

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236579253>

# Toward Understanding the Bonding Character in Complexes of Coinage Metals with Lone-Pair Ligands. CCSD(T) and DFT Computations

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · APRIL 2013

Impact Factor: 2.69 · DOI: 10.1021/jp401174p · Source: PubMed

CITATIONS

14

READS

38

## 3 AUTHORS:



Lukas Felix Pasteka

Massey University

8 PUBLICATIONS 33 CITATIONS

SEE PROFILE



Tomáš Rajský

Comenius University in Bratislava

1 PUBLICATION 14 CITATIONS

SEE PROFILE



Miroslav Urban

Comenius University in Bratislava

119 PUBLICATIONS 3,341 CITATIONS

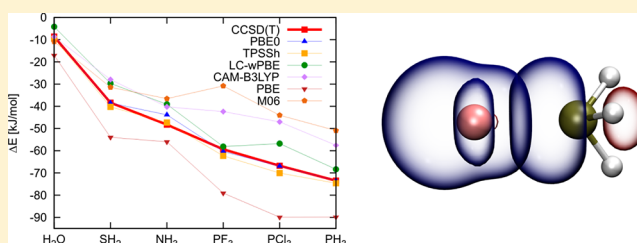
SEE PROFILE

# Toward Understanding the Bonding Character in Complexes of Coinage Metals with Lone-Pair Ligands. CCSD(T) and DFT Computations

Lukáš F. Pašteka,<sup>†</sup> Tomáš Rajský,<sup>†</sup> and Miroslav Urban<sup>\*,†,‡</sup><sup>†</sup>Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina, 841 04 Bratislava, Slovakia<sup>‡</sup>Faculty of Materials Science and Technology in Trnava, Institute of Materials Science, Slovak University of Technology in Bratislava, Bottova 25, 917 24 Trnava, Slovakia

## S Supporting Information

**ABSTRACT:** We present CCSD(T) interaction energies and the bonding analysis for complexes of Cu, Ag, and Au with the lone-pair ligands H<sub>2</sub>O, OF<sub>2</sub>, OMe<sub>2</sub>, NH<sub>3</sub>, NF<sub>3</sub>, NMe<sub>3</sub>, H<sub>2</sub>S, SF<sub>2</sub>, SMe<sub>2</sub>, PH<sub>3</sub>, PF<sub>3</sub>, PCl<sub>3</sub>, and PMe<sub>3</sub> (ML complexes). Both electron correlation and relativistic effects are crucial in the bonding of all complexes. AuPH<sub>3</sub>, AuPF<sub>3</sub>, and AuPCl<sub>3</sub> (AuPX<sub>3</sub>) complexes exhibit particularly large relativistic effects, 30–46 kJ/mol. Upon neglecting relativistic effects, the Au–P bonds almost vanish aside from weak long-range van der Waals interactions. Highest binding energies are computed for complexes with Au, followed by Cu and Ag. For all coinage metals the strongest interactions are computed for PX<sub>3</sub> ligands followed by SX<sub>2</sub> and NX<sub>3</sub> OX<sub>2</sub> ligands. Upon methylation the interaction energy rises significantly. Metal–thiol complexes, particularly AuSCH<sub>3</sub>, form a separate class. Exceptional stability of gold complexes is due to large relativistic enhancement of the electron affinity of Au. Along with the electron affinity of a metal, we link the pattern of interaction energies in ML complexes with ionization potentials (IPs) of ligands. Strong interaction with P containing ligands is attributed to their lower IP and the lone pair → metal electron donation accompanied with the back-donation characteristic for P containing ligand. Energy data are accompanied with the natural bond orbital analysis. Computationally less demanding DFT computations with the PBE0 functional provide correct pattern of interaction energies when compared with benchmark CCSD(T) results.



## 1. INTRODUCTION

For understanding phenomena associated with creation and stability of systems like self assembled monolayers (SAM),<sup>1–7</sup> large metal–ligand complexes,<sup>8–11</sup> ligand protected clusters,<sup>9</sup> organometallic complexes acting as efficient catalysts,<sup>12</sup> etc., it is useful to analyze the geometries, stability, and particularly the mechanism underlying the strength of the metal–ligand bond in typical complexes which participate in larger systems.

In a series of our previous papers we have computed ML complexes involving coinage metals, Cu, Ag, and Au, interacting with H<sub>2</sub>O or NH<sub>3</sub>,<sup>13</sup> H<sub>2</sub>S,<sup>14</sup> and PH<sub>3</sub>.<sup>15</sup> In assessing the interaction energy,  $\Delta E$ , of a complex with respect to the fragments (sum of energies of a metal atom and a ligand), it would be profitable having a quantity, preferably experimentally available, with a potential for predicting the pattern of stabilities within a group of a series of metal complexes with various ligands. Analyzing relativistic effects treated at the scalar relativistic level, as defined by Douglas, Kroll, and Hess (DKH),<sup>16,17</sup> we concluded that the mechanism of interaction can be explained by the charge transfer which depends on the electron affinity (EA) of the coinage metal and the ionization potential (IP) of the ligand. This view was supported by the

considerable enhancement of the electron affinity of gold due to relativistic effects<sup>8,18–21</sup> and related increase of stability of its 6s orbital accompanied by its shrinking.<sup>8,20,22</sup> This explains the much higher stability of the Au⋯L complexes in comparison with Ag⋯L complexes. The ligand–metal charge transfer ( $\sigma$  donation L → M) is supported by a lower IP of the ligand. Our previous results suggest that on the coinage metal side the participating orbital is the valence *ns* orbital of the metal. Some literature data suggest rather participation of the metal *d* orbitals.<sup>23</sup>

In our review paper on relativistic effects,<sup>21</sup> we were able to correlate the relativistic contribution to the total ML interaction energy with IP of the ligand. However, we noticed significantly higher interaction energy in the Au⋯PH<sub>3</sub> complex than expected. We should stress that the Au⋯PH<sub>3</sub> bonding is in fact due to relativist effects. By neglecting relativistic effects in the Au complex with PH<sub>3</sub>, the interaction energy disappears even at the highly correlated level considered by the coupled

Received: February 1, 2013

Revised: April 26, 2013

Published: April 29, 2013

cluster CCSD(T) method (forgetting the very weak van der Waals long-range interaction). A much stronger bond in the  $\text{Au}\cdots\text{PH}_3$  complex than expected using a simple model of the  $\text{L} \rightarrow \text{M} \sigma$  donation was attributed to the  $\pi$  back-donation, related to the charge transfer from the metal d orbitals to the ligand unoccupied p orbitals. There is rich literature on the back-donation in metal–ligand complexes particularly with  $\text{PX}_3$  ( $\text{X} = \text{H}, \text{F}, \text{Cl}$ ) as a ligand, frequently related to the organometallic chemistry and catalysis.<sup>12,23–28</sup> In order to relate the bonding energy and behavior of  $\text{M}\cdots\text{PX}_3$  complexes with properties of a ligand, we have extended the series of ligands in ML complexes by considering  $\text{PMe}_3$  ( $\text{Me} = \text{methyl group}$ ),  $\text{PF}_3$ , and  $\text{PCl}_3$  in addition to  $\text{PH}_3$  considered in our recent paper.<sup>15</sup> We also compared the behavior of  $\text{M}\cdots\text{PX}_3$  complexes with their isovalent  $\text{M}\cdots\text{NX}_3$  analogues. A comparison of  $\text{PX}_3$  and  $\text{NX}_3$  ligands interacting with  $\text{CN}\cdots\text{M}$ ,  $\text{NC}\cdots\text{M}$ , and  $\text{Br}\cdots\text{M}$  ( $\text{M}$  is  $\text{Cu}$ ,  $\text{Ag}$ , or  $\text{Au}$ ) molecules was published recently by Luo et al.<sup>24</sup> Comparison of ML complexes with  $\text{PX}_3$  and  $\text{NX}_3$  ligands that exhibit the  $\text{C}_{3v}$  symmetry with structurally different ML complexes in which  $\text{L}$  is  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{OMe}_2$ ,  $\text{SMe}_2$ ,  $\text{OF}_2$ , and  $\text{SF}_2$  as also interesting. The geometry of these complexes is characterized by a  $\text{M}\cdots\text{O}$  (or  $\text{M}\cdots\text{S}$ ) bond which is bent with respect to the symmetry axis of  $\text{H}_2\text{O}$  and analogous ligands.<sup>13,14,21</sup>

All complexes considered in our previous papers were doublets for which we used the CCSD(T) coupled cluster method with a restricted open-shell Hartree–Fock reference (ROHF),<sup>29</sup> applying an approximate spin adaptation (SA) of CC amplitudes. From the point of view of SAMs most important is the family of thiolate containing ligands.<sup>1,2,30,31</sup> The simplest representative of such complexes is the  $\text{SCH}_3$  radical, which is an open-shell system (doublet) in contrast to all ligands mentioned so far, which are closed-shell molecules. Upon interacting with  $\text{Cu}$ ,  $\text{Ag}$ , or  $\text{Au}$ , the  $\text{SCH}_3$  radical can create a closed-shell complex  $\text{M}\cdots\text{SCH}_3$  which exhibits a quite strong  $\text{M}-\text{S} \sigma$  bond. This results from the metal interacting with the singly occupied lone pair of  $\text{SCH}_3$ . The triplet state of  $\text{M}\cdots\text{SCH}_3$  exhibits a weaker bond. The bonding is characterized by the interaction of the valence  $ns$  electron of a metal with doubly occupied lone pair of  $\text{SCH}_3$ , similarly as in all other ligands.<sup>32,33</sup> One can thus expect that the binding energy of the triplet state fits into the pattern representing the closed-shell ligands.

Consideration of binding energies as a function of the electron affinity of a metal and the ionization potential of a ligand is suitable if the stability of ML complexes is determined by the  $\text{L} \rightarrow \text{M} \sigma$  donation. Once this mechanism is combined with other effects, particularly back-donation, we need yet another quantity potentially useful in predicting and explaining the pattern of stabilities of ML complexes. We were unable to find any parameter analogous to EA of the metal and IP of the ligand. Therefore we used a theoretical tool, the NBO analysis<sup>34,35</sup> for the assessment of contributions from the donation and back-donation effects, respectively.

Finally, we note that for large metal–ligand complexes it is computationally prohibitive using sophisticated relativistic and highly correlated methods like CCSD(T). Since our model complexes are tractable at this level with reasonably large basis sets, we expect that CCSD(T) results may serve as benchmark data for DFT methods which are mostly used for species containing several metal atoms and large ligands.

## 2. COMPUTATIONAL DETAILS

Energy data and the geometry optimizations for the series of coinage metal–ligand complexes were computed by the ROHF SA CCSD(T) method employing several basis sets ranging from smaller to larger ones: POL,<sup>36,37</sup> POL\_DK,<sup>38</sup> ANO-RCC-VTZP, and ANO-RCC-VQZP.<sup>39</sup> The formermost basis set was used without including the relativistic correction into the computation, while we used the scalar relativistic Douglas–Kroll–Hess correction of the second order (DKH2)<sup>40,41</sup> with the three latter basis sets, as it is intended. The smaller POL\_DK basis set was used with all investigated complexes, while we computed only selected complexes (with ligands  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ ,  $\text{PCl}_3$ , and  $\text{SCH}_3$ ) with the larger ANO-RCC basis sets.

Geometries of the ligand molecules were taken from the Landolt–Börnstein database<sup>42–44</sup> and other experimental works.<sup>45–48</sup> These were kept fixed during the optimization, since we were dealing with quite weakly bound complexes and no significant changes in the ligand geometries were expected. Thus only the relative position of metal and ligand was being optimized for each complex. We also examined the effect of this geometry constraint on selected complexes by reoptimizing the ligand geometry at the equilibrium metal–ligand distance. The counterpoise (CP) correction<sup>49</sup> was included throughout the whole optimization process to treat the BSSE, which is usually important for similar complexes.<sup>13,14,50</sup>

Systems optimized with the POL\_DK basis were afterward analyzed via natural bond orbital (NBO) analysis.<sup>34,35</sup> This was done at the UHF level as the analysis of the delocalizations is not applicable to the ROHF wave functions. The UHF orbitals, however, closely resemble the ROHF ones, hence the NBO analysis is still a meaningful interpretative tool.

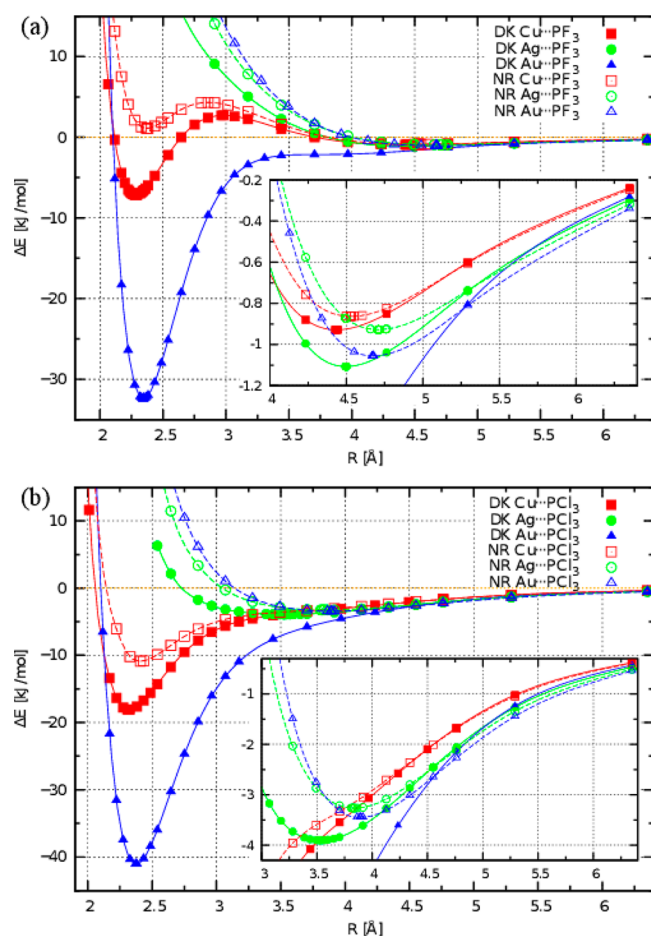
In addition, we computed the vertical ionization potentials of all investigated ligands at the CCSD(T)/POL\_DK and CCSD(T)/aug-cc-pVTZ<sup>51</sup> levels of theory.

