

## Estimation of Dissociation Energy in Donor–Acceptor Complex AuCl·PPh<sub>3</sub> via Topological Analysis of the Experimental Electron Density Distribution Function

Alexandra O. Borissova, Alexander A. Korlyukov, Mikhail Yu. Antipin, and Konstantin A. Lyssenko\*

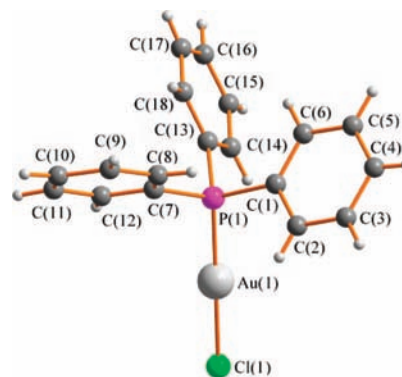
A. N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Vavilov Str., 28, 119991 Moscow, Russia

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The high-resolution X-ray diffraction analysis and plane-wave density functional theory were applied to the investigation of charge density distribution in the donor–acceptor complex of AuCl with PPh<sub>3</sub>. The approach allows us to estimate the atomic charges, the charge transfer, the energy of weak interactions (Au···H, Au···C, H···Cl, etc.), and Au–P bond energy directly from the experimental data.

The donor–acceptor complexes AuX·PR<sub>3</sub> (X = halide, R = H, alkyl or aryl) are frequently used as models for investigating the so-called auriphilic interactions.<sup>1</sup> These interactions are commonly attributed to rather strong d<sup>10</sup>–d<sup>10</sup> overlap<sup>2</sup> leading to the formation of Au(I) clusters.<sup>3</sup> The Au···Au interactions are also an important tool in supramolecular chemistry<sup>4</sup> and crystal engineering, in particular, dealing with the luminescent properties.<sup>5</sup> Although the strong Au···Au contacts were successfully described via “cheap” DFT calculations (see ref 6 and references therein), the investigations of the so-called intermediate type of auriphilic interactions,<sup>3b</sup> that play a major role in self-assembly in crystal and stabilization of large molecular aggregates, are still problematic. Accordingly, it is of interest to use the experimental methods, in particular, the high-resolution X-ray diffraction analysis (XRD) of the electron density distribution function,<sup>7</sup> for investigations of chemical bonding pattern. In addition to all necessary structural information, this approach can give a possibility to evaluate the properties, which were inherent earlier solely for quantum chemistry.

In particular, the use of topological analysis of the electron density distribution function  $\rho(\mathbf{r})$ , derived from experimental data and/or from ab initio calculations, within Bader’s “Atom in Molecules” (AIM) theory<sup>8</sup> in conjunction with Espinosa’s correlation scheme<sup>9</sup> allows one to estimate the interatomic interaction energy ( $E_{\text{cont}}$ ) with sufficient accuracy. This correlation scheme relates the value of local potential energy density in the critical point (3,–1) with the energy of interatomic interaction, for which this point was located. The good agreement between the sublimation enthalpy obtained by the summation of all the  $E_{\text{cont}}$  for molecular crystals and thermochemical data proves it.<sup>10</sup> It is valid not only for weak interactions, such as H···H and C–H···O contacts (i.e., so-called “closed-shell” interactions) but also for moderate and strong H-bonds, corresponding to the intermediate type of interatomic interactions in some limiting cases (see for instance refs 10e and 10f and references therein). Furthermore, this approach was successfully



**Figure 1.** (A) General view of AuCl·PPh<sub>3</sub>. (B) CP (3,–1) and (3,+1) (small points) and bond paths in the molecule of AuCl·PPh<sub>3</sub>.

applied in the DFT modeling of zeolites to estimate Mg···C and Ca···C interaction energies.<sup>11</sup> Assuming that chemical bonds formed by Au correspond at least to intermediate type of interatomic interactions (see ref 12), it was interesting to check the validity of this approach for such systems. All the interatomic interaction energies hereinafter were estimated by means of this approach.

Although a number of charge density investigations has already appeared for compounds containing heavy atoms,<sup>12</sup> to the best of our knowledge the topological analysis of  $\rho(\mathbf{r})$  in crystals and/or isolated complexes of Au(I) has not yet been performed.

