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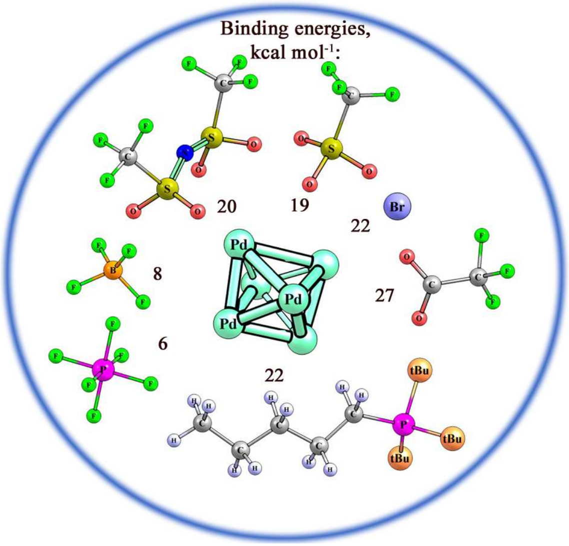

Pd nanoparticles interact with both the anions and cations of tri-*tert*-butyl-R-phosphonium-based ionic liquids. Dispersion forces dominate the cation-nanoparticle interactions.

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ARTICLE TYPE

Solvation and Stabilization of Palladium Nanoparticles in Phosphonium-Based Ionic Liquids: a Combined Infrared Spectroscopic and Density Functional Theory Study.

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Analysis of infrared spectra of palladium nanoparticles (NPs) immersed in the tri-*tert*-butyl-R-phosphonium-based ionic liquids (ILs) demonstrates that both cations and anions of the ILs interact with the NPs. According to quantum-chemical simulations of these interactions, binding energy of anions to the Pd_6 cluster, taken as minimal-size model of the NP, increases from ~6 to ~27 $kcal\cdot mol^{-1}$ in the order $[PF_6]^- \approx [BF_4]^- < [Tf_2N]^- < [OTf]^- < [Br]^- << [TFA]^-$. In contrast, the binding energy for all types of the $[Bu^t{}_3PR]^+$ cations slightly varies at about ~22 $kcal\cdot mol^{-1}$ only moderately depending on a choice of the moiety R (n-pentyl, 2-hydroxyethyl, 2-methoxyethyl, 2-ethoxy-2-oxoethyl). As a result, the energies of interaction between a Pd_6 cluster and various ion pairs, formed by the abovementioned counter-ions, follow the order found for the anions and vary from ~24 to ~47 $kcal\cdot mol^{-1}$. These values are smaller than the energy of addition of a Pd atom to a Pd_n cluster (~58 $kcal\cdot mol^{-1}$), which suggests kinetic stabilization of the NPs in phosphonium-based ILs rather than thermodynamic stabilization. The results are qualitatively similar to the trends found earlier for interactions between palladium clusters and components of imidazolium-based ILs, in spite of much larger contributions of the London dispersion forces to the binding of the $[Bu^t{}_3PR]^+$ cations to the cluster (up to 80%) relative to the case of 1-R-3-methylimidazolium cations (up to 40 %).

1. Introduction

Nowadays metal nanoparticles (M-NPs) find broad application in various areas of science due to their unique physicochemical properties based on an increased surface-area to volume ratio. At the same time as a result of high surface energy and relatively large surface area kinetically stable small M-NPs tend to form thermodynamically favoured larger metal particles. To avoid the agglomeration, that dramatically influences the NPs properties, M-NPs need to be stabilized with protective layers, created by polymers and surfactants[1,2,3] or within ionic liquids (IL).

As can be seem from the literature mainly imidazolium-based IL are used for solvation and stabilization of M-NPs that can be partially attributed to the moderate viscosities of these salts.[4,5,6] Using of phosphonium-based IL for stabilization of NPs is less recognized despite the obvious advantages such as a chemical inertness,[7] high thermal stability up to 300°C and a broad electrochemical window,[8] workability for the reaction involving strong bases.[9] For example, ultra-stable NPs can be synthesized in tetraalkylphosphonium halide ILs with an excess of the reducing agent ($LiBH_4$ or $LiAlH_4$).[10,11,12,13] Also Pd-NPs were prepared under an argon atmosphere by slow reduction of bis(benzonitrile)dichloropalladium(II) with ethylene glycol at 135°C and further extraction with tri-n-butyltetradecylphosphonium dodecylbenzenesulfonate.[14]

First steps in understanding of nature of interactions between metal clusters taken as models for NPs and various components of IL (imidazolium-[15,16,17,18] or ammonium-based cations[19] and different anions[15-20]) were performed using quantum chemical modeling. Density functional theory (DFT) calculations[15-20] suggested stronger interactions of gold, palladium and iron clusters with anions in comparison with the imidazolium- or ammonium-based cations.[21] At the same time, molecular dynamic simulations found both anions and cations in the first ordered layer of ions near the metal surface.[19] Direct evidence of

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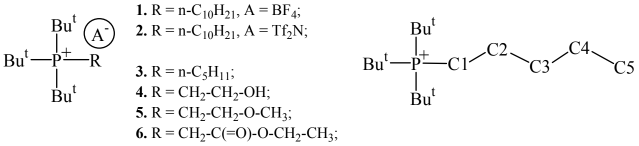
interactions between metal nanoparticles and both the anionic and cationic components of IL was delivered by various spectroscopic techniques (e.g., Ref. [16] and Refs. cited therein).