We also tested the applicability of the DFT method for computations of investigated complexes. We employed several functionals—PBE,<sup>52,53</sup> PBE0,<sup>54</sup> LC- $\omega$ PBE,<sup>55–57</sup> CAM-B3LYP,<sup>58</sup> TPSSH,<sup>59</sup> and M06<sup>60</sup>—together with several effective core potential (ECP) basis sets—larger sets DEF2-QZVP, DEF2-TZVP,<sup>61</sup> smaller sets LanL2DZ<sup>62</sup> and SBK<sup>63</sup>—as well as their counterparts LanL2DZdp and SBK\* with one set of polarization functions added to nonmetal atoms.

For all optimizations and energetics we used Molcas 7<sup>64</sup> and Gaussian 09<sup>65</sup> program packages. For the NBO analysis we used the NBO 5 program.<sup>66</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Complexes with  $\text{PF}_3$  and  $\text{PCl}_3$ .** Our group previously investigated the interaction of coinage metals with phosphine molecule.<sup>15</sup> In the present study we extend this investigation to substituted phosphine ligands  $\text{PF}_3$  and  $\text{PCl}_3$ . Nonrelativistic and scalar DKH relativistic potential energy curves obtained with ROHF SA CCSD(T) for complexes with  $\text{PF}_3$  and  $\text{PCl}_3$  ligands are depicted in Figure 1. At the nonrelativistic (NR) level all complexes with  $\text{PF}_3$  exhibit only shallow energy minima at the metal–ligand distances close to 4.5 Å corresponding to van der Waals (VdW) interaction. In addition,  $\text{Cu}\cdots\text{PF}_3$  potential curve shows another minimum at medium range around 2.3 Å. This indicates some charge-transfer (CT) interaction present already at the NR level. This can be attributed to the fact, that the NR valence  $ns$  orbital of copper is smaller than those of silver and



**Figure 1.** Comparison of BSSE corrected nonrelativistic (NR) and DK relativistic ROHF/SA CCSD(T) interaction energies [kJ/mol] with POL and POL\_DK basis sets for  $M \cdots PF_3$  (a) and  $M \cdots PCl_3$  (b) complexes as a function of metal–ligand distance [Å]. Full lines and closed symbols represent relativistic computations. Dashed lines and open symbols represent nonrelativistic computations. The inset shows magnified region of long-range interactions.

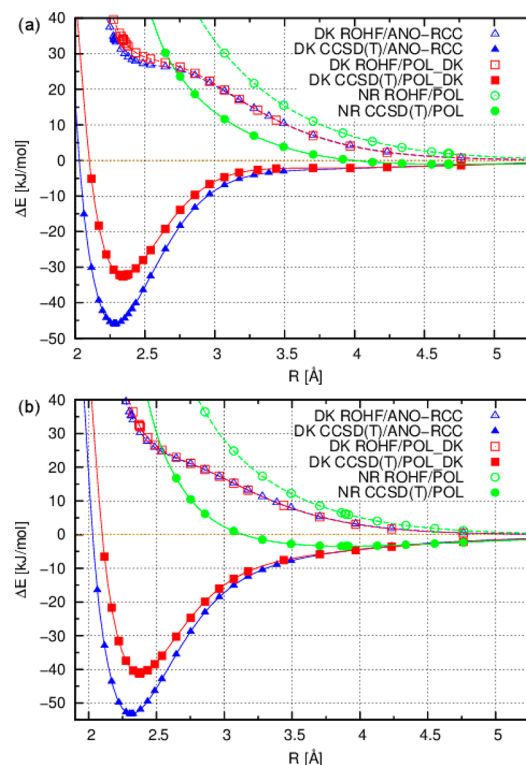
gold, allowing the ligand for closer interaction and orbital overlap. Nevertheless, this minimum is above the dissociation limit. We observe similar picture for the nonrelativistic curves of complexes with  $PCl_3$ . In this case, the VdW minima for  $Ag \cdots PCl_3$  and  $Au \cdots PCl_3$  appear at shorter distances, around 4.0 Å, and the interaction energies are about four times as high as in the case of  $PF_3$ . The  $Cu \cdots PCl_3$  complex in fact does not have a VdW minimum at all; we observe only a trace of VdW interaction, an inflection point in this region. The charge-transfer interaction is strong enough to create a minimum at about 2.4 Å already at the NR level.

Comparing the relativistic and nonrelativistic potential curves in Figure 1 reveals stabilization upon including the relativistic effects, magnitude of which (vertical energy difference) increases in the expected order from Cu to Au. In case of Au complexes, this relativistic contribution is dominant and accounts for the overall bonding. Inclusion of relativistic effects strengthens the bonding much less in Cu and Ag complexes; it is in fact not capable of overcoming the steric repulsion and allowing stronger CT interaction in Ag complexes, since silver atom has the largest van der Waals atomic radius of all coinage metals.<sup>67</sup> Very strong relativistic increase of interaction energy in Au complexes is dictated by relativistic enhancement of the

Au electron affinity and hence supporting the CT mechanism. While the values of electron affinity for Cu, Ag, and Au are similar in the NR limit ( $EA(Cu) = 1.17$  eV;  $EA(Ag) = 1.05$  eV;  $EA(Au) = 1.16$  eV), after inclusion of the relativistic effects, EA of gold almost doubles, while EAs for Cu and Ag increase only moderately ( $EA(Cu) = 1.24$  eV;  $EA(Ag) = 1.25$  eV;  $EA(Au) = 2.23$  eV).<sup>68</sup> Strong relativistic interactions in  $Au \cdots PF_3$  and  $Au \cdots PCl_3$  complexes discussed here are good examples of the aurophilic attraction.<sup>8,69</sup>

At the long-range limit over 5.5 Å we observe that NR potential curves in Figure 1 are below the relativistic curves. This can be explained by the relativistic decrease in dipole polarizabilities of all coinage metal atoms. Since the interaction in this region is dominated by induction, lowering the dipole polarizability means lowering the induced dipole and thus the whole interaction. Order of stabilities of the relativistic interactions in the long-range limit follows the order of relativistic mean dipole polarizabilities ( $\alpha(Cu) = 46.5$  au;  $\alpha(Ag) = 52.5$  au;  $\alpha(Au) = 36.1$  au),<sup>68</sup> Ag complexes being the most stable ones in this region.

Figure 2 serves for comparison of the relativistic effect, effect of electron correlation, and effect of basis set size on the



**Figure 2.** Nonrelativistic (NR) and DK relativistic BSSE corrected ROHF (dashed lines, open symbols) and CCSD(T) (full lines, closed symbols) potential energy curves [kJ/mol] with POL, POL\_DK, and ANO-RCC-VTZP basis sets for  $Au \cdots PF_3$  (a) and  $Au \cdots PCl_3$  (b) complexes as a function of metal–ligand distance [Å].

bonding  $Au \cdots PF_3$  and  $Au \cdots PCl_3$  complexes in a pictorial fashion. We have already discussed the role of the relativistic effect for ML bonding. Here we observe very similar stabilization effect due to the electron correlation and relativistic contribution in the bonding region. However, effect of electron correlation is more important than the effect of relativity in the longer range of ML distances over about 3 Å. Without electron correlation, the whole potential energy curves



**Table 1.** Optimized Metal–Ligand Distances  $R_e$  [Å], out-of-Plane Angles  $\theta$  [°] (for  $C_{2v}$  Ligands), and Interaction Energies  $\Delta E$  [kJ/mol] for Selected Metal–Ligand Complexes Obtained with SA CCSD(T) Method with Various Basis Sets<sup>a</sup>

M	basis set	H <sub>2</sub> O			NH <sub>3</sub>			SH <sub>2</sub>			PH <sub>3</sub>		PF <sub>3</sub>		PCl <sub>3</sub>	
		$\Delta E$	$R_e$	$\theta$	$\Delta E$	$R_e$		$\Delta E$	$R_e$	$\theta$	$\Delta E$	$R_e$	$\Delta E$	$R_e$	$\Delta E$	$R_e$
Cu	POL	−9.8	2.286	56.9	−39.1	2.092		−11.8	2.521	81.8	−19.0	2.389	−0.9	4.530	−10.9	2.409
	POL_DK	−9.9	2.239	58.3	−43.8	2.048		−15.6	2.436	80.3	−26.0	2.324	−7.1	2.282	−18.1	2.320
	ANO-RCC-VTZP	−9.0	2.222	53.0	−41.9	2.052		−12.0	2.419	79.6	−24.8	2.291	−6.8	2.251	−17.7	2.283
	ANO-RCC-VQZP	−14.5	2.162	54.3	−49.1	2.029		−20.1	2.357	78.5	−34.2	2.260	−16.6	2.220	−27.4	2.246
Ag	POL	−5.6	2.840	49.7	−16.9	2.572		−4.0	3.335	90.9	−3.0	3.281	−0.9	4.708	−3.3	3.839
	POL_DK	−4.7	2.884	54.7	−18.0	2.497		−5.2	3.125	89.7	−5.9	2.859	−1.1	4.497	−3.9	3.529
	ANO-RCC-VTZP	−3.8	2.915	45.8	−18.1	2.466		−4.0	3.171	91.0	−5.6	2.772	−0.9	4.622	−3.2	3.541
	ANO-RCC-VQZP	−6.6	2.726	54.8	−23.6	2.416		−8.6	2.917	88.1	−13.0	2.629	−1.4	4.271	−7.3	2.788
Au	POL	−4.5	3.053	47.2	−13.4	2.709		−3.6	3.563	93.4	−2.8	3.636	−1.1	4.673	−3.4	3.897
	POL_DK	−4.6	2.879	66.6	−38.4	2.271		−23.7	2.576	81.0	−48.1	2.399	−32.4	2.343	−41.1	2.376
	ANO-RCC-VTZP	−4.9	2.771	65.0	−40.9	2.261		−28.2	2.513	79.8	−60.5	2.337	−46.0	2.286	−53.2	2.314
	ANO-RCC-VQZP	−8.6	2.598	66.5	−48.3	2.236		−38.4	2.462	78.8	−73.5	2.312	−59.4	2.263	−66.7	2.288

<sup>a</sup>POL results are non-relativistic; other results are DKH relativistic.

are repulsive regardless of basis set size or inclusion of relativity. Correlation alone accounts for the induction interaction of investigated complexes forming the VdW minima on the potential energy curves. Considering the effect of the basis set size, this has very low importance at the uncorrelated ROHF level, as expected. At the correlated CCSD(T) level the extension of the basis set affects the optimized ML distances only slightly lowering them by about 0.1 Å. Its effect on the interaction energies is more notable, lowering them by about 15 kJ/mol. This is consistent with our discussion of data summarized in Table 1. We focused here only on the Au complexes because of their strong relativistic nature. Our findings for Au⋯PF<sub>3</sub> and Au⋯PCl<sub>3</sub> complexes are consistent with results in our previous study on Au⋯PH<sub>3</sub>.<sup>15</sup> Previously suggested term “relativistic bond” is applicable here as well.

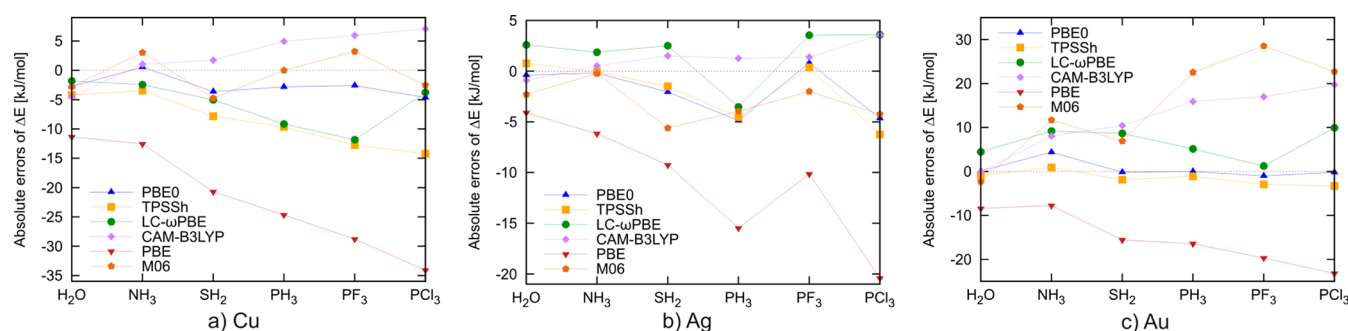
We have also investigated the validity of our assumption of fixed ligand geometry during the complex optimization. We reoptimized the PF<sub>3</sub> and PCl<sub>3</sub> ligand structures in their corresponding complexes with gold, where we observe the strongest interaction and supposedly also the largest geometry distortion. The P–F bond length decreased slightly from 1.563 Å to 1.552 Å and the F–P–F bond angle increased from 97.8° to 99.1° upon interaction with gold. Similarly, the P–Cl bond length decreased almost imperceptibly from 2.043 Å to 2.038 Å and the Cl–P–Cl bond angle increased from 100.1° to 101.8° upon complexation. Changes in interaction energies related to the ligand relaxation are quite small;  $\Delta E$  increased from −59.4 to −60.9 kJ/mol for Au⋯PF<sub>3</sub> complex, and from −66.7 to −68.1 kJ/mol for Au⋯PCl<sub>3</sub> complex. Such small changes in geometry parameters and interaction energies clearly can not affect our general discussion and the qualitative picture. Discussed ligand relaxation data were obtained with the ANO-RCC-VQZP basis set.

