Aurophilic Interactions in [(L)AuCl]...[(L')AuCl] Dimers: Calibration by **Experiment and Theory**

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Supporting Information

ABSTRACT: Attractive metallophilic (aurophilic, argentophilic, cuprophilic, etc.) interactions play an important role in arrangement and stabilization of oligonuclear metal ion complexes. We report a combined experimental and theoretical assessment of aurophilic interactions in closed-shell gold(I) dimers. The experimental binding energies were obtained for charged [(LH)AuCl]⁺...[(L')AuCl] dimers (L is either a phosphine or an N-heterocyclic carbene ligand) in the gas phase. These energies served for benchmarking of correlated quantum chemical calculations (CCSD(T)-calibrated SCS-MP2/CBS method) that were then applied to neutral [(L)AuCl]...[(L')AuCl] dimers. The overall attractive interactions between monomeric units are in the order of 100-165 kJ mol⁻¹ in the charged dimers and of 70-105 kJ mol⁻¹ in the corresponding neutral dimers. In the neutral dimers, pure aurophilic interactions account for 25-30 kJ mol⁻¹, the dipole-dipole interactions



for 30-45 kJ mol⁻¹, and the L···L' "inter-ligand" dispersion interactions for 5-25 kJ mol⁻¹. Energy of the aurophilic interactions is thus comparable or even larger than that of strong hydrogen bonds.

1. INTRODUCTION

Closed-shell metallophilic interactions are responsible for the formation of the metal-metal bound dimers or polynuclear metal clusters.^{1,2} Almost 30 years ago, Schmidbaur observed the first gold(I) complexes displaying short Au---Au distances in the solid state.³⁻⁵ His work paved the way for the ever-growing research on compounds exhibiting metallophilic interactions.⁶⁻⁹ For example, it was proposed that aurophilic interactions are important in materials science,¹⁰ medicinal chemistry,¹¹⁻¹⁴ and catalysis.¹⁵⁻²⁴ Pyykkö and co-workers pioneered theoretical investigation of aurophilic interactions.²⁵ They analyzed the role of intermolecular electrostatic, induction, and dispersion interactions in the overall attraction of closed-shell Au(I)...Au(I) dimers.²⁶ They also investigated the effect of a neutral ligand L in [(L)AuCl]2.26 Accurate treatment of the metallophilic interactions necessitated correlated ab initio methods, such as second order Møller-Plesset perturbation method (MP2) or coupled clusters method (CC).²⁵ Conversely, standard density functional theory (DFT) methods fail to provide satisfactory results. Andrejić and Mata used local correlation methods; local coupled clusters method LCCSD[T0] for small systems and local version of the spin-component scaling MP2 method (SCS-LMP2) for the

rest.²⁷ These methods with appropriate localization schemes provided a decomposition of the interaction energies into spatial domains; e.g., separation of gold, chlorine and ligand interactions in the [(L)AuCl]₂ dimers. Moreover, the SCS-LMP2 interaction energies were almost quantitatively correct with respect to the benchmark LCCSD[T0] values. Andrejić and Mata further advocated in favor of the dispersion-corrected DFT methods in cases when ab initio correlated calculations cannot be afforded.²⁷ De Proft and co-workers investigated a large set of dimers formed from coinage metal complexes with an N-heterocyclic carbene ligand and a halogen counterion.² All these studies led to the conclusion that the Au-Au binding energy is in the range of 20–65 kJ mol⁻¹. This energy range corresponds to weak forces and is comparable with that of hydrogen bonding.

The above studies represent the current state of the art in theoretical investigations of metallophilic interactions and set the guidelines for further computational studies. However, experimental benchmarks are missing. The ideal benchmarking experiment should provide the binding energy in an isolated

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Scheme 1. Ligands Investigated in This Study



[(L)AuCl]₂ dimer in vacuum. This goal cannot be achieved with available experimental methods. However, it is possible to obtain bond dissociation energies in charged complexes.² Herein, we studied a $[(L^1)AuCl]$ complex bearing a Nheterocyclic carbene ligand L1 (Scheme 1) with an easily protonable tertiary amine group. We investigated a series of charged dimers $[(L^1H)AuCl]^+...[(L^n)AuCl]$ $(L^n = L^1-L^6)$ L⁷AuCl, see Scheme 1) and determined the experimental binding energies between the monomeric units. These energies were then compared with calibrated high-level quantum chemical calculations (SCS-MP2 method benchmarked against CCSD(T) method). Finally, we separated the interaction energies between the ion-neutral $[(L^{1}H)AuCl]^{+}...[(L^{n})AuCl]$ and neutral-neutral [(L¹)AuCl]...[(Lⁿ)AuCl] species into various contributions and singled out "pure" aurophilic interactions from the dipole-dipole and ligand-ligand (through space) interactions.