To the best of our knowledge, there was no attempt to study interactions between Pd-NPs and phosphonium-based IL. Therefore, in the present paper we consider Pd-NPs in ILs composed of tri-*tert*-butyl(decyl)phosphonium, $[Bu^t_3PC_{10}H_{21}]^+$, cations and tetrafluoroborate, $[BF_4]^-$, and bis(trifluoromethylsulfonyl)imide, $[Tf_2N]^-$, anions (Scheme 1). We employ infrared (IR) spectroscopy and dispersion-corrected DFT-D3 computations to study binding of various components of the phosphonium-based IL (Scheme 1) to (i) a Pd atom; (ii) a Pd_6 cluster; and (iii) to Pd nanoparticles. Finally, we compare the results of present study with earlier reported data on the modes of interaction of imidazolium-based ILs with Pd NPs for better understanding of the role of different ionic components of IL in stabilization and formation of nano-sized metal species in ILs.



1. R = n-$C_{10}H_{21}$, A = BF_4;
2. R = n-$C_{10}H_{21}$, A = Tf_2N;

3. R = n-C_5H_{11};
4. R = CH_2-CH_2-OH;
5. R = CH_2-CH_2-O-CH_3;
6. R = CH_2-C(=O)-O-CH_2-CH_3;

Chart 1. Tri-*tert*-butyl(decyl)phosphonium-based ILs and tri-*tert*-butyl-R-phosphonium cations investigated in the present paper; and an atom numbering scheme for the tri-*tert*-butyl(pentyl)phosphonium cation.

2. Experimental section

2.1. Synthetic details

IL $[Bu^t_3PC_{10}H_{21}][BF_4]$ and $[Bu^t_3PC_{10}H_{21}][Tf_2N]$ were synthesized according to the earlier described protocol.[8] All other chemicals were obtained from commercial sources and were used as received. Palladium nanoparticles were obtained by the reduction of palladium acetate in the presence of phosphonium salt. $Pd(OAc)_2$ (0.4 mg, 0.178 mmol) and $[Bu^t_3PC_{10}H_{21}][BF_4]$ (0.076 g, 17.8 mmol) or $[Bu^t_3PC_{10}H_{21}][Tf_2N]$ (0.111 g, 17.8 mmol) were dissolved in ethanol (5 ml) and solutes were stirred for 15 min at room temperature. The solution was stirred until it turned pale gray in color indicating that Pd nanoparticles had formed. Solvent was removed under vacuum and sample was dried for 12h. The A&D Gemini GR-202 Analytical Balance (with dual resolutions starting at 0.1mg and with Automatic Internal Calibration) was used for precise measurements of reactants.

2.2. High-resolution transmission electron microscopy

HRTEM was carried out on a Philips Tecnai F30 electron microscope operated at 300 kV. For HRTEM analysis, the Pd NPs were dispersed in ethanol following their separation from the $[Bu^t_3PC_{10}H_{21}][BF_4]$ IL by centrifugation. One drop of the solution was placed onto a copper grid coated by a carbon film and dried under vacuum at 343 K for 24 h, and subject to HRTEM measurements. The average particle sizes of the Pd NPs were determined from ca. 300 NPs. TEM shows that these individual Pd-NPs have an average size of 1.68 ± 0.87 nm, but tend to aggregate with each other due to a low concentration of IL used. (Figure 1, top). In case of simple heating of mixture of 0.5 g neat $[Bu^t_3PC_{10}H_{21}][BF_4]$ IL and 0.4 mg palladium acetate we observed as a result only individual NPs with a larger average size of 3.45 ± 1.09 nm (Figure 1, bottom).

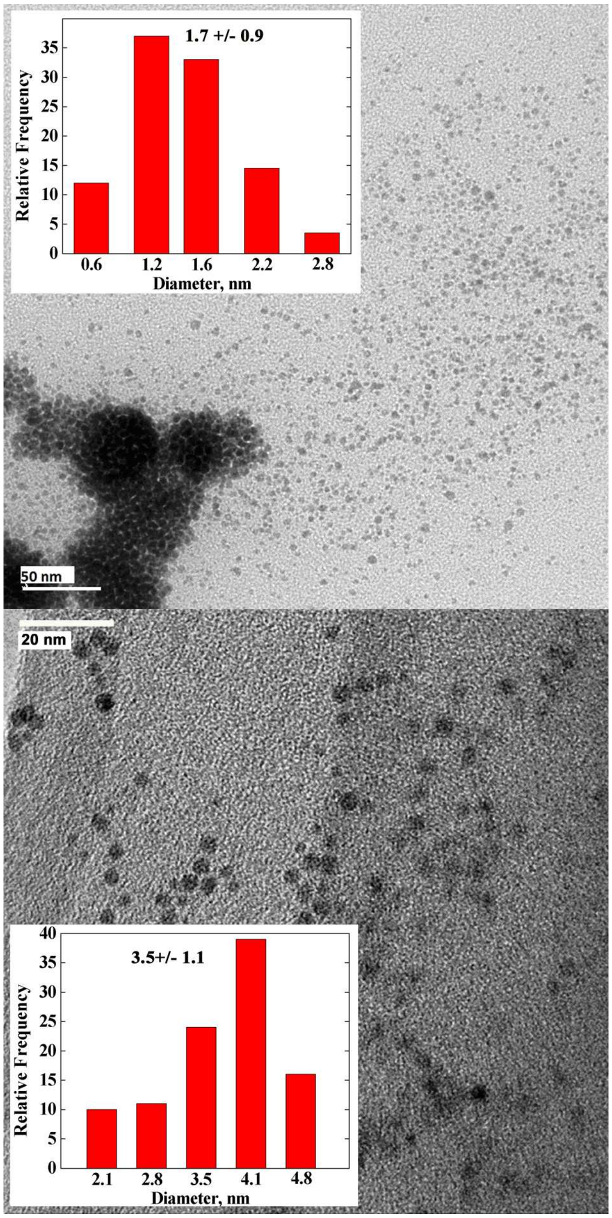


Figure 1. Typical TEM and HRTEM images of the Pd-NPs synthesized in $[Bu^t_3PC_{10}H_{21}][BF_4]$ (**1**).

