

Electronic Supplementary Information

Note 1. A role of a theoretical approximation level used for the BE computations.

As distinct from the earlier used approaches to modeling of adducts of IL components with the palladium clusters^{1,2} in the current study we use a triple-zeta quality basis set for Pd atoms and include van der Waals dispersion forces, which contribute substantially to the weak intermolecular interactions^{3,4} and must be regarded for a such kind of systems.^{5,6} At the same time for acceleration of calculations we work only with singlet ground state of Pd₅ and Pd₆ clusters. Nevertheless, our present approach produces addition energy (AE) of ~58 kcal/mol (see Eq. 1 of the main paper) for addition of a single Pd atom to Pd₅ cluster, which is only little less than ~64 kcal/mol obtained by the gas-phase PBE/6-31G*/LanL2DZ computations.¹ The value of binding energy (BE, Eq. 2 of the main paper) of *ca.* 21 kcal/mol for an adduct of the 1,3-dimethylimidazolium cation with the Pd₆ cluster (**f**, Figure 3 of the main paper) calculated within the framework of present approach also reasonably matches earlier obtained BE of ~14-15 kcal/mol (PBE/6-31G*/LanL2DZ or B3LYP/6-311+G**/LanL2DZ, gas phase).^{1,7} The difference should be attributed mainly to dispersion forces, which contribute almost 8 kcal/mol to the BE value.

In contrast, our present estimates of Pd₆ interactions with anions (Table 1S) differ essentially from our earlier published values of BE calculated at PBE/6-31G* level (e.g., ~40 kcal/mole for [BF₄]⁻/Pd₆ and ~31 kcal/mole for [PF₆]⁻/Pd₅ adducts).^{1,2} They differ also, though to a much lesser extent, from the B3LYP/6-311+G**/LanL2DZ estimates reported recently⁷ (~14 and ~10 kcal/mol for [BF₄]⁻/Pd₆ and [PF₆]⁻/Pd₆ adducts, respectively). The differences can be caused by the specific “anion problem” of DFT.⁸ In particular, the use of the hybrid functional PBE0 in present study instead of the semilocal functional PBE employed previously^{1,2} allowed to avoid overestimation of a charge transfer from anions to the palladium cluster. Namely, due to correct description of the HOMO - LUMO gap by the hybrid functionals, only 15-20% charge transfer was found at the present PBE0/def2-TZVP or at B3LYP/6-311+G**/LanL2DZ levels vs. almost 50% at the PBE/6-31G* level.^{1,2}

We performed test calculations of the binding energy (BE) for an adduct [PF₆]⁻/Pd₆ at the B3LYP/def2-TZVP level in the gas phase and obtained the BE of ~13 kcal/mole, which coincides with ~13 kcal/mol reported in Ref.7 Thus, only minor differences result from different choice of basis sets, provided that the latter are sufficiently large. Inclusion of dispersion corrections increases the BE up to ~21 kcal/mole (Table 1S).

In concern with the abovementioned “anion problem” of DFT special attention should be also paid to screening of charges by using of implicit solvation models to avoid erroneous shifts of the charges from the anionic centers. Our calculations of [PF₆]⁻/Pd₆ adduct in ethanol (COSMO model)⁹ demonstrate (Table 1S) that the implicit treatment of the media effects results in dramatic decrease of BE from ~21 to ~8 kcal/mol (~1 kcal/mole without inclusion of dispersion corrections). A comparison of these values with the corresponding BE ~11 kcal/mole computed⁷ at the B3LYP/6-311+G**/LanL2DZ level within the framework of PCM model¹⁰ confirms that interactions between anions and palladium clusters strongly depend on solvent effects. Smaller values of BE obtained from our computations can be explained by larger dielectric constant $\epsilon=24.85$ we used for COSMO modeling of medium effects relative to $\epsilon=11.4$ and 11.7 used in PCM computations.⁷

Data allowing to evaluate the role of various abovementioned factors influencing computed BEs (different DFT functional and basis sets, solvation effects and including of van der Waals dispersion forces) are collected in Table 1S.

