Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

σ-Donor/σ-Acceptor Plumbylene Ligands: Synergic σ-Donation Between Ambiphilic Pt^0 and Pb^{II} Fragments

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General Considerations. All manipulations were performed in an inert atmosphere of argon using standard Schlenk and glovebox techniques. Solvents were distilled over alkali metal, degassed, and stored over molecular sieves (4 Å) under argon. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored under argon over molecular sieves. NMR experiments were performed on a Bruker Avance 500 (^{1}H: 500.1 MHz; ^{13}C: 125.8 MHz; ^{31}P: 202.5 MHz, ^{195}Pt: 107.5 MHz) apparatus. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were calibrated to TMS. In the case of ^{31}P{^{1}H} NMR spectra 85% H_3PO_4 and ^{195}Pt{^{1}H} NMR $Na_2[PtCl_6]$ in D_2O were used as external standards. Elemental analyses were performed on an Elementar vario Micro Cube elemental analyzer and Leco Instrumente CHNS 932 elemental analyzer. The UV-Vis spectra were measured on a JASCO V-660 UV-Vis-spectrometer. $[(Cy_3P)_2Pt]$[1] was prepared according to known methods. Anhydrous $SnCl_2$ and $PbCl_2$ were purchased commercial and used after several sublimations.

$[(Cy_3P)_2Pt(PbCl_2)]$ (**2**): $PbCl_2$ (36.7 mg, 0.13 mmol) and $[(Cy_3P)_2Pt]$ (**1**) (100 mg, 0.13 mmol) were stirred in monofluorbenzene (1.0 mL) at 50 °C for 24 h. White $PbCl_2$ was filtered off and the solvent was removed in vacuum from the red solution. The orange residue was rinsed with hexane and to obtain **2** as orange solid. Suitable crystals were obtained by recrystallization from toluene and hexane at RT. (95.7 mg, 0.09 mmol, 70%). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.40 (br m, 6H, *Cy*), 2.15 (br d, $^{3}J_{H-H}$ = 12 Hz, 12 H, Cy), 1.79 (br d, $^{3}J_{H-H}$ = 12 Hz, 12 H, Cy), 1.71–1.57 (br m, 18H, Cy), 1.42–1.16 (br m, 18H, Cy) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 36.9 (vt, $N = |^{1}J_{P-C}+^{3}J_{P-C}|$ = 26 Hz, C1, Cy), 32.1 (s, C3 and C5, Cy), 27.9 (vt, $N = |^{2}J_{P-C}+^{4}J_{P-C}|$ = 12 Hz, C2 and C6, Cy), 26.7 (s, C4, Cy) ppm.[2] ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6): δ = 48.6 ($^{1}J_{P-Pt}$ = 3450 Hz) ppm. ^{195}Pt{^{1}H} NMR (107.7 MHz, C_6D_6): δ = −4025 ($^{1}J_{Pt-P}$ = 3450 Hz) ppm. Elemental analysis (%) calculated for $C_{36}H_{66}PbCl_2P_2Pt$: C 41.82; H 6.43; found: C 41.95; H 6.43.

$[\{(Cy_3P)_2Pt\}_2(PbCl_2)]$ (**3**): $PbCl_2$ (18.4 mg, 0.07 mmol) and $[(Cy_3P)_2Pt]$ (**1**) (100 mg, 0.13 mmol) were stirred in monofluorbenzene (1.0 mL) at 50 °C for 24 h. White $PbCl_2$ was filtered off and the solvent was removed in vacuum from the red solution. The orange residue was rinsed with hexane and to obtain **3** as orange solid. Suitable crystals were obtained by recrystallization from toluene and hexane at RT. (82.8 mg, 0.05 mmol, 70%). ^{1}H NMR (500.1 MHz, d_8-Tol, 233 K): δ = 2.23 (br m, 6H, *Cy*), 2.19 (br d, $^{3}J_{H-H}$ = 12 Hz, 12 H, Cy), 1.81 (br d, $^{3}J_{H-H}$ = 12 Hz, 12 H, Cy), 1.75–1.61 (br m, 18H, Cy), 1.40–1.19 (br m, 18H, Cy) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, d_8-Tol, 233 K): δ = 36.7 (vt, $N = |^{1}J_{P-C}+^{3}J_{P-C}|$ = 26 Hz,[2] C1, Cy), 31.5 (s, C3 and C5, Cy), 28.2 (vt, $N = |^{2}J_{P-C}+^{4}J_{P-C}|$ = 12 Hz, C2 and C6, Cy), 27.2 (s, C4, Cy) ppm.[2] ^{31}P{^{1}H} NMR (202.5 MHz, d_8-Tol, 233 K): δ = 50.4 ($^{1}J_{P-Pt}$ = 4032 Hz) ppm. ^{195}Pt{^{1}H} NMR (107.7 MHz, d_8-Tol, 233 K): δ = −5039 ($^{1}J_{Pt-P}$ = 4032 Hz) ppm. Elemental analysis (%) calculated for $C_{36}H_{66}PbCl_2P_2Pt$: C 48.31; H 7.43; found: C 48.43; H 7.31.

Crystal structure determination. The crystal data of **2** and **3** were collected on a Bruker Apex diffractometer with a CCD area detector and graphite monochromated $Mo_{K\alpha}$ radiation. The structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factors calculations.

Crystal data for **2**: $C_{84}H_{142}Cl_4F_2P_4Pb_2Pt_2$, M_r = 2260.22, yellow block, 0.32×0.24×0.12 mm^3, Monoclinic space group $P2_1/n$, a = 14.3019(5) Å, b = 9.7509(3) Å, c = 30.2920(9) Å, β = 92.6440(10)°, V = 4219.9(2) Å^3, Z = 2, ρ_{calcd} = 1.779 g·cm^{-3}, μ = 7.531 mm^{-1}, $F(000)$ = 2224, T = 100(2) K, R_1 = 0.0246, wR^2 = 0.0469, 8992 independent reflections [2θ≤53.56°] and 442 parameters.

