Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

for

SO_2 – Yet Another Two-Faced Ligand

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Our pilot calculations revealed two different conformers of both adducts, [L(CH_3)Pt·(SO_2)] and [L'(CH_3)Ir·(SO_2)], which are differed by the dihedral angle between S–O and M–C bonds. In order to get better understanding of the energetics of these systems, we have performed potential energy scan for the rotation of SO_2 moiety in [L(CH_3)Pt·(SO_2)] around S–O bond (Fig. S1). Two local minima were localized. The lowest one was found to correspond to the experimentally observed geometry of the target molecule. Nevertheless, we decided to investigate the electronic structure of both adducts. Hereafter, the energetically higher lying isomer is called as *i*-[L(CH_3)Pt·(SO_2)]. The same situation was observed for Ir-based system.

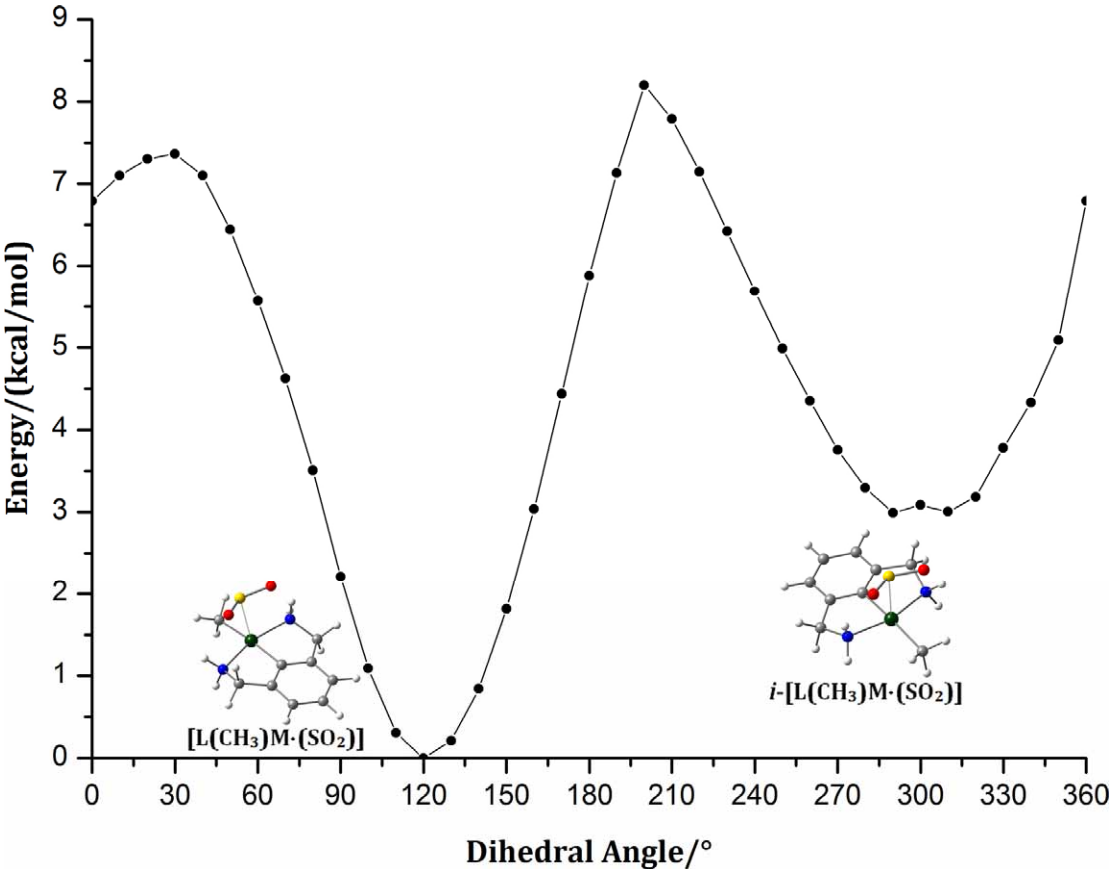


Figure S1. Potential energy surface (PES) scan for the rotation of the SO_2 fragment around the Pt–S bond in [L(CH_3)Pt·(SO_2)] adduct.

Table S1. Absolute energies of model adducts of SO_2 (in Hartree).

Compound	Energy
[L(CH_3)Pt·(SO_2)]	-20049.791818465896
i-[L(CH_3)Pt·(SO_2)]	-20049.787022596614
[L(CH_3)Pt]	-19499.481833309470
[L'(CH_3)Ir·(SO_2)]	-19443.638070171699
i-[L'(CH_3)Ir·(SO_2)]	-19443.627381455728
[L'(CH_3)Ir]	-18893.287360560771
[($P(CH_3)_3$)$_2$Pt·(SO_2)]	-20513.556258759090
[($P(CH_3)_3$)$_2$Pt]	-19963.235012413752
[($P(CH_3)_3$)$_2$Pd·(SO_2)]	-6578.502645078634
[($P(CH_3)_3$)$_2$Pd]	-6028.183740141637
SO_2	-550.271733265001

Table S2. Cartesian coordinates for [L(CH_3)Pt].

C	0.130249	0.400660	-5.204403
C	-1.008248	-0.183134	-4.649078
C	1.300917	0.557814	-4.461742
H	-1.896390	-0.305677	-5.263371
H	2.174397	1.001068	-4.932651
C	-0.978764	-0.597057	-3.323189
C	1.322779	0.140500	-3.137172
C	0.177925	-0.412835	-2.573025
H	0.107401	0.732436	-6.236354
C	-2.071924	-1.325925	-2.586649
H	-3.066681	-0.905094	-2.763684
H	-2.101969	-2.371015	-2.907796
C	2.513035	0.137838	-2.213957
H	3.172924	-0.697725	-2.464366
H	3.111257	1.052330	-2.275491
N	-1.789022	-1.338615	-1.101639
H	-2.340265	-0.618795	-0.643704
H	0.015208	-2.445135	1.560963
N	2.068101	-0.080367	-0.786796
H	2.761039	-0.627852	-0.286584
H	2.007896	0.812744	-0.306412
Pt	0.169509	-0.868217	-0.670146
C	0.144552	-1.363826	1.405288
H	1.062625	-1.097009	1.949055
H	-2.085589	-2.222768	-0.701693
H	-0.673044	-0.877378	1.957063

Table S3. Cartesian coordinates for [L(CH_3)Pt·(SO_2)].

C	0.341821	0.199731	-5.241845
C	-0.869735	-0.215145	-4.689847
C	1.490547	0.339562	-4.464266
H	-1.742660	-0.308744	-5.329361
H	2.414762	0.668780	-4.929910
C	-0.929504	-0.504923	-3.332485
C	1.420423	0.065443	-3.103914
C	0.212721	-0.351378	-2.560681

H	0.390814	0.419254	-6.302535
C	-2.117177	-1.032307	-2.572737
H	-3.050554	-0.522982	-2.831111
H	-2.254831	-2.097473	-2.779248
C	2.499082	0.250838	-2.077383
H	3.506631	0.037127	-2.445316
H	2.471494	1.281498	-1.711092
N	-1.868334	-0.897028	-1.093818
H	-2.149772	0.040071	-0.788124
H	0.286763	-2.845082	1.208239
N	2.204714	-0.603706	-0.867257
H	2.598802	-0.152092	-0.046613
H	2.652729	-1.510193	-0.963297
Pt	0.161039	-0.881670	-0.653076
C	0.150254	-1.759350	1.295239
H	0.946727	-1.388270	1.951499
H	-2.429541	-1.569802	-0.581868
H	-0.788637	-1.597555	1.838072
S	-0.110034	1.258950	0.576018
O	-1.364429	1.743774	-0.077277
O	1.127115	1.971663	0.146330

Table S4. Cartesian coordinates for *i*-[L(CH_3)Pt·(SO_2)].

C	0.213354	0.275683	-5.237662
C	-0.969576	-0.202343	-4.675010
C	1.376029	0.429921	-4.482234
H	-1.852081	-0.306337	-5.299666
H	2.275616	0.808431	-4.959041
C	-0.988425	-0.538257	-3.325944
C	1.349489	0.106305	-3.131301
C	0.169759	-0.374255	-2.582656
H	0.229923	0.534393	-6.290274
C	-2.143889	-1.134999	-2.559847
H	-3.090315	-0.620747	-2.749794
H	-2.280390	-2.181926	-2.844882
C	2.465296	0.289188	-2.133265
H	3.442030	-0.014027	-2.519704
H	2.542067	1.342907	-1.849910
N	-1.859733	-1.119607	-1.076075
H	-2.275449	-0.298357	-0.631564
H	0.342263	-2.801250	1.262791
N	2.173623	-0.469319	-0.856563
H	2.436005	0.099826	-0.053130
H	2.720679	-1.323106	-0.820753
Pt	0.160723	-0.908885	-0.682082
C	0.194014	-1.712430	1.289976
H	0.993728	-1.298898	1.914066
H	-2.279719	-1.929578	-0.631937
H	-0.737189	-1.533246	1.838825
S	-0.201557	1.485414	-0.087378
O	0.949506	1.696672	0.831742
O	-1.538045	1.368151	0.561119

Table S5. Cartesian coordinates for [L'(CH_3)Ir].

C	0.194981	0.352833	-5.216361
C	-0.968394	-0.147647	-4.632579
C	1.349909	0.462246	-4.441677
H	-1.878665	-0.244834	-5.214031
H	2.267152	0.849225	-4.871822

C	-0.945159	-0.543027	-3.312688
C	1.309121	0.096434	-3.113816
N	0.177657	-0.409680	-2.566933
H	0.201603	0.651592	-6.256767
C	-2.048022	-1.238281	-2.562891
H	-3.035218	-0.892377	-2.885869
H	-1.980196	-2.309000	-2.774940
C	2.399691	0.281259	-2.094701
H	3.392281	0.166199	-2.541802
H	2.323121	1.297013	-1.697065
N	-1.865827	-1.098140	-1.085482
H	-2.302827	-0.240766	-0.755194
H	0.118774	-2.662448	1.365997
N	2.205475	-0.633336	-0.927977
H	2.661633	-0.238258	-0.110551
H	2.646764	-1.532710	-1.107257
Ir	0.170665	-0.954578	-0.708147
C	0.171887	-1.562680	1.293237
H	1.063168	-1.273160	1.874128
H	-2.334856	-1.867212	-0.616651
H	-0.686886	-1.189580	1.874201

Table S6. Cartesian coordinates for [L'(CH_3)Ir·(SO_2)].

C	0.248710	0.141957	-5.290443
C	-0.936629	-0.286682	-4.701542
C	1.389208	0.320584	-4.516680
H	-1.831076	-0.430704	-5.295676
H	2.318224	0.652727	-4.963952
C	-0.946380	-0.539570	-3.343337
C	1.310267	0.085423	-3.155797
N	0.158485	-0.336175	-2.616068
H	0.283158	0.332580	-6.356274
C	-2.092528	-1.128333	-2.558932
H	-3.045187	-0.707199	-2.893077
H	-2.118465	-2.204558	-2.756772
C	2.377887	0.345199	-2.135961
H	3.381163	0.237597	-2.554231
H	2.226947	1.374453	-1.781957
N	-1.904605	-0.940670	-1.096228
H	-2.183593	0.022927	-0.836676
H	0.386432	-2.804990	1.139496
N	2.196252	-0.499432	-0.913674
H	2.549117	0.030784	-0.121032
H	2.740926	-1.354702	-0.978625
Ir	0.147642	-0.859125	-0.681530
C	0.228756	-1.717387	1.221704
H	1.046702	-1.337067	1.849431
H	-2.483541	-1.603024	-0.590490
H	-0.685592	-1.585664	1.815108
S	-0.218451	1.270839	0.175482
O	-1.505856	1.686079	-0.530785
O	0.975905	2.082440	-0.289960

Table S7. Cartesian coordinates for *i*-[L'(CH_3)Ir·(SO_2)].