Table 1S. Comparison of electronic energies (E, a.e.u) and binding energies (BE, kcal/mol) of several adducts of Pd_n (n=6, 15) and ions obtained within different functionals and the def2-TZVP basis set for the gas phase and the COSMO model simulations.

Energies	Gas phase			COSMO		
	B3LYP	TPSS	PBE0 ¹	B3LYP	TPSS	PBE0 ¹
E =	[Bu ₃ PC ₅ H ₁₁] ⁺ / Pd ₆ ²					
BE =	-1779.17554 (-1778.97045) ⁶ 26.5 (5.3) ⁶	-1779.76733 30.5	-1778.72354 24.2	-1779.23631 (-1779.03126) ⁶ 23.7 (2.6) ⁵	-1779.82855 27.4	-1778.78465 21.0
E =	[Bu ₃ PC ₅ H ₁₁] ⁺ / Pd ₁₅					
BE =		-2931.20405 35.4	-2930.18725 38.3		-2931.26793 33.4	-2930.25142 36.4
E =	[Mmim] ⁺ / Pd ₆ ³					
BE =	-1072.66066 (-1072.57313) ⁶ 26.6 (15.4) ⁶	-1072.85740 33.9	-1072.51936 29.6	-1072.73009 (-1072.64024) ⁶ 18.4 (5.7) ⁶	-1072.92652 25.0	-1072.58859 20.8
E =	[Mmim] ⁺ / Pd ₁₅					
BE =		-2224.28190 31.2	-2223.98341 44.0		-2224.35114 21.8	-2224.05099 33.5
E =	[PF ₆] ⁻ / Pd ₆ ⁴					
BE =	-1708.23991 (-1708.17206) ⁶ 21.0 (13.2) ⁶	-1708.48556 19.9	-1707.83208 18.8	-1708.30474 (-1708.23818) ⁶ 7.8 (0.9) ⁶	-1708.55112 6.4	-1707.89812 5.9
E =	[TFA] ⁻ / Pd ₆ ⁵					
BE =		-1294.02345 48.8	-1293.50367 24.3		-1294.08467 27.9	-1293.60284 26.9
E =	[TFA] ⁻ / Pd ₁₅					
BE =		-2445.46646 57.7	-2445.00656 63.0		-2445.51808 30.2	-2445.05815 35.1
E =	[Bu ₃ PC ₅ H ₁₁] ⁺					
BE =	-1011.68862 (-1011.56449) ⁶	-1012.32773	-1011.19989	-1011.75207 (-1011.62777) ⁶	-1012.39070	-1011.26374
E =	[Mmim] ⁺					
BE =	-305.17351 (-305.15113) ⁶	-305.41227	-304.98707	-305.25429 (-305.23188) ⁶	-305.49254	-305.06795
E =	[PF ₆] ⁻					
BE =	-940.76175 (-940.75352) ⁶	-941.06283	-940.31697	-940.84572 (-940.83749) ⁶	-941.14687	-940.40137
E =	[TFA] ⁻					
BE =		-526.55468	-525.97986		-526.64604	-526.07249
E =	Pd ₆					
BE =	-767.44468 (-767.39745) ⁶	-767.39095	-767.48512	-767.44651 (-767.39928) ⁶	-767.39411	-767.48741
E =	Pd ₁₅					
BE =		-1918.81988	-1918.92628		-1918.82393	-1918.92968

¹ Single point calculations based on TPSS-optimized structures.

² An adduct corresponds to the structure (d) from Figure 4 of the main manuscript.

³ An adduct corresponds to the structure (f) from Figure 4 of the main manuscript.

⁴ An adduct corresponds to the structure (o) from Figure 5 of the main manuscript.

⁵ An adduct corresponds to the structure (t) from Figure 5 of the main manuscript.

⁶ Values obtained WITHOUT including of the dispersion corrections are given in parenthesis.