**3.2. Benchmark Results.** Table 1 summarizes the most important results of the present study – the optimized geometry parameters ( $R_e$ ,  $\theta$ ) and interaction energies  $\Delta E$  for complexes of coinage metals with H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, PH<sub>3</sub>, PF<sub>3</sub>, and PCl<sub>3</sub> obtained with CP corrected ROHF SA CCSD(T) method. Nonrelativistic results were obtained with POL basis

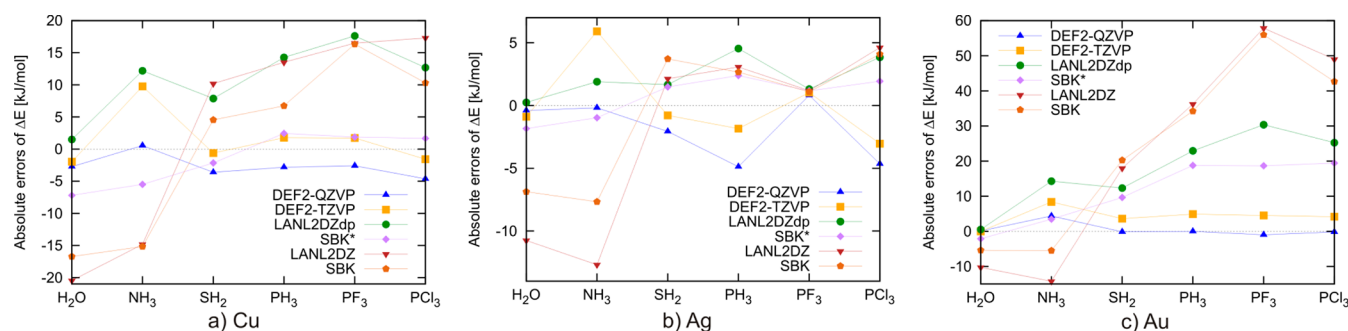
set, while results with POL\_DK, ANO-RCC-VTZP, and ANO-RCC-VQZP basis sets are scalar DKH relativistic. Although complexes with H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, and PH<sub>3</sub> ligands were studied by our group previously,<sup>13–15</sup> we present here new benchmark data obtained with the considerably larger ANO-RCC basis sets.

Generally, increasing the basis set size strengthens the ML interaction (i.e., shifts the interaction energies  $\Delta E$  toward more negative values and shortens the metal–ligand distances  $R_e$ ) without changing the overall qualitative picture. For Cu and Au complexes this is quite uniform, especially for the complexes with PX<sub>3</sub> ligands.

In complexes of copper the decrease of  $\Delta E$  connected with extending the basis set from POL\_DK to ANO-RCC-VQZP ranges from −5.3 to −9.5 kJ/mol and ML distance shortening ranges from −0.02 to −0.08 Å. Corresponding changes for complexes of gold vary from −9.8 to −27.0 kJ/mol and from −0.04 to −0.11 Å, respectively. In silver complexes we observe much larger ML distance shortenings, even when the ANO-RCC-VTZP basis set is extended to the ANO-RCC-VQZP basis set. Exceptionally large drop of −0.74 Å in ML distance appears in the Ag⋯PCl<sub>3</sub> complex. For the rest of the silver complexes this drop ranges from −0.08 to −0.23 Å. This can be attributed to the fact, that silver complexes are generally the weakest interacting ones balancing on the edge between charge-transfer and induction interaction, having very broad and shallow minima on the potential energy curve. Thus the small variation in computational approach might result in the change in the very nature of their interaction. We can support this by observing their ML distances. All complexes exhibiting large ML distance shortenings due to the basis set extension (over −0.2 Å), have their CCSD(T)/POL\_DK optimized  $R_e$  values over 2.8 Å, while the rest of the complexes are well below this threshold and have a dominant charge-transfer character. However, decrease of the interaction energies  $\Delta E$  of silver complexes is quite small, ranging from −0.3 to −7.1 kJ/mol. This is because they remain the weakest ones even after enlarging the basis set size.



**Figure 3.** Absolute errors of DFT interaction energies  $\Delta E$  obtained with PBE0, TPSSh, LC- $\omega$ PBE, CAM-B3LYP, PBE, and M06 functionals using the DEF2-QZVP basis set with respect to CCSD(T)/ANO-RCC-VQZP results. (a) Cu, (b) Ag, and (c) Au complexes with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ , and  $\text{PCl}_3$  ligands, respectively.



**Figure 4.** Absolute errors of DFT interaction energies  $\Delta E$  obtained with PBE0 functional using DEF2-QZVP, DEF2-TZVP, LanL2DZdp, SBK\*, LanL2DZ, and SBK basis sets with respect to CCSD(T)/ANO-RCC-VQZP results. (a) Cu, (b) Ag, and (c) Au complexes with  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_3$ ,  $\text{PF}_3$ , and  $\text{PCl}_3$  ligands, respectively.

**3.3. DFT Results.** Since the Density Functional Theory (DFT) method is much less computationally demanding than ab initio highly correlated methods (e.g., the CC method), it is expected to be very effective for computation of larger molecular systems. The major drawback is the uncertainty of accuracy of DFT results obtained with any of the numerous DFT functionals, unless they are benchmarked with respect to highly accurate ab initio method.

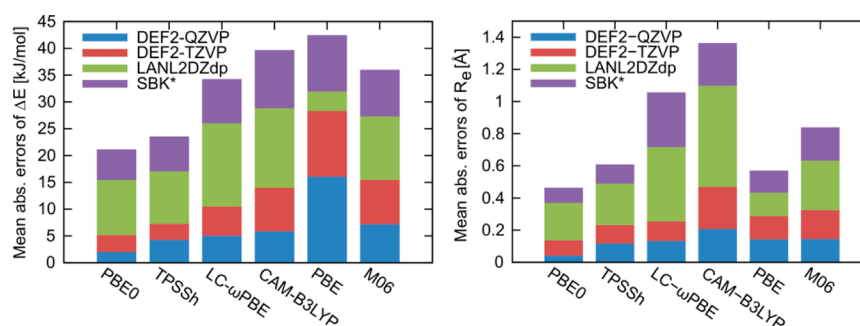
When treating transition metal complexes or organometallic compounds it is a common practice to use smaller effective core potential (ECP) basis sets<sup>4,30,70,71</sup> rather than full electron basis sets, which may be too large in the case of heavy metals and may result in excessive enhancement of the computational cost. Another advantage is the implicit inclusion of relativity in the ECP basis sets.

We provide a comparison of our benchmark CCSD(T) results with results obtained with several DFT functionals, where we have reoptimized the complex geometries in a fashion analogous to our CCSD(T) optimizations. We included commonly used local functional PBE as well as its hybrid version PBE0. Since we are dealing with CT and VdW complexes, we also chose functionals with long-range corrections, i.e., LC- $\omega$ PBE, CAM-B3LYP, and other functionals suitable for noncovalent interactions, i.e., TPSSh and M06. To evaluate the performance of the functional separately from the effect of the basis set size we used the DEF2-QZVP ECP basis set, which has a similar valence shell structure as the full electron ANO-RCC-VQZP basis set.

Figure 3 depicts the absolute errors of interaction energies obtained by the investigated DFT functionals with respect to the benchmark DKH2 CCSD(T)/ANO-RCC-VQZP interaction energies separately for Cu, Ag, and Au complexes. We

clearly recognize, that performance of PBE0 and TPSSh functionals stands out, PBE0 functional working slightly better (especially for the Cu complexes). CAM-B3LYP functional generally underestimates the interaction energies, especially for the Au complexes. Functionals LC- $\omega$ PBE and M06 are rather inconsistent in their performance. The LC- $\omega$ PBE functional overestimates  $\Delta E$  in Cu complexes and underestimates  $\Delta E$  in Au complexes. The M06 functional produces reasonable  $\Delta E$  for Cu complexes, but overestimates  $\Delta E$  in Ag complexes and underestimates  $\Delta E$  in Au complexes. Pure PBE functional considerably overbinds all investigated complexes, producing the largest overall error of over 34 kJ/mol in the case of  $\text{Cu}\cdots\text{PCl}_3$  complex. This is a well-known deficiency of this functional.<sup>72–75</sup>

The DEF2-QZVP basis set is still quite large and is often replaced with smaller basis sets. Hence we wanted to investigate the effect of basis set size as well. We spotted the PBE0 functional as the most suited for computation of examined ML complexes. Thus we used this functional with six different ECP basis sets—DEF2-QZVP, DEF2-TZVP, LanL2DZdp, LanL2DZ, SBK\*, and SBK. Results are summarized in Figure 4 for Cu, Ag, and Au complexes. The DEF2-QZVP basis set reproduces interaction energies the most accurately. Smaller DEF2-TZVP basis set still produces acceptable results. Interestingly, this basis seems to underestimate particularly  $\Delta E$  in  $\text{M}\cdots\text{NH}_3$  complexes. The LanL2DZdp basis set underestimates the  $\Delta E$  in Cu and Au complexes, and the SBK\* basis set reproduces  $\Delta E$  in Cu and Ag complexes, while still failing to reproduce  $\Delta E$  in Au complexes. Basis sets SBK and LanL2DZ lacking polarization functions on nonmetal atoms produce very large and very unsystematic errors. Therefore we omit them in further discussion. Since the silver



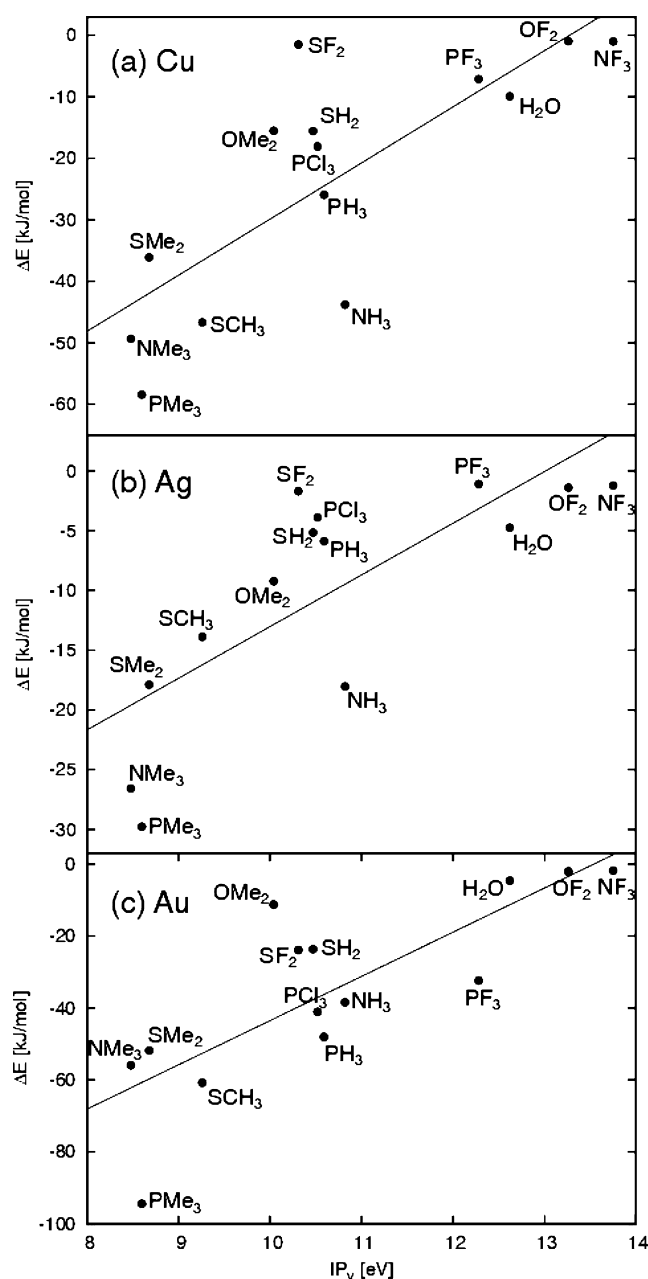
**Figure 5.** Mean absolute errors (MAE) of DFT interaction energies,  $\Delta E$ , and metal–ligand distances,  $R_e$ , for all combinations of DFT functionals and basis sets with respect to CCSD(T)/ANO-RCC-VQZP results. Height of each colored segment represents the MAE value.

complexes exhibit generally weaker interactions, even small absolute errors of PBE0 functional with DEF2-QZVP basis set turn into considerably large relative errors reaching up to 64% in the case of  $\text{Ag}\cdots\text{PCl}_3$  complex.