Crystal data for **3**: $C_{72}H_{132}Cl_2P_4PbPt_2$, M_r = 1789.93, orange plate, 0.14×0.11×0.04 mm^3, Triclinic space group P-1, a = 14.049(3) Å, b = 21.090(4) Å, c = 25.967(4) Å, α = 76.602(7)°, β = 85.335(7)°, γ = 78.047(9)°, V = 7318(2) Å^3, Z = 4, ρ_{calcd} = 1.625 g·cm^{-3}, μ = 6.308 mm^{-1}, $F(000)$ = 3584, T = 100(2) K, R_1 = 0.0576, wR^2 = 0.0628, 35781 independent reflections [2θ≤56.68°] and 1514 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 883009 and 883010. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

UV-Vis spectroscopy: A solution of the respective compound (c = $5.28*10^{-4}$ mol/l) in toluene was placed in a standard UV-Vis cuvette with screw cap. The cuvette was cold to -70°C. Before measuring the cuvette was put into cold ethanol to prevent the condensation of water on the surface of the cuvette.

Computational details for calculations of [$(Cy_3P)_2Pt–PbCl_2$] (2) and [{$(Cy_3P)_2Pt$}$_2$(μ-$PbCl_2$)] (3) complexes: Geometry optimizations in gas-phase were performed using the Gauss ian 09 (rev. B.01) series of programs[4] at the LC-ωPBE density functional[5] level of theory along with a mixed basis set: LANL2DZ ECPs[6] for Pt and Pb and 6-31G(d) for C, H and Cl atoms and 6-31G(2d) for P atoms (see Supporting Information for further details concerning the election and performance of this method). Energy values reported here contain the zero-point energy (ZPE) and thermal corrections as well as solvated energies. These were obtained by carrying out single-point calculations on the optimized geometries using the conductor-like polarizable continuum model (cPCM),[7] where a solvent cavity is formed as a surface of constant charge density of the solvated molecule with the UAKS radii and the dielectric constant set to 8.93 (dichloromethane).

We are reporting our theoretical results using the LC-ωPBE density functional since it reproduces UV-Vis spectra very well when compared with other tested levels of theory.[8] This long-range corrected density functional also provides a similar trend in calculated relative energies as can be seen in Table 1. The most significant difference is that LC-ωPBE predicts the formation of [{$(Cy_3P)_2Pt$}$_2$(μ-$PbCl_2$)] to be less favored than $(Cy_3P)_2Pt–PbCl_2$ + $Pt(PCy_3)_2$ in the scale of free-energies, which is more consistent with our experiments.

Table 1. Performance of our selected level of theory (LC-ωPBE) against other functionals and basis set. These relatives energies are calculated with respect to $(Cy_3P)_2Pt$ + $PbCl_2$ species. Values are enthalpies (free energies are given in parenthesis) in kJ mol^{-1}.

Method	[$(Cy_3P)_2Pt–PbCl_2$]	[{$(Cy_3P)_2Pt$}$_2$($PbCl_2$)]
B3LYP/mix-basis1[a]	-137.5 (-89.9)	-96.1 (-171.4)
B3LYP/mix-basis2[b]	-129.6 (-82.8)	-78.6 (-145.9)
B3PW91/mix-basis1[a]	-157.2 (-98.6)	-94.0 (-156.3)
LC-ωPBE/*mix-basis1*[a]	-160.5 (-95.3)	-118.7 (-53.5)

[a] LANL2DZ for Pt and Pb, 6-31G(2d) for Pt and 6-31G(d) for C, H and Cl.

[b] Stuttgart ECP for Pt (60e core) and Pb (78e core) and 6-31G(d) for C, H, P and Cl.

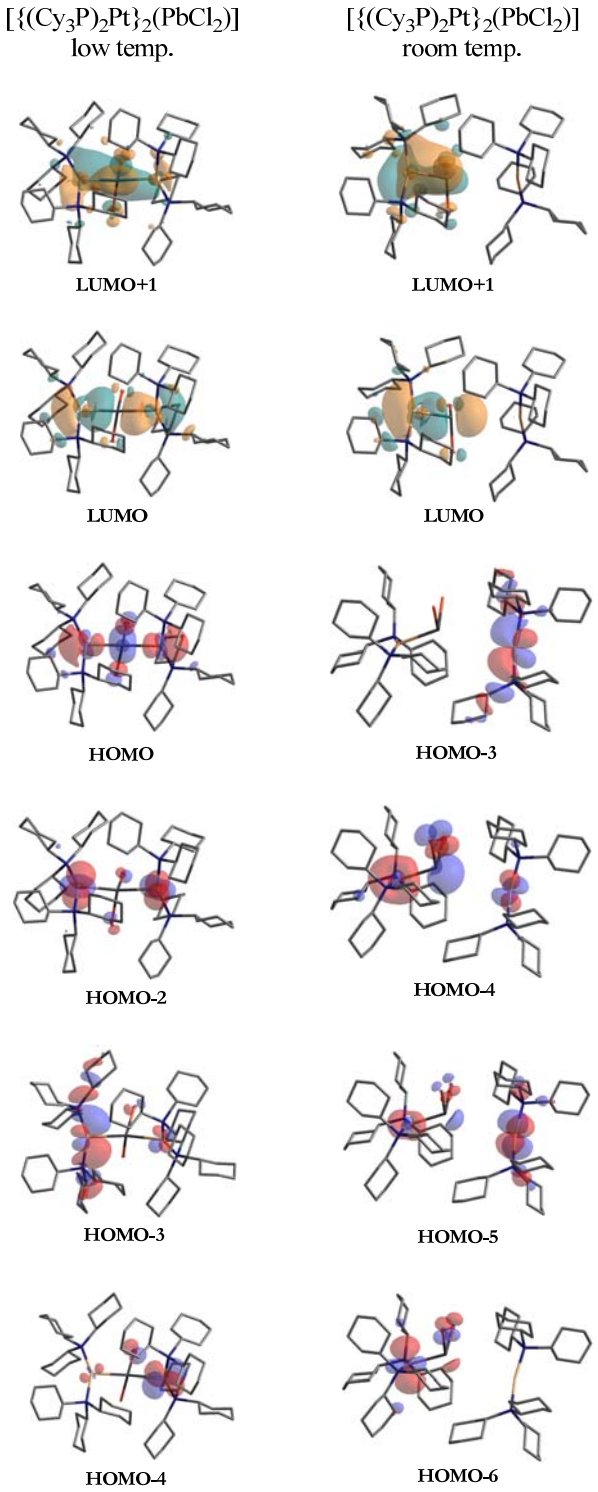


Figure S1. Comparison of molecular orbitals of $[(Cy_3P)_2Pt–PbCl_2–Pt(PCy_3)_2]$, the fully-bonded complex (left column) and the partially dissociated complex (right column) complexes (isosurface = 0.03 a.u.). Hydrogen atoms were omitted for clarity.