2.3. IR spectroscopy

Mid-IR spectra were recorded on a FTIR spectrometer "Tensor 27" (Bruker) at an optical resolution of 4 cm^{-1} at room temperature. 256 scans were averaged for each spectrum (for some comments see Note 2, ESI). The base-line correction and normalization relative to the strongest anion bands (as this procedure is implemented in the OPUS 6.0 suit of program[22]) were applied to all registered spectra in the 1700–400 cm^{-1} spectral range. In further comparison of spectra of pure ILs and IL-stabilized NPs the band of *tert*-butyl group bending vibrations (δCH_3)[23,24] at 1403 cm^{-1} was used as an internal standard: its intensity was supposed to remain constant in the spectra of the both systems. After equalization of the intensities of the band at 1403 cm^{-1} in the compared spectra the contours of this band in the both spectra always coincided as well as the contours of another δCH_3 band at 1386 cm^{-1} used for control.

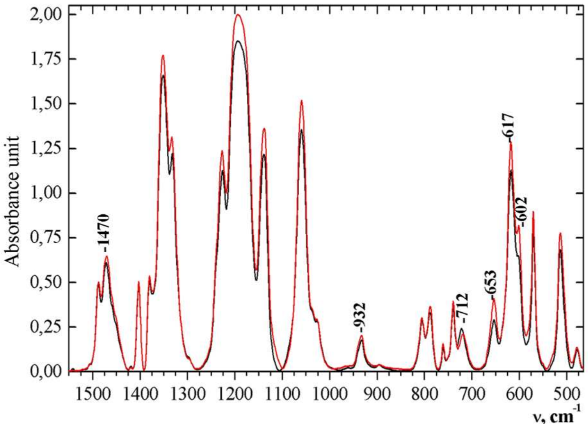


Figure 2. Experimental IR spectra of [$Bu^t_3PC_{10}H_{21}$][BF_4] (**1**, black) and [$Bu^t_3PC_{10}H_{21}$][BF_4]-stabilized Pd-NPs (red).

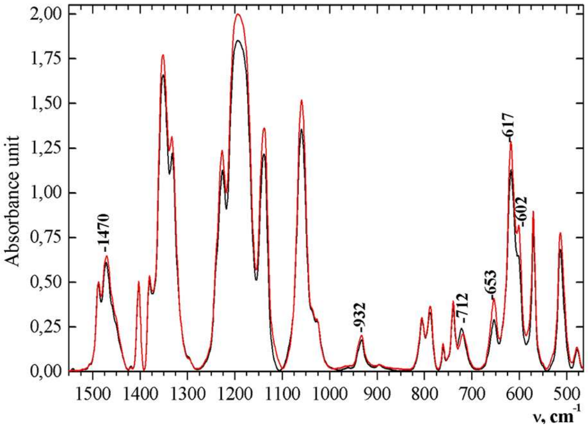


Figure 3. Experimental IR spectra of [$Bu^t_3PC_{10}H_{21}$][Tf_2N] (**2**, black) and [$Bu^t_3PC_{10}H_{21}$][Tf_2N]-stabilized Pd-NPs (red).

The solid samples of [$Bu^t_3PC_{10}H_{21}$][BF_4] (**1**) and [$Bu^t_3PC_{10}H_{21}$][BF_4]-stabilized NPs were prepared as KBr-pellets. For [$Bu^t_3PC_{10}H_{21}$][Tf_2N] (**2**) and [$Bu^t_3PC_{10}H_{21}$][Tf_2N]-stabilized NPs liquid samples of were placed between KBr plates.

2.4. Computational Details.

All gas-phase calculations were performed with the TURBOMOLE 6.4 program package.[25] The TPSS[26] functional and the Ahlrich's triple-ζ def2-TZVP[27] AO basis set (with effective core potentials for the Pd atom) and accompanying auxiliary basis set taken from the TURBOMOLE basis set library[28,29,30] were used for a preliminary optimization of all structures. Obtained stationary points were characterized as minima by frequency analysis of the Hessian matrices. Subsequently, optimization of the structures with the conductor-like screening model (COSMO)[31] with a dielectric constant ε=24.85 (to simulate the "real" environment[32]) was conducted employing the same functional and basis set. Based on these re-optimized structures single-point calculations within the hybrid PBE0 functional[33] (together with the def2-TZVP and COSMO, ε=24.85) were performed and electronic energies obtained were further used for the discussions. In all calculations the RI-JK approximation for the two-electron integrals[34,35,36,37] and the D3 approach[38] to describe the London dispersion interactions together with the Becke–Johnson (BJ) damping function[39,40,41] were employed as implemented in the TURBOMOLE program. DFT-D3 was recently benchmarked for various prototype IL interactions and found to provide results close to those of CCSD(T) benchmark quality.[42]

On the grounds of a computational analysis published elsewhere,[17] the Pd_6 cluster in the octahedral structure (as the most stable one),[43] was used as a minimal-size model for a Pd-NP. Previous modelling of palladium clusters with the various accessible spin multiplicities[15,18,43,44,45,46,47] demonstrates that the spin multiplicities of low-energy states are higher than singlet. In particular Pd_n clusters with $2 \leq n \leq 6$ have a triplet ground state. But calculations of metallic clusters with an open-shell electronic configuration are more CPU time expensive and often show SCF convergence problems, therefore in the current study a palladium cluster Pd_6 with a closed-shell configuration in the singlet ground state were used. Several preliminary investigations for the systems under study with different multiplicities and different-size Pd clusters (Table 1S, 2S) have shown that at least the trends in the relative interaction strength between Pd_n particles and various components of ILs remain the same in all cases.