2. EXPERIMENTAL DETAILS

The [(L¹)AuCl] and [(L²)AuCl] complexes were prepared according to literature procedures.³¹ Complexes [(Lⁿ)AuCl] for n = 3-6 and ligand L⁷ were obtained from commercial sources.

Mass spectrometry experiments were performed using a TSQ 7000 (Finnigan) quadrupole-octopole-quadrupole tandem mass spectrometer equipped with an electrospray ionization (ESI) source. The clusters were generated by ESI of < 1 mM methanolic solutions of $[(L^n)AuCl]$ (n = 2-7, see Scheme 1) with 3 equiv of $[(L^1)AuCl]$ and 10 equiv of HCl (Figure S3). The ions of interest were mass-selected by the first quadrupole and collided in an octopole collision cell at variable collision energies with xenon at 40 °C and at typical pressures 0.2, 0.1, and 0.05 mTorr, measured with 120AA Baratron absolute capacitance manometer (MKS Instruments). The ionic products were mass-analyzed by the second quadrupole and detected using a Dalytype detector. The second quadrupole was kept at the offset corresponding to the sum of the first quadrupole and the octopole offsets. The nominally zero collision energy and the shape of the kinetic energy distribution were determined from the stopping potential analysis (Figure S1).³² The thermalization of the generated ions was tested by their collisional cooling in an additional collision cell placed to the region of a transfer quadrupole in the ESI source region. Because we did not detect any change in the evaluated data, we collected the data without this additional collisional thermalization.

The reaction cross-section for the *i*th dissociation channel σ_i was calculated as follows,

$$\sigma_i dl = -\ln[1 - \sum I_n / (\sum I_n + I_p)]I_i / \sum I_n$$
⁽¹⁾

where *d* is the gas number density in the collision cell, $d = p/k_{\rm B}T$ (*T* is the collision cell temperature (313.15 K), *p* is the collision gas pressure, and $k_{\rm B}$ is the Boltzmann constant), *l* is the collision cell length (18.5 cm), $\sum I_n$ is a sum of the intensities of all product ions, $I_{\rm P}$ is the intensity of parent ions, and I_i is the intensity of ions belonging to the *i*th channel. Each of the cross-section measurements was repeated at least three times on different days. The zero-pressure dissociation curve was extrapolated from the pressure dependence of normalized dissociation curves, (Figure S2) and fitted with a modified version of the L-CID program (Figures S4–S10).³⁰ The modifications of the fitting program account for the spontaneous decomposition of ions from the high-energy tail of their internal energy distribution. In addition, the ion kinetic energy broadening function was set to Lorentzian, which better describes the experimentally measured distribution (cf. Figure S1).³⁴ A full account of the changes to the L-CID program is described in the Supporting Information. We note that in the L-CID program, the nature of the transition structure assumed for a given dissociation channel has to be specified. It can be either loose (usually for neutral ligand elimination) or tight (dissociations proceeding via entropically constrained transition structures). The cluster cleavage described here as well as HCl elimination were modeled with the "loose" option, which provided results in good agreement with the observed branching ratios (i.e., the branching ratios can be rationalized based on the determined appearance energies (AEs) for both channels). Additional support comes from the theoretical calculations that localized transition structures for HCl elimination with imaginary frequencies smaller than *i*100 cm⁻¹. Furthermore, the L-CID requires specification of a number of free rotors in the molecule. This was assumed to be equal to the number of methyl groups in each complex (Table S1). We ran the L-CID simulation 16 times on each set of data (both dissociation channels were fitted simultaneously). The reported energies were calculated as an average of the energies obtained, when the genetic algorithm of the L-CID converged and the results fitted the experimental data. We tested the hypothesis that the two dissociation channels originate from different isomers of the parent ions and fitted them independently by L-CID. This fitting did not converge in most cases.