C	0.197286	0.312310	-5.208656
C	-0.976535	-0.157695	-4.629557
C	1.359165	0.422040	-4.451365
H	-1.890852	-0.224317	-5.207042
H	2.271410	0.808150	-4.890689

C	-0.950721	-0.539307	-3.300096
C	1.316952	0.056315	-3.118145
N	0.184461	-0.432833	-2.601107
H	0.203907	0.605745	-6.251420
C	-2.100356	-1.140208	-2.521634
H	-3.042311	-0.657712	-2.796772
H	-2.178995	-2.194426	-2.803898
C	2.430026	0.247963	-2.110208
H	3.395172	-0.029240	-2.540793
H	2.473676	1.314853	-1.873149
N	-1.877451	-1.092687	-1.048006
H	-2.224546	-0.219201	-0.623491
H	0.302888	-2.806924	1.237946
N	2.193643	-0.471371	-0.820046
H	2.339527	0.184765	-0.046394
H	2.835480	-1.249604	-0.715703
Ir	0.168595	-0.949560	-0.671988
C	0.198883	-1.708442	1.265432
H	1.026119	-1.331495	1.878821
H	-2.372116	-1.860564	-0.605721
H	-0.715543	-1.497349	1.832548
S	-0.166036	1.337013	-0.249234
O	0.965982	1.622173	0.715082
O	-1.549974	1.320931	0.373131

Table S8. Cartesian coordinates for [$(P(CH_3)_3)_2Pt$].

Pt	-1.339055	0.665845	1.640786
P	-3.088108	-0.742639	1.524521
P	0.359766	2.132839	1.533077
C	1.882523	1.552562	0.675201
H	2.283607	0.687070	1.203902
H	1.624009	1.239061	-0.336921
H	2.641147	2.338913	0.632163
C	1.049277	2.800034	3.105628
H	0.253703	3.296604	3.662230
H	1.421715	1.974218	3.713043
H	1.859898	3.509104	2.916637
C	-0.014829	3.684301	0.612857
H	0.855990	4.344491	0.570379
H	-0.331125	3.431652	-0.399964
H	-0.840620	4.200235	1.103942
C	-3.770567	-0.979764	-0.169698
H	-2.984540	-1.365719	-0.819985
H	-4.615566	-1.673645	-0.166498
H	-4.091613	-0.014808	-0.563286
C	-4.601992	-0.280873	2.466691
H	-5.400886	-1.013217	2.323101
H	-4.357669	-0.211330	3.527282
H	-4.942971	0.699966	2.132949
C	-2.825249	-2.483005	2.066892
H	-3.732569	-3.080980	1.947941
H	-2.019852	-2.922128	1.476724
H	-2.519472	-2.488892	3.113730

Table S9. Cartesian coordinates for [$(P(CH_3)_3)_2Pt\cdot(SO_2)$].

Pt	-1.128286	0.401059	1.391933
P	-3.028714	-0.898986	1.360207
P	0.505549	2.013085	1.357238
S	-0.026582	-1.051392	2.892347

O	-1.044808	-1.297498	3.962990
O	1.177128	-0.302465	3.374840
C	2.179837	1.480125	0.840740
H	2.514376	0.715721	1.542750
H	2.136553	1.051279	-0.161180
H	2.875503	2.322413	0.847418
C	0.791787	2.825576	2.971459
H	-0.133148	3.292787	3.311229
H	1.084067	2.053883	3.684504
H	1.576085	3.581982	2.891874
C	0.145508	3.422716	0.234425
H	0.943427	4.168136	0.277772
H	0.046297	3.061072	-0.789768
H	-0.796706	3.886692	0.528462
C	-4.176220	-0.561221	-0.034407
H	-3.671877	-0.769922	-0.978790
H	-5.073605	-1.179697	0.040298
H	-4.461663	0.491383	-0.023161
C	-4.064926	-0.677725	2.851869
H	-4.935556	-1.337048	2.828808
H	-3.441067	-0.903639	3.718258
H	-4.392572	0.360565	2.915320
C	-2.798530	-2.715779	1.276526
H	-3.762153	-3.229233	1.240134
H	-2.213417	-2.973042	0.392635
H	-2.251628	-3.033087	2.165170

Table S10. Cartesian coordinates for [($P(CH_3)_3)_2Pd$].

Pd	-1.341144	0.669422	1.538608
P	-3.111854	-0.755349	1.498613
P	0.380746	2.151958	1.481605
C	1.970428	1.564454	0.753386
H	2.333959	0.711982	1.329080
H	1.793188	1.226083	-0.268517
H	2.731871	2.349942	0.748399
C	0.967293	2.854873	3.082809
H	0.135440	3.355333	3.580522
H	1.303811	2.042842	3.728981
H	1.785196	3.566966	2.938873
C	0.089820	3.691733	0.508845
H	0.964422	4.349041	0.513238
H	-0.158592	3.425525	-0.519527
H	-0.763920	4.223626	0.931366
C	-3.932639	-0.990078	-0.135980
H	-3.203678	-1.377404	-0.849324
H	-4.779597	-1.679490	-0.071918
H	-4.279097	-0.023474	-0.504468
C	-4.557311	-0.321454	2.558318
H	-5.364115	-1.054484	2.466416
H	-4.236050	-0.265422	3.599309
H	-4.928040	0.663042	2.269201
C	-2.818482	-2.506028	2.000176
H	-3.730277	-3.106812	1.935359
H	-2.052732	-2.939767	1.355412
H	-2.443693	-2.527163	3.024543

Table S11. Cartesian coordinates for [($P(CH_3)_3)_2Pd\cdot(SO_2)$].

Pd	-1.083399	0.351256	1.374007
P	-3.051492	-0.927159	1.348811

P	0.530252	2.030899	1.337377
S	0.008218	-1.065672	2.899917
O	-1.009631	-1.282526	3.973215
O	1.230575	-0.343259	3.365563
C	2.222120	1.535179	0.830203
H	2.560797	0.756885	1.514985
H	2.199424	1.130427	-0.182641
H	2.909551	2.384045	0.866076
C	0.813224	2.829701	2.962397
H	-0.111861	3.293393	3.307404
H	1.105780	2.053357	3.670969
H	1.597747	3.587688	2.896574
C	0.178590	3.462535	0.234222
H	0.971577	4.212528	0.294240
H	0.089758	3.117737	-0.797055
H	-0.768910	3.919442	0.523459
C	-4.221391	-0.619655	-0.039141
H	-3.733300	-0.857295	-0.985505
H	-5.124695	-1.226776	0.061219
H	-4.498378	0.435395	-0.055367
C	-4.085622	-0.662109	2.839046
H	-4.961482	-1.315664	2.838313
H	-3.465793	-0.868197	3.713266
H	-4.408399	0.379239	2.876738
C	-2.866521	-2.753329	1.312742
H	-3.839808	-3.249827	1.322930
H	-2.317368	-3.050655	0.418212
H	-2.294902	-3.059840	2.189724

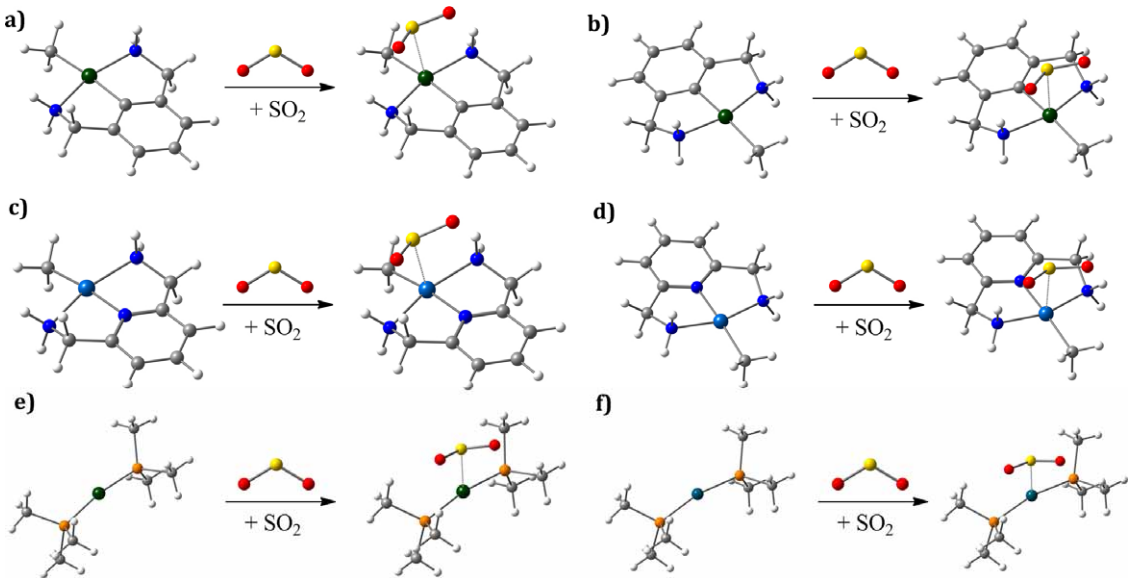


Figure S2. The optimized equilibrium geometries for model adducts (along with its parent metal fragments): (*a*) [L(CH$_3$)Pt·(SO$_2$)], (*b*) *i*-[L(CH$_3$)Pt·(SO$_2$)] (*c*) [L'(CH$_3$)Ir·(SO$_2$)], (*d*) *i*-[L'(CH$_3$)Ir·(SO$_2$)], (*e*) [(P(CH$_3$)$_3$)$_2$Pt·(SO$_2$)], and (*f*) [(P(CH$_3$)$_3$)$_2$Pd·(SO$_2$)].

Table S12. NBO charges in [L(CH_3)Pt·(SO_2)].

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
C	1	-0.21665	1.99928	4.20194	0.01542	6.21665
C	2	-0.21139	1.99912	4.19786	0.01440	6.21139
C	3	-0.21190	1.99912	4.19837	0.01440	6.21190
H	4	0.21194	0.00000	0.78654	0.00152	0.78806
H	5	0.21267	0.00000	0.78582	0.00152	0.78733
C	6	-0.08588	1.99908	4.06872	0.01807	6.08588
C	7	-0.08393	1.99909	4.06642	0.01842	6.08393
C	8	-0.25733	1.99899	4.22371	0.03463	6.25733
H	9	0.21473	0.00000	0.78386	0.00140	0.78527
C	10	-0.23950	1.99933	4.22731	0.01286	6.23950
H	11	0.20832	0.00000	0.78980	0.00188	0.79168
H	12	0.20993	0.00000	0.78814	0.00194	0.79007
C	13	-0.25088	1.99931	4.23823	0.01334	6.25088
H	14	0.20137	0.00000	0.79687	0.00176	0.79863
H	15	0.25186	0.00000	0.74590	0.00223	0.74814
N	16	-0.72595	1.99960	5.70674	0.01961	7.72595
H	17	0.43878	0.00000	0.55897	0.00225	0.56122
H	18	0.19570	0.00000	0.80315	0.00115	0.80430
N	19	-0.71663	1.99961	5.69733	0.01969	7.71663
H	20	0.41895	0.00000	0.57918	0.00186	0.58105
H	21	0.39976	0.00000	0.59861	0.00162	0.60024
Pt	22	0.64214	67.98878	9.32561	0.04347	77.35786
C	23	-1.06917	1.99950	5.05169	0.01798	7.06917
H	24	0.19356	0.00000	0.80508	0.00136	0.80644
H	25	0.40178	0.00000	0.59665	0.00157	0.59822
H	26	0.19496	0.00000	0.80370	0.00134	0.80504
S	27	1.44937	9.99942	4.36576	0.18546	14.55063
O	28	-0.89533	1.99987	6.88100	0.01446	8.89533
O	29	-0.88130	1.99988	6.86673	0.01468	8.88130
* Total *		0.00000	103.97998	87.53973	0.48029	192.00000

Table S13. NBO charges in *i*-[L(CH_3)Pt·(SO_2)].