We also provide an error analysis for all combinations of DFT functionals and basis sets (excluding LanL2DZ and SBK). Mean absolute errors (MAE), root mean squared errors (RMSE) and mean signed errors (MSE) for interaction energies, ML distances and out-of-plane angles (for complexes with  $C_{2v}$  ligands) throughout all investigated complexes are collected in Table S1 in the Supporting Information. MAEs are the most informative statistical values, which describe the average magnitude of errors of the examined method with respect to the benchmark reference. MAEs for  $\Delta E$  and  $R_e$  are briefly summarized in Figure 5. RMSEs and MSEs are useful as a tool for systematic understanding of errors. The closer the MSE is to zero, the better the accuracy of the result as the systematic shift is smaller. RMSE gives higher weight to larger errors and lower weight to smaller ones. Hence, the greater the difference between the RMSEs and MAEs, the greater is the variance in error magnitudes. Once again, these data point out the superiority of the PBE0/DEF2-QZVP combination over all other tested combinations, giving MAE = 1.99 kJ/mol, RMSE = 2.66 kJ/mol, and MSE = −1.34 kJ/mol for interaction energies and MAE = 0.041 Å, RMSE = 0.056 Å, and MSE = −0.001 Å for ML distances.

**3.4. Analysis of ML Interactions.** In our previous works<sup>13–15</sup> we considered the metal–ligand interaction as an interplay between charge-transfer stabilization and steric valence repulsion. The assumed charge transfer from ligand lone-pair orbital to the metal singly occupied valence  $ns$  orbital was supported by much larger relativistic stabilization of the Au 6s orbital in comparison to Cu and Ag, which in turn increased the interaction energies of the gold complexes compared to the silver ones. Another supporting argument for such interpretations was the qualitative correlation between decreasing IP of various ligands and increasing metal–ligand interaction energies.<sup>21</sup> To investigate this matter more thoroughly we computed in addition to the previously studied ligands  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{PH}_3$  their fluorinated and methylated counterparts ( $\text{OF}_2$ ,  $\text{NF}_3$ ,  $\text{SF}_2$ ,  $\text{PF}_3$ ,  $\text{OMe}_2$ ,  $\text{NMe}_3$ ,  $\text{SMe}_2$ , and  $\text{PMe}_3$ ) as well as one chlorinated ligand  $\text{PCl}_3$ .

We optimized all metal–ligand complexes at the CCSD(T)/POL\_DK level of theory and correlated the resulting interaction energies ( $\Delta E$ ) with collected experimental vertical ionization potentials. Results are displayed in Figure 6. We observe qualitative correlation between the interaction energies and IPs, however, no quantitative conclusions can be drawn



**Figure 6.** Correlation between interaction energies of (a) copper, (b) silver, and (c) gold complexes ( $\Delta E$ ) and experimental vertical ionization potentials ( $\text{IP}_v$ ) of corresponding ligands taken from refs 76 and 77.

**Table 2. Optimized Metal–Ligand Distances  $R_e$  [Å], out-of-Plane Angles  $\theta$  [°] (for  $C_{2v}$  Ligands), and Interaction Energies  $\Delta E$  [kJ/mol] for Copper Complexes Obtained with CCSD(T)/POL\_DK<sup>a</sup>**

complex	$R_e$	$\theta$	$\Delta E$	$\Delta E_{CT}$	$\Delta E_{L \rightarrow M}^D$	$\Delta E_{i \rightarrow j}^D$	$\Delta \epsilon_{ji}^D$	$f_{ij}^D$	$\Delta E_{L \leftarrow M}^B$	$\Delta E_{j \leftarrow i}^B$	$\Delta \epsilon_{ji}^B$	$f_{ij}^B$
Cu...OH <sub>2</sub>	2.237	58.3	−9.9	−92.6	−39.7	−29.7	0.85	0.111	−52.0	−48.5	1.35	0.150
Cu...OF <sub>2</sub>	3.787	47.2	−1.0	−5.6	−4.9	−2.7	0.88	0.032	−0.7	0.0	1.79	0.003
Cu...OMe <sub>2</sub>	2.217	35.2	−15.5	−104.1	−47.4	−22.7	0.71	0.094	−56.7	−40.7	0.78	0.113
Cu...NH <sub>3</sub>	2.048		−43.8	−179.8	−81.9	−59.6	0.69	0.149	−100.5	−75.9	1.64	0.213
Cu...NF <sub>3</sub>	3.885		−1.0	−9.0	−8.3	−5.2	0.90	0.042	−0.7	0.0	1.60	0.000
Cu...NMe <sub>3</sub>	2.110		−49.4	−143.4	−66.3	−37.9	0.59	0.119	−75.6	−36.0	1.02	0.139
Cu...SH <sub>2</sub>	2.434	80.3	−15.7	−130.3	−85.5	−69.2	0.66	0.157	−50.9	−41.6	1.08	0.129
Cu...SF <sub>2</sub>	3.912	42.4	−1.5	−14.2	−12.4	−7.5	0.63	0.043	−1.8	0.0	1.03	0.002
Cu...SMe <sub>2</sub>	2.367	71.1	−36.1	−183.3	−118.5	−86.2	0.57	0.169	−75.8	−55.9	0.97	0.132
Cu...PH <sub>3</sub>	2.323		−26.0	−198.1	−117.0	−108.0	0.68	0.196	−90.7	−53.7	0.88	0.137
Cu...PF <sub>3</sub>	2.282		−7.1	−271.7	−197.0	−146.9	0.57	0.239	−88.4	−40.4	1.02	0.139
Cu...PCl <sub>3</sub>	2.320		−18.1	−236.5	−138.4	−106.7	0.61	0.201	−109.9	−33.6	1.16	0.118
Cu...PMe <sub>3</sub>	2.283		−58.4	−253.6	−169.0	−140.2	0.53	0.212	−106.4	−61.0	0.77	0.137

<sup>a</sup>Total charge-transfer stabilization energies  $\Delta E_{CT}$  [kJ/mol], total donation stabilization energies  $\Delta E_{L \rightarrow M}^D$  [kJ/mol]; discussed single donation stabilization energies  $\Delta E_{i \rightarrow j}^D$  [kJ/mol]; corresponding orbital energy differences  $\Delta \epsilon_{ji}^D$  [a.u.] and Fock matrix elements  $f_{ij}^D$  [a.u.]. Analogous parameters for the back-donation are superscripted with B.

**Table 3. Optimized Metal–Ligand Distances  $R_e$  [Å], out-of-Plane Angles  $\theta$  [°] (for  $C_{2v}$  Ligands), and Interaction Energies  $\Delta E$  [kJ/mol] for Silver Complexes Obtained with CCSD(T)/POL\_DK<sup>a</sup>**

complex	$R_e$	$\theta$	$\Delta E$	$\Delta E_{CT}$	$\Delta E_{L \rightarrow M}^D$	$\Delta E_{i \rightarrow j}^D$	$\Delta \epsilon_{ji}^D$	$f_{ij}^D$	$\Delta E_{L \leftarrow M}^B$	$\Delta E_{j \leftarrow i}^B$	$\Delta \epsilon_{ji}^B$	$f_{ij}^B$
Ag...OH <sub>2</sub>	2.887	54.7	−4.8	−32.5	−14.5	−10.1	0.78	0.060	−17.9	−15.0	1.05	0.072
Ag...OF <sub>2</sub>	3.927	92.0	−1.4	−6.6	−5.8	−2.3	0.77	0.028	−0.9	0.0	1.76	0.002
Ag...OMe <sub>2</sub>	2.763	37.9	−9.2	−38.9	−18.3	−5.9	0.61	0.048	−20.9	−13.0	0.75	0.075
Ag...NH <sub>3</sub>	2.497		−18.0	−101.4	−46.1	−33.5	0.66	0.109	−54.0	−47.9	1.95	0.168
Ag...NF <sub>3</sub>	3.974		−1.2	−9.9	−9.0	−5.4	0.91	0.043	−0.9	0.0	1.59	0.000
Ag...NMe <sub>3</sub>	2.536		−26.6	−85.1	−41.9	−24.2	0.59	0.100	−42.7	−22.4	1.21	0.133
Ag...SH <sub>2</sub>	3.122	89.7	−5.2	−45.8	−30.1	−23.0	0.55	0.083	−16.1	−13.4	0.90	0.067
Ag...SF <sub>2</sub>	4.069	44.2	−1.7	−14.2	−12.7	−7.3	0.61	0.039	−1.5	0.0	1.03	0.001
Ag...SMe <sub>2</sub>	2.832	75.8	−17.9	−104.1	−69.9	−46.9	0.51	0.121	−39.3	−27.3	1.02	0.114
Ag...PH <sub>3</sub>	2.858		−5.9	−93.6	−59.4	−52.9	0.67	0.131	−37.9	−24.5	0.83	0.092
Ag...PF <sub>3</sub>	4.498		−1.1	−11.9	−11.3	−6.7	0.68	0.019	−0.7	−0.1	0.57	0.028
Ag...PCl <sub>3</sub>	3.529		−3.9	−31.6	−23.1	−15.6	0.73	0.071	−8.8	0.0	0.86	0.000
Ag...PMe <sub>3</sub>	2.626		−29.8	−178.0	−122.6	−102.1	0.48	0.177	−69.3	−38.5	0.82	0.129

<sup>a</sup>Remaining symbols concerning the charge transfer analysis are explained in the caption of Table 2.

**Table 4. Optimized Metal–Ligand Distances  $R_e$  [Å], out-of-Plane Angles  $\theta$  [°] (for  $C_{2v}$  Ligands), and Interaction Energies  $\Delta E$  [kJ/mol] for Gold Complexes Obtained with CCSD(T)/POL\_DK<sup>a</sup>**

complex	$R_e$	$\theta$	$\Delta E$	$\Delta E_{CT}$	$\Delta E_{L \rightarrow M}^D$	$\Delta E_{i \rightarrow j}^D$	$\Delta \epsilon_{ji}^D$	$f_{ij}^D$	$\Delta E_{L \leftarrow M}^B$	$\Delta E_{j \leftarrow i}^B$	$\Delta \epsilon_{ji}^B$	$f_{ij}^B$
Au...OH <sub>2</sub>	2.880	66.6	−4.6	−31.4	−15.9	−11.0	0.68	0.061	−15.4	−8.4	1.35	0.062
Au...OF <sub>2</sub>	3.813	104.8	−2.0	−8.2	−6.0	−1.6	0.72	0.023	−2.2	0.0	1.92	0.001
Au...OMe <sub>2</sub>	2.630	46.7	−11.3	−55.7	−26.1	−15.8	0.64	0.079	−30.0	−13.3	0.96	0.086
Au...NH <sub>3</sub>	2.271		−38.4	−193.9	−111.2	−97.8	0.65	0.193	−84.5	−53.2	1.61	0.182
Au...NF <sub>3</sub>	3.698		−1.8	−13.7	−10.4	−6.0	0.91	0.046	−3.3	0.0	1.64	0.000
Au...NMe <sub>3</sub>	2.313		−56.0	−193.1	−103.8	−78.2	0.52	0.166	−88.7	−39.1	0.99	0.130
Au...SH <sub>2</sub>	2.577	81.0	−23.8	−165.7	−119.2	−106.2	0.54	0.187	−56.3	−35.6	1.07	0.121
Au...SF <sub>2</sub>	2.437	65.6	−23.9	−274.9	−207.7	−170.1	0.53	0.242	−88.5	−16.3	1.52	0.142
Au...SMe <sub>2</sub>	2.502	70.7	−51.8	−240.9	−177.2	−147.7	0.46	0.215	−81.7	−41.5	1.13	0.139
Au...PH <sub>3</sub>	2.397		−48.1	−328.5	−215.3	−204.9	0.54	0.258	−144.7	−56.2	0.92	0.148
Au...PF <sub>3</sub>	2.343		−32.4	−425.4	−301.3	−241.1	0.45	0.293	−159.7	−32.4	1.14	0.149
Au...PCl <sub>3</sub>	2.376		−41.1	−397.8	−227.4	−190.8	0.52	0.257	−195.2	−35.1	1.29	0.101
Au...PMe <sub>3</sub>	2.371		−94.4	−456.8	−323.9	−276.6	0.43	0.279	−176.5	−68.9	0.85	0.147

<sup>a</sup>Remaining symbols concerning the charge transfer analysis are explained in the caption of Table 2.

from this correlation. Coefficient of determination is largest for Au complexes and lowest for the Ag complexes ( $R^2(\text{Cu}) = 0.624$ ;  $R^2(\text{Ag}) = 0.590$ ;  $R^2(\text{Au}) = 0.637$ ) agreeing with the trend of the magnitude of interaction energies  $\Delta E(\text{Au}) >$

$\Delta E(\text{Cu}) > \Delta E(\text{Ag})$ . Interestingly enough the interaction energies correlate a little better with adiabatic IPs ( $R^2(\text{Cu}) = 0.675$ ;  $R^2(\text{Ag}) = 0.625$ ;  $R^2(\text{Au}) = 0.729$ ), retaining the qualitative picture. However, since results used in this



correlation were obtained with frozen geometries of ligands, interaction energies should be correlated with vertical IPs.