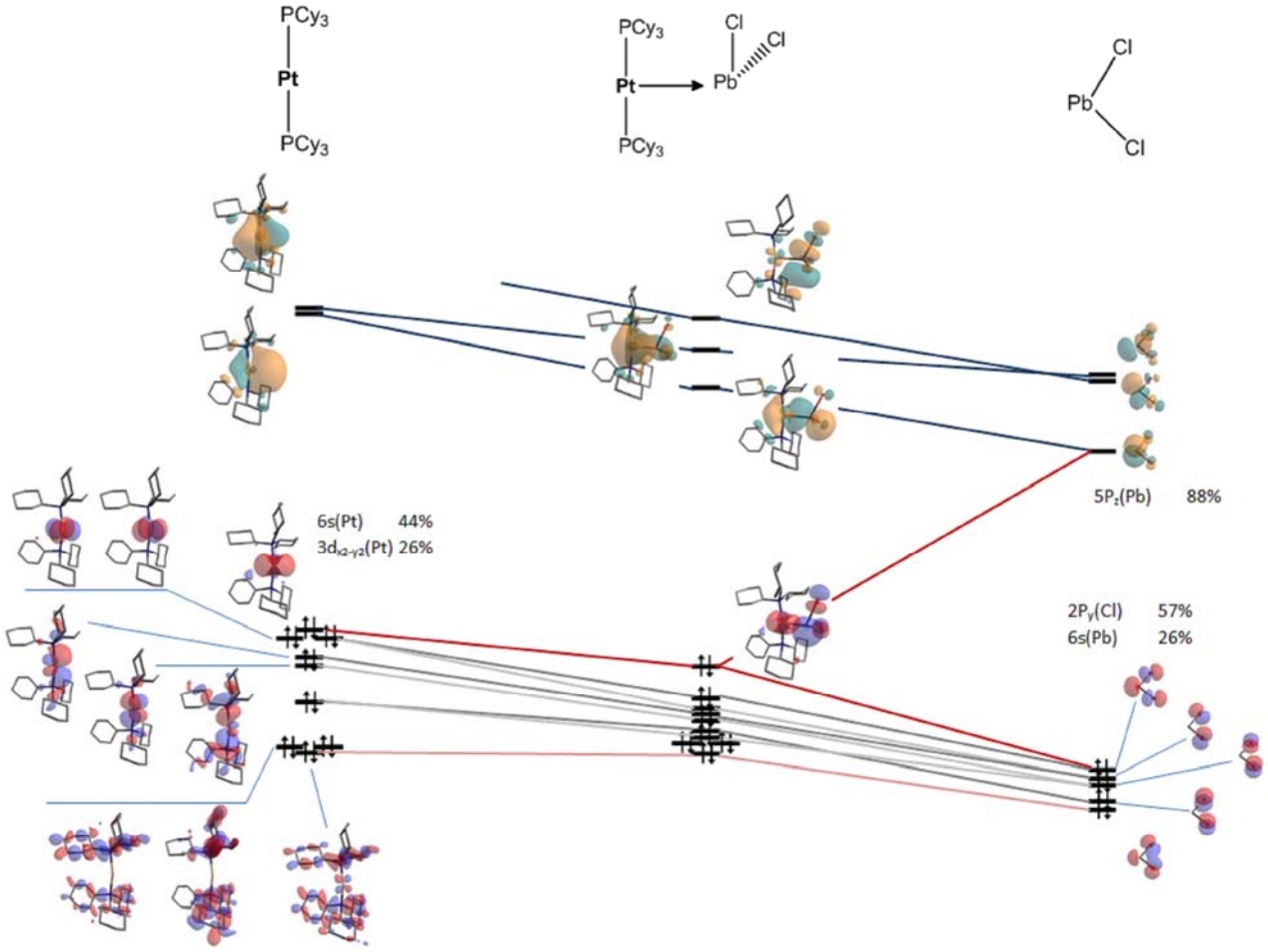
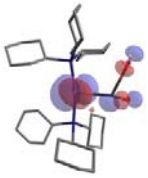


Figure S2. Energy correlation diagram of molecular orbitals of **[**$Pt(PCy_3)_2$] (left), [$(Cy_3P)_2Pt–PbCl_2$**]** (middle) and $PbCl_2$ (right) (isosurface = 0.03 a.u.). Hydrogen atoms were omitted for clarity.

List of HOMOs not shown in the correlation diagram above:

HOMO-1

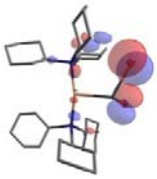


HOMO-2

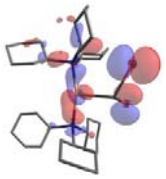
HOMO-3

HOMO-4

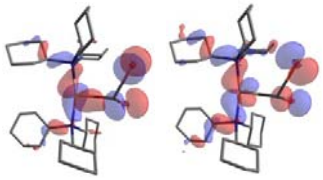
HOMO-5



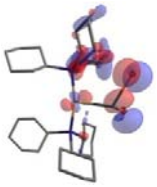
HOMO-6



HOMO-7 HOMO-8



HOMO-9



Cartesian coordinates

(x y z format) of the gas-phase optimized geometries at the LC-ωPBE/(LANL2DZ,6-31G(d)) level listed below:

$(Cy_3P)_2Pt$

E(scf) = -2212.49264272 a.u.