Atom	No	Natural Charge	Natural Population			
			Core	Valence	Rydberg	Total
C	1	-0.22269	1.99928	4.20792	0.01549	6.22269
C	2	-0.20985	1.99913	4.19631	0.01441	6.20985
C	3	-0.21085	1.99912	4.19732	0.01441	6.21085
H	4	0.21213	0.00000	0.78637	0.00151	0.78787
H	5	0.21227	0.00000	0.78622	0.00151	0.78773
C	6	-0.09641	1.99906	4.07904	0.01830	6.09641
C	7	-0.09503	1.99906	4.07736	0.01860	6.09503
C	8	-0.25248	1.99900	4.21767	0.03582	6.25248
H	9	0.21539	0.00000	0.78321	0.00140	0.78461
C	10	-0.24119	1.99932	4.22894	0.01293	6.24119
H	11	0.21021	0.00000	0.78804	0.00175	0.78979
H	12	0.21143	0.00000	0.78662	0.00194	0.78857
C	13	-0.24598	1.99932	4.23312	0.01355	6.24598
H	14	0.20836	0.00000	0.78991	0.00173	0.79164
H	15	0.22389	0.00000	0.77388	0.00223	0.77611
N	16	-0.72373	1.99961	5.70472	0.01940	7.72373
H	17	0.43294	0.00000	0.56500	0.00206	0.56706
H	18	0.19211	0.00000	0.80670	0.00119	0.80789
N	19	-0.72239	1.99961	5.70289	0.01989	7.72239
H	20	0.43286	0.00000	0.56530	0.00184	0.56714
H	21	0.40327	0.00000	0.59523	0.00150	0.59673
Pt	22	0.65101	67.98852	9.31789	0.04258	77.34899
C	23	-1.09372	1.99952	5.07716	0.01704	7.09372

H 24	0.20302	0.00000	0.79579	0.00119	0.79698
H 25	0.40652	0.00000	0.59195	0.00153	0.59348
H 26	0.20424	0.00000	0.79456	0.00120	0.79576
S 27	1.44082	9.99941	4.37149	0.18828	14.55918
O 28	-0.86993	1.99988	6.85562	0.01442	8.86993
O 29	-0.87623	1.99988	6.86214	0.01422	8.87623
* Total *	0.00000	103.97972	87.53838	0.48190	192.00000

Table S14. NBO charges in [L'(CH_3)Ir·(SO_2)].

	Natural	Natural Population			
Atom No	Charge	Core	Valence	Rydberg	Total
C 1	-0.17510	1.99927	4.16082	0.01501	6.17510
C 2	-0.23872	1.99911	4.22662	0.01299	6.23872
C 3	-0.23651	1.99911	4.22433	0.01306	6.23651
H 4	0.22886	0.00000	0.76982	0.00132	0.77114
H 5	0.22965	0.00000	0.76904	0.00131	0.77035
C 6	0.20510	1.99921	3.77556	0.02013	5.79490
C 7	0.20186	1.99922	3.77831	0.02060	5.79814
N 8	-0.41383	1.99938	5.38077	0.03368	7.41383
H 9	0.22638	0.00000	0.77228	0.00134	0.77362
C 10	-0.26494	1.99934	4.25284	0.01276	6.26494
H 11	0.21732	0.00000	0.78099	0.00169	0.78268
H 12	0.22022	0.00000	0.77798	0.00180	0.77978
C 13	-0.29367	1.99930	4.28123	0.01314	6.29367
H 14	0.20605	0.00000	0.79237	0.00158	0.79395
H 15	0.29552	0.00000	0.70221	0.00227	0.70448
N 16	-0.72786	1.99962	5.70874	0.01950	7.72786
H 17	0.44705	0.00000	0.54980	0.00315	0.55295
H 18	0.18727	0.00000	0.81138	0.00135	0.81273
N 19	-0.70913	1.99963	5.69002	0.01947	7.70913
H 20	0.42235	0.00000	0.57533	0.00232	0.57765
H 21	0.39180	0.00000	0.60619	0.00201	0.60820
Ir 22	0.33023	67.98816	8.63015	0.05146	76.66977
C 23	-0.97602	1.99955	4.96163	0.01485	6.97602
H 24	0.18884	0.00000	0.80967	0.00150	0.81116
H 25	0.39670	0.00000	0.60138	0.00192	0.60330
H 26	0.19436	0.00000	0.80419	0.00145	0.80564
S 27	1.37000	9.99940	4.44835	0.18224	14.63000
O 28	-0.96701	1.99988	6.95346	0.01367	8.96701
O 29	-0.95679	1.99989	6.94294	0.01397	8.95679
* Total *	0.00000	103.98006	87.53839	0.48155	192.00000

Table S15. NBO charges in *i*-[L'(CH_3)Ir·(SO_2)].

	Natural	Natural Population			
Atom No	Charge	Core	Valence	Rydberg	Total
C 1	-0.17732	1.99927	4.16315	0.01490	6.17732
C 2	-0.23664	1.99911	4.22455	0.01298	6.23664
C 3	-0.23800	1.99911	4.22592	0.01297	6.23800
H 4	0.22980	0.00000	0.76889	0.00131	0.77020
H 5	0.22973	0.00000	0.76896	0.00131	0.77027
C 6	0.19557	1.99921	3.78417	0.02105	5.80443
C 7	0.19897	1.99920	3.77952	0.02231	5.80103
N 8	-0.40641	1.99937	5.37359	0.03345	7.40641
H 9	0.22757	0.00000	0.77111	0.00132	0.77243
C 10	-0.26724	1.99933	4.25503	0.01287	6.26724
H 11	0.21854	0.00000	0.77981	0.00165	0.78146
H 12	0.22321	0.00000	0.77495	0.00185	0.77679

C	13	-0.27711	1.99932	4.26408	0.01370	6.27711
H	14	0.21658	0.00000	0.78183	0.00159	0.78342
H	15	0.24746	0.00000	0.75025	0.00229	0.75254
N	16	-0.72461	1.99962	5.70557	0.01941	7.72461
H	17	0.44568	0.00000	0.55133	0.00299	0.55432
H	18	0.18465	0.00000	0.81392	0.00143	0.81535
N	19	-0.72494	1.99963	5.70530	0.02002	7.72494
H	20	0.44808	0.00000	0.54932	0.00260	0.55192
H	21	0.39542	0.00000	0.60259	0.00199	0.60458
Ir	22	0.33293	67.98838	8.62747	0.05122	76.66707
C	23	-0.98208	1.99956	4.96825	0.01427	6.98208
H	24	0.19995	0.00000	0.79872	0.00133	0.80005
H	25	0.40047	0.00000	0.59754	0.00200	0.59953
H	26	0.20531	0.00000	0.79336	0.00133	0.79469
S	27	1.32332	9.99942	4.48665	0.19061	14.67668
O	28	-0.94265	1.99989	6.92870	0.01406	8.94265
O	29	-0.94621	1.99988	6.93248	0.01385	8.94621
* Total *		0.00000	103.98029	87.52704	0.49267	192.00000

Table S16. NBO charges in [(P(CH$_3$)$_3$)$_2$Pt·(SO$_2$)].

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Pt	1	-0.25907	67.99070	10.22947	0.03890	78.25907
P	2	0.95494	9.99892	3.98930	0.05684	14.04506
P	3	0.96578	9.99891	3.97856	0.05675	14.03422
S	4	1.37729	9.99939	4.42512	0.19821	14.62271
O	5	-0.89462	1.99989	6.87924	0.01550	8.89462
O	6	-0.90137	1.99989	6.88570	0.01578	8.90137
C	7	-0.94348	1.99948	4.93283	0.01117	6.94348
H	8	0.27631	0.00000	0.72244	0.00125	0.72369
H	9	0.24048	0.00000	0.75843	0.00109	0.75952
H	10	0.22516	0.00000	0.77268	0.00217	0.77484
C	11	-0.94442	1.99948	4.93354	0.01140	6.94442
H	12	0.24210	0.00000	0.75681	0.00109	0.75790
H	13	0.28236	0.00000	0.71607	0.00157	0.71764
H	14	0.22461	0.00000	0.77330	0.00209	0.77539
C	15	-0.93842	1.99949	4.92816	0.01077	6.93842
H	16	0.22818	0.00000	0.76956	0.00226	0.77182
H	17	0.24240	0.00000	0.75648	0.00112	0.75760
H	18	0.24345	0.00000	0.75540	0.00115	0.75655
C	19	-0.93629	1.99949	4.92615	0.01065	6.93629
H	20	0.24414	0.00000	0.75476	0.00111	0.75586
H	21	0.22851	0.00000	0.76924	0.00225	0.77149
H	22	0.24409	0.00000	0.75479	0.00112	0.75591
C	23	-0.94395	1.99948	4.93316	0.01131	6.94395
H	24	0.22477	0.00000	0.77314	0.00209	0.77523
H	25	0.28264	0.00000	0.71605	0.00131	0.71736
H	26	0.24200	0.00000	0.75691	0.00109	0.75800
C	27	-0.94324	1.99949	4.93178	0.01197	6.94324
H	28	0.22762	0.00000	0.77022	0.00216	0.77238
H	29	0.24398	0.00000	0.75494	0.00108	0.75602
H	30	0.26407	0.00000	0.73425	0.00168	0.73593
* Total *		0.00000	113.98459	79.53849	0.47692	194.00000

Table S17. NBO charges in [(P(CH$_3$)$_3$)$_2$Pd·(SO$_2$)].

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total

Pd	1	-0.06738	35.99227	10.04081	0.03430	46.06738
P	2	0.86430	9.99892	4.08237	0.05441	14.13570
P	3	0.87803	9.99892	4.06902	0.05403	14.12197
S	4	1.36762	9.99937	4.44152	0.19149	14.63238
O	5	-0.87790	1.99989	6.86226	0.01576	8.87790
O	6	-0.88382	1.99989	6.86799	0.01595	8.88382
C	7	-0.94054	1.99949	4.92920	0.01185	6.94054
H	8	0.27215	0.00000	0.72666	0.00119	0.72785
H	9	0.23725	0.00000	0.76168	0.00107	0.76275
H	10	0.22291	0.00000	0.77468	0.00241	0.77709
C	11	-0.94169	1.99948	4.93006	0.01215	6.94169
H	12	0.23897	0.00000	0.75993	0.00111	0.76103
H	13	0.27751	0.00000	0.72100	0.00149	0.72249
H	14	0.22286	0.00000	0.77484	0.00230	0.77714
C	15	-0.93558	1.99949	4.92477	0.01132	6.93558
H	16	0.22595	0.00000	0.77158	0.00247	0.77405
H	17	0.23979	0.00000	0.75911	0.00111	0.76021
H	18	0.24052	0.00000	0.75832	0.00115	0.75948
C	19	-0.93346	1.99949	4.92276	0.01121	6.93346
H	20	0.24105	0.00000	0.75788	0.00108	0.75895
H	21	0.22598	0.00000	0.77156	0.00246	0.77402
H	22	0.24116	0.00000	0.75773	0.00111	0.75884
C	23	-0.94025	1.99949	4.92888	0.01188	6.94025
H	24	0.22278	0.00000	0.77487	0.00235	0.77722
H	25	0.27675	0.00000	0.72203	0.00122	0.72325
H	26	0.23870	0.00000	0.76020	0.00110	0.76130
C	27	-0.93967	1.99949	4.92775	0.01243	6.93967
H	28	0.22544	0.00000	0.77219	0.00238	0.77456
H	29	0.24049	0.00000	0.75844	0.00107	0.75951
H	30	0.26009	0.00000	0.73835	0.00156	0.73991
* Total *		0.00000	81.98619	79.54843	0.46538	162.00000

Table S18. Selected calculated geometrical parameters for [L(CH_3)Pt·(SO_2)], *i*-[L(CH_3)Pt·(SO_2)], [L'(CH_3)Ir·(SO_2)] adducts and their parent complexes.[a]

Parameter	SO_2	[L(CH_3)Pt]	[L'(CH_3)Ir]	[L(CH_3)Pt·(SO_2)]		[L'(CH_3)Ir·(SO_2)]	
				n[b]	*i*[b]	*n*[b]	*i*[b]
M[c]–C		1.96	1.937	1.98	1.97	2.004	2.00
M[c]–N		2.06	2.074	2.07	2.07	2.094	2.08
M[c]–CH_3		2.13	2.092	2.14	2.13	2.089	2.08
M[c]–S				2.48	2.49	2.349	2.35
∠C–M[c]–C		180°	179°	171°	173°	170°	173°
∠N–M[c]–N		162°	163°	160°	163°	161°	163°
∠C–M[c]–S				104°	88°	97°	86°
S–O	1.46			1.49	1.49	1.52	1.52
∠O–S–O	118°			114°	116°	112°	115°
∠M[c]–plane[d]				108°	108°	115°	111°

[a] All bond lengths are in angstroms; angles are in degrees. [b] *n* and *i* here mean "normal" and "isomeric" conformer of SO_2 adduct. [c] M=Pt for Y=C, M=Ir for Y=N [d] This parameter designates the angle between M–S vector and plane formed by three atoms of SO_2.