Infrared photodissociation spectra were acquired with the ISORI instrument, equipped with an ESI ion source from the TSQ 7000,³ and Nd:YAG-pumped IR optical parametric oscillator/amplifier system from LaserVision calibrated by WS-600 wavelength meter from HighFinesse GmbH as the IR light source. The generated ions were mass-selected by first quadrupole and captured by a helium pulse in a cryogenic (3 K) linear quadrupole ion trap. At these conditions, the ions form weakly bound [M.He]+ complexes. The absorption of the IR light by the complexes was monitored by comparing two filling cycles. To obtain the base count $N_{\rm i0}$, the ions were stored for a specified amount of time, ejected from the trap, mass-selected for the [M.He]⁺ by second quadrupole and counted. To obtain the wavelength-dependent ion count N_{i} , the above sequence was repeated, but this time, the contents of the trap were irradiated by IR light, which caused, upon absorption, depletion of the [M.He]⁺ complexes. The IR spectra were then plotted as $1 - N_i/N_{i0}$.

3. COMPUTATIONAL DETAILS

We performed the calculations using the Turbomole 7.1 program.³⁷ Geometry optimizations were carried out at the DFT level, employing the Perdew–Burke–Ernzerhof (PBE) functional,³⁸ which included Grimme's dispersion correction³⁹ in its version 3 (PBE-D3) and the def2-SVP basis set on all of the atoms.^{40,41} Along with the PBE-D3 geometry optimization, we have also carried out optimization at the



Figure 1. (a) Helium tagging infrared photodissociation spectra of the $[(L^1H)AuCl]^+...[(L^1)AuCl]$ (black trace) and $[(L^1D)AuCl]^+...[(L^1)AuCl]$ (blue trace) complexes. The pink trace shows the difference spectrum. (b–d) Theoretical IR spectra and relative energies (at 0 K) of different dimeric clusters calculated at the B3LYP-D3/def2-SVP level of theory. Additional isomers are shown in Figure S13. Frequency scaling factors of 0.98 and 0.955 were used in the lower and upper frequency range and were chosen to fit the NHC ligand bands.⁵²

TPSS⁴²-D3/def2-SVP level and for one model system also at the B3LYP⁴³-D3/def2-SVP level. The resulting equilibrium geometries differed only marginally which is further indication of the robustness of the adopted protocol and of the reliability of the results obtained. Moreover, the obtained SCS-MP2/CBS interaction energies (*vide infra*) for separation of the dimer into the monomers computed for the $[(L^1H)AuC1]^+...[(L^5)AuC1]$ system at PBE versus B3LYP equilibrium geometries only differed by less than 1 kJ mol⁻¹. Most of the reported interaction energies were obtained as single-point energies using the spin-component scaling second order Møller–Plesset perturbation method (SCS-MP2) with the recommended $c_{OS} = 6/5$ and $c_{SS} = 1/3$ parameters⁴⁴ and extrapolated to the complete basis set limit (CBS) using the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets⁴⁵ and Helgaker's formula:⁴⁶

$$E^{\text{MP2/CBS[D:T]}} = E^{\text{HF/aug-cc-pVTZ}} + \frac{3^{3}E^{\text{MP2_corr/aug-cc-pVTZ}} - 2^{3}E^{\text{MP2_corr/aug-cc-pVDZ}}}{3^{3} - 2^{3}}$$
(2a)

 $E^{\text{MP2/CBS[T:Q]}} = E^{\text{HF/aug-cc-pVQZ}}$

+
$$\frac{4^{3}E^{MP2_corr/aug-cc-pVQZ} - 3^{3}E^{MP2_corr/aug-cc-pVTZ}}{4^{3} - 3^{3}}$$
 (2b)

The Hartree–Fock energy is not extrapolated but taken from the calculation in the larger basis set used for the extrapolation, whereas the $E^{\text{MP2}_\text{corr}}$ denotes the MP2 correlation energy, i.e., $E^{\text{MP2}_\text{tot/BS}} - E^{\text{HF/BS}}$, in the given basis set (BS).