Pt	0.087226	0.988996	0.278949
P	-2.170944	1.083476	0.439491
P	2.345895	0.902436	0.121024
C	-3.035747	-0.147924	-0.637962
H	-2.777138	-1.089751	-0.133308
C	-4.560866	-0.077868	-0.733299
H	-4.849416	0.824888	-1.285604
H	-5.017240	-0.002730	0.259991
C	-5.111703	-1.297370	-1.471696
H	-6.202803	-1.228760	-1.547362
H	-4.893113	-2.201597	-0.887765
C	-4.491271	-1.429558	-2.859294
H	-4.799969	-0.572701	-3.473368
H	-4.870088	-2.327167	-3.360572
C	-2.967645	-1.465975	-2.780729
H	-2.653154	-2.380290	-2.259426
H	-2.536805	-1.515703	-3.786985
C	-2.416483	-0.251547	-2.036732
H	-1.326436	-0.309726	-1.944635
H	-2.636492	0.652706	-2.615984
C	-2.804230	2.791682	0.096225
H	-2.120246	3.394996	0.710908
C	-4.233671	3.159451	0.505351
H	-4.423398	2.896883	1.551095
H	-4.955851	2.596615	-0.095627
C	-4.478313	4.655871	0.304559
H	-3.825470	5.220199	0.984146
H	-5.508865	4.905460	0.581192
C	-4.196675	5.084546	-1.132441
H	-4.919467	4.598390	-1.801634
H	-4.345265	6.164558	-1.241933
C	-2.783928	4.694722	-1.555111
H	-2.054764	5.258650	-0.958399
H	-2.611139	4.966878	-2.602367
C	-2.544553	3.200585	-1.356828
H	-3.221252	2.646049	-2.019378
H	-1.520581	2.929894	-1.638640
C	-2.823500	0.716923	2.131175
H	-3.917465	0.819492	2.123193
C	-2.475208	-0.711870	2.563936
H	-1.388838	-0.846886	2.475281
H	-2.939605	-1.443582	1.895024
C	-2.920713	-0.998863	3.996278
H	-2.632237	-2.018814	4.273960
H	-4.017200	-0.957218	4.050730
C	-2.332967	0.006998	4.978431
H	-2.688179	-0.197904	5.994481
H	-1.240338	-0.099434	4.995911
C	-2.691793	1.428788	4.564360

$(Cy_3P)_2Pt–PbCl_2$

E(scf) = -3136.22432695 a.u.

Pt	0.021339	0.272870	-0.056956
Pb	-0.019828	-2.424141	-0.579156
Cl	-2.307994	-3.505211	-0.325442
Cl	0.875149	-3.151668	1.663471
P	-2.218795	0.662762	0.288751
P	2.330512	0.494965	-0.133256
C	-3.461550	-0.202704	-0.755338
H	-3.424083	-1.222225	-0.350400
C	-4.909813	0.282526	-0.653465
H	-5.001917	1.274696	-1.112477
H	-5.220845	0.380988	0.392224
C	-5.842440	-0.680687	-1.386354
H	-6.876387	-0.325762	-1.311253
H	-5.804979	-1.661483	-0.895874
C	-5.436131	-0.829613	-2.849000
H	-5.569880	0.133963	-3.360175
H	-6.093262	-1.546408	-3.352924
C	-3.981562	-1.273278	-2.971403
H	-3.868179	-2.280649	-2.554077
H	-3.689492	-1.327793	-4.026162
C	-3.043911	-0.325534	-2.226146
H	-2.010630	-0.685166	-2.293984
H	-3.060068	0.656705	-2.712309
C	-2.401711	2.500984	0.104774
H	-1.526761	2.874397	0.655902
C	-3.632844	3.168731	0.729864
H	-3.755592	2.870076	1.774987
H	-4.540666	2.855761	0.204841
C	-3.509660	4.690326	0.649221
H	-2.654342	5.015119	1.257247
H	-4.399077	5.156835	1.086587
C	-3.315479	5.162902	-0.787871
H	-4.217604	4.930579	-1.369419
H	-3.195326	6.251275	-0.817180
C	-2.114449	4.478081	-1.431902
H	-1.196373	4.796317	-0.920720
H	-2.014937	4.786858	-2.478279
C	-2.234032	2.958584	-1.348120
H	-3.107382	2.643100	-1.931265
H	-1.357964	2.477272	-1.798832
C	-2.725343	0.349005	2.031804
H	-3.757531	0.708028	2.145697
C	-2.692003	-1.141619	2.385124
H	-1.676203	-1.527334	2.231520
H	-3.343947	-1.721481	1.727211
C	-3.096865	-1.375928	3.838011
H	-3.045219	-2.447160	4.056166
H	-4.143279	-1.072526	3.981305
C	-2.207111	-0.593476	4.796213