The strength of the metal-metal interaction was characterized by the addition energy (AE) defined as the difference of the energies of the optimized Pd_n cluster and a single Pd atom to the energy of the optimised Pd_{n+1} cluster:

$$AE = E(Pd_n) + E(Pd) - E(Pd_{n+1}) \qquad (1)$$

The strength of the metal-IL stabilizing interaction was characterized by the binding energy (BE) defined as the difference of the energies of the optimized stabilizing substrates (cations, anions, ion pairs and aggregates of these IL entities) and the Pd_n clusters relative to the energy of their adducts:

$$BE = E(\text{substrate}) + E(Pd_n) - E(\text{substrate}/Pd_n \text{ adduct}) \qquad (2)$$

The ball-and-stick pictures were created with ChemCraft 1.6,[48] the diagrams using Xmgrace.[49]

3. Results and discussion

3.1. IR spectra

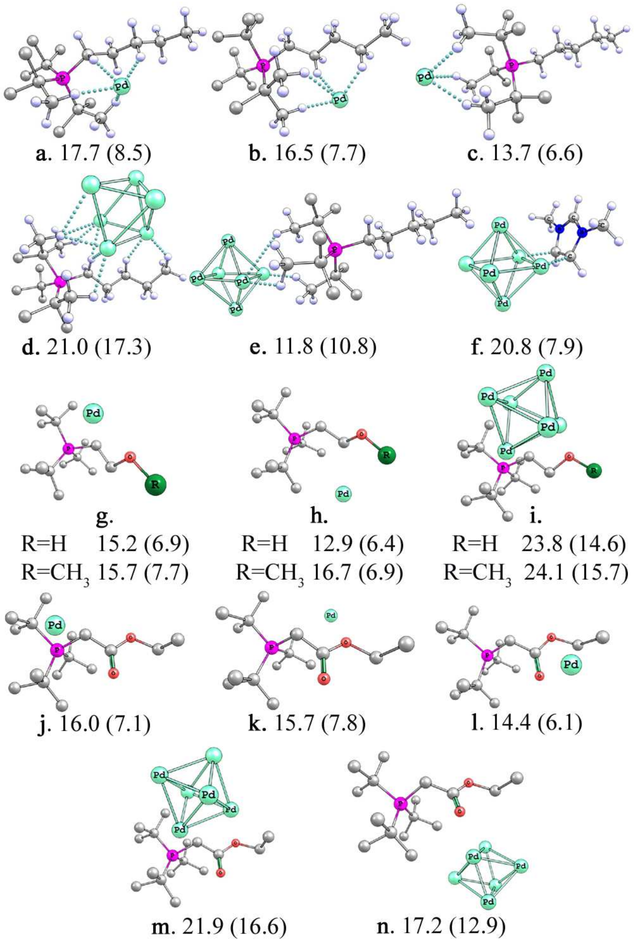
An IR spectrum of the [$Bu^t_3PC_{10}H_{21}$][BF_4]-stabilized NPs compared with a spectrum of the pure IL **1** is given in Figure 2. As in the case of [Emim][BF_4]-stabilized NPs the "anion - NP" interaction manifests itself in the appearance of an additional band at ~1250 cm^{-1} (Figure 2, red), which is assigned to the $\nu_{as}BF_4^-$ stretching vibrations of the anion interacting with the Pd-NP surface.[16] This band is very weak relative to the main broad $\nu_{as}BF_4^-$ feature at ~1050 cm^{-1}, because intensity of the latter is a sum of intensities of the overlapping $\nu_{as}BF_4^-$ bands of the bulk IL and of the IL/palladium interface. This strongest complex band also changes due to the interaction of the anion with the Pd-NP surface (the intensity of 1082 and 1057 cm^{-1} peaks noticeably increases, Figure 2, red). Another new band at 532 cm^{-1} (Figure 2, red), which is absent in the spectrum of the pure IL (Figure 2, black), can be assigned to asymmetric bending vibrations of the anion BF_4^-.[16,50,51] A comparison of spectra reveals also small changes of some IR bands of the phosphonium cation, which can be caused by "cation – NP" interactions. For example, the growth of bands of the wagging vibrations of methylene groups at 1309, 1319 and 1340 cm^{-1} is clearly observed.

In the spectra of $[Bu^t_3PC_{10}H_{21}][Tf_2N]$ - stabilized NPs (Figure 3, red) small frequency shifts and intensity redistributions of some IR bands of cation can be seen as a result of "cation - NP interactions" (for example, the band 1470 cm^{-1} of -CH$_2$-scissoring, the band 932 cm^{-1} of -C(CH$_3$)$_3$ rocking and the band 712 cm^{-1} with contributions of P-C stretching and -CH$_2$- rocking). The "anion – NP" interactions are revealed by growth of bands of $[Tf_2N]^-$ vibrations below 1400 cm^{-1} (the origin of all $[Tf_2N]^-$ bands has been carefully investigated earlier in a number of papers[52,53,54,55,56,57,58]). For example, bands of the symmetric and asymmetric stretching vibrations of SO$_2$ groups at 1139 and 1353 cm^{-1}, respectively,[56,59] grow, similar to the reported effects found in time-resolved IR reflection/absorption spectra of [BMIM][Tf$_2$N] layers on Pd nanoparticles supported on an ordered alumina film.[60] Moreover, intensity of bands of a *cis*-conformer of the $[Tf_2N]^-$ anion at 653/602 cm^{-1} grows relative to the band of a *trans*-conformer at 617 cm^{-1} (Table 3S, ESI), which indicates a partial transformation of the *trans*-conformers into the *cis*-form.[61] Similar effects were reported to happen during interaction of the $[Tf_2N]^-$ anion with the surface of Pd-NPs.[52] Thus, the IR spectra provide an evidence of interactions of all ionic components of the studied ILs with Pd-NPs immersed in the ILs.

3.2. Quantum-chemical study of interaction between the palladium atom or Pd$_6$ cluster and the IL ions

To simplify computations of binding energies (BE) of a phosphonium cation to a palladium atom and a Pd$_6$ cluster, the $[Bu^t_3PC_5H_{11}]^+$ cation (**3**, Chart 1) in the most stable all-*trans* conformation of n-pentyl moiety was regarded as a model for the $[Bu^t_3PC_{10}H_{21}]^+$ cation. According to the published X-Ray data this zig-zag conformation is preferred for the nearest to the phosphorus atom part of the alkyl chain.[8] Possible adducts of the Pd atom or the Pd$_6$ cluster with the abovementioned cation **3** were optimized from various starting configurations.