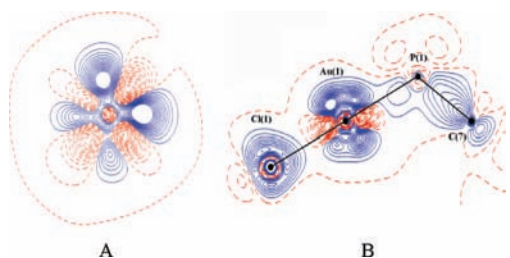
As the model compound for estimation of accuracy and applicability of this experimental approach for investigation of gold complexes we have chosen the donor–acceptor complex of AuCl with PPh<sub>3</sub> (Figure 1). This compound was intended for intensive study owing to the single crystals of excellent quality, which can be easily obtained. This allows carrying out an accurate determination of electron density function in the solid state. In addition, the various theoretical and experimental data, such as molecular geometry,<sup>13</sup> atomic charges,<sup>14</sup> and even the energy of Au–P bond in complex under consideration (see, e.g., ref 14), is available for it.

\* Corresponding author. E-mail: kostya@xrlab.ineos.ac.ru. Fax: +7499 135 5085. Tel: 7 499 135 9214.

**TABLE 1: Bond Lengths and Topological Parameters of  $\rho(\mathbf{r})$  Function in CP(3,-1)<sup>a</sup>**

bond	distance, Å	$\rho(\mathbf{r})$ , e Å <sup>-3</sup>	$\nabla^2\rho(\mathbf{r})$ , e Å <sup>-5</sup>	$\epsilon^b$	$V(\mathbf{r})$ , au	$h_c(\mathbf{r})$ , au
Au-Cl	2.2915(5)	0.698	7.304	0.209	-0.1565	-0.0404
	2.319	0.699	6.070	0.211	-0.1527	-0.0448
Au-P	2.2308(5)	0.845	1.251	0.093	-0.1846	-0.0858
	2.253	0.865	0.942	0.429	-0.1906	-0.0904

<sup>a</sup> The upper line gives the average value for XRD, the lower line gives the calculation data. <sup>b</sup> The value of ellipticity.



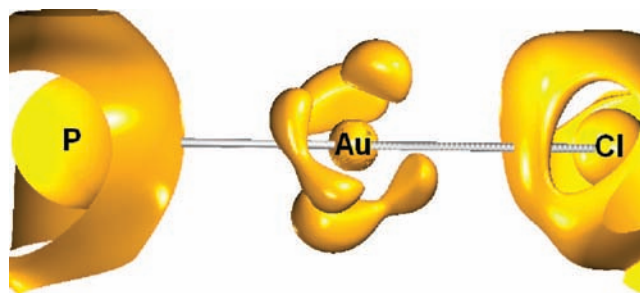
**Figure 2.** (A) Distribution of DED in the area of Au atom in the section perpendicular to Cl-Au-P line. (B) Distribution of DED in the area of Au(1), P(1) and C(7) atoms. The contours are drawn with 0.1 e Å<sup>-3</sup> step, the negative contours are dashed and red, the positive contours are blue.

Assuming that quantum chemical investigations of Au-containing compounds were mainly devoted to molecular geometry of such systems, the estimation of the energy of aurophilic interactions and d-orbital population of gold (see, e.g., ref 6), we performed the PW-PBE (plane-wave-PBE) calculations of AuCl·PPh<sub>3</sub> crystal structure as a reference for the experimental data.

The PW-PBE calculation of the orthorhombic polymorph of AuCl·PPh<sub>3</sub> complex reproduces the experimental geometry very well. In particular, the Au-P and Au-Cl bond lengths are equal to 2.253 and 2.319 Å, which are only slightly differing from the corresponding experimental values (2.2313(4) and 2.2903(4) Å). One notes that PW-PBE geometry is close to the obtained by MP2 calculation of AuCl·PH<sub>3</sub> molecule in the gas phase (Au-P and Au-Cl bond lengths are 2.250 and 2.272 Å).<sup>6</sup> Thus, the chosen functional and computational procedure reproduces the experimental geometry satisfactorily to make an attempt to compare the topological parameters of experimental and theoretical  $\rho(\mathbf{r})$  functions.