H	-2.237844	2.153444	5.249483	H	-2.529224	-0.746893	5.831988
H	-3.779538	1.564187	4.639463	H	-1.180034	-0.973483	4.722501
C	-2.240641	1.720250	3.135237	C	-2.222057	0.891353	4.451906
H	-2.520051	2.744707	2.866887	H	-1.547358	1.446639	5.113009
H	-1.145242	1.669095	3.071852	H	-3.230069	1.294425	4.621300
C	3.281142	2.165884	1.117654	C	-1.822853	1.129628	2.997327
H	3.470984	1.648575	2.069693	H	-1.847623	2.203851	2.784311
C	2.408730	3.384435	1.443273	H	-0.786134	0.801760	2.842332
H	1.450244	3.046955	1.850711	C	2.753920	2.292764	0.124364
H	2.169499	3.922269	0.516612	H	2.912627	2.353466	1.210142
C	3.114399	4.328450	2.413374	C	1.589454	3.233822	-0.203547
H	3.251900	3.817611	3.376284	H	0.684873	2.890572	0.311366
H	2.483026	5.202034	2.610341	H	1.369714	3.193810	-1.278555
C	4.474677	4.766022	1.880147	C	1.907653	4.671106	0.203913
H	4.330823	5.368139	0.972933	H	2.010913	4.718194	1.296395
H	4.982973	5.409259	2.607058	H	1.071635	5.327986	-0.059491
C	5.341785	3.557161	1.544764	C	3.195348	5.166703	-0.444402
H	6.301423	3.880050	1.125502	H	3.056476	5.221524	-1.532335
H	5.571114	3.007468	2.467751	H	3.426464	6.182119	-0.105306
C	4.635958	2.621508	0.563916	C	4.353675	4.226096	-0.133276
H	4.484478	3.156181	-0.381956	H	5.266189	4.563753	-0.636416
H	5.280986	1.766955	0.339223	H	4.562515	4.248014	0.944658
C	2.968675	1.075048	-1.611526	C	4.034022	2.793020	-0.555674
H	4.063649	1.155715	-1.593679	H	3.904597	2.769700	-1.645088
C	2.391219	2.348281	-2.242340	H	4.884468	2.145259	-0.324603
H	2.673287	3.231275	-1.659158	C	3.207391	0.023294	-1.688490
H	1.295978	2.286249	-2.193805	H	4.187008	0.516114	-1.664746
C	2.839666	2.517668	-3.691121	C	2.433477	0.544246	-2.905223
H	3.929563	2.652191	-3.725270	H	2.261823	1.623232	-2.821572
H	2.397846	3.427582	-4.112377	H	1.438845	0.078567	-2.914445
C	2.455017	1.303198	-4.528373	C	3.166540	0.232723	-4.207467
H	2.806815	1.420080	-5.559462	H	4.118299	0.780633	-4.228317
H	1.360496	1.228465	-4.572641	H	2.578761	0.592223	-5.058918
C	3.021072	0.027169	-3.916169	C	3.441278	-1.260993	-4.343486
H	2.708966	-0.847155	-4.498300	H	4.003180	-1.462993	-5.261556
H	4.118122	0.060453	-3.964532	H	2.487643	-1.797762	-4.433547
C	2.587949	-0.142377	-2.461341	C	4.201287	-1.787702	-3.130995
H	1.499483	-0.280915	-2.408375	H	4.358293	-2.868000	-3.217541
H	3.042575	-1.052978	-2.057531	H	5.197683	-1.326878	-3.097131
C	3.028866	-0.719287	0.689932	C	3.462089	-1.479579	-1.830269
H	2.546356	-1.436766	0.011961	H	2.505781	-2.016721	-1.836017
C	4.543327	-0.909278	0.595362	H	4.034236	-1.864469	-0.980723
H	4.907490	-0.674682	-0.411290	C	3.219898	-0.370662	1.226277
H	5.039950	-0.214099	1.284508	H	3.056986	-1.436161	1.016009
C	4.939308	-2.336306	0.971037	C	4.725485	-0.106352	1.309398
H	6.027426	-2.451677	0.911620	H	5.217450	-0.299807	0.349098
H	4.508416	-3.034100	0.240478	H	4.897769	0.951127	1.549100
C	4.442731	-2.697209	2.367612	C	5.364895	-0.961239	2.402247
H	4.955070	-2.064981	3.105384	H	6.440170	-0.756552	2.451816
H	4.703203	-3.733935	2.608064	H	5.255071	-2.021930	2.142155
C	2.936235	-2.486017	2.485971	C	4.708277	-0.701189	3.753736
H	2.418103	-3.194387	1.825861	H	4.907473	0.336102	4.056784
H	2.600483	-2.705089	3.505692	H	5.154347	-1.343276	4.520805
C	2.537269	-1.063318	2.100276	C	3.202326	-0.932121	3.682177
H	1.450068	-0.936268	2.145368	H	2.997234	-1.990489	3.483419

H	2.969095	-0.362922	2.828350
H	2.734812	-0.696530	4.644373
C	2.551657	-0.099776	2.579869
H	1.486115	-0.341266	2.513087
H	2.633889	0.966267	2.834945

$(Cy_3P)_2Pt–PbCl_2$ – as a dimer
E(scf) = -6272.47593122 a.u.

Pt	0.043395	-1.678461	4.165964
Pb	-0.899113	-1.177666	1.614096
Cl	-3.270424	-0.161012	1.389322
Cl	0.242574	1.157764	1.425402
P	-1.873347	-1.297106	5.366299
P	2.251605	-2.079573	3.568498
C	-3.491235	-1.783790	4.630934
H	-3.614883	-1.029696	3.842006
C	-4.721375	-1.705688	5.538827
H	-4.669486	-2.495212	6.298845
H	-4.760752	-0.749002	6.071013
C	-5.997274	-1.900666	4.720768
H	-6.872446	-1.846445	5.378033
H	-6.089468	-1.080880	3.997185
C	-5.973054	-3.232028	3.976545
H	-5.981134	-4.053309	4.706603
H	-6.877814	-3.342641	3.369138
C	-4.731120	-3.346092	3.097481
H	-4.773704	-2.590509	2.304065
H	-4.701795	-4.325941	2.607824
C	-3.454521	-3.137304	3.909698
H	-2.574258	-3.194884	3.258442
H	-3.349857	-3.953241	4.633731
C	-1.624466	-2.158161	6.990766
H	-0.587200	-1.884579	7.232131
C	-2.487880	-1.724502	8.181165
H	-2.463077	-0.638663	8.312096
H	-3.533870	-1.996669	8.007889
C	-2.001627	-2.400247	9.463583
H	-0.985529	-2.050314	9.691040
H	-2.633110	-2.095196	10.305252
C	-1.993211	-3.919649	9.330512
H	-3.024628	-4.276583	9.208515
H	-1.608615	-4.379355	10.247436
C	-1.165896	-4.359664	8.127003
H	-0.112100	-4.100641	8.294321
H	-1.207986	-5.448388	8.012519
C	-1.651482	-3.683216	6.847634
H	-2.678509	-4.011050	6.647019
H	-1.042051	-3.993567	5.990663
C	-2.073832	0.473317	5.840213
H	-2.930738	0.542990	6.524309
C	-2.353733	1.364382	4.625837
H	-1.528708	1.264262	3.908970
H	-3.259032	1.049068	4.100597
C	-2.486395	2.830326	5.030678
H	-2.667863	3.435960	4.136726

$[\{(Cy_3P)_2Pt\}_2(PbCl_2)]$
E(scf) = -5348.73820028 a.u.

