-0.0018	0.9008
		2.618	Cl···H	0.0116	0.0370	0.0075	-0.0058	0.0017	1.2948
6···$TeCH_2$	-8.76	3.163	Hg···Te	0.0305	0.0518	0.0157	-0.0184	-0.0027	0.8512
		2.636	Cl···H	0.0111	0.0355	0.0072	-0.0055	0.0017	1.3046

Table S4 Major NBO results for the complexes $HgLCl_2$···ZH_3(L= pyrrole **1**, pyrazole **2**, imidazole **3**, pyridazine **5**, and pyrimidine **6**; Z = N, P, As, and Sb) (energy, in kcal/mol, charge, in e)

Complex	Donor NBO	Acceptor NBO	$E^{(2)}$	Q_{CT}	WBI(Hg···Z)
1···NH_3	LP(N)	p_Z*(Hg)	8.9	0.1040	0.18
	LP(N)	p_Z*(Hg)	10.9		
1···PH_3	LP(P)	p_Z*(Hg)	6.5	0.0778	0.16
	LP(P)	p_Z*(Hg)	5.8		
1···AsH_3	LP(As)	p_Z*(Hg)	4.7	0.0391	0.09
	LP(As)	p_Z*(Hg)	4.7		
1···SbH_3	LP(Sb)	p_Z*(Hg)	3.0	0.0113	0.07
	LP(Sb)	p_Z*(Hg)	2.9		
2···NH_3	LP(N)	p_Z*(Hg)	25.0	0.1085	0.19
2···PH_3	LP(P)	p_Z*(Hg)	20.5	0.0981	0.19
2···AsH_3	LP(As)	p_Z*(Hg)	8.0	0.0477	0.11
2···SbH_3	LP(Sb)	p_Z*(Hg)	6.0	0.0387	0.09
3···NH_3	LP(N)	p_Z*(Hg)	19.6	0.1034	0.18
3···PH_3	LP(P)	p_Z*(Hg)	12.7	0.0723	0.15
3···AsH_3	LP(As)	p_Z*(Hg)	9.3	0.0194	0.09
3···SbH_3	LP(Sb)	p_Z*(Hg)	5.7	0.0287	0.07
5···NH_3	LP(N)	p_Z*(Hg)	36.5	0.1070	0.20
5···PH_3	LP(P)	p_Z*(Hg)	25.1	0.0918	0.19
5···AsH_3	LP(As)	p_Z*(Hg)	7.8	0.0488	0.11
5···SbH_3	LP(Sb)	p_Z*(Hg)	6.0	0.0367	0.09
6···NH_3	LP(N)	p_Z*(Hg)	28.3	0.1024	0.18
6···PH_3	LP(P)	p_Z*(Hg)	19.0	0.0828	0.16
6···AsH_3	LP(As)	p_Z*(Hg)	7.2	0.0506	0.11
6···SbH_3	LP(Sb)	p_Z*(Hg)	6.4	0.03682	0.09

Table S5 Major NBO results for the complexes $HgLCl_2\cdots YCH_2$ (L= pyrrole **1**, pyrazole **2**, imidazole **3**, pyridazine **5**, and pyrimidine **6**; Y = O, S, Se, and Te) (energy, in kcal/mol, charge, in e)

Complex	Donor NBO	Acceptor NBO	$E^{(2)}$	Q_{CT}	WBI(Hg···Y)
1···OCH_2	LP(O)	p_Z*(Hg)	3.2	0.0331	0.06
	LP(O)	p_Z*(Hg)	2.7		
1···SCH_2	LP(S)	p_Z*(Hg)	15.5	0.1238	0.21
	LP(S)	p_Z*(Hg)	15.7		
1···$SeCH_2$	-	-	-	-	0.26
1···$TeCH_2$	-	-	-	-	0.35
2···OCH_2	LP(O)	p_Z*(Hg)	6.9	0.0365	0.07
2···SCH_2	LP(S)	p_Z*(Hg)	33.9	0.1358	0.23
2···$SeCH_2$	LP(Se)	p_Z*(Hg)	43.2	0.1677	0.28
2···$TeCH_2$	LP(Te)	p_Z*(Hg)	59.1	0.2406	0.38
3···OCH_2	LP(O)	p_Z*(Hg)	6.6	0.0332	0.06
3···SCH_2	LP(S)	p_Z*(Hg)	30.2	0.1219	0.21
3···$SeCH_2$	LP(Se)	p_Z*(Hg)	38.8	0.1551	0.25
3···$TeCH_2$	-	-	-	-	0.34
5···OCH_2	LP(O)	p_Z*(Hg)	5.3	0.0305	0.06
5···SCH_2	LP(S)	p_Z*(Hg)	29.4	0.1290	0.22
5···$SeCH_2$	LP(Se)	p_Z*(Hg)	34.9	0.1593	0.26
5···$TeCH_2$	LP(Te)	p_Z*(Hg)	38.5	0.2244	0.36
6···OCH_2	LP(O)	p_Z*(Hg)	6.1	0.0346	0.07
6···SCH_2	LP(S)	p_Z*(Hg)	28.6	0.1249	0.21
6···$SeCH_2$	LP(Se)	p_Z*(Hg)	33.6	0.1540	0.25
6···$TeCH_2$	LP(Te)	p_Z*(Hg)	37.6	0.2175	0.34

The symbol '-' indicates that the complex is regarded as a single fragment by NBO analysis.