The accuracy of SCS-MP2 energies was validated by its benchmarking against the reference CCSD(T) method on a set of smaller model complexes. At the same time, the performance of several popular DFT functionals—B3LYP,⁴³ TPSS,⁴² and PBE³⁸—was investigated as well (both with and without the D3 dispersion correction). In these benchmark calculations, the def2-TZVP⁴¹ and aug-cc-pVTZ⁴⁷ basis sets were employed. All calculations (both DFT and wave function) were expedited by expanding the Coulomb integrals in an auxiliary basis set, the resolution-of-identity, RI-J (or density-fitting, DF) approximation,^{48,49} or RI-JK in case of Hartree–Fock method, wherever possible. It was carefully checked that the two adopted RI approximations have only marginal effect on the final

interaction energies, ~ 0.2 kJ mol⁻¹. The standard Boys–Bernardi counterpoise correction method was used to estimate the basis set superposition error (BSSE), and the interaction energies also account for the relaxation of the monomers. The BSSE accounts for $\sim 35\%$ of the overall interaction energies of the investigated complexes at the SCS-MP2/aug-cc-pVTZ level of calculation. Therefore, the BSSE-uncorrected values would be quite meaningless and far from the experimental values.

In all calculations, the Stuttgart/Dresden/Köln effective core potentials ($N_{core} = 60$, $l_{max} = 3$ for def2-SVP and $l_{max} = 5$ for aDZ and aTZ basis sets) were used.⁵⁰ Since the d¹⁰ electronic configuration on the gold atom(s) is not significantly changing upon interaction with the other monomer and across the series of studied complexes, we do not expect strong nonscalar relativistic effects to affect the computed interaction energies. In correlated calculations (MP2, CCSD(T)), 1s electrons on all atoms (except Au where these are described by the ECP), 2s, 2p electrons on Cl, P (except Au), and 5s electrons on Au were frozen (\$freeze; implicit core).

The zero-point vibrational energy ($\Delta E_{\rm ZPVE}$) thermal contributions to enthalpy and entropic contributions at 298 K and 1 bar (10⁵ Pa) were calculated using the analytical harmonic vibrational frequencies calculated at the RI-PBE-D3/def2-SVP level.⁵¹ Infrared spectra predictions were performed at the B3LYP-D3/def2-SVP level of theory.

4. RESULTS

4.1. Mass Spectrometry and Infrared Spectroscopy Measurements. Electrospray ionization of a solution of gold(I) complexes with ligand L¹ and one of the ligands L¹– L⁷ generated the desired $[(L^1H)(L^n)Au_2Cl_2]^+$ complexes with protonated L¹. The structures of the complexes most likely correspond to the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ dimers (note that L⁷ is a bisphosphine ligand and thus coordinates two AuCl units; therefore, n = 7 in a listing refers to the cluster $[(L^1H)AuCl]^+...[(L^7)Au_2Cl_2])$. This assumption was verified for the $[(L^1H)AuCl]^+...[(L^1)AuCl]$ complex by measuring its infrared photodissociation (IRPD) spectrum (Figure 1a). IR spectra of possible isomers of $[(L^1H)AuCl]^+...[(L^1)AuCl]$ differ mainly in positions of the bands associated with the proton (cf. Figure 1b and Figure S13). Hence, we measured IRPD spectra of protonated as well as deuterated dimer (black and blue spectra in Figure 1a). The bands associated with protonation can be visualized as the difference spectrum (Figure 1a, pink trace). The difference spectrum shows a broad band at 2680 cm⁻¹, followed by a band at 2760 cm⁻¹ and a continuum, featuring another maximum at 2930 cm⁻¹, ending below 3000 cm⁻¹.