The critical point (CP) search revealed the presence of CP(3,-1) for all Au-Cl, P-Cl, P-C, C-C and C-H bonds and of three CP(3,+1) for phenyl rings. The topological parameters of CPs (3,-1) for experimental and theoretical  $\rho(\mathbf{r})$  functions are in qualitative and even quantitative agreement (see Table 1). As it was expected, both the Au-Cl and Au-P bonds are characterized by the positive value of  $\nabla^2\rho(\mathbf{r})$  and the negative electron energy density ( $h_c(r)$ ) in CP(3,-1) and, thus, correspond to intermediate type of interatomic interactions.

Inspection of the deformation electron density (DED)<sup>15</sup> distribution in the sections perpendicular and parallel to Cl(1)-Au(1)-P(1) line shows that DED maxima are localized in the vicinity of Au and Cl atoms (Figure 2) and can be associated with 5d-orbitals of Au and the electron lone pairs (Lp) of chlorine atoms. The chlorine's Lps are characterized by tetrahedral arrangement with one of them directed toward the area of charge depletion around the gold atom. The same chemical bonding pattern is observed for Au-P bond. Thus, both the Au-P and Au-Cl bonds belong to the so-called "peak-hole" type of interactions, which is typical for donor-



**Figure 3.** 3D map of ELF in the area of Au, P and Cl atoms.

acceptor complexes.<sup>16</sup> One notes that the same conclusion could be drawn from the analysis of the more theoretically sound electron localization function (ELF),<sup>17</sup> which was shown to be homeomorphically related with DED for some ionic systems.<sup>18</sup> It was obtained from the experimental XRD data within the approach proposed by Tsirelson and Stash.<sup>19</sup> The applicability of this method to localize domains corresponding to metal orbitals and the atom electron lone pairs was demonstrated by a number of investigations.<sup>10b,12c,20</sup> The 3D map of ELF distribution (0.7 envelope) also reveals the presence of domains that can be associated with Au 5d-orbitals and the directionality of electron localization domains that can be associated with lone pairs toward the area near Au atom with lower electron localization (Figure 3).

To estimate the extent of charge transfer upon the formation of donor-acceptor complex, we have estimated the atomic charges via the integration of  $\rho(\mathbf{r})$  over the atomic basins ( $\Omega$ ) surrounded by zero-flux surface.<sup>8</sup> The accuracy of obtained charges can be in part justified by the values of Lagrangian [ $L(r) = -1/4\nabla^2\rho(\mathbf{r})$ ] and volumes, obtained by the analogues procedure. In particular, the  $L(r)$  value for Au(1), P(1) and Cl(1) are quite small and equal to  $9.6 \times 10^{-5}$ ,  $1.6 \times 10^{-4}$  and  $1.4 \times 10^{-4}$  e Å<sup>-5</sup>, respectively.<sup>21</sup> The summation of estimated atomic charges led to a charge leakage equal to 0.01 e. In turn, the sum of atomic volumes in the crystal (401.00 Å<sup>3</sup>) reproduces well the volume of the independent part of the unit cell (402.21(5) Å<sup>3</sup>), the error being only 0.3%. The charge values of Au, P and Cl atoms are 0.003, 1.135 and -0.963 e, respectively. The corresponding charges obtained from PW-DFT calculations are 0.045, 1.737 and -0.782 e. Thus, the charge transfer from PPh<sub>3</sub> to AuCl moiety is 0.96 e according to the experiment data and 0.74 e in the case of the PW-PBE calculation. The charge of gold is far from the formal oxidation state +1 due to the electron donation by Cl<sup>-</sup> and PPh<sub>3</sub> into the Au 6s and 6p valence shell. This data agrees well with the calculations of Au···Au bonded clusters,<sup>6</sup> which demonstrated that the Mulliken charge of Au atoms has a very low value being in the neighborhood of zero. Investigating the Au···Au bonded clusters with PH<sub>3</sub> as a ligand, the authors of ref 6 came to the conclusion that, as a rule, the gold atom carries nearly vanishing charge owing to the electron transfer from the soft base PH<sub>3</sub> ligand. One can expect that in the case of PPh<sub>3</sub> such transfer will be slightly higher.

The variation of charge transfer according to experimental and theoretical data can be the result of intermolecular interactions. Moreover, some difference can be the consequence of DFT calculations that does not describe the van-der-Waals interactions properly.

