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Electronic Supplementary Material

Investigation of the effect of solvation on ^{1}J(Metal-P) spin-spin coupling

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Table S1. Atomic radii for PCM-1 and PCM-2

	PCM-1 (uff)		PCM-2 (bondi)	
	bohr	Angstrom	bohr	Angstrom
Hg	2.81	1.49	2.93	1.55
Se	4.37	2.31	3.59	1.90
Cl	4.10	2.17	3.31	1.75
P	4.31	2.28	3.40	1.80

Table S2. FC, PSO and DSO contributions to 1J(Zn-P) / Hz.

	$ZnLCl_2$, gas phase	$ZnLCl_2$, frozen	$ZnLCl_2$ + 6 $CHCl_3$
FC	132.0	154.4	178.3
DSO	0.1	0.1	0.1
PSO	3.1	3.3	2.8

Table S3. LMO contributions to J(Zn-P) / Hz. Boys localization. Only the dominating Fermi-contact contribution was considered.

	$ZnLCl_2$, gas phase	$ZnLCl_2$, frozen	$ZnLCl_2$ + 6 $CHCl_3$
Zn-P	371.3	411.0	439.5
2 x (Zn-Cl)	-81.0	-80.7	-66.2
Zn-Se	-25.3	-29.7	-34.5
3 x (P-C)	-110.3	-124.8	-141.8
Sum	154.6	175.8	197.0
FC	132.0	154.4	178.3

Computational procedure for obtaining LMO contributions.

All occupied and the first (lowest) layer of vacant MOs were localised using the Pipek-Mezey localization. The number of vacant MOs in the layer was equal to the number of valence MOs. The occupied and vacant MOs were localized separately in order to preserve the orthogonality of their subspaces. In order to obtain individual contributions, the linear response density matrix was transformed to the LMO basis. The contributions from individual excitations depend on which atom was chosen as a center of perturbation. The results were averaged between the two calculations. Among thus selected contributions all vacant LMOs were visualized to ensure the similarity for the two structures (that is the correctness of pair-wise matching).

Notes on computations

Spin-orbit effects on ^{1}J(Hg-P) were found to be small (about 2% of the total value), especially in comparison with the magnitude of solvent effects (about 50% or more of the total value). The use of a different functional (BP86 instead of PBE0) for the geometry optimization lead to practically the same value of ^{1}J(Hg-P) (2042.7 Hz versus 2041.5 Hz, gas-phase optimisation). The use of BP86-D3 resulted in the Cl-Hg-Cl angle of 123.7 deg. and R(Hg-P) = 2.52 Å, also close to the PBE0-D3 values (122.8 deg. and 2.53 Å, correspondingly).
For the X-ray structure with relaxed hydrogens the inclusion of PCM-1, $CHCl_3$ gave ^{1}J(Hg-P) = 4120.3 Hz whereas the gas-phase value was 3485.5 Hz. The direct solvent effect for this structure is consistent with graphs in Figure 3 (compare points for the Cl-Hg-Cl angle close to the X-Ray value, 100 deg.).