During the optimization the Pd atom or cluster tended to shift closer to the phosphorus atom. As a result, three stable structures were found for adducts with the Pd atom (Figure 4). The most energetically preferred forms correspond to (**a**) and (**b**) structures with Pd···P distances of 3.85 and 4.51 Å, respectively. These structures are characterized by short contacts between the Pd atom and two hydrogen atoms of the n-alkyl chain (with Pd···H distances of 2.02 – 2.11 Å) and two hydrogen atoms of a *tert*-butyl group (distances of 2.09 – 2.24 Å). In the third stable structure (**c**) the Pd atom is located between the CH$_3$-groups of *tert*-butyl moieties at a distance of 4.05 Å from the P atom and has short contacts with three hydrogen atoms (distances of 2.06, 2.07 and 2.19 Å). According to our computations, the structure (**c**) is *ca.* 2-4 kcal·mol^{-1} less stable than the (**a**) and (**b**). Similar structures were obtained after optimization of $[Bu^t_3PC_5H_{11}]^+/Pd_6$ adducts (Figure 4, **d** and **e**). These are characterized by more multiple short contacts between palladium atoms and hydrogens of the cation in comparison with (**a**), (**b**), (**c**) structures. For example, in the case of structure (**d**) the Pd$_6$ cluster interacts with six hydrogen atoms, that increases the BE by *ca.* 3 kcal·mol^{-1} in comparison to the form (**a**). It should be noted that similar orientations of a butyl moiety of a n-butyltrimethylammonium cation parallel to a metal / IL interface was also found during MD simulations of ammonium-based ILs at the iron surface.[19]



a. 17.7 (8.5) **b.** 16.5 (7.7) **c.** 13.7 (6.6)

d. 21.0 (17.3) **e.** 11.8 (10.8) **f.** 20.8 (7.9)

g. **h.** **i.**

R=H 15.2 (6.9) R=H 12.9 (6.4) R=H 23.8 (14.6)

R=CH$_3$ 15.7 (7.7) R=CH$_3$ 16.7 (6.9) R=CH$_3$ 24.1 (15.7)

j. 16.0 (7.1) **k.** 15.7 (7.8) **l.** 14.4 (6.1)

m. 21.9 (16.6) **n.** 17.2 (12.9)

Figure 4. Optimized structures of associations of $[Bu^t_3PC_5H_{11}]^+$ (**3**, **a-e**), $[Mmim]^+$ (**f**), $[Bu^t_3PC_2H_4OR]^+$ (**4-5**, **g-i**) and $[Bu^t_3PCH_2C(O)OC_2H_5]^+$ (**6**, **j-n**) cations with a Pd atom and a Pd$_6$ 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}). Short contacts are shown with dotted lines. Some hydrogen atoms are omitted for clarity.

According to the present computations all the abovementioned contacts of hydrogen atoms with Pd atoms induce small elongations (2-4%) of the corresponding CH-bonds and a pronounced red shift of IR bands of CH stretching vibrations. A concomitant two- and four-fold increase of IR intensities is also found for νC3-H/νC5-H and νC3-H bands. In contrast, the formation of short contacts with CH-groups of *t*-Bu moieties produces practically negligible changes of IR intensities of the corresponding νC-H bands.

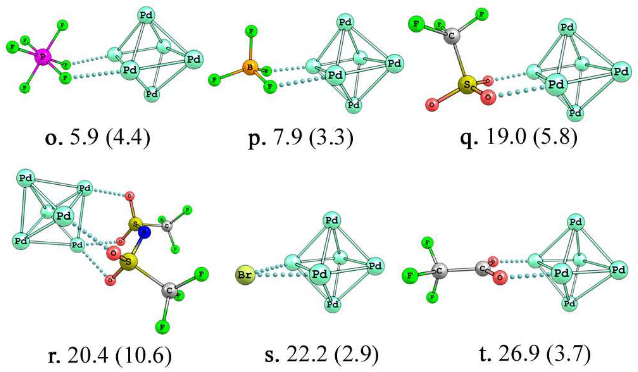
Adducts of the Pd atom or the Pd$_6$ cluster with two $[Bu^t_3PC_5H_{11}]^+$ cations were also optimized (Figure 1S, ESI). BEs for the most energetically stable adducts of this kind amount to ~33 and ~39 kcal·mol^{-1} for Pd and Pd$_6$, respectively, which correspond to a BE per cation of ~16 and ~19 kcal·mol^{-1}, respectively. Thus, the gross energy of the interaction of two cations with the palladium species roughly equals the doubled values of the corresponding energies computed for 1:1 species shown in Figure 4.

It is known that properties of ILs can be tuned by functionalization of cations. For example, the insertion of a hydroxyl group to alkyl moiety of 1-alkyl-3-methylimidazolium cation accelerates the formation of Pd NPs in the corresponding ILs compared with the case of non-functionalized imidazolium-based ILs, and also helps to protect the NPs once formed from oxidation.[17,62,63] To estimate possible influence of functionalization of phosphonium cations on formation and stabilization of Pd NPs in the phosphonium-based ILs, we optimized the adducts of some functionalized cations $[Bu^t_3PC_2H_4OR]^+$ (**4-5**, Chart 1 and **g-i**, Figure 4) and $[Bu^t_3PCH_2C(O)OC_2H_5]^+$ (**6**, Chart 1 and **j-n**, Figure 4) with the Pd atom or the Pd_6 cluster. Comparison of the computed BEs with those found for $[Bu^t_3PC_5H_{11}]^+$ (**a-e**, Figure 4) demonstrates that functionalization of the phosphonium cations influences their binding with the palladium species only moderately. Moreover, as can be seen from Figure 4, the average strength of interactions with the Pd_6 cluster/Pd atom amounts to *ca.* 22/16 kcal·mol^{-1} for all types of cations studied, including 1,3-dimethylimidazolium cation (**f**, Figure 4).