Geometries and interaction energies ( $\Delta E$ ) are collected in the first three columns of Tables 2–4. Gold complexes are in general the strongest (i.e., having the most negative  $\Delta E$ ) and silver complexes are generally the weakest ones. Considering the substitution effects we clearly see, that fluorination weakens the interaction, while methylation strengthens it. This is expected as fluorine is very electronegative and draws charge from the donor atom (and effectively from the lone-pair orbital) via  $-I$  inductive effect, while methyl group affects the electron density on the donor atom in the opposite way via the  $+I$  inductive effect. There are only few minor exceptions to the stated general  $\Delta E$  ordering. Copper is interacting stronger than gold with water and dimethylether, gold having the weakest interaction with water of all coinage metals. Since IPs of water,  $\text{OF}_2$  and  $\text{NF}_3$  are highest of all ligands, the charge transfer is hindered and contributes to the stabilization of their complex with gold substantially less than ligands having lower IPs. Also, the sequence of interaction energies of coinage metals with fluorinated ligands  $\text{OF}_2$ ,  $\text{NF}_3$ , and  $\text{SF}_2$  is  $\Delta E(\text{Au}) > \Delta E(\text{Ag}) > \Delta E(\text{Cu})$ , i.e., different than with other ligands. This is due to the different bonding mechanism in complexes with most of the fluorinated species, which are better described as VdW complexes. The second trend has only one exception, interaction of Au with  $\text{SF}_2$ , which is slightly stronger than the interaction with  $\text{H}_2\text{S}$ .

Following our argument about the charge transfer from the lone-pair orbital of ligand to the metal, corresponding ionization should also take place at that lone-pair orbital. In order to verify that experimental first ionization potentials used in Figure 6 correspond to the ionization from the lone-pair orbital we computed IPs as well. We would also like to demonstrate that with methods applied to computations of interaction energies we are able to reproduce experimental IPs with sufficient accuracy. In the first step we used the same level of theory as for above-mentioned optimizations, i.e., CCSD-(T)/POL\_DK. Improved accuracy is achieved with larger aug-cc-pVTZ basis set. Obtained ionization potentials are collected in Table 5 alongside the experimental values.<sup>76,77</sup> Without any effort to provide benchmark IPs by, e.g., extrapolation to the CBS limit, all computed values agree very well with experiment.

**Table 5. Computed and Experimental Vertical Ionization Potentials [eV] of Investigated Ligands**

ligand	CCSD(T)		experiment <sup>a</sup>
	POL_DK	aug-cc-pVTZ	
$\text{H}_2\text{O}$	12.47	12.68	12.62
$\text{OF}_2$	13.06	13.30	13.26
$\text{OMe}_2$	9.97	10.15	10.04
$\text{NH}_3$	10.73	10.90	10.82
$\text{NF}_3$	13.61	13.61	13.75
$\text{NMe}_3$	8.37	8.51	8.48
$\text{H}_2\text{S}$	10.18	10.40	10.47
$\text{SF}_2$	10.08	10.27	10.31 <sup>b</sup>
$\text{SMe}_2$	8.54	8.72	8.68
$\text{PH}_3$	10.43	10.57	10.59
$\text{PF}_3$	12.08	12.14	12.28
$\text{PCl}_3$	10.31	10.45	10.52
$\text{PMe}_3$	8.50	8.62	8.6

<sup>a</sup>Reference 76. <sup>b</sup>Reference 77.

The aug-cc-pVTZ errors stay within  $\pm 0.15$  eV margin, and POL\_DK results, being quite systematically lower by about 0.1–0.2 eV with respect to the former results, are still very reasonable.

The charge transfer interaction mechanism requires ligand and metal to be close enough so that their frontier orbitals can effectively overlap and electrons can redistribute. Looking at the optimized metal–ligand distances  $R_e$  in Tables 2–4, we find there is an obvious gap between two groups of complexes. Complexes with shorter metal–ligand distances can be considered as CT complexes while longer distances imply VdW complexes. For copper all CT complex distances range from 2.0 to 2.5 Å and VdW complex distances range from 3.7 to 4.0 Å; for silver these intervals are 2.5–3.2 and 3.9–4.5 Å, respectively; for gold these intervals are 2.2–2.9 and 3.7–3.8 Å, respectively. All complexes in the CT interval are lower in energy than complexes in VdW interval, as expected. An intermediate between the specified intervals (and supposedly interaction mechanism) is the  $\text{Ag}\cdots\text{PCl}_3$  complex with its metal–ligand distance of 3.529 Å. Enlarging the basis sets size to ANO-RCC-VQZP, however, places the  $\text{Ag}\cdots\text{PCl}_3$  complex well into the interval for the CT complexes with the ML distance of 2.788 Å, as we discussed in section 3.2.

All complexes with  $\text{C}_{3v}$  ligands ( $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{NF}_3$ ,  $\text{PF}_3$ ,  $\text{PCl}_3$ ,  $\text{NMe}_3$ , and  $\text{PMe}_3$ ) are quasilinear. This is expected as there is no ambiguity in the orientation of the lone-pair orbital in  $\text{C}_{3v}$  ligands and, which coincides with the  $\text{C}_3$  axis of the ligand itself and the complex as well. The same holds for the dipole moment.

Complexes with  $\text{C}_{2v}$  ligands ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ ,  $\text{OF}_2$ ,  $\text{SF}_2$ ,  $\text{OMe}_2$ , and  $\text{SMe}_2$ ) on the other hand are bent with respect to the orientation of the ligand dipole moment, so that the metal lies in a plane perpendicular to molecular plane of the ligand, thus retaining the  $\text{C}_s$  symmetry of the complex. The corresponding out-of-plane angles  $\theta$  are collected in Tables 2–4. This was previously explained by the metal interacting with the lone-pair orbital oriented away from the molecular axis (CT mechanism) rather than forming an electrostatic dipole–induced dipole pair (induction VdW mechanism).<sup>13</sup>

Out-of-plane angles of water complexes are around  $60^\circ$ , while angles of  $\text{SH}_2$  complexes are closer to  $90^\circ$ . This addresses the problem of lone pair hybridization. The former value suggests that water orbitals undergo hybridization and form so-called “rabbit ears”, while sulfane according to the latter value keeps unhybridized s and p orbitals. Similar findings were made in the case of interaction between metal cations and water.<sup>70</sup> Comparing the H–O–H and H–S–H bond angles ( $104.5^\circ$  and  $92.1^\circ$ , respectively) it is clear, that S–H bonding is due to the unhybridized p orbitals on sulfur, while O–H bonding is due to  $\text{sp}^3$  hybrid orbitals. Similarly, bond angles in ammonia and phosphine ( $106.7^\circ$  and  $93.4^\circ$ , respectively) suggest the same picture for P–H and N–H bonding. Generally, hybridization concerns the second row elements only. Reasons for this are manifold and are thoroughly covered in the review paper concerning bonding in amines and phosphines.<sup>78</sup> There are several theoretical studies dealing with hybridization in other small molecules, mostly hydrides.<sup>79–81</sup>

**3.5. NBO Analysis.** The charge transfer nature of the metal–ligand interaction was analyzed in terms of interacting NBOs at the optimized geometry of each complex. Following the procedure described by Reed et al. in their study of bimolecular complexes,<sup>82</sup> we have computed the total charge-transfer stabilization energies  $\Delta E_{\text{CT}}$  for all complexes by

forbidding all intermolecular delocalizations, i.e., zeroing all NBO Fock matrix off-diagonal elements between occupied orbitals of the first subsystem and virtual orbitals of the second subsystem and vice versa, and constructing a new density matrix for energy evaluation. Similarly, total donation stabilization energies  $\Delta E_{L \rightarrow M}^D$  and back-donation stabilization energies  $\Delta E_{L \leftarrow M}^B$  were obtained by forbidding delocalizations from ligand to metal and from metal to ligand, respectively. These energies are collected in Tables 2–4. Since  $\Delta E_{CT}$  increases almost exponentially with decreasing metal–ligand distance (similarly as steric repulsion),<sup>82</sup> it comes as no surprise, that VdW complexes have quite small  $\Delta E_{CT}$  values, while for CT complexes we observe stabilization energies 2 orders of magnitude larger (up to  $-450$  kJ/mol). Naturally,  $\Delta E_{CT}$  values are not solely dictated by distance, they rely heavily on the nature of interaction, and we can see very different values for complexes with quite similar metal–ligand distances.

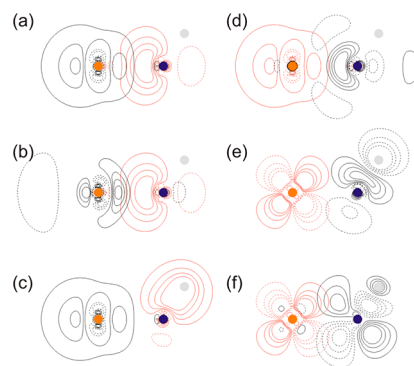
The commonly accepted explanation for quite strong interactions of (substituted) phosphines with metals is increased back-donation in phosphines compared to amines, partially attributed to accessible empty 3d orbitals on phosphorus combining with the P–H  $\sigma^*$  antibonding orbitals.<sup>83–86</sup> Our results for coinage metal complexes contradict this picture. Complexes with  $H_2O$ ,  $OMe_2$ ,  $NH_3$ , and  $NMe_3$  ligands are actually more stabilized through back-donation than through donation, and the opposite is true for complexes with  $H_2S$ ,  $SMe_2$ ,  $PH_3$ , and  $PMe_3$ , regardless of the complexing coinage metal. When we compare ligands containing oxygen and nitrogen with ligands containing sulfur and phosphorus, it is clear that donation stabilization energies increase considerably more than back-donation stabilization energies, when we go down one period. Actually, for complexes of copper and silver with water and ammonia we observe a decrease in back-donation stabilization energies when we compare them to complexes with sulfane and phosphine. Complexes with fluorinated ligands are excluded from this discussion for the time being due their predominant VdW nature and weak interaction.

We investigated the metal–ligand interactions in more detail and found a dominant donation from ligand lone-pair orbital to singly occupied metal  $ns$  orbital (Figure 7a) and dominant back-donation from the same metal  $ns$  orbital to virtual lone-pair orbital  $n^*$  on ligand – orbital having same direction as valence lone pair and built from  $(n + 1)$  shell AOs (Figure 7d). Stabilization energies for described interactions collected in Tables 2–4 are denoted  $\Delta E_{i \rightarrow j}^D$  and  $\Delta E_{j \leftarrow i}^B$ , respectively, and were obtained in the same fashion as described for  $\Delta E_{CT}$ . For better interpretation we also provide corresponding orbital energy differences ( $\Delta \epsilon_{ji} = \epsilon_j - \epsilon_i$ ) and Fock matrix elements  $f_{ij}$  for the discussed donation and back-donation orbital pairs. These are used for evaluation of second order estimates of stabilization energy according to the equation

$$E^{(2)} = -q_i f_{ij}^2 / (\epsilon_j - \epsilon_i)$$

where  $q_i$  stands for the donor orbital occupation number.

Part of the donation stabilization energy ( $\Delta E_{L \rightarrow M}^D$ ) not covered by the dominant interaction ( $\Delta E_{i \rightarrow j}^D$ ) is composed of number of different interactions, all of which contribute with stabilization energies considerably smaller than  $\Delta E_{i \rightarrow j}^D$  in the hydrogenated and methylated ligand complexes. Most of these interactions are completely negligible; however, some weak but



**Figure 7.** Interacting natural bond orbitals (NBOs) of  $Au \cdots PH_3$  complex, donating orbitals are contoured in red, accepting orbitals are contoured in black. Atoms Au, P, and H (from left to right) are represented by orange, blue and light gray dot, respectively. (a)  $n \rightarrow 6s$  donation ( $6s$  is slightly  $d$  polarized, by about 7%); (b)  $n \rightarrow 6p_z$  donation; (c)  $\sigma \rightarrow 6s$  donation; (d)  $6s \rightarrow n^*$  back-donation ( $n^*$  is a mixture of  $4s$  and  $4p_z$ ); (e)  $5d \rightarrow \sigma^*$  back-donation; and (f)  $5d \rightarrow 3d$  back-donation.

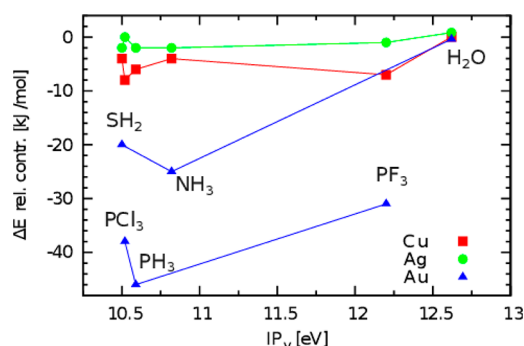
notable interactions include donation from ligand lone-pair orbital to metal virtual  $np_z$  orbital (Figure 7b), donation from ligand  $\sigma$  bonds to metal singly occupied  $ns$  orbital (Figure 7c), back-donation from metal  $(n - 1)d$  orbitals to ligand  $\sigma^*$  antibonds (Figure 7e), and back-donation from metal  $(n - 1)d$  orbitals to ligand virtual  $d$  orbital (Figure 7f). For example, second order estimates ( $E^{(2)}$ ) for these interactions in  $Au \cdots PH_3$  complex are  $-32.8$ ,  $-12.9$ ,  $-46.9$ , and  $-16.2$  kJ/mol, respectively. Note that  $E^{(2)}$  values are typically overestimated by about 30–70% with respect to the stabilization energies obtained from the Fock matrix deletion analysis.