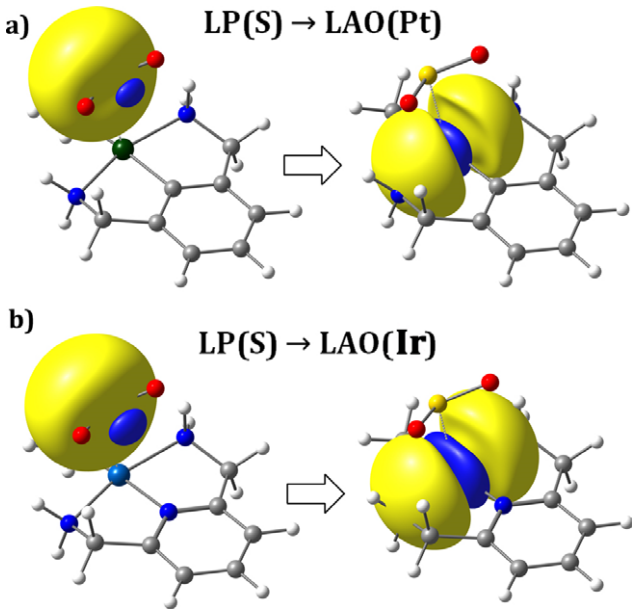


Figure S3. The major contribution to the $SO_2 \rightarrow M$ component of the bonding in: (*a*) [L(CH_3)Pt·(SO_2)], and (b) [L'(CH_3)Ir·(SO_2)].

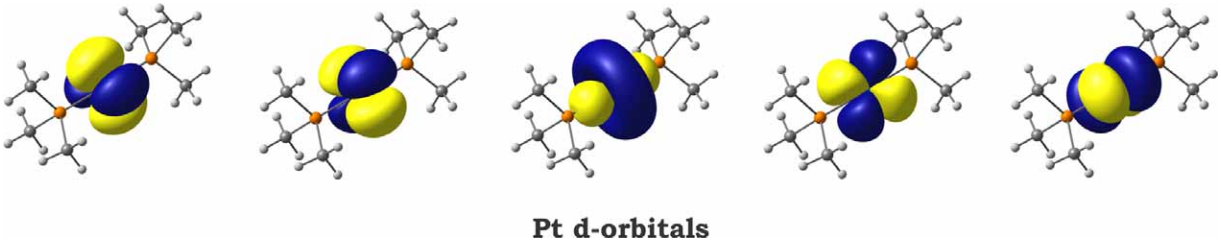


Figure S4. Selected NBOs of [($P(CH_3)_3)_2$Pt] (PBE0/TZVP/ZORA, analogous orbitals for the Pd-complex can be found in SI).

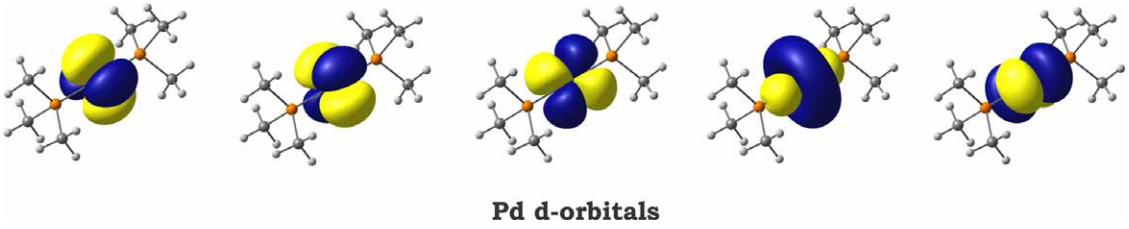


Figure S5. Selected d-type NBOs of [($P(CH_3)_3)_2$Pd].

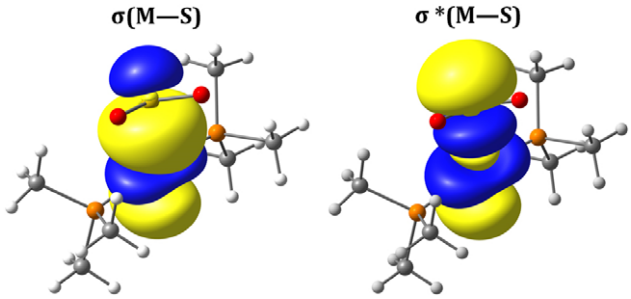


Figure S6. The bonding and anti-bonding NBOs for [$(P(CH_3)_3)_2Pd\cdot(SO_2)$] adduct.

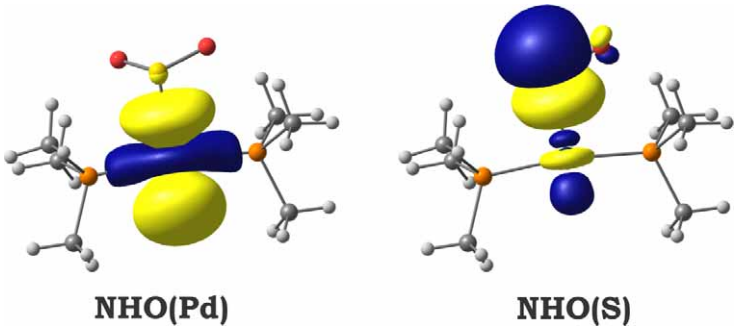


Figure S7. Two NHOs, which take part in formation of the bonding NBO in [$(P(CH_3)_3)_2PD\cdot(SO_2)$].

Adducts of SO_2 with pure organic donors

Table S19. Absolute energies of model adducts of SO_2 (in Hartree).

Compound	Energy, a.u.
$[(C_7H_{13}N)\cdot(SO_2)]$	-879.549119172807
$[C_7H_{13}N]$	-329.251572173780
$[(C_5H_8N_2)\cdot(SO_2)]$	-855.062253607391
$[C_5H_8N_2]$	-304.760143903783
$[(NH_3)\cdot(SO_2)]$	-606.846989972469
$[NH_3]$	-56.560712083653
$[(N(CH_3)_3)\cdot(SO_2)]$	-724.736430821009
$N(CH_3)_3$	-174.440217030339

Table S20. Cartesian coordinates for $[C_7H_{13}N]$.

N	0.759765	0.332993	-4.145253
C	2.104734	0.501774	-3.603957
C	0.828764	-0.454297	-5.372410
C	-0.070540	-0.365055	-3.168457
C	2.777786	-0.859864	-3.299390
C	0.510346	-1.754778	-2.806333
C	1.415720	-1.865774	-5.119596
C	1.777168	-1.966398	-3.636879
H	2.211044	-2.945334	-3.419774
H	3.688734	-0.988268	-3.892047
H	3.069575	-0.927349	-2.246923
H	0.750260	-1.814515	-1.740317
H	-0.211404	-2.550155	-3.015363
H	2.304873	-2.037160	-5.733999
H	0.692422	-2.644466	-5.380571
H	-0.180015	-0.516122	-5.789641
H	1.436644	0.101025	-6.092144
H	-1.075674	-0.455621	-3.589317
H	-0.153036	0.271004	-2.282863
H	2.026573	1.113555	-2.700970
H	2.688869	1.076929	-4.327661

Table S21. Cartesian coordinates for $[(C_7H_{13}N)\cdot(SO_2)]$.

N	1.329166	0.413237	-3.777033
C	2.616174	0.079565	-3.160559
C	1.280507	-0.095519	-5.152003
C	0.223943	-0.144052	-2.991857
C	2.864445	-1.440740	-3.254005
C	0.428511	-1.663506	-2.803009
C	1.261836	-1.637781	-5.141159
C	1.569631	-2.109692	-3.719387
H	1.673396	-3.196385	-3.692813
H	3.669437	-1.656772	-3.961581

H	3.175067	-1.836452	-2.283872
H	0.672925	-1.895484	-1.762620
H	-0.489784	-2.204432	-3.044192
H	1.999418	-2.030661	-5.845033
H	0.285083	-2.015564	-5.456007
H	0.398451	0.334015	-5.631361
H	2.155442	0.301836	-5.669966
H	-0.700153	0.080729	-3.527757
H	0.185792	0.382364	-2.035216
H	2.579257	0.419537	-2.122497
H	3.384737	0.663490	-3.670170
S	1.156556	2.659091	-3.980122
O	2.517955	2.870725	-4.519315
O	0.073704	2.651743	-4.987811

Table S22. Cartesian coordinates for [^{Me}NHC].

C	-0.591951	0.088503	-4.991740
N	0.462476	0.408745	-4.196438
C	0.079807	0.875444	-2.954321
C	-1.270093	0.855289	-2.948777
N	-1.648915	0.377438	-4.187889
H	0.780491	1.175973	-2.192371
H	-1.973093	1.134849	-2.181007
C	-3.018208	0.199292	-4.606064
H	-2.998598	-0.209589	-5.613644
H	-3.540202	-0.495814	-3.944213
H	-3.551949	1.152710	-4.614559
C	1.832842	0.273766	-4.626914
H	2.385411	-0.394973	-3.962741
H	1.817451	-0.147239	-5.629570
H	2.332951	1.244957	-4.651852

Table S23. Cartesian coordinates for [^{Me}NHC·(SO_2)].

C	-0.823565	0.687508	-5.038174
N	0.309045	0.964557	-4.374023
C	0.070369	1.008783	-3.019309
C	-1.246061	0.754922	-2.848401
N	-1.778044	0.562595	-4.103252
H	0.850571	1.203173	-2.302591
H	-1.840335	0.683321	-1.952982
S	-1.079360	0.618499	-7.112274
O	-2.162746	-0.409989	-7.178839
O	0.271461	0.102824	-7.494336
C	-3.179622	0.263371	-4.358249
H	-3.281550	-0.043569	-5.397992
H	-3.495112	-0.550484	-3.705615
H	-3.787520	1.147456	-4.160054
C	1.613650	1.188060	-4.980298
H	2.361409	0.609509	-4.438408
H	1.571275	0.856688	-6.016745
H	1.865814	2.248572	-4.931756

Table S24. Cartesian coordinates for [NH_3].

N	-0.195295	-2.057929	-3.711234
H	0.257175	-2.799343	-3.192234
H	0.175142	-2.072625	-4.652604
H	0.076663	-1.179449	-3.289163

Table S25. Cartesian coordinates for [$H_3N{\cdot}(SO_2)$].

N	-0.077112	-1.928616	-3.634213
H	0.670278	-2.608578	-3.703022
H	-0.244178	-1.536979	-4.554240
H	0.211856	-1.180228	-3.016321
S	-2.328722	-2.982978	-3.202478
O	-3.077948	-1.900189	-3.852159
O	-2.081046	-4.180082	-4.015012

Table S26. Cartesian coordinates for [$(CH_3)_3N$].

N	0.172280	-0.222775	-3.483098
C	-0.688964	-0.701062	-2.427206
H	-1.290538	-1.538175	-2.788809
H	-0.128019	-1.042412	-1.536565
H	-1.370192	0.093318	-2.114208
C	0.927038	0.935386	-3.065918
H	1.614641	0.722067	-2.225518
H	1.521412	1.313719	-3.900735
H	0.245101	1.728828	-2.751849
C	1.036671	-1.269999	-3.974289
H	1.725705	-1.658615	-3.200399
H	0.437074	-2.105837	-4.341871
H	1.638966	-0.896045	-4.805357

Table S27. Cartesian coordinates for [$(CH_3)_3N{\cdot}(SO_2)$].

N	0.612601	-1.111996	-3.945495
C	-0.364319	-1.663374	-3.022713
H	-0.650564	-2.660773	-3.359429
H	0.039961	-1.721394	-2.004539
H	-1.252499	-1.029568	-3.024436
C	0.941926	0.271706	-3.654068
H	1.428046	0.371775	-2.675457
H	1.614900	0.655653	-4.422999
H	0.026030	0.863651	-3.666267
C	1.778330	-1.962592	-4.105420
H	2.342538	-2.052651	-3.168397
H	1.455748	-2.954138	-4.425652
H	2.433700	-1.542698	-4.870642
S	-0.498360	-1.108048	-5.943653
O	-1.537604	-0.135019	-5.546587
O	-0.905309	-2.528028	-5.899089

Table S28. NBO charges in [$(C_7H_{13}N)\cdot(SO_2)$].