It should be mentioned that for all discussed structures the calculations show significant contributions of London dispersion forces to the total interactions between cations and the palladium species. In the case of adducts of phosphonium cations with a Pd atom the dispersion contributions are about 7-8 kcal·mol^{-1} (or *ca.* 50% of the BE), while for adducts with the Pd_6 cluster dispersion effects amount up to 18 kcal·mol^{-1} (or *ca.* 80% of BEs). In contrast, the corresponding value for the adduct $[Mmim]^+$ / Pd_6 is comparatively moderate (about 8 kcal·mol^{-1} or *ca.* 40% of BE).

The different character of the Pd_6 interactions with phosphonium- and imidazolium-based cations is exhibited also in different patterns of structural changes caused by formation of the cation/ Pd_6 adducts. The Pd_6 cluster strongly interacts with non-hydrogen atoms of the imidazolium ring causing a noticeable distortion of the ring structure as a result.[16] In case of the tetraalkylphosphonium cations the Pd_6 cluster forms multiple short contacts with CH-bonds, leading to moderate elongation of the latter and concomitant IR spectroscopic effects reminiscent of the effects of hydrogen bond formation. Despite of these pronounced differences in character of the cation- Pd_6 interactions, both imidazolium- and phosphonium-based cations bind to palladium species with roughly the same strength, irrespective of their functionalization.

Optimized structures of adducts of the Pd_6 cluster with various anions are shown in Figure 5. The present calculations indicate that perflouroanions $[BF_4]^-$ and $[PF_6]^-$ can interact with two Pd atoms of the Pd_6 cluster *via* two F atoms, in contrast to the earlier reported structure where one F atom is shared by two Pd atoms.[17,18] The optimization of $[BF_4]^-/Pd_6$ and $[PF_6]^-/Pd_6$ entities results in Pd···F distances of 2.39 and 2.54 Å, respectively (Figure 5, **p**, **o**). The $[OTf]^-$ anion also forms two short contacts of 2.26 Å with two Pd atoms of the Pd_6 cluster (Figure 5, **q**). Two even shorter Pd…O contacts of 2.18 Å are found for $[TFA]^-/Pd_6$ adduct (Figure 4, **t**). Optimization of $[Br]^-/Pd_6$ entity (Figure 5, **s**) results in two Pd…Br short contacts of 2.61 Å. For $[Tf_2N]^-/Pd_6$ adduct only a *cis*-conformer of the anion was regarded (Figure 4, **r**) because both present IR experiments (*vide supra*) and earlier reported studies[52] indicate that this conformer represents the major form of the anions interacting through the sulfonyl groups with the surface of Pd-NPs.



o. 5.9 (4.4) **p.** 7.9 (3.3) **q.** 19.0 (5.8)

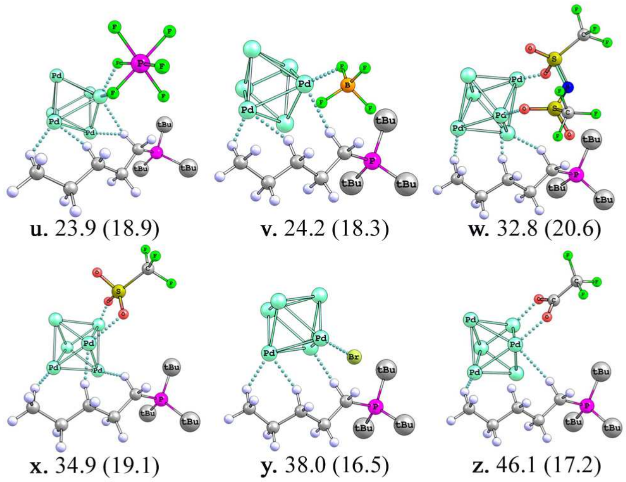
r. 20.4 (10.6) **s.** 22.2 (2.9) **t.** 26.9 (3.7)

Figure 5. Optimized structures of the associations of anions with a Pd_6 cluster, including their binding energies (BE, kcal·mol^{-1}) with fractions of London dispersion energy contributions to binding in parenthesis (in kcal·mol^{-1}). Short contacts are shown with dotted lines.

According to present simulations the *cis*-conformer of the $[Tf_2N]^-$ anion strongly interacts *via* four oxygen atoms with three Pd atoms of the Pd_6 cluster (corresponding distances are 2.35, 2.35, 2.49 and 2.52 Å). According to the computations all the abovementioned contacts between the anions and the Pd_6 induce distortions of structures and small elongations (2-4%) of the bonds participating in the interactions.

The energy of binding of the anions to the Pd_6 cluster varies from *ca.* 6 to *ca.* 27 kcal·mol^{-1} (Figure 5) with dispersion contributions varying from 3 to 11 kcal·mol^{-1} (13 - 75% of the BEs). The profound contribution of London forces takes place in the case of the $[PF_6]^-$, $[Tf_2N]^-$, $[BF_4]^-$ anions while their role in the interactions with participation of $[OTf]^-$, $[TFA]^-$, $[Br]^-$ anions is rather moderate. The obtained BE values are much smaller than the “gas-phase” PBE/6-31G* computational estimates (ca. 31 - 47 kcal·mol^{-1})[16,17] and are closer to the BEs computed within the framework of the polarizable continuum model.[18] Detailed discussion of the influence of theoretical approximations on the BE values can be found in the ESI. Here we just note that the BE values for the anions are strongly dependent on the effects of the surrounding media taken into account implicitly.[64] Explicit treatment of the interactions of the anions with other IL components also has an impact on the BE. Our computations show, that simultaneous binding of the both counterions to the Pd_6 cluster (optimized structures **u** - **z** shown in Figure 6) results in BEs, which are smaller than just sums of BE values obtained separately for the corresponding cation/Pd_6 and anion/Pd_6 adducts. These anti-cooperativity effects are maximal for the $[Bu^t_3PC_5H_{11}][Tf_2N]$ ion pair: the BE for the adduct (**w**, Figure 6) is ~8 kcal·mol^{-1} less than the sum of the BEs computed separately for the cation/Pd_6 (**d**, Figure 4) and anion/Pd_6 (**r**, Figure 5) adducts.