Protonation site and binding between the monomeric units can be deduced by comparing the experimental bands associated with the protonation and the theoretical IR spectra. We can exclude the covalent bond of hydrogen to chlorine or gold atoms, because stretching vibrations of such bonds would be located at lower wavenumbers than experimentally observed. The alternative protonation at the nitrogen atom has to be associated with further hydrogen bonding, because the free N-H stretch would be located around 3400 cm⁻¹ (Figure S13c,f). The only possibility is thus protonation at the amino group that is surrounded by possible hydrogen-bond acceptors. Further, we exclude interaction of the protonated amino group with the chlorine anion directly, because such interaction would redshift the N-H bond well below 2600 cm^{-1} (Figure S13b,d). The only structures consistent with the observed spectra are thus the expected dimeric clusters [(L¹H)AuCl]⁺...[(L¹)AuCl] (Figure 1b-d), in which the N-H unit is bound either to the chlorine atom in the Au-Cl unit of the other subunit (Figure 1b,c) or to the gold atom of the same subunit (Figure 1d). Also, theory predicts these structures as the lowest energy isomers (Figure S13). We will not further attempt to assign the experimental spectrum to one, two, or all three of these isomers, because the main goal of this work is calibration of energetics, which is almost the same for all of them. The assignment would be complicated by the diffuse character of the N-H band (Figure 1a, pink trace) which is typical for stretches involving hydrogen bonds. Moreover, we probably observe a whole progression of these vibrational bands.

The lower frequency range is dominated by ligand vibrations. The ligand vibrations are very little affected by the interaction between the monomeric units. Therefore, the lower frequency range offers little or no information on how the units in the dimeric cluster interact.

Collision-induced dissociation (CID) of the $[(L^1H)AuCl]^+...$ $[(L^n)AuCl]$ clusters led to the cluster cleavage, forming the mononuclear complexes $[(L^1H)AuCl]^+$ and $[(L^n)AuCl]$ (Scheme 2, Pathway A). We observed this fragmentation pathway in competition with HCl elimination (Scheme 2,

Scheme 2. Observed Fragmentation Pathways of the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ Clusters (n = 1-7)



Pathway B). The branching ratios between the cluster cleavage and the HCl elimination were drastically dependent on the collision energy (Figure 2). For most complexes, the HCl



Figure 2. Energy dependence of the fragmentation yields in dissociation of the $[(L^1H)AuCl]^+...[(L^4)AuCl]$ cluster (*m*/*z* 1187) to $[(L^1H)AuCl]^+$ (*m*/*z* 567) + $[(L^4)AuCl]$ and to $[(L^1)(L^4)Au_2Cl]^+$ (*m*/*z* 1151) + HCl. The experimental data (points) were fitted with the L-CID program (lines). The inset shows the CID spectrum at P(Xe) = 0.04 mTorr and $E_{coll} = 4$ eV.

elimination was the dominant fragmentation process at small collision energies (e.g., in Figure 2). At large collision energies, cluster cleavage plays a much more important role (Figures S4-S10). This suggests that HCl eliminates via a transition structure lying slightly below the energy required for the cluster cleavage. Hence, HCl elimination prevails at low collision energies and becomes disfavored at high collision energies due to entropic reasons.

Next, we extracted the dissociation energies of the cluster cleavage as well as of the HCl loss from the energy-dependent fragmentation curves of the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ clusters (Figure 2 and Table 1; for details see the Supporting Information). We have used the L-CID program of Chen and co-workers to evaluate the curves.³⁰ This approach proved suitable for evaluating dissociation energies in metal–metal bound complexes.⁵³ Chen also demonstrated that this method can address complexes bound by weak interactions.⁵⁴

The L-CID simulation of all data provided smaller appearance energies (*AEs*) for the HCl elimination than for the cluster cleavage. Further, both *AEs* grow with the size of the ligand L^n in $[(L^1H)AuCl]^+...[(L^n)AuCl]$ (Table 1 and Figures 3, S11). The largest energies are required for fragmenting clusters bearing N-heterocyclic carbene ligands IMes (L^3) and IPr (L^4), and the bisphosphine ligand (L^7AuCl). The smallest *AEs* were observed for fragmentation of $[(L^1H)AuCl]^+...$ [(L^5)AuCl]; with L^5 being trimethylphosphine. Hence, the binding energies correlate with the size (mass) of the ligand L^n in $[(L^1H)AuCl]^+...$ [(L^n)AuCl] (Figure 3b), which might be due to dispersion interactions.

The difference between the HCl elimination and cluster cleavage *AEs* correlates well with the relative abundance of the HCl elimination. Hence, the small *AEs* difference found for $[(L^1H)AuCl]^+...[(L^5)AuCl]$ implicates almost complete kinetic suppression of HCl elimination. Conversely, for other clusters, HCl elimination demands approximately 10–20 kJ mol⁻¹ less energy than cluster cleavage and, therefore, HCl elimination prevails at lower collision energies (e.g., Figure 2).