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
N	1	-0.37402	1.99953	5.34130	0.03318	7.37402
C	2	-0.25586	1.99940	4.24189	0.01458	6.25586
C	3	-0.26757	1.99939	4.25199	0.01619	6.26757
C	4	-0.25119	1.99940	4.23695	0.01484	6.25119
C	5	-0.43106	1.99943	4.42200	0.00963	6.43106
C	6	-0.43087	1.99944	4.42178	0.00965	6.43087
C	7	-0.42887	1.99943	4.41982	0.00961	6.42887
C	8	-0.21442	1.99942	4.20378	0.01122	6.21442
H	9	0.22652	0.00000	0.77192	0.00156	0.77348
H	10	0.21534	0.00000	0.78314	0.00152	0.78466
H	11	0.21846	0.00000	0.78013	0.00142	0.78154
H	12	0.21287	0.00000	0.78561	0.00152	0.78713
H	13	0.22020	0.00000	0.77838	0.00142	0.77980
H	14	0.22030	0.00000	0.77830	0.00140	0.77970
H	15	0.21334	0.00000	0.78513	0.00152	0.78666
H	16	0.24074	0.00000	0.75723	0.00204	0.75926
H	17	0.22536	0.00000	0.77244	0.00220	0.77464
H	18	0.22219	0.00000	0.77590	0.00192	0.77781
H	19	0.21220	0.00000	0.78530	0.00250	0.78780
H	20	0.20747	0.00000	0.79046	0.00207	0.79253
H	21	0.24005	0.00000	0.75805	0.00190	0.75995
S	22	1.52432	9.99935	4.29091	0.18542	14.47568
O	23	-0.87344	1.99989	6.85909	0.01447	8.87344
O	24	-0.87206	1.99989	6.85773	0.01445	8.87206
* Total *		0.00000	29.99457	63.64922	0.35621	94.00000

Table S29. NBO charges in [^{Me}NHC$\cdot(SO_2)$].

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
C	1	0.15232	1.99911	3.81072	0.03785	5.84768
N	2	-0.49776	1.99940	5.48199	0.01638	7.49776
C	3	-0.08294	1.99918	4.06622	0.01754	6.08294
C	4	-0.09422	1.99919	4.07731	0.01772	6.09422
N	5	-0.49345	1.99944	5.47912	0.01489	7.49345
H	6	0.24141	0.00000	0.75731	0.00129	0.75859
H	7	0.23801	0.00000	0.76065	0.00134	0.76199
H	8	0.43331	0.00000	0.56524	0.00145	0.56669
H	9	0.47229	0.00000	0.52494	0.00277	0.52771
S	10	1.46905	9.99935	4.35309	0.17851	14.53095
O	11	-0.88708	1.99989	6.87264	0.01455	8.88708
O	12	-0.95096	1.99988	6.93700	0.01407	8.95096
* Total *		0.00000	23.99544	43.68622	0.31835	68.00000

Table S30. NBO charges in [$H_3N\cdot(SO_2)$].

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
N	1	-1.03768	1.99966	6.01596	0.02206	8.03768
H	2	0.37900	0.00000	0.61942	0.00158	0.62100
H	3	0.38145	0.00000	0.61598	0.00257	0.61855
H	4	0.37658	0.00000	0.62184	0.00158	0.62342
S	5	1.52999	9.99935	4.28447	0.18618	14.47001

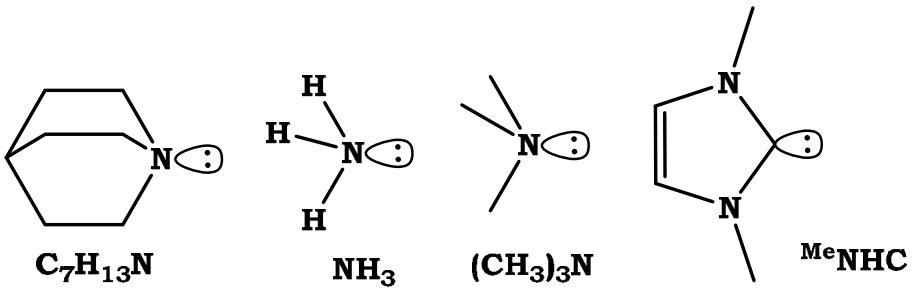
O	6	-0.81628	1.99989	6.80108	0.01531	8.81628
O	7	-0.81305	1.99989	6.79782	0.01535	8.81305
* Total *		0.00000	15.99879	25.75658	0.24463	42.00000

Table S31. NBO charges in [((CH$_3$)$_3$N·(SO$_2$)].

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
N	1	-0.38156	1.99958	5.35342	0.02857	7.38156
C	2	-0.45471	1.99941	4.44010	0.01521	6.45471
H	3	0.23595	0.00000	0.76236	0.00168	0.76405
H	4	0.19405	0.00000	0.80316	0.00279	0.80595
H	5	0.23254	0.00000	0.76562	0.00184	0.76746
C	6	-0.44223	1.99941	4.42921	0.01360	6.44223
H	7	0.19248	0.00000	0.80448	0.00305	0.80752
H	8	0.21253	0.00000	0.78571	0.00176	0.78747
H	9	0.23593	0.00000	0.76255	0.00152	0.76407
C	10	-0.44139	1.99941	4.42820	0.01378	6.44139
H	11	0.19334	0.00000	0.80362	0.00304	0.80666
H	12	0.23108	0.00000	0.76736	0.00156	0.76892
H	13	0.21295	0.00000	0.78520	0.00186	0.78705
S	14	1.51076	9.99936	4.30312	0.18676	14.48924
O	15	-0.86587	1.99989	6.85136	0.01463	8.86587
O	16	-0.86583	1.99989	6.85126	0.01468	8.86583
* Total *		0.00000	21.99694	43.69672	0.30634	66.00000

NBO analysis of SO$_2$-adducts with organic donors. The final step in the part about acceptor behavior of the SO$_2$ molecule was to investigate its reactions with pure donors, which are not expected to show any acceptor properties. This should provide the final piece of information in order to complete the picture of the binding of sulfur dioxide with available donor and help to quantify the strength of such interactions. The specific donor systems include ammonia (NH$_3$), trimethylamine ((CH$_3$)$_3$N), azabicyclooctane (C$_7$H$_{13}$N), and methyl-substituted N-heterocyclic carbene (^{Me}NHC). ChemDraw representation of all model systems is given in Scheme 1.

Scheme 1



The bent coordination mode of the SO_2 moiety is well reproduced in all optimized equilibrium geometries (Fig. S8). Such adducts are well-known experimentally and their bent shape is established.[i] Selected calculated geometrical parameters are collected in Table S32. The shortest bond between donor atom (N in amines and C in ^{Me}NHC) was expectedly found in the case of [^{Me}NHC·(SO_2)]. In contrast, the adduct with unsubstituted ammonia showed the longest N–S bond. This fully agrees with the total bonding energy, which was calculated to be the largest for [^{Me}NHC·(SO_2)] (-18 kcal/mol) and the smallest for [H_3N·(SO_2)] (-10 kcal/mol). Interestingly, the bonding energies for the amine adducts are smaller than those for complexes with any organometallic fragment considered in this paper (Table S32). The lower stabiltiy is also supported by the Wiberg bond orders (see Fig. S9).

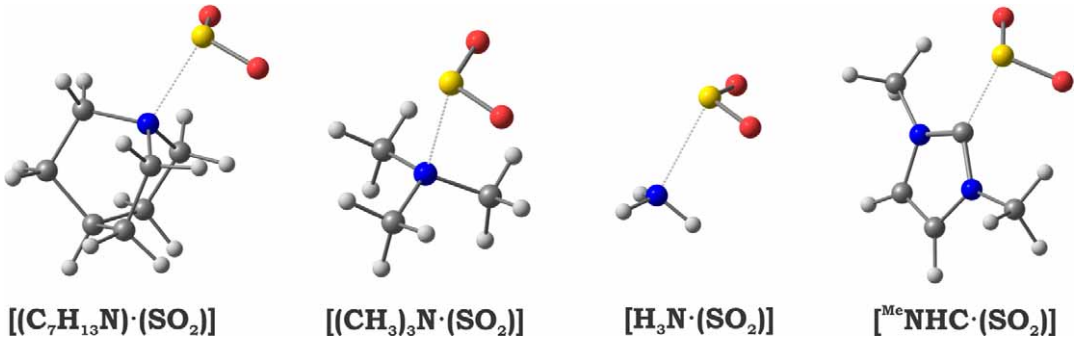


Figure S8. The opitmized geometries (PBE0/TZVP/ZORA) for model adducts [($C_7H_{13}N$)·(SO_2)], [(CH_3)$_3$N·(SO_2)], [H_3N·(SO_2)], [^{Me}NHC·(SO_2)].

Table S32. Selected calculated parameters of adducts of SO_2 with pure organic donors (PBE0/TZVP/ZORA).[a]

Parameter	[($C_7H_{13}N$)·(SO_2)]	[^{Me}NHC·(SO_2)]	[H_3N·(SO_2)]	[(CH_3)$_3$N·(SO_2)]
N–S	2.26	2.09[b]	2.52	2.27
S–O	1.48	1.50	1.47	1.48
∠O–S–O	115°	114°	117°	116°
∠N–plane[c]	102°	107°[b]	99°	102°
$E^{(2)}_{i\rightarrow j}$[d]	49	-	22	44
E_{bonding}	-17	-18	-10	-16

[a] All bond lengths are in angstroms; angles are in degrees. [b] Carbon atom is used instead of nitrogen in adducts with ^{Me}NHC. [c] ∠N–plane is the angle between N–S bond and plane of attached SO_2 (analogous to ∠M–plane in adducts with metal fragments). [d] $E^{(2)}_{i\rightarrow j}$ designates the major donor→SO_2 contribution to the acceptor-donor interaction (LP(N)→LAO(S) term), estimated by second order perturbation theory.

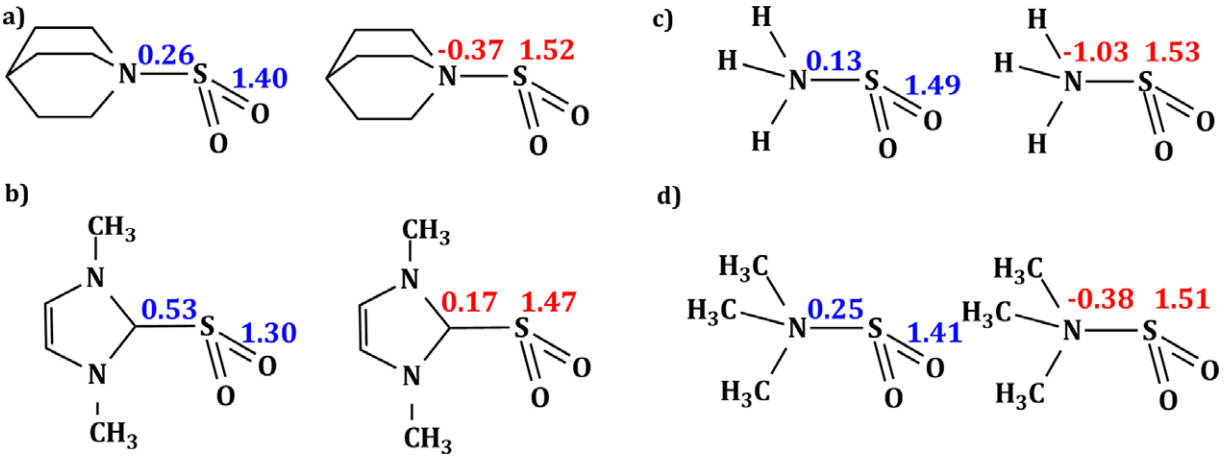


Figure S9. The Wiberg bond orders and atomic charges in the SO_2 adducts with pure organic donors (PBE0/TZVP/ZORA). Blue color is for bond orders, red – for charges.