Indeed, in the crystal of AuCl·PPh<sub>3</sub>, in addition to expected C···C, C···H, H···H, and H···Cl contacts, one observes the presence of weak Au···H and Au···C contacts. It should be noted that at least Au···C ( $\pi$ ) contacts are rather unusual.

**TABLE 2: Interatomic Separation ( $d$ ) and Topological Parameters of  $\rho(\mathbf{r})$  Function in CP(3,−1) of Intermolecular Contacts<sup>a</sup>**

	$d, \text{Å}$	$\rho(\mathbf{r}),$ $\text{e Å}^{-3}$	$\nabla^2\rho(\mathbf{r}),$ $\text{e Å}^{-5}$	$V(\mathbf{r}) \times$ $10^3, \text{au}$	$H_e(\mathbf{r}) \times$ $10^4, \text{au}$	$E_{\text{cont}},$ $\text{kcal/mol}$
Au(1)⋯H(16)	2.96	0.032	1.56	−2.1	9.72	0.7
		0.057	0.49	−3.7	6.85	1.2
Au(1)⋯H(6)	3.08	0.041	1.65	−2.6	8.48	0.8
		0.046	0.45	−2.9	8.42	0.9
Au(1)⋯H(9)	3.31	0.039	1.48	−2.4	7.48	0.7
Au(1)⋯C(10)	3.773(1)	0.036	1.37	−2.1	7.14	0.7
		0.042	0.39	−2.6	7.52	0.8
Au(1)⋯C(17)	3.992(1)	0.025	0.85	−1.2	4.80	0.4

<sup>a</sup> The upper line gives the value for XRD, the lower line gives the calculation data.

According to the CSD<sup>22</sup> search, the average/shortest Au⋯H and Au⋯C contacts are 3.0/2.7 and 3.9/3.2 Å. Moreover, the only Au⋯C contact attributed to Au⋯ $\pi$  type of interactions was found in the golden complex with anthracene, where the Au⋯C distance is ca. 3.2 Å.<sup>23</sup> Although the Au⋯C and Au⋯H contacts are clearly uncharacteristic for the complexes of gold, the CP search has revealed three Au⋯H and two Au⋯C contacts (see Table 2). The same contacts are located in the case of PW-DFT calculations. Although all these contacts are rather weak, some of them are characterized by specific directionality with Cl–Au–H angles varying in the range 68–94°. The chlorine atom participates in four C–H⋯Cl interactions with H⋯Cl distances equal to 2.85–3.12 Å. One notes that the energy of all these interactions as well as the rest of C⋯C, C⋯H and H⋯H bonds does not exceed 1.8 kcal/mol. As estimated by means of Espinosa's correlation scheme,<sup>9</sup> the summarized energy of Cl⋯H and Au⋯X interatomic interactions is only 4.1 and 3.3 kcal/mol. The energy of Cl⋯H interatomic interactions (0.69–1.2 kcal/mol) are in line with those observed in ionic liquids and some chloride salts with organic cations.<sup>24</sup> According to available data (see ref 24a) the Cl⋯H interatomic interactions as weak as in AuCl⋯PPh<sub>3</sub> complex practically do not affect the chlorine charge.

The Au⋯C contacts are weaker than Au⋯H ones with the average energy of 0.5 and 0.7 kcal/mol, respectively. It is noteworthy, that energy of Au⋯H is comparable with available data on the estimation of molecular hydrogen adsorption by Au clusters. In particular, according to PW-DFT calculation, the Au⋯H interactions with interatomic separation equal to 2.31 Å are characterized by  $E_{\text{cont}}$  equal to 1.4 kcal/mol.<sup>25</sup>

Thus, we can conclude that crystal packing negligibly effects the charge distribution in AuCl⋯PPh<sub>3</sub> molecule and one can use the topological parameters at CP (3,−1) of Au–P bond to estimate its energy in crystal. The usage of Espinosa correlation<sup>9</sup> leads to its value of 57.9 kcal/mol for experimental  $\rho(\mathbf{r})$  and 59.8 for PW-DFT data. The absence of pronounced charge redistribution upon the formation of this complex as well as of strong intermolecular interactions allows us to compare the energy of Au–P bond with the dissociation energy of AuCl⋯PPh<sub>3</sub> complex into two neutral fragments AuCl and PPh<sub>3</sub>. Indeed, both above values are close to the dissociation energies of MeAu⋯PPh<sub>3</sub> and AuCl⋯PH<sub>3</sub> complexes that are 58.9 and 53.2 kcal/mol according to LCGTO-LDF<sup>14</sup> and MP2 calculations.<sup>26</sup>