Pb	-0.021676	0.051442	-0.625070
Cl	0.138358	2.237450	-1.971002
Cl	-0.432245	-1.416753	-2.714854
Pt	2.733596	0.105395	0.067948
P	2.922824	2.086135	1.236640
P	3.641273	-1.596088	-1.184904
Pt	-2.745266	-0.154193	0.121804
P	-2.717715	-2.049731	1.416305
P	-3.821106	1.473838	-1.089671
C	1.914208	2.377340	2.753540
H	2.317430	3.270767	3.246712
C	2.037260	1.197727	3.720893
H	1.642689	0.302352	3.225332
H	3.086706	0.982747	3.947196
C	1.272374	1.465298	5.014831
H	1.353485	0.600757	5.683536
H	1.736600	2.311642	5.539187
C	-0.193400	1.783020	4.737552
H	-0.714000	2.026200	5.670584
H	-0.681363	0.890817	4.327251
C	-0.335603	2.925408	3.737397
H	0.040702	3.854284	4.187162
H	-1.392369	3.094863	3.502535
C	0.438857	2.642788	2.451939
H	0.004717	1.763412	1.956683
H	0.324361	3.482399	1.759875
C	4.684713	2.314397	1.817667
H	5.150372	2.834742	0.968332
C	5.446277	0.996433	1.990529
H	5.018560	0.425179	2.825043
H	5.309765	0.382087	1.095564
C	6.930862	1.244457	2.247902
H	7.451309	0.290029	2.386356
H	7.373205	1.716508	1.359949
C	7.149145	2.147187	3.457256
H	6.805605	1.628843	4.362484
H	8.216757	2.349561	3.596545
C	6.375832	3.451985	3.304672
H	6.787291	4.023399	2.461746
H	6.500107	4.075920	4.196737
C	4.890170	3.191953	3.059660
H	4.475121	2.686344	3.940289
H	4.363046	4.144876	2.968890
C	2.621792	3.581292	0.194006
H	1.557743	3.504383	-0.062562
C	2.872970	4.939013	0.854856
H	2.330495	5.024795	1.803442

H	-3.364565	2.953829	5.679660	H	3.941157	5.044229	1.084376
C	-1.243283	3.321059	5.763012	C	2.468315	6.081445	-0.075676
H	-1.366771	4.364515	6.073450	H	1.388420	6.028004	-0.265058
H	-0.387439	3.291574	5.076352	H	2.657254	7.043735	0.413820
C	-0.950163	2.439726	6.971335	C	3.218586	5.998648	-1.400514
H	-0.031867	2.766760	7.471586	H	2.899038	6.805628	-2.069144
H	-1.762172	2.545015	7.704094	H	4.291452	6.148988	-1.216095
C	-0.819609	0.972240	6.570354	C	2.999203	4.643212	-2.062976
H	-0.613315	0.368813	7.460956	H	3.578037	4.575847	-2.991115
H	0.041771	0.847873	5.900791	H	1.944593	4.532088	-2.340422
C	3.193011	-2.618232	5.086016	C	3.376718	3.489644	-1.136676
H	3.596526	-1.671960	5.473709	H	3.139985	2.535358	-1.616505
C	2.288999	-3.193874	6.181739	H	4.461868	3.509890	-0.959892
H	1.460082	-2.502926	6.371349	C	4.483349	-0.859264	-2.654761
H	1.836541	-4.132382	5.835104	H	4.983599	-1.672929	-3.197029
C	3.070232	-3.444847	7.469992	C	5.551618	0.171874	-2.277214
H	3.419877	-2.482936	7.868869	H	5.088194	0.954878	-1.663415
H	2.409647	-3.877043	8.229767	H	6.337760	-0.287413	-1.667957
C	4.270154	-4.355057	7.232174	C	6.188623	0.792228	-3.519340
H	3.916182	-5.351561	6.936114	H	6.929387	1.541495	-3.217738
H	4.839489	-4.485807	8.158831	H	6.735906	0.015008	-4.070418
C	5.164470	-3.794219	6.132777	C	5.143305	1.415352	-4.437096
H	6.001042	-4.473888	5.936984	H	4.663261	2.256967	-3.921130
H	5.602957	-2.844568	6.467618	H	5.620821	1.824585	-5.334382
C	4.378566	-3.560139	4.843913	C	4.079792	0.391657	-4.817576
H	4.009359	-4.526648	4.478088	H	4.539231	-0.400674	-5.425002
H	5.046848	-3.166035	4.073423	H	3.306120	0.855976	-5.437723
C	2.588443	-3.383060	2.306238	C	3.435335	-0.224408	-3.579087
H	3.644201	-3.662507	2.406740	H	2.893274	0.550573	-3.021565
C	1.729773	-4.621229	2.589307	H	2.679989	-0.957374	-3.880018
H	1.893757	-4.982330	3.611190	C	2.650377	-2.968276	-1.927344
H	0.670987	-4.333140	2.535479	H	1.789319	-2.427640	-2.338358
C	2.012434	-5.738513	1.588084	C	2.089727	-3.916991	-0.865462
H	3.047922	-6.083579	1.712967	H	2.900506	-4.517211	-0.432568
H	1.367200	-6.598143	1.800908	H	1.649382	-3.336568	-0.045587
C	1.810063	-5.259256	0.154390	C	1.050170	-4.856682	-1.471622
H	2.050264	-6.061561	-0.551892	H	0.663714	-5.536695	-0.702746
H	0.751601	-5.010956	0.000143	H	0.205704	-4.260241	-1.836572
C	2.658780	-4.025959	-0.132366	C	1.641492	-5.650801	-2.631201
H	2.469438	-3.651592	-1.143094	H	2.435812	-6.311265	-2.256202
H	3.722763	-4.295652	-0.085866	H	0.877977	-6.297424	-3.077384
C	2.379415	-2.907004	0.866940	C	2.218333	-4.711175	-3.683900
H	1.342917	-2.578918	0.723977	H	1.406140	-4.114181	-4.117281
H	3.008216	-2.045447	0.628210	H	2.666728	-5.284400	-4.503291
C	3.152023	-0.581706	2.989539	C	3.261717	-3.766906	-3.085611
H	2.686160	-0.346377	2.023426	H	3.622903	-3.098823	-3.872683
C	4.657508	-0.754686	2.771013	H	4.122827	-4.352287	-2.744819
H	4.862245	-1.597254	2.101070	C	5.026745	-2.312881	-0.183907
H	5.143403	-0.977482	3.730485	H	5.689677	-1.444440	-0.069954
C	5.271406	0.520592	2.196169	C	5.854367	-3.429296	-0.824874
H	6.349777	0.380964	2.059627	H	5.243057	-4.335114	-0.913209
H	4.845460	0.705394	1.202676	H	6.164983	-3.155007	-1.838905
C	5.000876	1.715500	3.104403	C	7.080986	-3.747849	0.028920
H	5.512958	1.565269	4.065344	H	7.658321	-4.556089	-0.433613
H	5.419695	2.627401	2.664709	H	7.738772	-2.868648	0.058619