The nature of the bonding between pure organic donors and SO_2 was found to be essentially the same as revealed by NBO and EDA analysis (Table S32 and Table S33). Estimations of the strength of donor-acceptor interaction through an NBO perturbation analysis are in good agreement with the trend observed from analysis of Wiberg bond indexes and bond dissociation energies. Indeed, in all adducts of SO_2 with substituted amines it shows the leading (amine)→(SO_2) term to be equal to 46±3 kcal/mol, whereas for the adduct with ammonia it is half the magnitude (22 kcal/mol). This component of the bonding corresponds to electron donation from the lone pair of amine (LP(N)) to the empty acceptor orbital of SO_2 (LAO(S)). Graphically it is depicted in Fig. S10a. The calculated values are much smaller than that in [L(CH_3)Pt·(SO_2)], the least stable adduct with a metal fragment. One may also note the mixing with p-orbitals of one of oxygen atoms to the acceptor

LAO(S). Such mixing was found to be most pronounced for unperturbed SO_2 molecule.

Table S33. Results of EDA analysis of the bonding between SO_2 and pure organic donors (in kcal/mol, PBE0/TZ2P/ZORA).

Parameter	$[(C_7H_{13}N)\cdot(SO_2)]$	$[^{Me}NHC\cdot(SO_2)]$	$[H_3N\cdot(SO_2)]$	$[(CH_3)_3N\cdot(SO_2)]$
ΔE_{int}	-17	-24	-7	-16
ΔE_{elstat}	-52(54%)	-117(53%)	-23(59%)	-47(53%)
ΔE_{Pauli}	80	195	32	73
ΔE_{orb}	-45(46%)	-102(47%)	-16(41%)	-42(47%)
$-D_e$	-14	-17	-6	-13
ΔE_{prep}	3	7	1	3

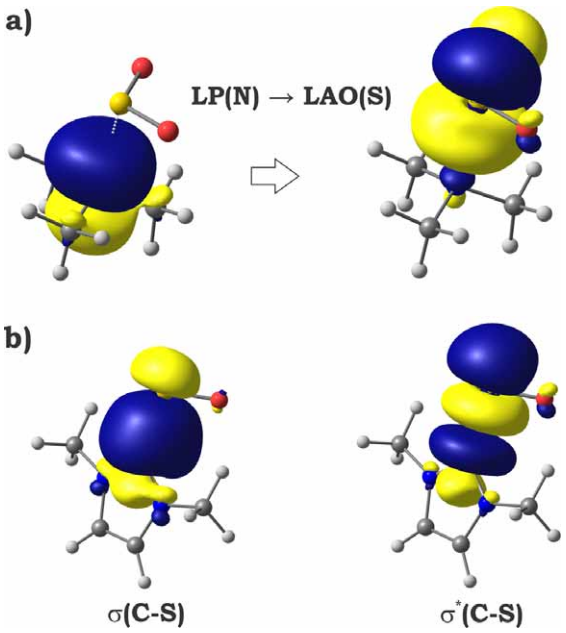


Figure S10. (a) The major contribution to the (amine)→(SO_2) interaction in NBO analysis of $[(CH_3)_3N\cdot(SO_2)]$ (PBE0/TZVP/ZORA, analogous for other adducts of amines); (b) bonding and anti-bonding NBOs in the case of $[^{Me}NHC\cdot(SO_2)]$.

High stability of the adduct [^{Me}NHC·(SO_2)] prevented analysis of the bonding in terms of NBO second order perturbation theory. Instead, we turned to an analysis of localized bonding and anti-bonding NBOs (Fig. S10b), describing this interaction. This bond can be considered as a result of interaction of two NHOs (Fig. S11), localized on different fragments:

$$\mathrm{NBO} = 0.84 \cdot h(\mathrm{C}) + 0.55 \cdot h(\mathrm{S}) = 70\% h(\mathrm{C}) + 30\% h(\mathrm{S})$$

where h(C) has 65% of p-character and 35% of s-orbital, whereas h(S) is mainly formed by the p_x-orbital of S (95%) with a small (~4%) contribution from an s-orbital. The anti-bonding NBO corresponds to an opposite combination of these NHOs.

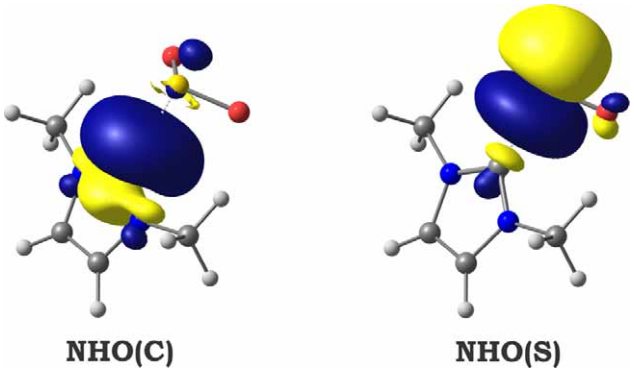


Figure S11. Two NHOs, which take part in formation of the bonding NBO in [^{Me}NHC·(SO_2)] (PBE0/TZVP/ZORA).

Adducts of SO_2-donor

Table S34. Absolute energies of model adducts of SO_2 (in Hartree).

Compound	Energy, a.u.
$[Rh_2(O_2CCF_3)_4 \cdot (SO_2)]$	-12330.246233883241
$[Rh_2(O_2CCF_3)_4]$	-11779.961889362379
$[Cr(CO)_5 \cdot (SO_2)]$	-2171.443384593723
$[Cr(CO)_5]$	-1621.131063475442
$[W(CO)_5 \cdot (SO_2)]$	-17747.981959948123
$[W(CO)_5]$	-17197.667280303882

Table S35. Cartesian coordinates for $[Rh_2(O_2CCF_3)_4]$.

Rh	0.040670	-0.154140	-3.129612
Rh	0.036193	-0.131574	-0.749247
O	-1.990598	-0.292416	-3.069174
O	0.202299	-2.183858	-3.042032
O	-0.108343	1.878292	-3.085970
O	2.070298	-0.003108	-3.068809
O	-0.108186	1.897334	-0.832348
O	0.189336	-2.161882	-0.788564
O	-1.998131	-0.266639	-0.815793
O	2.067990	0.012427	-0.815388
C	-2.538452	-0.302075	-1.943442
C	-0.144056	2.430960	-1.963852
C	0.255456	-2.713929	-1.909774
C	2.612026	0.048901	-1.942597
C	-0.202012	3.977871	-1.965961
F	-0.922402	4.420807	-0.944363
F	1.039758	4.454705	-1.850261
F	-0.728990	4.435603	-3.091492
C	4.153652	0.191813	-1.922322
F	4.477585	1.383912	-1.421057
F	4.686984	-0.753322	-1.153930
F	4.665185	0.089371	-3.138318
C	-4.087000	-0.327922	-1.972520
F	-4.530898	0.859014	-2.390682
F	-4.519273	-1.260030	-2.815272
F	-4.589601	-0.570062	-0.772505
C	0.479107	-4.245680	-1.884095
F	1.781419	-4.482517	-1.707739
F	-0.190416	-4.805712	-0.884899
F	0.097559	-4.803815	-3.022911

Table S36. Cartesian coordinates for $[Rh_2(O_2CCF_3)_4 \cdot (SO_2)]$.

Rh	0.031559	-0.114159	-3.138528
Rh	0.106420	-0.095752	-0.736886
O	-1.999690	-0.236483	-3.011065
O	0.171266	-2.145179	-3.063711
O	-0.079166	1.921787	-3.092232

O	2.064272	0.006660	-3.145669
O	-0.013368	1.941531	-0.840022
O	0.239038	-2.134543	-0.811101
O	-1.932634	-0.227653	-0.759320
O	2.141811	0.026227	-0.893401
C	-2.508160	-0.271039	-1.871144
C	-0.063837	2.474911	-1.974028
C	0.260580	-2.680287	-1.939647
C	2.645119	0.048269	-2.042013
C	-0.080493	4.024448	-1.957089
F	-1.033922	4.465297	-1.143178
F	1.096208	4.466185	-1.510930
F	-0.288103	4.517306	-3.167083
C	4.190600	0.153319	-2.071458
F	4.561815	1.326120	-1.557886
F	4.724629	-0.821630	-1.342113
F	4.656339	0.063845	-3.306138
C	-4.052011	-0.399913	-1.838634
F	-4.601554	0.559270	-2.576955
F	-4.402791	-1.583215	-2.343174
F	-4.521485	-0.308442	-0.605395
C	0.471559	-4.214772	-1.924809
F	1.772543	-4.463265	-1.759230
F	-0.196964	-4.774744	-0.924658
F	0.076874	-4.760717	-3.064396
S	0.094842	-0.048364	1.685336
O	-0.854957	0.841134	2.332335
O	0.962526	-0.905573	2.476081

Table S37. Cartesian coordinates for [$Cr(CO)_5$].

Cr	0.056931	-0.888869	3.481694
C	-0.985919	-0.125287	4.870349
C	1.100380	-1.651812	2.092013
C	-0.629347	-2.605794	3.909742
C	0.734444	0.831710	3.057126
C	1.437485	-1.140239	4.653845
O	2.302270	-1.294480	5.389809
O	-1.572778	0.327845	5.735851
O	-1.002792	-3.641765	4.203457
O	1.773409	-2.117476	1.298696
O	1.182063	1.857653	2.842667

Table S38. Cartesian coordinates for [$Cr(CO)_5 \cdot (SO_2)$].

Cr	0.001490	-0.885121	3.432150
C	-1.025664	-0.080461	4.816533
C	1.049052	-1.706104	2.073492
C	-0.652390	-2.601780	3.934926
C	0.716937	0.830881	3.026368
C	1.427676	-1.125516	4.632941
O	2.295776	-1.271380	5.354653
O	-1.615313	0.398411	5.661236
O	-1.024565	-3.626893	4.254246
O	1.695429	-2.205969	1.284576
O	1.154582	1.857409	2.811938
S	-1.648118	-0.581247	1.963764
O	-2.599884	0.522247	2.105593
O	-1.804481	-1.452085	0.796994

Table S39. Cartesian coordinates for [$W(CO)_5$].

W	0.031669	-0.882724	3.454961
C	-1.076770	-0.066168	4.960615
C	1.169470	-1.708237	1.975892
C	-0.695033	-2.729437	3.932625
C	0.777680	0.965604	3.019749
C	1.485027	-1.151323	4.690846
O	2.354043	-1.311152	5.427740
O	-1.660316	0.383543	5.831820
O	-1.067344	-3.764034	4.236858
O	1.846108	-2.177239	1.186049
O	1.231614	1.992652	2.818095

Table S40. Cartesian coordinates for [$W(CO)_5{\cdot}(SO_2)$].

W	0.009069	-0.893253	3.453951
C	-1.104378	-0.017034	4.933820
C	1.117987	-1.779375	1.976368
C	-0.694067	-2.748449	3.986428
C	0.767819	0.964613	3.023494
C	1.552662	-1.144106	4.725196
O	2.438027	-1.281819	5.429814
O	-1.705356	0.472545	5.765931
O	-1.064317	-3.776844	4.299063
O	1.742586	-2.280730	1.169333
O	1.195355	1.997377	2.815115
S	-1.734647	-0.561428	1.871359
O	-2.686854	0.543507	2.006442
O	-1.863358	-1.422611	0.693095

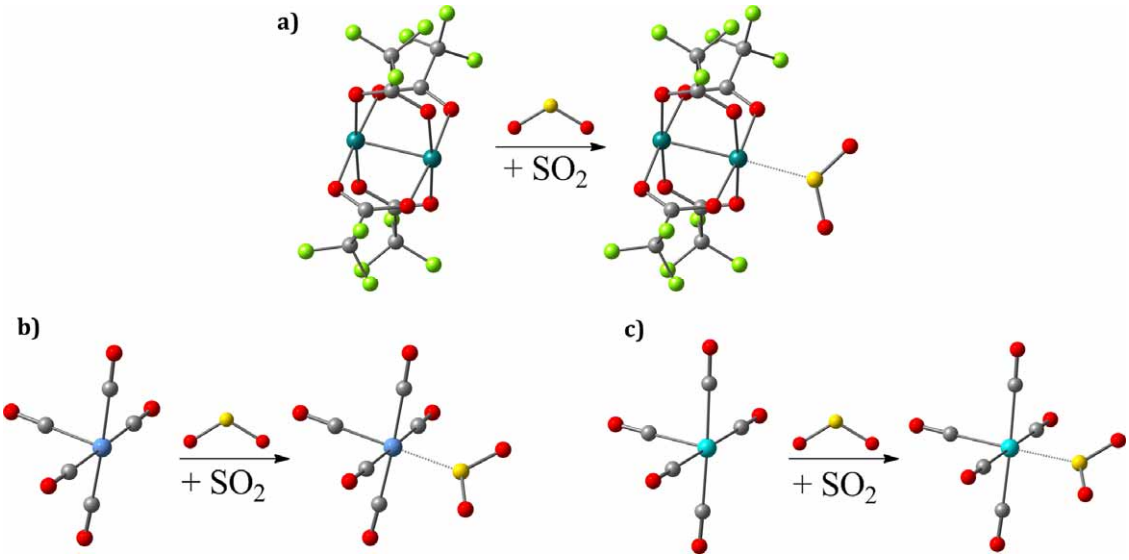


Figure S12. Optimized equilibrium geometries for model adducts: (*a*) [$Rh_2(O_2CCF_3)_4{\cdot}(SO_2)$], (*b*) [$Cr(CO)_5{\cdot}(SO_2)$], and (*c*) [$W(CO)_5{\cdot}(SO_2)$].