## Conclusion

Therefore, one assume that our approach is reliable to obtain such important characteristics of golden complexes in crystal, as atomic charge, the charge transfer, the atomic volume and

the energy of rather weak Au⋯H, Au⋯C and rather strong Au–P interatomic interactions. This gives the wide opportunities to investigate a series of organometallic golden derivatives and, in particular, to study the strong and intermediate aurophilic interactions.

## Experimental Section

**X-ray Structure Analysis.** Crystals of PPh<sub>3</sub> AuCl (PPh<sub>3</sub>·AuCl, M = 494.69) are orthorhombic, space group  $P2_12_12_1$ , at 100(2) K:  $a = 10.1077(2)$ ,  $b = 12.2492(4)$ ,  $c = 12.9943(3)$  Å,  $V = 1608.84(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calc}} = 2.042 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo K}\alpha) = 9.399 \text{ cm}^{-1}$ ,  $F(000) = 936$ . Intensities of 147456 reflections were measured with a “Bruker SMART APEX2” CCD diffractometer and 18742 independent reflections [ $R_{\text{int}} = 0.0505$ ] were used in further refinement. The refinement converged to  $wR2 = 0.0437$  and  $\text{GOF} = 1.000$  for all independent reflections ( $R1 = 0.0230$  was calculated against  $F$  for 16546 observed reflections with  $I > 2\sigma(I)$ ). All calculations were performed using SHELXTL PLUS 5.0.<sup>27</sup> Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

**The multipole refinement** was carried out within the Hansen–Coppens formalism<sup>28</sup> using the XD program package.<sup>29</sup> Before the refinement C–H bond distances were normalized to the values obtained in the B3LYP/6-311G(d,p) calculation. The level of multipole expansion was hexadecapole for all atoms. The refinement was carried out against  $F$  and converged to  $R = 0.0150$ ,  $wR = 0.0178$  and  $\text{GOF} = 0.9075$  for 6470 merged reflections with  $I > 3\sigma(I)$ . All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria.<sup>30</sup> The average value of difference of the mean square displacement amplitudes along the bond was  $6 \times 10^{-4} \text{ Å}^2$ . The residual electron density was not more than  $0.72 \text{ e Å}^{-3}$ . Analysis of topology of the  $\rho(\mathbf{r})$  function as well as the calculation of ELF was carried out using the WINXPRO program package.<sup>31</sup>

**The quantum chemical calculations** of crystal structure AuCl⋯PPh<sub>3</sub> were carried out using the VASP 4.6.31 code.<sup>32</sup> Conjugated gradient technique was used for optimizations of the atomic positions (started from experimental data) and minimization of total energy. The projected augmented wave (PAW) method was applied to account for core electrons, and valence electrons were approximated by plane-wave expansion with 400 eV cutoffs. Exchange and correlation terms of total energy were described by PBE<sup>33</sup> exchange-correlation functional. Kohn–Sham equations were integrated with three irreducible  $k$ -points. Using the DFT method, it is not possible to take into account the dispersion interactions. For this reason calculated cell parameters may be systematically overestimated or underestimated up to 5%. Thus, the experimental values of cell parameters were used in the calculations. At a final step of our calculations atomic displacements converged were better than  $0.01 \text{ eV Å}^{-1}$ , as well as energy variations were less than  $10^{-3} \text{ eV}$ . To carry out the topological analysis of electron density distribution function in terms of AIM theory the dense FFT grid ( $140 \times 168 \times 180$ ) was used. The latter was obtained by separate single point calculation of optimized geometry with hard PAWs for each atom type. The topological analysis of electron density distribution function was carried out using AIM program—part of ABINIT software package.<sup>34</sup>

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**Supporting Information Available:** Full structural data and details of the multipole refinement as well as the full values of integrated atomic charges, volumes and Laplacians. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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