Aggregation of the ionic components of the IL slightly weakens their binding to palladium clusters and is accompanied by increase of distances between the Pd_6 cluster and the ions. The optimization of $[Bu^t_3PC_5H_{11}][BF_4]/Pd_6$ and $[Bu^t_3PC_5H_{11}][PF_6]/Pd_6$ entities results in Pd···P and Pd···F distances of 4.04 - 4.03 Å and 2.38 - 2.86 Å, respectively (**v** and **u,** Figure 6). Perflouroanions $[BF_4]^-$ and $[PF_6]^-$ interact with only one Pd atom of the Pd_6 cluster *via* one or two F atoms. In the presence of the $[Bu^t_3PC_5H_{11}]^+$ cation separated by 3.89 Å from the Pd_6 cluster, two oxygen atoms of the *cis*-conformer of the



u. 23.9 (18.9) **v.** 24.2 (18.3) **w.** 32.8 (20.6)

x. 34.9 (19.1) **y.** 38.0 (16.5) **z.** 46.1 (17.2)

Figure 6. Optimized structures of ion pair associations with a Pd_6 cluster, including their binding energies (BE, kcal·mol^{-1}) with fractions of London dispersion energy contributions to binding in parenthesis (in kcal·mol^{-1}). Some short contacts are shown with dotted lines.

$[Tf_2N]^-$ anion form two short contacts of 2.29 and 2.34 Å with two Pd atoms of the Pd_6 cluster (**w**, Figure 6). In case of the $[OTf]^-$ anion these short contacts are of 2.27 and 2.33 Å (**x**, Figure 6), while the minimal separation of Pd_6 cluster from the phosphorus atom of the $[Bu^t_3PC_5H_{11}]^+$ cation is equal to 3.97 Å. Optimization of $[Bu^t_3PC_5H_{11}][Br]/Pd_6$ entity (**y**, Figure 6) results in one Pd…Br short contact of 2.49 Å, while the Pd_6 cluster is separated by 4.18 Å from the phosphorus atom of the cation. Two shortest Pd…O contacts of 2.14 – 2.15 Å are found for $[Bu^t_3PC_5H_{11}][TFA]/Pd_6$ adduct (**z**, Figure 6). The corresponding Pd···P distance is 4.04 Å. All the abovementioned contacts between the ion pairs and the Pd_6 induce distortions of structures and small elongations (2-4%) of the interacting bonds.

Association of the Pd_6 cluster with the ion pairs represents a more realistic model for the Pd-NP/IL interface, because both anionic and cationic components of the ILs under study interact with Pd NPs according to the present experimental evidence (*vide supra*). Indeed, the simulation of IR spectrum of the $[Bu^t_3PC_5H_{11}][BF_4]/Pd_6$ adduct (Figure 2S, ESI) reproduces the experimentally registered (Figure 2) increase of intensities of the bands νBF_4 (~1000-1100 cm^{-1}) and appearance of a new band of δBF_4 at ~530 cm^{-1} due to interaction of the anion with the surface palladium atoms. The redistribution of intensities of the bands in the spectral range above 1300 cm^{-1} assigned to bendings of the methylene groups of the phosphonium cation is reproduced by the computations as well. In the case of the $[Bu^t_3PC_5H_{11}][Tf_2N]/Pd_6$ adduct (Figure 3S, ESI) the simulated IR bands of the $[Tf_2N]^-$ anion (at ~1400-1000 cm^{-1} and ~600 cm^{-1}) show intensities enhanced relative to the case of $[Bu^t_3PC_5H_{11}][Tf_2N]$ ion pair in full agreement with the experimental IR spectra (Figure 3) and earlier reported data.[60] Interaction between the cation and Pd_6 entities of the same model results in intensity redistribution for the bands of the phosphonium cation in the spectral range above 1400 cm^{-1}, at ~ 700 cm^{-1} and at ~900 cm^{-1}, which also matches the corresponding IR spectroscopic experiment (Figure 3).

The interaction energies between a Pd_6 cluster and various ion pairs vary from *ca.* 24 to *ca.* 48 kcal·mol^{-1} and follow the order $[Bu^t_3PC_5H_{11}][PF_6] \approx [Bu^t_3PC_5H_{11}][BF_4] < [Bu^t_3PC_5H_{11}][Tf_2N] < [Bu^t_3PC_5H_{11}][OTf] < [Bu^t_3PC_5H_{11}][Br] \ll [Bu^t_3PC_5H_{11}][TFA]$ (Figure 5). Dispersion contributions to the interactions are about 17-21 kcal·mol^{-1} (*ca.* 37-80% of the BEs), being more significant for $[PF_6]^-$, $[Tf_2N]^-$, $[BF_4]^-$ than for $[OTf]^-$, $[Br]^-$, $[TFA]^-$ anions. Interactions between ion pairs and the Pd_6 cluster are partly formed via multiple short contacts with CH-bonds of the tetraalkylphosphonium cation, leading to the effects similar to ones of hydrogen bond formation (*vide supra*).