C	3.505104	1.886605	3.348201	C	6.680742	-4.128268	1.450986
H	3.004662	2.135950	2.405127	H	7.571799	-4.322421	2.058155
H	3.321942	2.721150	4.034448	H	6.107878	-5.064981	1.424480
C	2.874224	0.614067	3.907934	C	5.828086	-3.036949	2.091353
H	1.792591	0.747892	4.012899	H	6.435235	-2.130101	2.216074
H	3.279404	0.421461	4.911818	H	5.510622	-3.341571	3.095003
Pt	-0.043395	1.678461	-4.165964	C	4.606346	-2.705177	1.237486
Pb	0.899113	1.177666	-1.614096	H	3.942423	-3.576735	1.208696
Cl	3.270424	0.161012	-1.389322	H	4.033625	-1.886290	1.687290
Cl	-0.242574	-1.157764	-1.425402	C	-1.136650	-2.863413	1.946161
P	1.873347	1.297106	-5.366299	H	-0.542957	-2.834833	1.019760
P	-2.251605	2.079573	-3.568498	C	-1.203910	-4.326064	2.401307
C	3.491235	1.783790	-4.630934	H	-1.806287	-4.407052	3.312844
H	3.614883	1.029696	-3.842006	H	-1.690059	-4.948957	1.645220
C	4.721375	1.705688	-5.538827	C	0.194725	-4.879287	2.675123
H	4.669486	2.495212	-6.298845	H	0.117849	-5.914771	3.025036
H	4.760752	0.749002	-6.071013	H	0.759475	-4.907678	1.734764
C	5.997274	1.900666	-4.720768	C	0.952775	-4.030484	3.688879
H	6.872446	1.846445	-5.378033	H	1.964413	-4.425177	3.833898
H	6.089468	1.080880	-3.997185	H	0.448278	-4.092150	4.662829
C	5.973054	3.232028	-3.976545	C	1.010374	-2.572788	3.245770
H	5.981134	4.053309	-4.706603	H	1.611238	-2.480962	2.332042
H	6.877814	3.342641	-3.369138	H	1.510549	-1.966940	4.009315
C	4.731120	3.346092	-3.097481	C	-0.389127	-2.023686	2.985341
H	4.773704	2.590509	-2.304065	H	-0.947989	-2.037187	3.928822
H	4.701795	4.325941	-2.607824	H	-0.337133	-0.978648	2.657209
C	3.454521	3.137304	-3.909698	C	-3.605162	-3.408147	0.530567
H	2.574258	3.194884	-3.258442	H	-3.650722	-4.277818	1.199625
H	3.349857	3.953241	-4.633731	C	-2.820825	-3.794604	-0.728839
C	1.624466	2.158161	-6.990766	H	-2.706885	-2.906974	-1.363199
H	0.587200	1.884579	-7.232131	H	-1.805388	-4.111683	-0.471290
C	2.487880	1.724502	-8.181165	C	-3.515611	-4.904596	-1.512020
H	2.463077	0.638663	-8.312096	H	-2.936931	-5.130756	-2.413837
H	3.533870	1.996669	-8.007889	H	-3.536377	-5.823728	-0.909788
C	2.001627	2.400247	-9.463583	C	-4.941599	-4.511550	-1.878642
H	0.985529	2.050314	-9.691040	H	-4.914082	-3.653146	-2.562306
H	2.633110	2.095196	-10.305252	H	-5.439771	-5.327702	-2.413484
C	1.993211	3.919649	-9.330512	C	-5.731572	-4.135935	-0.630582
H	3.024628	4.276583	-9.208515	H	-5.838975	-5.021954	0.010149
H	1.608615	4.379355	-10.247436	H	-6.745753	-3.819607	-0.899171
C	1.165896	4.359664	-8.127003	C	-5.041228	-3.024813	0.158285
H	0.112100	4.100641	-8.294321	H	-5.013776	-2.106460	-0.442606
H	1.207986	5.448388	-8.012519	H	-5.630806	-2.804579	1.054750
C	1.651482	3.683216	-6.847634	C	-3.792306	-1.718877	2.888400
H	2.678509	4.011050	-6.647019	H	-4.737309	-1.459597	2.388640
H	1.042051	3.993567	-5.990663	C	-3.393516	-0.468732	3.680356
C	2.073832	-0.473317	-5.840213	H	-2.474828	-0.657862	4.245069
H	2.930738	-0.542990	-6.524309	H	-3.177504	0.353787	2.989142
C	2.353733	-1.364382	-4.625837	C	-4.497036	-0.082572	4.662581
H	1.528708	-1.264262	-3.908970	H	-4.194167	0.801268	5.234976
H	3.259032	-1.049068	-4.100597	H	-5.398712	0.199202	4.102315
C	2.486395	-2.830326	-5.030678	C	-4.825719	-1.236162	5.605924
H	2.667863	-3.435960	-4.136726	H	-3.954039	-1.439416	6.242568
H	3.364565	-2.953829	-5.679660	H	-5.645791	-0.959027	6.277319
C	1.243283	-3.321059	-5.763012	C	-5.182889	-2.500839	4.830691