⁷ The most stable structure of Pd₁₅ with O_h symmetry (a fragment of the fcc lattice with six corner atoms and eight off-plane face-centered atoms, plus an additional body-centered atom) was taken.¹¹ The results demonstrated that though BEs depended on the size of Pd cluster, their RELATIVE values practically did not change. Namely, the BE values in the case of [TFA]⁻/Pd₁₅, [Mmim]⁺/Pd₁₅ and [Bu₃PC₅H₁₁]⁺/Pd₁₅ are very close to each other and amount to *ca.* 35 kcal·mol⁻¹. The similar trend was obtained for the BEs of adducts [TFA]⁻/Pd₆, [Mmim]⁺/Pd₆ and [Bu₃PC₅H₁₁]⁺/Pd₆: the BE values were approximately equal to each other (*ca.* 25 kcal·mol⁻¹). Thus, the results of the computations of the RELATIVE strength of the cluster-cation interactions are practically independent of the size of the model chosen for the computations.

Table 2S. Atom charges of Pd_n clusters (n=6, 15, 23) obtained from atomic populations analysis of total density.^{1,2}

Pd ₆		Pd ₁₅		Pd ₂₃	
Number of an atom	Charge	Number of an atom	Charge	Number of an atom	Charge
1	0.00	1	-1.51	1	-2.20
2	0.00	2	-0.07	2	-1.32
3	0.00	3	-1.31	3	-2.20
4	0.00	4	-0.94	4	-0.12
5	0.00	5**	10.57	5	-1.47
6	0.00	6	-0.27	6**	20.52
		7	-1.03	7	-1.32
		8	-0.20	8	-1.47
		9	-1.30	9	-0.09
		10	-1.02	10	-1.34
		11	-0.14	11	-1.47
		12	-0.20	12	-2.20
		13	-1.51	13	-0.07
		14	-0.94	14	-0.09
		15	-0.12	15	-1.34
				16	-1.47
				17	-0.12
				18	-2.20
				19	-0.07
				20	0.01
				21	0.01
				22	0.01
				23	0.01

¹ Single point PBE0/def2-TZVP/COSMO calculations based on TPSS/def2-TZVP/COSMO optimized structures. Body-centered atoms are marked in bold.

² We checked if a surface of clusters is partially charged by population analysis on the bare clusters Pd₆, Pd₁₅ and Pd₂₃. The most stable structures of Pd₁₅ and Pd₂₃ species were taken from the work of H. Zhang et al.¹¹ According to our calculations, all atoms in the cluster Pd₆ are uncharged, and hence the surface charge has no influence on interaction between the cluster and either cations or anions. For Pd₁₅ and Pd₂₃ clusters charge redistribution takes place, leading to a negatively charged surface and a positively charged body-centered atom. This suggests preferable interaction of these larger clusters with cationic rather than with anionic components of IL. Indeed, the computed BE for the [TFA]/Pd₁₅ adduct (Table 1S) increases relative to the [TFA]/Pd₆ adduct to lesser extent (*ca.* 35 kcal·mol⁻¹ vs *ca.* 27 kcal·mol⁻¹), than the BEs for [Mmim]⁺/Pd₁₅ and [Bu₃PC₅H₁₁]⁺/Pd₁₅ adducts relative to [Mmim]⁺/Pd₆ and [Bu₃PC₅H₁₁]⁺/Pd₆ adducts (*ca.* 36 kcal·mol⁻¹ vs *ca.* 21 kcal·mol⁻¹).

Note 2. Discussions of a possibility to use more concentrated solutions of Pd NPs in ILs.

The use of a concentrated solution of Pd NPs in IL would be preferable from the spectroscopic point of view, but, regretfully, NPs can be stabilized only in solutions of low concentrations. At higher concentrations NPs agglomerate much faster and form a “palladium black” precipitate after a shorter period of time. Moreover, our experience shows that even at maximal possible concentrations of Pd NPs in imidazolium-based IL (~ 1:5) IR spectroscopic markers of interactions between Pd NPs and components of the IL are utterly weak.¹² Thus, the moderate changes of IR spectra presented in the current manuscript are quite typical for such systems. It should be noted that the positions of the bands dependent on the interactions between Pd NPs and ILs agree well with previously published reliable experimental data.^{12,13}

Table 3S. Peak intensities of some bands of the [Tf₂N]⁻ anion in the IR spectra of [Bu₃PC₁₀H₂₁][Tf₂N] (A) and [Bu₃PC₁₀H₂₁][Tf₂N]-stabilized Pd-NPs (B) (see Figure 2 of the main Manuscript).