Moreover, strength of binding follows the same trend as enthalpy of the hydrogen bond between the 1-(2′- hydroxylethyl)-3-methylimidazolium cation and various anions: $[PF_6]^- < [BF_4]^- < [Tf_2N]^- < [OTf]^- < [TFA]^-$.[65] At the same time BE values grow roughly in the same order as the estimates reported previously[17] for interaction strength between $[Tf_2N]^-$, $[PF_6]^-$, $[OTf]^-$, $[BF_4]^-$ and $[TFA]^-$ anions and Pd_5 cluster. The size of Pd-NPs, prepared from the decomposition of $Pd(OAc)_2$ in series of hydroxyl-functionalized ILs comprising the 1-(2'-hydroxylethyl)-3-methylimidazolium cation and various anions follows the same trend.[17] Thus, our present computations suggest that similar trends should be expected for the Pd-NPs formed in phosphonium-based ILs. Quite strong interactions of the cationic components of both the phosphonium- and imidazolium-based ILs with palladium species are characterised by almost constant BEs. In contrast, the strength of binding of the anions to the Pd-NPs varies over wider limits, thus determining the gross changes of magnitude of interactions at the NP/IL interface in passing from one IL to another.

The BEs discussed above for all ionic components of ILs (Figures 3, 4) or their associations (Figure 5) remain smaller than the computed energy of addition of a single Pd atom onto a Pd_n cluster resulting in a larger Pd_{n+1} cluster (~58 kcal·mol^{-1}). This suggests kinetic stabilization of Pd-NPs in the phosphonium-based ILs rather than thermodynamic stabilization. The same conclusion was obtained previously on the grounds of the gas-phase PBE/6-31G*/Lanl2DZ computations of Pd_n clusters immersed in imidazolium-based ILs.[16,17]

4. Conclusions

Interactions of various components of the tri-*tert*-butyl-R-phosphonium-based ILs with a Pd atom, a Pd_6 cluster, and Pd-NPs were studied both experimentally and computationally. IR spectroscopic experiments provide an evidence of interactions of both cationic and anionic components of the studied ILs with Pd-NPs immersed in the ILs. These interactions were modeled at a microscopic level within the framework of density functional theory (DFT) in combination with an atom pair-wise correction method for London dispersive forces (DFT-D3). It was shown that the tri-*tert*-butyl-R-phosphonium cations tend to form multiple short contacts between hydrogen atoms of alkyl moieties and palladium atoms. An average energy of binding of the cations to the Pd_6 cluster/Pd atom amounts to *ca*. 22/16 kcal·mol^{-1} for all types of cations studied, irrespective of substituents. This suggests that chemical modification of the phosphonium cations influences their interactions with the palladium species only moderately. London dispersion energy contributions to the abovementioned binding energies (BE) amount up to 80% of the BE values, which suggests that their consideration in theoretical studies of the metal-IL interactions is mandatory. These forces seem to be of lesser importance in case of palladium species bound to 1,3-dialkylimidazolium cations because this binding being characterized by stronger interactions of Pd atoms with π-system of the aromatic ring rather than with hydrogen atoms of the cation. In spite of these differences in mode of binding and quite dissimilar structures, both the phosphonium- and imidazolium-based cations interact with the palladium species with approximately the same strength.

The computed energy of binding of the anions $[PF_6]^-$, $[BF_4]^-$, $[Tf_2N]^-$, $[OTf]^-$, $[Br]^-$, $[TFA]^-$ to the Pd_6 cluster varies from *ca.* 6 to *ca.* 27 kcal·mol^{-1}, being strongly influenced by the effects of the surrounding media. Our computations show, that simultaneous binding of the both counter-ions to the Pd_6 cluster results in BEs, which are smaller than just sums of BE values obtained separately for the corresponding cation/ Pd_6 and anion/ Pd_6 adducts. The interaction energies between a Pd_6 cluster and various ion pairs follow the order $[Bu^t_3PC_5H_{11}][PF_6] \approx [Bu^t_3PC_5H_{11}][BF_4] < [Bu^t_3PC_5H_{11}][Tf_2N] < Bu^t_3PC_5H_{11}][OTf] < [Bu^t_3PC_5H_{11}][Br] << [Bu^t_3PC_5H_{11}][TFA]$ and vary from *ca.* 24 to *ca.* 48 kcal·mol^{-1}. This trend is determined mainly by variation of the strength of binding between the palladium species and anionic components of ILs, because quite large contributions of the cationic components to gross BE values remain almost constant for the whole series. Thus, our present computations suggest that changes of magnitude of interactions at the NP/IL interface in passing from one IL to another and, hence, the corresponding changes of properties of the NPs immersed in these ILs should be determined by variation of the anionic rather than cationic components of the ILs.

Interactions of palladium species with all the components of IL as well as with their associations are weaker than Pd–Pd interactions of ~58 kcal·mol^{-1}. This suggests kinetic stabilization of Pd-NPs in phosphonium-based ILs rather than thermodynamic stabilization, similar to the case of imidazolium-based ILs described earlier.

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Electronic Supplementary Information

Note 1. Discussions of a role of a theoretical approximation level used for the BE computations. **Table 1S**. Comparison of electronic energies and binding energies of several adducts of Pd_n clusters (n=6, 15) and ions obtained within different functionals for the gas phase and COSMO simulations. **Table 3S.** Atom charges of Pd_n clusters (n=6, 15, 23). **Note 2.** Discussions of a possibility to use more concentrated solutions of Pd NPs in ILs. **Table 3S.** Experimental peak intensities of some bands of the $[Tf_2N]^-$ anion in the IR spectra of $[Bu^t_3PC_{10}H_{21}][Tf_2N]$ and $[Bu^t_3PC_{10}H_{21}][Tf_2N]$-stabilized Pd-NPs. **Figure 1S.** Optimized structures of the associations of the two $[Bu^t_3PC_5H_{11}]^+$ cations with a Pd atom and a Pd_6 cluster. **Figure 2S.** Simulated IR spectra of the ion pair $[Bu^t_3PC_{10}H_{21}][BF_4]$ and the $[Bu^t_3PC_{10}H_{21}][BF_4]/Pd_6$ adduct. **Figure 3S.** Simulated IR spectra of the ion pair $[Bu^t_3PC_{10}H_{21}][Tf_2N]$ and the $[Bu^t_3PC_{10}H_{21}][Tf_2N]/Pd_6$ adduct.

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