In Tables 2–4 we observe that methylation of the ligand generally improves its donation and back-donation by lowering the orbital energy difference  $\Delta \epsilon_{ji}$ . Simultaneously, it lowers the Fock matrix elements of donation and back-donation for oxygen and nitrogen donors, while the opposite holds for sulfur and phosphorus donors. Hence, effect of methylation is more pronounced in the S, P donors, where the  $\Delta \epsilon_{ji}$  decrease goes hand in hand with the  $f_{ij}$  increase. Fluorinated and hydrogenated ligands cannot be directly compared due to the large differences of metal–ligand distance for most of the complex pairs. Nevertheless, for  $Cu \cdots PX_3$  ( $X = H, F$ ),  $Au \cdots SX_2$  ( $X = H, F$ ), and  $Au \cdots PX_3$  ( $X = H, F$ ), where changes in geometry are not as severe, we observe fluorination enhances the  $n \rightarrow ns$  donation primarily through the increase of  $f_{ij}^D$  elements, while it hinders the  $ns \rightarrow n^*$  back-donation primarily via increase of the  $\Delta \epsilon_{ji}^B$  values. Regarding the general increase in donation and back-donation when comparing the second and third row donor atoms, this is a concerted effect of decreasing  $\Delta \epsilon_{ji}$  values and increasing  $f_{ij}$  values, former being more important for donation when going from oxygen to sulfur ligands, latter being more important for donation when going from nitrogen to phosphorus ligands.

According to a previous study,<sup>87</sup> methylation of the phosphine ligand ought to stabilize the  $n^*$  virtual lone-pair orbital and thus should promote the dominant  $ns \rightarrow n^*$  back-donation, while the effect of the fluorination should be opposite. Indeed, we can confirm this by comparing the corresponding second order estimates of the stabilization energies for the dominant  $6s \rightarrow n^*$  back-donation in  $Au \cdots PH_3$ ,  $Au \cdots PF_3$ , and  $Au \cdots PMe_3$  complexes,  $-62.6$ ,  $-51.4$ , and  $-66.8$  kJ/mol, respectively. Effects of methylation and fluorination on

the phosphine  $\sigma^*$  antibonding orbital and the corresponding ( $n - 1$ )d  $\rightarrow \sigma^*$  back-donation should be reversed.<sup>83,86,87</sup> However, comparing the second order estimates of the stabilization energies for the 5d  $\rightarrow \sigma^*$  back-donation in Au...PH<sub>3</sub>, Au...PF<sub>3</sub>, and Au...PMe<sub>3</sub> complexes (−46.9, −73.6, and −51.2 kJ/mol, respectively) reveals, that in fact both, methylation and fluorination, promote the 5d  $\rightarrow \sigma^*$  back-donation, although the effect of fluorination is much stronger.

Figure 8 depicts the contribution of relativity to interaction energies of complexes with H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, PH<sub>3</sub>, PF<sub>3</sub>, and PCl<sub>3</sub>



**Figure 8.** Energy difference between relativistic (DK CCSD(T)/POL\_DK) and nonrelativistic (NR CCSD(T)/POL) minima of interaction energies of M(Au, Ag, Cu)...L(NH<sub>3</sub>, H<sub>2</sub>O, PH<sub>3</sub>, PF<sub>3</sub>, PCl<sub>3</sub>, and SH<sub>2</sub>) complexes as a function of experimental vertical IP<sub>v</sub> of ligand. IP<sub>v</sub> values taken from ref 76.

as a function of experimental vertical ionization potentials.<sup>76</sup> Figure 8 clearly supports our assumption, that the CT interaction of metal–ligand complexes is supported by increasing of metal electron affinity and decreasing the ligand ionization potential. The Au complexes exhibit the largest relativistic contributions to interaction for all investigated complexes, as the EA of gold doubles after the inclusion of relativity.<sup>68</sup> Relativistic contributions for Cu and Ag complexes are an order of a magnitude smaller. Ionization potential of water is high enough to hinder the CT interaction, not allowing even gold to form a stable strong CT complex with it. We also observe a clear separation of phosphine ligands from the rest of the ligands in terms of relativistic contributions to interaction energy. Phosphine–gold complexes are much stronger than the complexes of Au with H<sub>2</sub>O, NH<sub>3</sub>, and H<sub>2</sub>S. Same picture, but far less pronounced holds for the Cu...PX<sub>3</sub> complexes. This can

be attributed to exceptionally large donation and back-donation stabilization of phosphine complexes.

**3.6. Complexes with the SCH<sub>3</sub> Radical.** Methylthio-radical is an open-shell doublet system. There are three nonbonding (lone-pair) orbitals on the sulfur atom. The energetically lower one lies along the C<sub>3v</sub> axis of the molecule and has mostly 3s character with some 3p<sub>z</sub> admixture. Two higher nonbonding orbitals are perpendicular to the C<sub>3v</sub> axis and are almost purely 3p<sub>x</sub> and 3p<sub>y</sub> orbitals. One of these two orbitals is singly occupied and the other is doubly occupied. This basically offers two types of interaction between coinage metals and SCH<sub>3</sub>. The physical background for the interaction with the doubly occupied lone-pair orbital leads to formation of a triplet complex and is in principle the same as was described for all investigated closed-shell ligands in the previous sections. Interaction with the singly occupied orbitals leads to formation of a singlet complex, where the two unpaired electrons (one on the metal, one on the ligand) form a classical covalent bond.

We optimized the complexes of both types to obtain minima at expected bent geometry with M–S–C angles of about 100°. Coinage metal atoms interact with the SCH<sub>3</sub> radical at the trans site with respect to one of the hydrogens (i.e., dihedral angle  $\phi_{\text{MSCH}} = 180^\circ$ ). Optimized geometry parameters and interaction energies are collected in Table 6. The triplet complexes (<sup>3</sup>A'') have interaction energies and ML distances similar to complexes with phosphines. They follow the same trends,  $\Delta E(\text{Au}) > \Delta E(\text{Cu}) > \Delta E(\text{Ag})$  and  $R_e(\text{Ag}) > R_e(\text{Au}) > R_e(\text{Cu})$ , based on relativistic stabilization and atomic radii as was discussed in the previous sections. Similarly, considerations concerning the basis set size are analogous to previously discussed complexes. Since the triplet M...SCH<sub>3</sub> complexes resemble all other lone-pair donor ligand complexes presented in this study, we included the triplet M...SCH<sub>3</sub> complexes into the correlation with vertical IPs in Figure 6. For the sake of completeness we computed the vertical IPs as we did for the rest of the ligands in section 3.4. Obtained IP<sub>v</sub> values of electron detached from the doubly occupied lone-pair orbital and the singly occupied lone-pair orbital are 8.93 eV and 10.44, respectively, with the POL\_DK basis set, and 9.19 and 10.58 eV, respectively, with the aug-cc-pVTZ basis set. All values agree satisfactorily with the corresponding experimental values of 9.26 eV and 10.32, respectively.<sup>88</sup>

We have also performed the NBO analysis of the triplet M...SCH<sub>3</sub> complexes to reveal the CT interactions are essentially of the same nature as for the previously discussed lone-pair donor complexes with the dominant  $n \rightarrow ns$  donation

**Table 6.** Optimized Metal–Ligand Distances  $R_e$  [Å], M–S–C Angles  $\theta$  [°] (for C<sub>2v</sub> Ligands), and Interaction Energies  $\Delta E$  [kJ/mol] for Singlet and Triplet Complexes of Coinage Metals with SCH<sub>3</sub> Radical Obtained with DK Relativistic SA CCSD(T)

M	basis set	M...SCH <sub>3</sub> singlet <sup>a</sup>			M...SCH <sub>3</sub> triplet <sup>b</sup>		
		$\Delta E$	$R_e$	$\theta$	$\Delta E$	$R_e$	$\theta$
Cu	POL_DK	−230.3	2.128	104.5	−46.7	2.216	103.7
	ANO-RCC-VTZP	−237.9	2.112	104.3	−43.0	2.197	74.3
	ANO-RCC-VQZP	−252.5	2.097	104.3	−54.5	2.152	76.0
Ag	POL_DK	−178.2	2.371	103.9	−13.9	2.825	97.8
	ANO-RCC-VTZP	−188.5	2.335	103.8	−11.8	2.804	82.7
	ANO-RCC-VQZP	−202.6	2.317	103.8	−18.8	2.676	81.7
Au	POL_DK	−203.0	2.286	102.8	−60.8	2.389	103.7
	ANO-RCC-VTZP	−220.6	2.245	102.9	−67.1	2.334	75.9
	ANO-RCC-VQZP	−237.7	2.228	102.9	−79.8	2.307	75.9

<sup>a</sup>Spectroscopic term is <sup>1</sup>A'. <sup>b</sup>Spectroscopic term is <sup>3</sup>A''.



and  $ns \rightarrow n^*$  back-donation. However, there is also another strong back-donation from the metal ( $n - 1$ )d orbital to the singly occupied nonbonding p orbital on sulfur. For the  $\text{Au}\cdots\text{SCH}_3$  complex we obtained total CT interaction energy  $\Delta E_{\text{CT}} = 301.7$  kJ/mol, total donation stabilization energy  $\Delta E_{\text{L} \rightarrow \text{M}}^{\text{D}} = 221.2$  kJ/mol, single dominant donation stabilization energy  $\Delta E_{\text{i} \rightarrow \text{j}}^{\text{D}} = 204.7$  kJ/mol, total back-donation stabilization energy  $\Delta E_{\text{L} \leftarrow \text{M}}^{\text{B}} = 106.6$  kJ/mol, and the two dominant back-donation stabilization energies  $\Delta E_{\text{i} \rightarrow \text{j}}^{\text{B}1} = 48.1$  kJ/mol and  $\Delta E_{\text{i} \rightarrow \text{j}}^{\text{B}2} = 24.8$  kJ/mol.

In contrast to the triplet state of the  $\text{M}\cdots\text{SCH}_3$  complex, ( $^3\text{A}''$ ), the binding mechanism of the singlet  $\text{M}\cdots\text{SCH}_3$  complexes ( $^1\text{A}'$ ) is very different. Due to the pairing of radical electrons they form a very stable  $\sigma$  M–S bond. This leads to much larger interaction energies and shorter ML distances reported in Table 6. In the case of singlet  $\text{M}\cdots\text{SCH}_3$  complexes the energy ordering ( $\Delta E(\text{Cu}) > \Delta E(\text{Au}) > \Delta E(\text{Ag})$ ) closely follows the trend in ML distances strictly dictated by the VdW atomic radius<sup>67</sup> and the corresponding steric repulsion.

The  $^2\text{S}$  electronic states of coinage metals do not split due to spin–orbit (SO) coupling,<sup>21</sup> however, the  $\text{SCH}_3$  radical as well as the triplet  $\text{M}\cdots\text{SCH}_3$  complexes do. Nevertheless, these corrections are quite small. Using the RASSI<sup>89</sup> CASPT2/ANO-RCC-VDZP level of theory with minimal active space (formally equivalent to the ROHF reference) we computed the SO splitting of the  $\text{SCH}_3$  radical to be  $371.2\text{ cm}^{-1}$ . This is in good agreement with the reported experimental value of  $356\text{ cm}^{-1}$ .<sup>90</sup> Triplet  $\text{Cu}\cdots\text{SCH}_3$  complex splits almost negligibly into three states of relative energies 0, 0.3, and  $1.2\text{ cm}^{-1}$ . Similarly, for the  $\text{Ag}\cdots\text{SCH}_3$  complex these relative energies are 0, 0.1, and  $5.2\text{ cm}^{-1}$ . For the  $\text{Au}\cdots\text{SCH}_3$  complex the relative energies of SO split states are somewhat larger, but still quite small  $-0$ ,  $3.5$ , and  $64.9\text{ cm}^{-1}$ . Singlet complexes do not split as they are closed-shell systems.

#### 4. CONCLUSIONS

Stabilities of complexes created by a coinage metal interacting with a lone-pair ligand follow the irregular order  $\text{Au} > \text{Cu} > \text{Ag}$ . Large binding energy of gold with ligands is attributed mainly to the charge transfer mechanism supported in the gold complexes by relativistic enhancement of its electron affinity. Both, electron correlation and relativistic effects, are essential for the stability of all complexes. Since the binding energy in most complexes almost vanishes upon neglecting relativistic effects, we can talk about the “relativistic bond” particularly in case of complexes with gold. Geometries of all  $\text{M}\cdots\text{AX}_3$  ( $\text{C}_{3v}$ ) and  $\text{M}\cdots\text{AX}_2$  ( $\text{C}_s$ ) complexes correspond to the picture of creating the  $\text{M}\cdots\text{A}$  bond through the lone pair of a ligand. Charge transfer from the ligand to the metal ( $\text{L} \rightarrow \text{M}$ ) is supported by low IPs corresponding to the electron detachment from the lone-pair orbital of a ligand. Binding energies for a series of ML complexes roughly correlate with IPs of the ligand. The order of stabilities follow the pattern  $\text{M}\cdots\text{PX}_3 > \text{M}\cdots\text{NX}_3 > \text{M}\cdots\text{SX}_2 > \text{M}\cdots\text{OX}_2$ . Within  $\text{M}\cdots\text{PX}_3$  complexes the order of binding energies is  $\text{M}\cdots\text{PMe}_3 \gg \text{M}\cdots\text{PH}_3 > \text{M}\cdots\text{PCl}_3 > \text{M}\cdots\text{PF}_3$ . Fluorinated ligands are the most weakly bound also in species containing another halogen atom Y away from the  $\text{PX}_3$  or  $\text{NX}_3$  group ( $\text{Y}\cdots\text{M}\cdots\text{PX}_3$  or  $\text{Y}\cdots\text{M}\cdots\text{NX}_3$ ) complexes,<sup>24,26</sup> in accord with previous metallophilicity studied by Pyykkö.<sup>8,10,18,69,91</sup> Addition of  $\text{PH}_3$  ligands to such complexes leads to enhancement of the aurophilicity.<sup>92</sup> In general, substitution of the hydrogen by the methyl group enhances the interaction energy in all cases. In contrast, fluorinated

ligands (and to a lesser extent chlorinated) have lower binding energies than their  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  counterparts, similarly as it was with  $\text{M}\cdots\text{PX}_3$  complexes. One exception are gold complexes,  $\text{AuSH}_2$  and  $\text{AuSF}_2$ , which have almost the same binding energies. We believe that this can be attributed to the fact, that IP of  $\text{SF}_2$  is lower than is IP of  $\text{H}_2\text{S}$ . All other fluorinated ligands have higher IPs than unsubstituted species.