Table S41. NBO charges in $[Rh_2(O_2CCF_3)_4 \cdot (SO_2)]$.

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Rh	1	0.86341	35.99000	8.11070	0.03590	44.13659
Rh	2	0.75633	35.99211	8.19780	0.05376	44.24367
O	3	-0.56892	1.99970	6.55328	0.01595	8.56892
O	4	-0.56449	1.99970	6.54879	0.01601	8.56449
O	5	-0.56331	1.99970	6.54761	0.01600	8.56331
O	6	-0.56320	1.99970	6.54745	0.01606	8.56320
O	7	-0.56919	1.99970	6.55301	0.01648	8.56919
O	8	-0.56725	1.99971	6.55109	0.01645	8.56725
O	9	-0.56445	1.99970	6.54820	0.01655	8.56445
O	10	-0.56849	1.99970	6.55241	0.01638	8.56849
C	11	0.67925	1.99953	3.27381	0.04740	5.32075
C	12	0.67880	1.99953	3.27420	0.04747	5.32120
C	13	0.67835	1.99953	3.27465	0.04746	5.32165
C	14	0.67842	1.99953	3.27459	0.04745	5.32158
C	15	0.85561	1.99946	3.08872	0.05621	5.14439
F	16	-0.28390	1.99992	7.27696	0.00701	9.28390
F	17	-0.28816	1.99992	7.28143	0.00681	9.28816
F	18	-0.27881	1.99992	7.27167	0.00722	9.27881
C	19	0.85563	1.99946	3.08870	0.05621	5.14437
F	20	-0.28752	1.99992	7.28077	0.00683	9.28752
F	21	-0.28432	1.99992	7.27741	0.00698	9.28432
F	22	-0.27879	1.99992	7.27164	0.00723	9.27879
C	23	0.85572	1.99946	3.08861	0.05621	5.14428
F	24	-0.28447	1.99992	7.27757	0.00698	9.28447
F	25	-0.28761	1.99992	7.28087	0.00681	9.28761
F	26	-0.27895	1.99992	7.27179	0.00725	9.27895
C	27	0.85568	1.99946	3.08871	0.05615	5.14432
F	28	-0.28844	1.99992	7.28176	0.00675	9.28844
F	29	-0.28275	1.99992	7.27574	0.00708	9.28275
F	30	-0.27961	1.99992	7.27249	0.00720	9.27961
S	31	1.58572	9.99919	4.22168	0.19342	14.41428
O	32	-0.70478	1.99988	6.68888	0.01602	8.70478
O	33	-0.70553	1.99988	6.68985	0.01580	8.70553
* Total *		0.00000	141.97365	199.08286	0.94349	342.00000

Table S42. NBO charges in $[Cr(CO)_5 \cdot (SO_2)]$.

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
Cr	1	-1.67096	17.96839	7.65151	0.05105	25.67096
C	2	0.70737	1.99930	3.23266	0.06068	5.29263
C	3	0.70688	1.99930	3.23297	0.06085	5.29312
C	4	0.70144	1.99930	3.23863	0.06063	5.29856
C	5	0.70089	1.99929	3.23906	0.06076	5.29911
C	6	0.71965	1.99929	3.21537	0.06569	5.28035
O	7	-0.43199	1.99976	6.40955	0.02268	8.43199
O	8	-0.42249	1.99976	6.40023	0.02251	8.42249
O	9	-0.42388	1.99976	6.40145	0.02267	8.42388
O	10	-0.42241	1.99976	6.40001	0.02265	8.42241
O	11	-0.42407	1.99976	6.40149	0.02281	8.42407
S	12	1.78368	9.99824	4.05107	0.16701	14.21632
O	13	-0.76217	1.99988	6.74714	0.01515	8.76217
O	14	-0.76193	1.99988	6.74693	0.01513	8.76193
* Total *		0.00000	51.96166	73.36808	0.67026	126.00000

Table S43. NBO charges in $[W(CO)_5 \cdot (SO_2)]$.

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
W	1	-1.16190	67.95853	7.13640	0.06697	75.16190
C	2	0.60494	1.99938	3.34222	0.05345	5.39506
C	3	0.60566	1.99938	3.34120	0.05376	5.39434
C	4	0.60263	1.99939	3.34415	0.05383	5.39737
C	5	0.60313	1.99939	3.34334	0.05415	5.39687
C	6	0.61172	1.99939	3.33043	0.05845	5.38828
O	7	-0.41551	1.99976	6.39342	0.02234	8.41551
O	8	-0.40875	1.99976	6.38684	0.02215	8.40875
O	9	-0.40751	1.99976	6.38539	0.02236	8.40751
O	10	-0.40843	1.99976	6.38633	0.02234	8.40843
O	11	-0.40834	1.99976	6.38607	0.02251	8.40834
S	12	1.70424	9.99852	4.12735	0.16990	14.29576
O	13	-0.76070	1.99988	6.74568	0.01514	8.76070
O	14	-0.76120	1.99988	6.74617	0.01515	8.76120
* Total *		0.00000	101.95252	73.39499	0.65248	176.00000

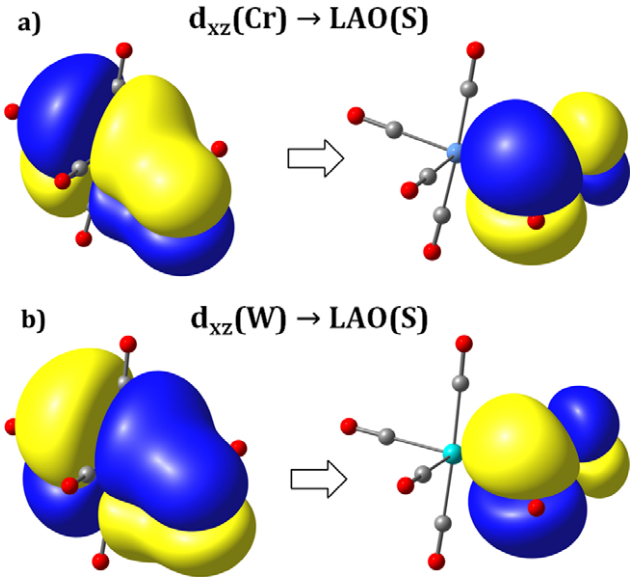


Figure S13. The major contribution to M→(SO_2) interaction in (*a*) $[Rh_2(O_2CCF_4) \cdot (SO_2)]$ and (*b*) $[M(CO)_5 \cdot (SO_2)]$ (M = Cr, W).

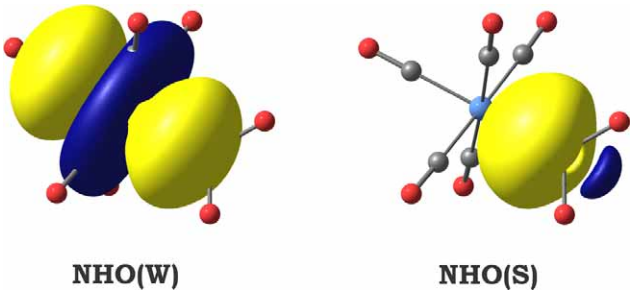


Figure S14. Two NHOs, which take part in formation of the bonding NBO in [$W(CO)_5 \cdot (SO_2)$].

Adducts of SO_2 with pure organic acceptor

Table S44. Absolute energies of model adducts of SO_2 with pure acceptors (in Hartree).

Compound	Energy, a.u.
$[(BH_3)\cdot(SO_2)]$	-576.861805667299
$[BH_3]$	-26.577348364588
$[(B(CF_3)_3)\cdot(SO_2)]$	-1588.815859823129
$[B(CF_3)_3]$	-1038.540852762250

Table S45. Cartesian coordinates for $[BH_3]$.

B	0.086477	0.020051	-2.319699
H	0.931960	0.841770	-2.132892
H	-1.063735	0.339384	-2.330156
H	0.390699	-1.120781	-2.497132

Table S46. Cartesian coordinates for $[(BH_3)\cdot(SO_2)]$.

S	-1.694891	-1.297486	-2.297901
O	-2.083755	-0.077225	-1.613935
O	-1.359565	-2.485529	-1.532702
B	-1.593039	-1.290801	-4.225598
H	-0.746543	-0.435159	-4.332100
H	-1.301540	-2.421506	-4.473957
H	-2.700148	-0.886121	-4.474282

Table S47. Cartesian coordinates for $[B(CF_3)_3]$.

B	-2.011941	-0.314082	-0.492423
C	-2.770224	-0.583248	-1.882675
F	-2.311371	0.326311	-2.765457
F	-2.565856	-1.793411	-2.404408
F	-4.092608	-0.418071	-1.756449
C	-2.318159	1.017296	0.353212
F	-3.249137	1.814778	-0.171795
F	-2.732565	0.664699	1.582000
F	-1.191288	1.737237	0.474966
C	-0.933509	-1.376372	0.047212
F	-0.272197	-0.999381	1.142478
F	-1.585273	-2.516769	0.339897
F	-0.024615	-1.639615	-0.903179

Table S48. Cartesian coordinates for [(B(CF$_3$)$_3$)·(SO$_2$)].

B	-1.818666	-0.157594	-0.602229
C	-2.786402	-0.555308	-1.852785
F	-3.113545	0.505285	-2.615328
F	-2.234136	-1.459249	-2.679057
F	-3.919850	-1.079372	-1.376537
C	-2.421519	0.953548	0.432201
F	-3.165743	1.893873	-0.160915
F	-3.185169	0.348990	1.346651
F	-1.436042	1.603798	1.094666
C	-1.029370	-1.391318	0.109824
F	-0.158997	-0.964570	1.044469
F	-1.923019	-2.182565	0.716782
F	-0.333192	-2.155392	-0.744410
S	-0.286141	0.939542	-1.532296
O	-0.572103	2.301410	-1.916140
O	0.994911	0.309234	-1.746100

Table S49. NBO charges in [(BH$_3$)·(SO$_2$)].

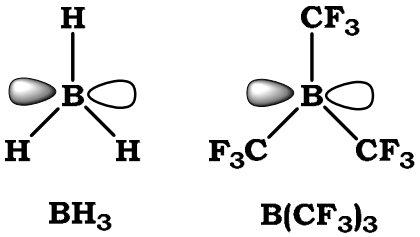
			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
S	1	1.87395	9.99870	3.96302	0.16433	14.12605
O	2	-0.72219	1.99987	6.70661	0.01571	8.72219
O	3	-0.71756	1.99987	6.70199	0.01569	8.71756
B	4	-0.59831	1.99944	3.58884	0.01004	5.59831
H	5	0.06541	0.00000	0.93292	0.00167	0.93459
H	6	0.03795	0.00000	0.96024	0.00181	0.96205
H	7	0.06075	0.00000	0.93756	0.00168	0.93925
* Total *		0.00000	15.99788	23.79118	0.21094	40.00000

Table S50. NBO charges in [(B(CF$_3$)$_3$)·(SO$_2$)].