Frequencies, cm ⁻¹	Peak intensities, absorbance unit	
	A	B
653 (<i>cis</i>)	0.29	0.41
602 (<i>cis</i>)	0.65	0.82
617 (<i>trans</i>)	1.13	1.29
Ratio of intensities		
I_{653}/I_{617}	0.57	0.63
I_{602}/I_{617}	0.26	0.32
$I_{653+602}/I_{617}$	0.83	0.95

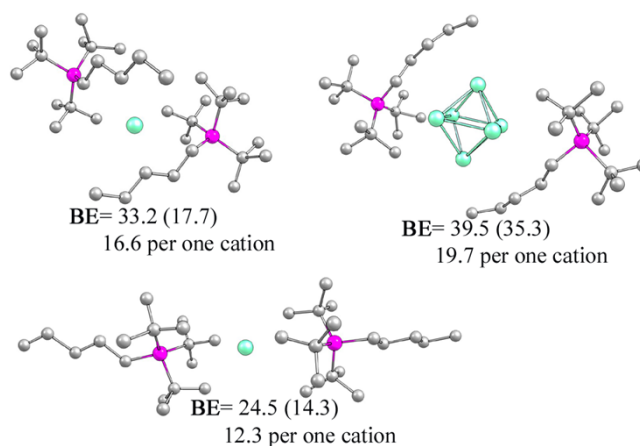


Figure 1S. Optimized structures of the associations of two [Bu₃PC₅H₁₁]⁺ cations with a Pd₆ cluster, including their binding energies (BE, kcal·mol⁻¹). The contribution of the D3 computed London dispersion energy to binding is given in parenthesis (kcal·mol⁻¹). Hydrogen atoms are omitted for clarity.

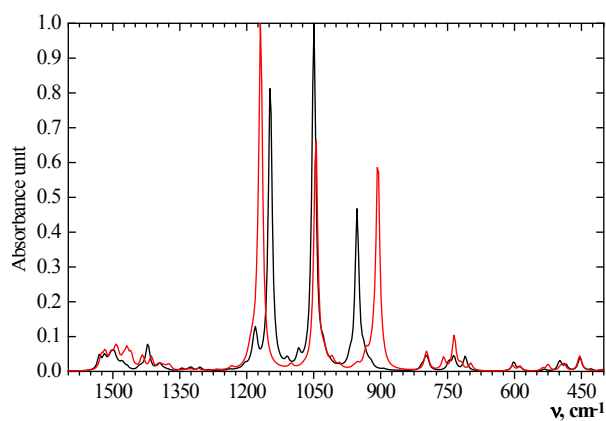


Figure 2S. Simulated IR spectra of the ion pair $[\text{Bu}^t_3\text{PC}_{10}\text{H}_{21}][\text{BF}_4]$ and the $[\text{Bu}^t_3\text{PC}_{10}\text{H}_{21}][\text{BF}_4]/\text{Pd}_6$ adduct.

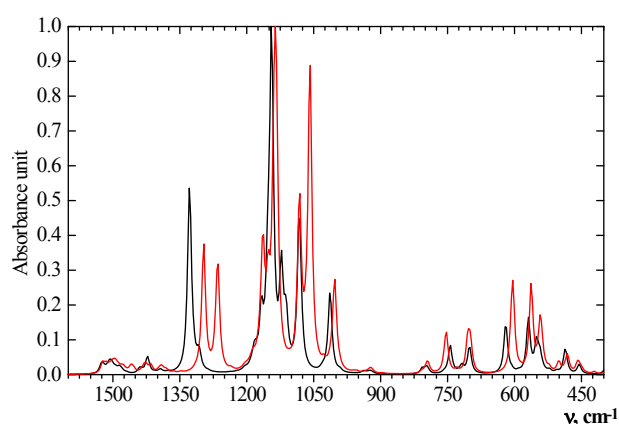


Figure 3S. Simulated IR spectra of the ion pair $[\text{Bu}^t_3\text{PC}_{10}\text{H}_{21}][\text{Tf}_2\text{N}]$ and the $[\text{Bu}^t_3\text{PC}_{10}\text{H}_{21}][\text{Tf}_2\text{N}]/\text{Pd}_6$ adduct.

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