We should note that the interpretation based on the  $\text{L} \rightarrow \text{M}$  charge transfer is oversimplified. The fit of  $\Delta E$ s with respect to IPs of ligands supported by the analysis of relativistic effects demonstrate the importance of the relativistic stabilization of the 6s orbital of gold. Figures 6 and 8 also show somewhat specific position of phosphorus containing ligands in  $\text{Au}\cdots\text{L}$  complexes. We have speculated<sup>15</sup> that the  $\text{L} \rightarrow \text{M}$  charge transfer is supplemented by the back-donation which is also related to relativistic effects, namely shrinking of valence  $ns$  and  $(n - 1)p$  orbitals and destabilization of  $(n - 1)d$  orbitals. Relativistic shrinkage of the orbital size affects the overlap between metal and ligand orbitals. The NBO analysis provides more detailed insight into the binding mechanism. Charge transfer mechanism for complexes of coinage metals with lone-pair donor ligands seems to operate through dominant  $n \rightarrow ns$  donation and  $ns \rightarrow n^*$  back-donation, while other commonly accepted mechanisms, such as  $(n - 1)d \rightarrow \sigma^*$  back-donation, play only a minor role. Proposed mechanism might also take place in complexes of other  $ns^1$  metals (Cr, Nb, Mo, Ru, Rh, and Pt). However, these metals do not have closed d shell, hence other interactions might be of importance, e.g.,  $n \rightarrow (n - 1)d$  donation or  $\sigma \rightarrow (n - 1)d$  donation. Some theoretical investigations of donation and back-donation in ML complexes of Pd, Cr, Mo, and W are available.<sup>93–95</sup>

Finally, we conclude that the DFT method with hybrid PBE0 functional reproduce relative stabilities of a series of coinage metal–ligand complexes quite well. Reasonable performance shows also TPSSh functional. Quantitative results should be taken with care, unless a larger basis set (e.g., DEF2-QZVP) is used. Employing PBE0/DEF2-QZVP approach the largest errors with respect to our best CCSD(T) calculation for complexes with Cu, Ag, and Au, respectively, are  $-4.6$  kJ/mol for  $\text{Cu}\cdots\text{PCl}_3$  (16.9%),  $-4.9$  kJ/mol for  $\text{Ag}\cdots\text{PH}_3$  (37.4%), and  $+4.4$  kJ/mol for  $\text{Au}\cdots\text{NH}_3$  (9.1%). Simplest DFT methods combined with small basis sets missing polarization functions are completely unreliable.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Table of mean errors of several DFT approaches with respect to the benchmark CC calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

\*E-mail: [urban@fns.uniba.sk](mailto:urban@fns.uniba.sk).

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

This research was supported by the Slovak Research and Development Agency APVV (Contract Nos. APVV-LPP-0155-09 and APVV-0059-10) and Comenius University Young Scientists Grants (Contract Nos. UK/614/2013 and UK/634/2013).



## REFERENCES

- (1) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.
- (2) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533–1554.
- (3) Akinaga, Y.; Nakajima, T.; Hirao, K. A Density Functional Study on the Adsorption of Methanethiolate on the (111) Surfaces of Noble Metals. *J. Chem. Phys.* **2001**, *114*, 8555–8564.
- (4) Azzaroni, O.; Vela, M. E.; Andreasen, G.; Carro, P.; Salvarezza, R. C. Electrodesorption Potentials of Self-Assembled Alkanethiolate Monolayers on Ag(111) and Au(111). An Electrochemical, Scanning Tunneling Microscopy and Density Functional Theory. *J. Phys. Chem. B* **2002**, *106*, 12267–12273.
- (5) Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. Self-Assembled Monolayers of Thiols and Dithiols on Gold: New Challenges for a Well-Known System. *Chem. Soc. Rev.* **2010**, *39*, 1805–1834.
- (6) Maksymovych, P.; Voznyy, O.; Dougherty, D. B.; Sorescu, D. C.; Yates, J. T., Jr. Gold Adatom as a Key Structural Component in Self-Assembled Monolayers of Organosulfur Molecules on Au(111). *Prog. Surf. Sci.* **2010**, *85*, 206–240.
- (7) Ford, M. J.; Masens, C.; Cortie, M. B. The Application of Gold Surfaces and Particles in Nanotechnology. *Surf. Rev. Lett.* **2006**, *13*, 297–307.
- (8) Pyykkö, P. Theoretical Chemistry of Gold. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412–4456.
- (9) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Groenbeck, H.; Hakkinen, H. A Unified View of Ligand-Protected Gold Clusters as Superatom Complexes. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 9157–9162.
- (10) Pyykkö, P.; Runeberg, N. Comparative Theoretical Study of N-Heterocyclic Carbenes and Other Ligands Bound to Au<sup>I</sup>. *Chem. Asian J.* **2006**, *1*, 623–628.
- (11) Schwerdtfeger, P.; Krawczyk, R. P.; Hammerl, A.; Brown, R. A. Comparison of Structure and Stability between the Group 11 Halide Tetramers M<sub>4</sub>X<sub>4</sub> (M = Cu, Ag, or Au; X = F, Cl, Br, or I) and the Group 11 Chloride and Bromide Phosphanes (XMPH<sub>3</sub>)<sub>4</sub>. *Inorg. Chem.* **2004**, *43*, 6707–6716.
- (12) Fey, N.; Orpen, A. G.; Harvey, J. N. Building Ligand Knowledge Bases for Organometallic Chemistry: Computational Description of Phosphorus(III)-Donor Ligands and the Metal-Phosphorus Bond. *Coord. Chem. Rev.* **2009**, *253*, 704–722.
- (13) Antušek, A.; Urban, M.; Sadlej, A. J. Lone Pair Interactions with Coinage Metal Atoms: Weak Van der Waals Complexes of the Coinage Metal Atoms with Water and Ammonia. *J. Chem. Phys.* **2003**, *119*, 7247–7262.
- (14) Granatier, J.; Urban, M.; Sadlej, A. J. Van der Waals Complexes of Cu, Ag, and Au with Hydrogen Sulfide. The Bonding Character. *J. Phys. Chem. A* **2007**, *111*, 13238–13244.
- (15) Granatier, J.; Urban, M.; Sadlej, A. J. 'Relativistic Bond' in Complexes of Cu, Ag, and Au Elements with Phosphine. *Chem. Phys. Lett.* **2010**, *484*, 154–159.
- (16) Douglas, M.; Kroll, N. M. Quantum Electrodynamical Corrections to the Fine Structure of Helium. *Ann. Phys.* **1974**, *82*, 89–155.
- (17) Hess, B. A. Relativistic Electronic-Structure Calculations Employing a Two-Component No-Pair Formalism with External-Field Projection Operators. *Phys. Rev. A* **1986**, *33*, 3742–3748.
- (18) Pyykkö, P. Theoretical Chemistry of Gold. III. *Chem. Soc. Rev.* **2008**, *37*, 1967–1997.
- (19) Schwerdtfeger, P. Gold Goes Nano - from Small Clusters to Low-Dimensional Assemblies. *Angew. Chem., Int. Ed.* **2003**, *42*, 1892–1895.
- (20) Pyykkö, P. Relativistic Effects in Structural Chemistry. *Chem. Rev.* **1988**, *88*, 563–594.
- (21) Iliaš, M.; Kellö, V.; Urban, M. Relativistic Effects in Atomic and Molecular Properties. *Acta Phys. Slov.* **2010**, *60*, 259–391.
- (22) Schwerdtfeger, P.; Michal, S. Relativistic Effects of the Superheavy Elements. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; John Wiley & Sons: Chichester, U.K., 1998; pp 2480–2499.
- (23) Li, J.; Qiu, Y.-X.; Wang, S.-G. Metal-Phosphorus Bonding in Complexes W@Au<sub>12</sub>PX<sub>3</sub> (X = H, F, Cl, Br, I, Me, OMe) and [M@Au<sub>12</sub>]<sup>q</sup>PH<sub>3</sub> (M<sup>q</sup> = Hf<sup>2+</sup>, Ta<sup>+</sup>, W, Re<sup>+</sup>, Os<sup>2+</sup>, Ir<sup>3+</sup>, Pt<sup>4+</sup>, Au<sup>5+</sup>): Relativistic DFT Investigations. *J. Phys. Chem. A* **2009**, *113*, 1646–1652.
- (24) Luo, Q.; Li, Q.; Xie, Y.; King, R. B.; Schaefer, H. F. Substantial Dissociation Energies for the Recently Synthesized NC-Ag-NH<sub>3</sub> and Br-Ag-NH<sub>3</sub> Molecules and Their Isovalent Family Members M(CN)-XY<sub>3</sub> and M(Br)XY<sub>3</sub> (M = Cu, Ag, Au; X = N, P; Y = H, F). *J. Chem. Theory Comput.* **2011**, *7*, 131–137.
- (25) Häberlen, O. D.; Rösch, N. Effect of Phosphine Substituents in Gold(I) Complexes: A Theoretical Study of MeAuPR<sub>3</sub>, R = H, Me, Ph. *J. Phys. Chem.* **1993**, *97*, 4970–4973.
- (26) Assadollahzadeh, B.; Schwerdtfeger, P. A Comparison of Metallophilic Interactions in Group 11[X-M-PH<sub>3</sub>]<sub>n</sub> (n = 2–3) Complex Halides (M = Cu, Ag, Au; X = Cl, Br, I) from Density Functional Theory. *Chem. Phys. Lett.* **2008**, *462*, 222–228.
- (27) Lim, I. S.; Botschwina, P.; Oswald, R.; Barone, V.; Stoll, H.; Schwerdtfeger, P. Calculated Spectroscopic and Electric Properties of the Alkali Metal-Ammonia Complexes from K<sup>n</sup>-NH<sub>3</sub> to Fr<sup>n</sup>-NH<sub>3</sub> (n = 0, 1). *J. Chem. Phys.* **2007**, *127*, 104313.
- (28) Frenking, G. Understanding the Nature of the Bonding in Transition Metal Complexes: From Dewar's Molecular Orbital Model to an Energy Partitioning Analysis of the Metal-Ligand Bond. *J. Organomet. Chem.* **2001**, *635*, 9–23.
- (29) Neogrády, P.; Urban, M. Spin-Adapted Restricted Hartree-Fock Reference Coupled-Cluster Theory for Open-Shell Systems - Non-iterative Triples for Noncanonical Orbitals. *Int. J. Quantum Chem.* **1995**, *55*, 187–203.
- (30) Askerka, M.; Pichugina, D.; Kuz'menko, N.; Shestakov, A. Theoretical Prediction of S-H Bond Rupture in Methanethiol Upon Interaction with Gold. *J. Phys. Chem. A* **2012**, *116*, 7686–7693.
- (31) Ning, C.-G.; Xiong, X.-G.; Wang, Y.-L.; Li, J.; Wang, L.-S. Probing the Electronic Structure and Chemical Bonding of the "Staple" Motifs of Thiolate Gold Nanoparticles: Au(SCH<sub>3</sub>)<sub>2</sub><sup>−</sup> and Au<sub>2</sub>(SCH<sub>3</sub>)<sub>3</sub><sup>−</sup>. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9323–9329.
- (32) Neogrády, P.; Pitoňák, M.; Granatier, J.; Urban, M. Coupled Cluster Calculations: OVOS as an Alternative Avenue Towards Treating Still Larger Molecules. In *Recent Progress in Coupled Cluster Methods: Theory and Applications*; Čársky, P., Paldus, J., Pittner, J., Eds.; Springer: Netherlands, 2010; Vol. 11, pp 429–454.
- (33) Granatier, J. Interactions of Copper, Silver, and Gold with Electron-Donating Ligands. Dissertation (Ph.D.); Comenius University: Bratislava, Slovakia, 2009.
- (34) Foster, J. P.; Weinhold, F. Natural Hybrid Orbitals. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
- (35) Glendenning, E. D.; Landis, C. R.; Weinhold, F. Natural Bond Orbital Methods. *WIREs Comput. Mol. Sci.* **2012**, *2*, 1–42.
- (36) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level Correlated Calculations of Molecular Electric Properties. *Collect. Czech. Chem. Commun.* **1988**, *53*, 1995–2016.
- (37) Sadlej, A. J. Medium-Size Polarized Basis Sets for High-Level-Correlated Calculations of Molecular Electric Properties. *Theoret. Chim. Acta* **1991**, *79*, 123–140.
- (38) Kellö, V.; Sadlej, A. J.; Hess, B. A. Relativistic Effects on Electric Properties of Many-Electron Systems in Spin-Averaged Douglas-Kroll and Pauli Approximations. *J. Chem. Phys.* **1996**, *105*, 1995–2003.
- (39) Widmark, P.-O.; Malmqvist, P.-Å.; Roos, B. O. Density Matrix Averaged Atomic Natural Orbital (ANO) Basis Sets for Correlated Molecular Wave Functions. *Theoret. Chim. Acta* **1990**, *77*, 291–306.
- (40) Reiher, M.; Wolf, A. Exact Decoupling of the Dirac Hamiltonian. I. General Theory. *J. Chem. Phys.* **2004**, *121*, 2037–2047.
- (41) Barysz, M.; Sadlej, A. J.; Snijders, J. G. Nonsingular Two/One-Component Relativistic Hamiltonians Accurate through Arbitrary High Order in α<sup>2</sup>. *Int. J. Quantum Chem.* **1997**, *65*, 225–239.