H	1.366771	-4.364515	-6.073450	H	-6.118187	-2.337249	4.278613
H	0.387439	-3.291574	-5.076352	H	-5.367883	-3.331053	5.521319
C	0.950163	-2.439726	-6.971335	C	-4.079110	-2.879764	3.843254
H	0.031867	-2.766760	-7.471586	H	-3.169695	-3.121937	4.407096
H	1.762172	-2.545015	-7.704094	H	-4.364275	-3.783868	3.294538
C	0.819609	-0.972240	-6.570354	C	-3.199128	3.204487	-1.046438
H	0.613315	-0.368813	-7.460956	H	-2.318863	3.128458	-1.698208
H	-0.041771	-0.847873	-5.900791	C	-2.652629	3.618629	0.323287
C	-3.193011	2.618232	-5.086016	H	-3.466644	3.719906	1.050646
H	-3.596526	1.671960	-5.473709	H	-1.987119	2.834235	0.699030
C	-2.288999	3.193874	-6.181739	C	-1.907728	4.947073	0.215062
H	-1.460082	2.502926	-6.371349	H	-1.538321	5.251247	1.201686
H	-1.836541	4.132382	-5.835104	H	-1.030447	4.804060	-0.428917
C	-3.070232	3.444847	-7.469992	C	-2.797191	6.039496	-0.371827
H	-3.419877	2.482936	-7.868869	H	-3.624790	6.244474	0.321244
H	-2.409647	3.877043	-8.229767	H	-2.234729	6.974191	-0.474222
C	-4.270154	4.355057	-7.232174	C	-3.368099	5.616931	-1.722033
H	-3.916182	5.351561	-6.936114	H	-2.549185	5.508685	-2.444769
H	-4.839489	4.485807	-8.158831	H	-4.036145	6.392673	-2.113137
C	-5.164470	3.794219	-6.132777	C	-4.116688	4.288999	-1.614601
H	-6.001042	4.473888	-5.936984	H	-4.983414	4.425290	-0.955460
H	-5.602957	2.844568	-6.467618	H	-4.504689	4.000264	-2.597612
C	-4.378566	3.560139	-4.843913	C	-5.556537	1.401544	-0.409533
H	-4.009359	4.526648	-4.478088	H	-5.709914	0.317297	-0.308856
H	-5.046848	3.166035	-4.073423	C	-6.704604	1.936451	-1.273695
C	-2.588443	3.383060	-2.306238	H	-6.604427	3.018751	-1.411339
H	-3.644201	3.662507	-2.406740	H	-6.684878	1.487821	-2.270879
C	-1.729773	4.621229	-2.589307	C	-8.055311	1.631948	-0.624693
H	-1.893757	4.982330	-3.611190	H	-8.862610	2.039539	-1.243211
H	-0.670987	4.333140	-2.535479	H	-8.200784	0.543449	-0.597695
C	-2.012434	5.738513	-1.588084	C	-8.143226	2.183402	0.793895
H	-3.047922	6.083579	-1.712967	H	-9.105677	1.919550	1.245920
H	-1.367200	6.598143	-1.800908	H	-8.101397	3.280322	0.759428
C	-1.810063	5.259256	-0.154390	C	-6.991383	1.666215	1.648820
H	-2.050264	6.061561	0.551892	H	-7.087186	0.578238	1.769457
H	-0.751601	5.010956	-0.000143	H	-7.036676	2.100431	2.653997
C	-2.658780	4.025959	0.132366	C	-5.644717	1.984162	1.004311
H	-2.469438	3.651592	1.143094	H	-5.527895	3.073804	0.958999
H	-3.722763	4.295652	0.085866	H	-4.823358	1.598475	1.618826
C	-2.379415	2.907004	-0.866940	C	-4.078321	1.122538	-2.883767
H	-1.342917	2.578918	-0.723977	H	-4.881637	1.788723	-3.226228
H	-3.008216	2.045447	-0.628210	C	-4.535282	-0.330051	-3.064702
C	-3.152023	0.581706	-2.989539	H	-3.740797	-0.985806	-2.685740
H	-2.686160	0.346377	-2.023426	H	-5.431442	-0.535301	-2.466605
C	-4.657508	0.754686	-2.771013	C	-4.808893	-0.654599	-4.530986
H	-4.862245	1.597254	-2.101070	H	-5.111182	-1.703912	-4.626344
H	-5.143403	0.977482	-3.730485	H	-5.654459	-0.049844	-4.888120
C	-5.271406	-0.520592	-2.196169	C	-3.582634	-0.372367	-5.391162
H	-6.349777	-0.380964	-2.059627	H	-2.767533	-1.041334	-5.089029
H	-4.845460	-0.705394	-1.202676	H	-3.799919	-0.581539	-6.444818
C	-5.000876	-1.715500	-3.104403	C	-3.128012	1.071798	-5.216605
H	-5.512958	-1.565269	-4.065344	H	-3.904956	1.747671	-5.602221
H	-5.419695	-2.627401	-2.664709	H	-2.224381	1.259710	-5.805715
C	-3.505104	-1.886605	-3.348201	C	-2.847274	1.396997	-3.751163
H	-3.004662	-2.135950	-2.405127	H	-2.005767	0.790662	-3.402635

H	-3.321942	-2.721150	-4.034448	H	-2.534808	2.441807	-3.668216
C	-2.874224	-0.614067	-3.907934	C	-2.874224	-0.614067	-3.907934
H	-1.792591	-0.747892	-4.012899	H	-1.792591	-0.747892	-4.012899
H	-3.279404	-0.421461	-4.911818	H	-3.279404	-0.421461	-4.911818

$PbCl_2$
E(scf) = -923.674595192 a.u.

Pb	0.000000	0.000000	0.462507
Cl	0.000000	1.850048	-1.115458
Cl	0.000000	-1.850048	-1.115458

[1] T. Yoshida, S. Otsuka, D. G. Jones, J. L. Spencer, P. Binger, A. Brinkmann, P. Wedemann, *Inorg. Synth.* **1990**, *28*, 113-119.
[2] J. P. Fackler Jr., J. A. Fetchin, J. Mayhew, W. C. Seidel, T. J. Swift, M. Weeks, *J. Am. Chem. Soc.* **1969**, *91*, 1941-1947.
[3] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122.
[4] 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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, **2010**.
[5] (a) Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, K. Hirao, *J. Chem. Phys.* **2004**, *120*, 8425-8433; (b) O. A. Vydrov, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 234109-234117; (c) O. A. Vydrov, J. Heyd, A. V. Krukau, G. E. Scuseria, *J. Chem. Phys.* **2006**, *125*, 074106-074114; (d) O. A. Vydrov, G. E. Scuseria, J. P. Perdew, *J. Chem. Phys.* **2007**, *126*, 154109-154117.
[6] (a) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284-298; (b) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299-310.
[7] (a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001; (b) R. Cammi, B. Mennucci, J. Tomasi, *J. Phys. Chem. A* **1999**, *103*, 9100-9108; (c) A. Klamt, G. Schüürmann, *J. Chem. Soc. Perkin. Trans 2* **1993**, *2*, 799-805; (d) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3094.
[8] (a) J. Aragó, J. C. Sancho-García, E. Ortí, D. Beljonne, *J. Chem. Theory Comput.* **2011**, *7*, 2068-2077; (b) L. Goerigk, H. Kruse, S. Grimme, *ChemPhysChem* **2011**, *12*, 3421-3433.