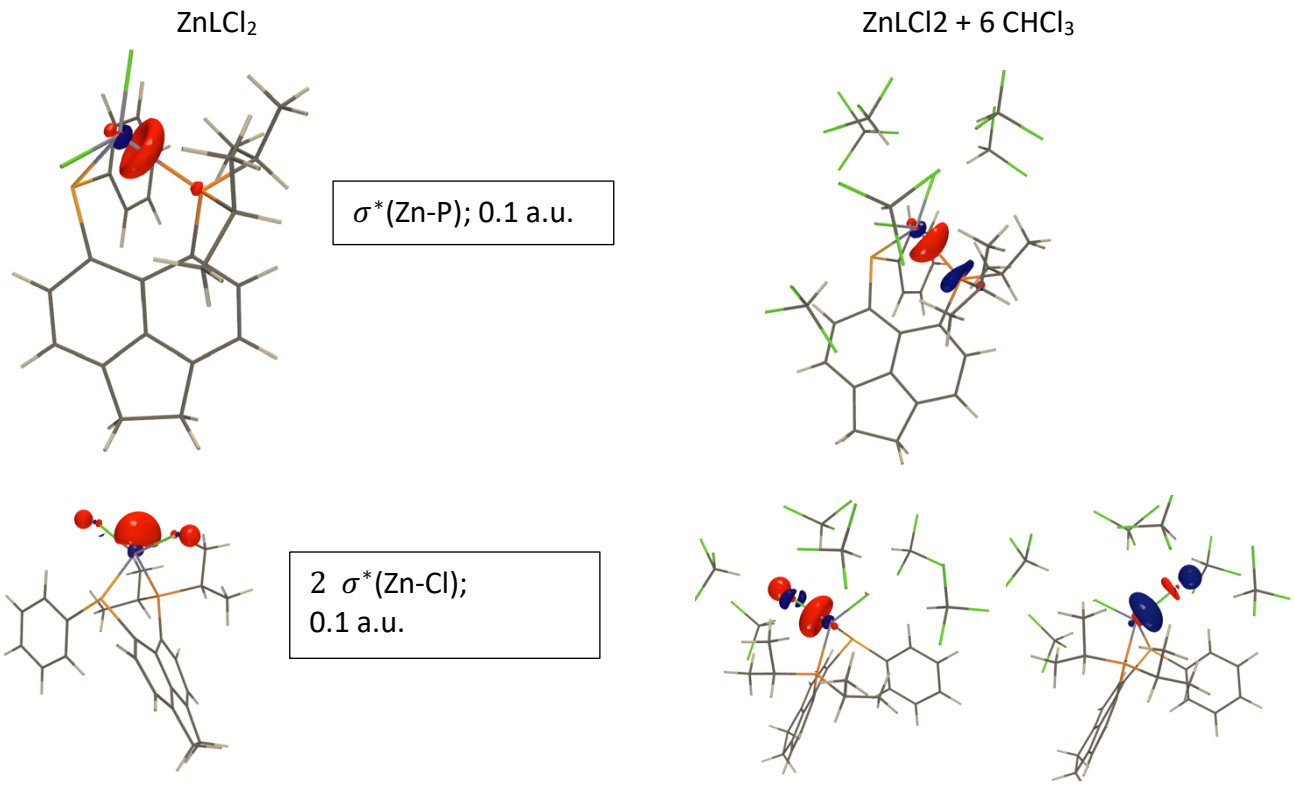

Figure S1. Plots of vacant LMOs mentioned in Table 6.

Table S4. The overlap of densities (in a.u.) of LMOs representing σ(Zn-P) and σ^*(Zn-Cl) orbitals. The overlap of densities is defined as

$$\Omega = \iint \varphi_i^2(\vec{r}_1)\delta(\vec{r}_1 - \vec{r}_2)\varphi_j^2(\vec{r}_2)dV_1\,dV_2 = \int \varphi_i^2(\vec{r})\varphi_j^2(\vec{r})dV$$

	Gas-phase	„Frozen“	+6 $CHCl_3$
Ω	7.33E-04	9.22E-04	7.71E-03

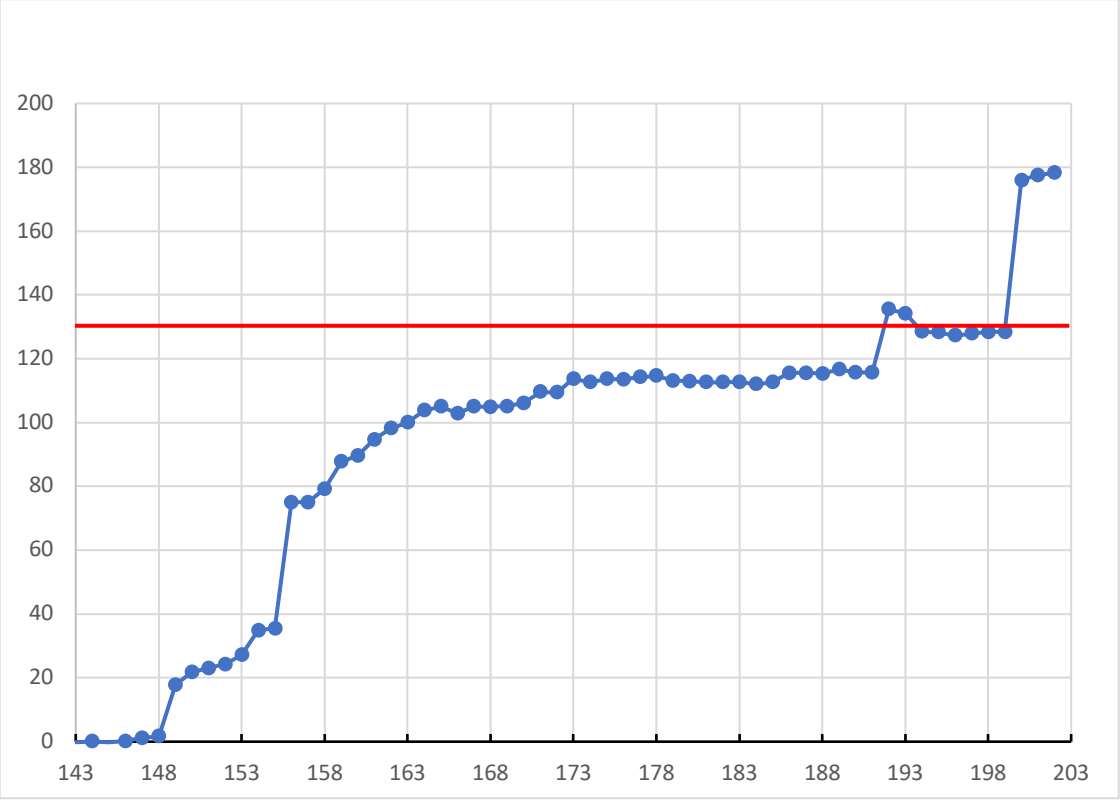

Figure S2. Convergence of the calculated ^{1}J(Zn-P) for the gas-phase structure with number of canonical vacant MOs included into consideration. The red line approximately corresponds to the total value of ^{1}J(Zn-P). In this calculation, the total number of MOs was 942 from which 142 were occupied.

Table S5. The average Hg-P bond lengths and Cl-Hg-Cl angles for differently optimised Hg dimer structures.

	Gas phase	PCM-1, $CHCl_3$	PCM-1, $CHCl_3$
Cl-Hg-Cl/deg.	102.9	100.9	100.1
R(Hg-P)/Å	2.47	2.48	2.48

The basis set used for Zn in non-relativistic calculations

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 8
405924.31028     .22442017483E-03
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