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
B	1	-0.01713	1.99899	2.99369	0.02445	5.01713
C	2	0.74189	1.99873	3.20530	0.05408	5.25811
F	3	-0.31143	1.99993	7.30401	0.00750	9.31143
F	4	-0.30740	1.99993	7.29994	0.00753	9.30740
F	5	-0.28978	1.99992	7.28201	0.00785	9.28978
C	6	0.74036	1.99875	3.20651	0.05438	5.25964
F	7	-0.30024	1.99993	7.29263	0.00768	9.30024
F	8	-0.28982	1.99992	7.28214	0.00776	9.28982
F	9	-0.32061	1.99993	7.31345	0.00722	9.32061
C	10	0.73633	1.99873	3.21064	0.05430	5.26367
F	11	-0.31183	1.99993	7.30449	0.00741	9.31183
F	12	-0.29259	1.99992	7.28501	0.00765	9.29259
F	13	-0.30438	1.99993	7.29690	0.00755	9.30438
S	14	1.84417	9.99887	3.99324	0.16371	14.15583
O	15	-0.65836	1.99987	6.64202	0.01647	8.65836
O	16	-0.65920	1.99987	6.64289	0.01644	8.65920
* Total *		0.00000	39.99316	95.55488	0.45196	136.00000

NBO analysis of SO_2-adducts with organic acceptors. Might the donor behavior of SO_2 also emerge in bonding with other molecules as we have just seen in adducts with Lewis acidic organometallic fragments? We are going now to answer this question. The final logical step to complete our investigation of the donor-acceptor behavior of the SO_2 molecule was to consider it in complexes with systems expected to be pure acceptors. These specific acceptor systems are borane (BH_3) and tris-trifluoromethylborane, $B(CF_3)_3$ (Scheme 2), both having available empty orbitals of p-type.

Scheme 2



The linear coordination mode of SO_2 is well-reproduced in optimized equilibrium geometries of both $[(BH_3)\cdot(SO_2)]$ and $[(B(CF_3)_3)\cdot(SO_2)]$ (Fig. S15), with the angle between the B–S bond vector and the plane of SO_2 moiety being equal to ~180°. The B–S bond length was found to be shorter in the former (Table S51). It agrees with larger bonding energy between fragments in $[(BH_3)\cdot(SO_2)]$ (-9 kcal/mol) in comparison with that in $[(B(CF_3)_3)\cdot(SO_2)]$ (-3 kcal/mol). The lower stability of the latter is also supported by the smaller Wiberg bond orders (Fig. S16). It is important to note here that the stability (as estimated by the bonding or bond dissociation energy) of adducts with pure acceptors is, in general, significantly lower than those of adducts with pure organic donors (Table S32). This finding supports

the previous conclusion that the SO_2 molecule is a strong acceptor rather than a strong donor species. However, the Wiberg bond orders show an opposite trend, being notably smaller for the adducts of pure organic donors (Fig. S9). This seeming disagreement prompted us to perform a detailed study of the bonding in the adducts.

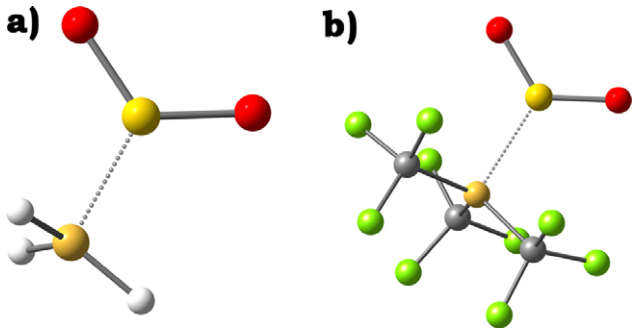


Figure S15. The optimized geometries for [$(BH_3)\cdot(SO_2)$] (*a*) and [$(B(CF_3)_3)\cdot(SO_2)$] (*b*) adducts (PBE0/TZVP/ZORA).

Table S51. Selected calculated geometrical parameters of adducts of SO_2 with pure organic acceptors (PBE0/TZVP/ZORA).[a]

Parameter	[$(BH_3)\cdot(SO_2)$]	[$(B(CF_3)_3)\cdot(SO_2)$]
B–S[b]	1.93	2.10
S–O	1.45	1.44
∠O–S–O	120°	123°
∠B–plane[c]	179°	180°
$E_{bonding}$	-9	-3

[a] All bond lengths are in angstroms; angles are in degrees. [c] ∠B–plane parameter designates the angle between B–S vector and plane formed by three atoms of SO_2 (analogous to previously used ∠M–plane and ∠N–plane parameters).

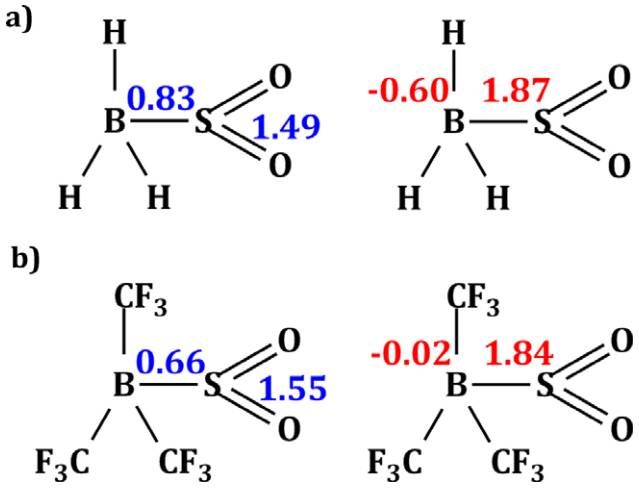


Figure S16. The Wiberg bond orders and NBO atomic charges for the adducts of SO_2 with pure organic acceptors (PBE0/TZVP/ZORA). Blue color is for bond orders and red is for charges.

The bonding between the SO_2 molecule and the acceptor organic species can be described as a polar covalent bond as provided by NBO analysis (Fig. S17). The bonding orbitals are mainly formed by the lone pair of SO_2 moiety, whereas the anti-bonding NBOs have a major contribution from the borane fragment. This conclusion clearly arrives from analysis of bonding (anti-bonding) NBOs in terms of hybrid orbitals (Fig. S18):

$[(BH_3)\cdot(SO_2)]$: NBO = $0.52\cdot h(B) + 0.85\cdot h(S) = 27\% h(B) + 73\% h(S)$

$[(B(CF_3)_3)\cdot(SO_2)]$: NBO = $0.51\cdot h(B) + 0.86\cdot h(S) = 26\% h(B) + 74\% h(S)$

where h(B) has 89% and 87% of p-character and 10% and 13% of s-orbital for $[(BH_3)\cdot(SO_2)]$ and $[(B(CF_3)_3)\cdot(SO_2)]$, respectively. The h(S) is formed by s-orbital

(~50%) and p-orbital (~50%) of S in both cases. The anti-bonding partners have an opposite combination of these hybrid orbitals.

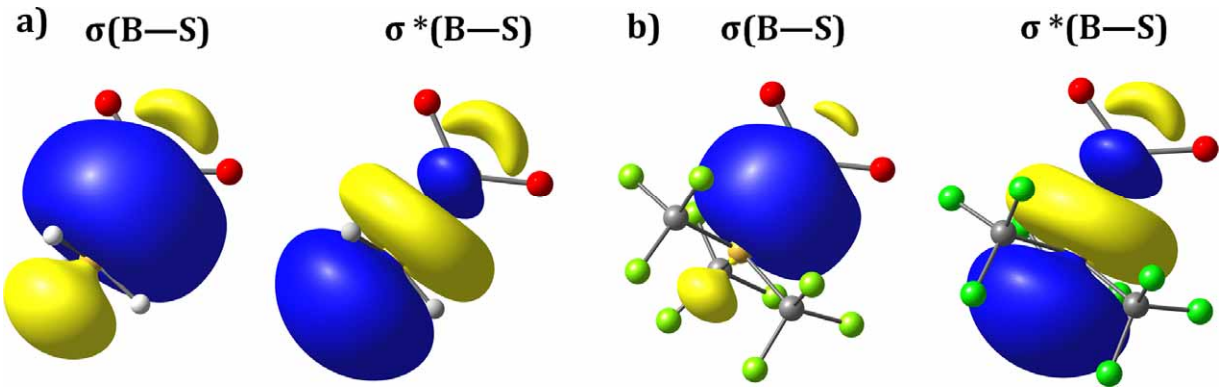


Figure S17. Bonding and anti-bonding NBOs for (*a*) [$(BH_3)\cdot(SO_2)$] and (*b*) [$(B(CF_3)_3)\cdot(SO_2)$] (PBE0/TZVP/ZORA).

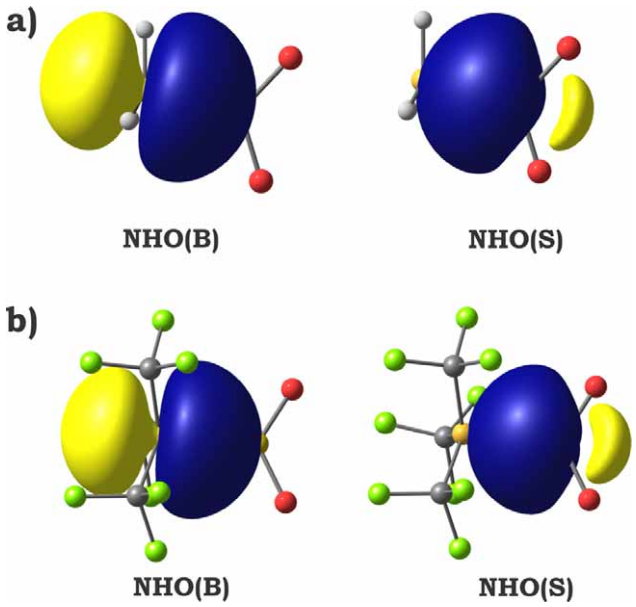


Figure S18. Two NHOs, which take part in formation of the bonding NBO in (*a*) [$(BH_3)\cdot(SO_2)$] and (*b*) [$(B(CF_3)_3)\cdot(SO_2)$] (PBE0/TZVP/ZORA).

Subsequent *EDA analysis* revealed significant dominance of the orbital component over the electrostatic one, which was found to be ~2.5 times smaller in magnitude (Table S52). These findings are in opposite to what was observed for adducts of SO_2 with pure organic donors (Table S33), where the balance ΔE_{elstat}:ΔE_{orb}=55:45 was established. Thus, the ionic contribution in the latter is significantly larger. Considering that almost all techniques for bond order calculation (including Wiberg scheme) are based on orbital overlap, and, thus, on the orbital component of the bonding, rather than on the classic electrostatic one, it is now possible to resolve the aforementioned inconsistency between bond orders and bonding energy. Larger contribution of the electrostatic term makes adducts of SO_2 with pure donors more stable (as estimated by the bonding energy) without increasing N–S bond order. On the other hand, the adducts of sulfur dioxide with pure acceptors have a relatively large contribution from ΔE_{orb} (reflected in calculated bond order) and small participation of the ΔE_{elstat} (Table S52). Altogether, it leads to a smaller stability of the final adducts. Thus, one can make two conclusions: (*i*) both components orbital and electrostatic are of equal importance for the total stability of the adduct, and (*ii*) complexes of SO_2 with pure organic donors represent an unusual case, where the higher bond order does not correspond to higher stability of the final product.

Table S52. Results of EDA analysis of the bonding in [$(BH_3)\cdot(SO_2)$] and [$(B(CF_3)_3)\cdot(SO_2)$] (in kcal/mol, PBE0/TZ2P/ZORA).

Parameter	[$(BH_3)\cdot(SO_2)$]	[$(B(CF_3)_3)\cdot(SO_2)$]
ΔE_{int}	-15	-12
ΔE_{elstat}	-28(28%)	-13(19%)
ΔE_{Pauli}	86	59
ΔE_{orb}	-73(72%)	-57(81%)
$-D_{\text{e}}$	-10	-2
ΔE_{prep}	5	10

[i] *See for instance*: (a) Oh, J.J.; LaBarge, M.S.; Matos, J.; Kampf, J.W.; Hilling II, K.W.; Kuczkowski, R.L. *J. Am. Chem. Soc.*, **1991**, *113*, 4732. (b) Denk, M.K.; Hatano, K.; Lough, A.J. *Eur. J. Inorg. Chem.*, **2003**, 224.