- (42) Graner, G.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Ramsay, D. A.; Vogt, J.; Vogt, N. Structure Data of Free Polyatomic Molecules: Inorganic Molecules. In *Landolt-Börnstein, New Series II*; Martienssen, W., Ed.; Springer-Verlag: Berlin, 1998; Vol. 25A, p 359.
- (43) Graner, G.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Ramsay, D. A.; Vogt, J.; Vogt, N. Structure Data of Free Polyatomic Molecules: Molecules Containing One or Two Carbon Atoms. In *Landolt-Börnstein, New Series II*; Martienssen, W., Ed.; Springer-Verlag: Berlin, 1999; Vol. 25B, p 512.
- (44) Graner, G.; Hirota, E.; Iijima, T.; Kuchitsu, K.; Ramsay, D. A.; Vogt, J.; Vogt, N. Structure Data of Free Polyatomic Molecules: Molecules Containing Three or Four Carbon Atoms. In *Landolt-Börnstein, New Series II*; Martienssen, W., Ed.; Springer-Verlag: Berlin, 2000; Vol. 25C, p 481.
- (45) Bryan, P. S.; Kuczkowski, R. L. Structure and Conformation of Trimethylphosphine. *J. Chem. Phys.* **1971**, *55*, 3049–3051.
- (46) Endo, Y.; Saito, S.; Hirota, E. The Microwave Spectrum of the Thiomethoxy Radical  $\text{CH}_3\text{S}$ . *J. Chem. Phys.* **1986**, *85*, 1770–1777.
- (47) Marenich, A. V.; Boggs, J. E. Jahn–Teller Effect Versus Spin–Orbit Coupling in  $\text{X}^2\text{E}$   $\text{CH}_3\text{S}$ : An ab Initio Study by the Equation-of-Motion Coupled Cluster Method and Multiconfiguration Quasi-Degenerate Second-Order Perturbation Theory. *J. Phys. Chem. A* **2004**, *108*, 10594–10601.
- (48) Kirchhoff, W. H.; Johnson, D. R.; Powell, F. X. Centrifugal Distortion Effects in  $\text{SF}_2$ : Calculation of the Force Field and Infrared Spectrum. *J. Mol. Spectrosc.* **1973**, *48*, 157–164.
- (49) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.
- (50) Van Lenthe, J. H.; Duijneveldt-Van Deven Rijdt, J. G. C. M.; Van Duijneveldt, F. B. Weakly Bonded Systems. In *Adv. Chem. Phys.*; John Wiley & Sons, Inc.: New York, 2007; pp 521–566.
- (51) Dunning, J. T. H. Gaussian Basis Sets for Use in Correlated Molecular Calculations. I. The Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (52) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (53) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple [Phys. Rev. Lett. **77**, 3865 (1996)]. *Phys. Rev. Lett.* **1997**, *78*, 1396–1396.
- (54) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (55) Vydrov, O. A.; Scuseria, G. E. Assessment of a Long-Range Corrected Hybrid Functional. *J. Chem. Phys.* **2006**, *125*, 234109–234109.
- (56) Vydrov, O. A.; Heyd, J.; Krukau, A. V.; Scuseria, G. E. Importance of Short-Range Versus Long-Range Hartree-Fock Exchange for the Performance of Hybrid Density Functionals. *J. Chem. Phys.* **2006**, *125*, 074106–074109.
- (57) Vydrov, O. A.; Scuseria, G. E.; Perdew, J. P. Tests of Functionals for Systems with Fractional Electron Number. *J. Chem. Phys.* **2007**, *126*, 154109–154109.
- (58) Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (59) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Phys. Rev. Lett.* **2003**, *91*, 146401.
- (60) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Non-covalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (61) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (62) Dunning, J. T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 2.
- (63) Binkley, J. S.; Pople, J. A.; Hehre, W. J. Self-Consistent Molecular Orbital Methods. 21. Small Split-Valence Basis Sets for First-Row Elements. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.
- (64) Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Roos, B. O.; Ryde, U.; Veryazov, V.; Widmark, P.-O.; Cossi, M.; Schimmelpfennig, B.; Neogrády, P.; Seijo, L. Molcas: A Program Package for Computational Chemistry. *Comput. Mater. Sci.* **2003**, *28*, 222–239.
- (65) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.
- (66) Glendening, E. D. J.; Badenhoop, K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. NBO 5.0; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2001.
- (67) Atomic Radii of the Elements. In *CRC Handbook of Chemistry and Physics*, 89th ed.; Lide, D. R., Ed.; CRC Press/Taylor and Francis: Boca Raton, FL, 2009.
- (68) Neogrády, P.; Kellö, V.; Urban, M.; Sadlej, A. J. Ionization Potentials and Electron Affinities of Cu, Ag, and Au: Electron Correlation and Relativistic Effects. *Int. J. Quantum Chem.* **1997**, *63*, 557–565.
- (69) Pyykkö, P.; Zaleski-Ejgierd, P. Basis-Set Limit of the Aurophilic Attraction Using the MP2 Method: The Examples of  $[\text{ClAuPH}_3]_2$  Dimer and  $[\text{P}(\text{AuPH}_3)_4]^+$  Ion. *J. Chem. Phys.* **2008**, *128*, 124309.
- (70) Gourlaouen, C.; Piquemal, J.-P.; Saue, T.; Parisel, O. Revisiting the Geometry of  $\text{nd}^{10}(\text{n}+1)\text{s}^0[\text{M}(\text{H}_2\text{O})]^{p+}$  Complexes Using Four-Component Relativistic DFT Calculations and Scalar Relativistic Correlated Cso Energy Decompositions ( $\text{M}^{p+}=\text{Cu}^+, \text{Zn}^{2+}, \text{Ag}^+, \text{Cd}^{2+}, \text{Au}^+, \text{Hg}^{2+}$ ). *J. Comput. Chem.* **2006**, *27*, 142–156.
- (71) Sosibo, N. M.; Mdululi, P. S.; Mashazi, P. N.; Dyan, B.; Revaprasadu, N.; Nyokong, T.; Tshikhudo, R. T.; Skepu, A.; van der Lingen, E. Synthesis, Density Functional Theory, Molecular Dynamics and Electrochemical Studies of 3-Thiophenecetic Acid-Capped Gold Nanoparticles. *J. Mol. Struct.* **2011**, *1006*, 494–501.
- (72) Orita, H.; Itoh, N. Adsorption of CO on Ni(7 5 5) Surface: Ab Initio Periodic Density Functional Study. *Chem. Phys. Lett.* **2003**, *369*, 305–310.
- (73) Griffiths, G. I. G.; Misquitta, A. J.; Fortes, A. D.; Pickard, C. J.; Needs, R. J. High Pressure Ionic and Molecular Crystals of Ammonia Monohydrate within Density Functional Theory. *J. Chem. Phys.* **2012**, *137*, 064506.
- (74) Xu, X.; Goddard, W. A., III The Extended Perdew-Burke-Ernzerhof Functional with Improved Accuracy for Thermodynamic and Electronic Properties of Molecular Systems. *J. Chem. Phys.* **2004**, *121*, 4068–4082.
- (75) Csonka, G. I.; Ruzsinszky, A.; Perdew, J. P. Proper Gaussian Basis Sets for Density Functional Studies of Water Dimers and Trimers. *J. Phys. Chem. B* **2005**, *109*, 21471–21475.
- (76) NIST Chemistry Webbook, NIST Standard Reference Database Number 69; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, 2013.
- (77) De Leeuw, D. M.; Mooyman, R.; De Lange, C. A. He(I) Photoelectron Spectroscopy of Transient Species: The  $\text{SF}_2$  Molecule. *Chem. Phys.* **1978**, *34*, 287–294.
- (78) Gilheany, D. G.; No, D. Orbitals but Walsh Diagrams and Maybe Banana Bonds: Chemical Bonding in Phosphines, Phosphine Oxides, and Phosphonium Ylides. *Chem. Rev.* **1994**, *94*, 1339–1374.
- (79) Magnusson, E. sp Hybridization Reconsidered: Effect of Substitution on the Utilization of s and p Orbitals. *J. Am. Chem. Soc.* **1984**, *106*, 1185–1191.
- (80) Magnusson, E. sp Hybridization Reconsidered: The Composition of Orbitals in Main-Group Hydrides. *J. Am. Chem. Soc.* **1984**, *106*, 1177–1185.

- (81) Trindle, C.; Sinanoğlu, O. Local Orbital and Bond Index Characterization of Hybridization. *J. Am. Chem. Soc.* **1969**, *91*, 853–858.
- (82) Reed, A. E.; Weinhold, F.; Curtiss, L. A.; Pochatko, D. J. Natural Bond Orbital Analysis of Molecular Interactions: Theoretical Studies of Binary Complexes of HF, H<sub>2</sub>O, NH<sub>3</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, CO, and CO<sub>2</sub> with HF, H<sub>2</sub>O, and NH<sub>3</sub>. *J. Chem. Phys.* **1986**, *84*, 5687–5705.
- (83) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley & Sons: Hoboken, NJ, 2005.
- (84) Dunne, B. J.; Morris, R. B.; Orpen, A. G. Structural Systematics. Part 3. Geometry Deformations in Triphenylphosphine Fragments: A Test of Bonding Theories in Phosphine Complexes. *J. Chem. Soc., Dalton Trans.* **1991**, *0*, 653–661.
- (85) Orpen, A. G.; Connelly, N. G. Structural Evidence for the Participation of P-X  $\sigma^*$  Orbitals in Metal-PX<sub>3</sub> Bonding. *J. Chem. Soc., Chem. Commun.* **1985**, *0*, 1310–1311.
- (86) Orpen, A. G.; Connelly, N. G. Structural Systematics: The Role of P-A  $\sigma^*$  Orbitals in Metal-Phosphorus  $\pi$ -Bonding in Redox-Related Pairs of M-PA<sub>3</sub> Complexes (A = R, Ar, or; R = Alkyl). *Organometallics* **1990**, *9*, 1206–1210.
- (87) Xiao, S.; Trogler, W. C.; Ellis, D. E.; Berkovitch-Yellin, Z. Nature of the Frontier Orbitals in Phosphine, Trimethylphosphine, and Trifluorophosphine. *J. Am. Chem. Soc.* **1983**, *105*, 7033–7037.
- (88) Zhu, X. J.; Ge, M. F.; Wang, J.; Sun, Z.; Wang, D. X. First Experimental Observation on Different Ionic States of Both Methylthio (CH<sub>3</sub>S·) and Methoxy (CH<sub>3</sub>O·) Radicals. *Angew. Chem.* **2000**, *112*, 2016–2019.
- (89) Malmqvist, P. Å.; Roos, B. O.; Schimmelpfennig, B. The Restricted Active Space (RAS) State Interaction Approach with Spin–Orbit Coupling. *Chem. Phys. Lett.* **2002**, *357*, 230–240.
- (90) Bent, G. D. Approximate Calculation of the Jahn–Teller Energy and Ham Reduction Factor for CH<sub>3</sub>S. *J. Chem. Phys.* **1988**, *89*, 7298–7300.
- (91) Pyykkö, P.; Zhao, Y. Ab Initio Calculations on the (ClAuPH<sub>3</sub>)<sub>2</sub> Dimer with Relativistic Pseudopotential: Is the “Aurophilic Attraction” a Correlation Effect? *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 604–605.
- (92) Liu, R.-F.; Franzese, C. A.; Malek, R.; Żuchowski, P. S.; Ángyán, J. n. G.; Szczęśniak, M. M.; Chłasiński, G. Aurophilic Interactions from Wave Function, Symmetry-Adapted Perturbation Theory, and Rangehybrid Approaches. *J. Chem. Theory Comput.* **2011**, *7*, 2399–2407.
- (93) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Van, D. L.; Krebs, B.; Läge, M. Nature of the Metal–Ligand Bond in M(CO)<sub>5</sub>PX<sub>3</sub> Complexes (M = Cr, Mo, W; X = H, Me, F, Cl): Synthesis, Molecular Structure, and Quantum-Chemical Calculations. *Organometallics* **2002**, *21*, 2921–2930.
- (94) Leyssens, T.; Peeters, D.; Orpen, A. G.; Harvey, J. N. How Important Is Metal–Ligand Back-Bonding toward YX<sub>3</sub> Ligands (Y = N, P, C, Si)? An NBO Analysis. *Organometallics* **2007**, *26*, 2637–2645.
- (95) Pacchioni, G.; Bagus, P. S. Metal-Phosphine Bonding Revisited.  $\sigma$ -Basicity,  $\pi$ -Acidity, and the Role of Phosphorus d Orbitals in Zerovalent Metal-Phosphine Complexes. *Inorg. Chem.* **1992**, *31*, 4391–4398.

#### ■ NOTE ADDED AFTER ASAP PUBLICATION

This article posted ASAP on May 15, 2013. A minor text revision was made to figure captions 3 and 4. The correct version posted on May 20, 2013.