4.2. Theoretical Calculations: Calibration of the Quantum Chemical Methods on the Model [(L)AuCl]...

Complex	Γ_u	AE([(L ¹ H)AuCl] ⁺) [kJ mol ⁻¹]	AE(HCl) [kJ mol ⁻¹]
$[(L^{1}H)AuCl]^{+}[(L^{1})AuCl]$		134 ± 5	121 ± 6
[(L1H)AuCl]+[(L2)AuCl]	Me N ^m N ^m N ^m N ^m N ^m N ^m	132 ± 5	121 ± 4
$[(L^{1}H)AuCl]^{+}[(L^{3})AuCl]$	IMes	147 ± 7	130 ± 6
$[(L^1H)AuCl]^+[(L^4)AuCl]$	IPr	144 ± 7	128 ± 7
$[(L^{1}H)AuCl]^{+}[(L^{5})AuCl]$	Me ₃ P	102 ± 11	100 ± 12
$[(L^{1}H)AuCl]^{+}[(L^{6})AuCl]$	PPh ₃	123 ± 7	115 ± 8
$[(L^{1}H)AuCl]^{+}[(L^{7}AuCl)AuCl]$	$Ph_2P(CH_2)_3PPh_2$	154 ± 6^{b}	128 ± 5

Table 1. Experimental Appearance Energies^{*a*} (*AE*) of the Fragmentation Channels for the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ (n = 1-7) Complexes Studied

"The values were obtained by fitting the experimental CID curves using the L-CID program (see the Supporting Information for details). They are given in the center-of-mass reference frame. The uncertainties are the standard deviations of the mean of fits of the experimental data (always three independent experimental curves were analyzed). ^bThe AE was associated with elimination of $[(L^7)Au_2Cl_2]$.



Figure 3. (a) Correlation between the appearance energies (*AEs*) for the HCl elimination and the *AEs* determined for the cluster cleavage of the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ complexes (n = 1-7, n is denoted at each point in the graph). (b) Dependence of the *AEs* of the HCl elimination (red square) and the cluster cleavage (black square) on the m/z ratio of parent complexes $[(L^1H)AuCl]^+...[(L^n)AuCl]$ (n = 1-7, n is denoted at each point in the graph). Note that n = 7 refers to $[(L^1H)AuCl]^+...[((L^7)AuCl)AuCl]$ cluster.

[(L')AuCl] Dimers. First, we have benchmarked various computational methods (both ab initio and DFT methods) by calculation of the interaction energies in smaller model systems, some of them previously studied by other authors.²⁶⁻²⁸ The models include $[(N_2C)AuCl]_2$, $[(N_2C)-$ AuCl]...[$(H_3P)AuCl$], [(NHC)AuCl]...[$(N_2C)AuCl$], $[(NHC)AuCl]...[(H_3P)AuCl], [(NHC^{CT})AuCl]⁺...[(N_2C)-$ AuCl], $[(NHC^{CT})AuCl]^+...[(H_3P)AuCl]$, and $[(H_3P)AuCl]_2$ homo- or heterodimers, where N2C stands for 3H-diazirineylidene, and NHC stands for 1,4-dihydro- $5\lambda^2$ -1,2,4-triazole (the core 1,2,4-triazole ring present in ligands 1 and 2; the aryl/alkyl substituents are replaced by hydrogen atoms). The chargetagged NHC ligand (NHC^{CT}) bears the protonated $NH_3^+CH_2$ – group at position 4 of triazole ring. We optimized the geometries at the PBE-D3/def2-SVP level (Figure S12). Our key aim is the direct comparison between theoretical and experimental data. Therefore, we assessed the performance of the quantum chemical methods mostly for experimentally relevant structures corresponding to the global minima on the respective potential energy surfaces.

One important aspect concerning the aurophilic interactions, thoroughly discussed in the previous studies^{26,28} is the orientation of the monomers in the [(L)AuCl]₂ dimers. In order to suppress the leading dipole-dipole interaction term and single out the "pure" gold(I)-gold(I) interactions, the dimers are often considered in a constrained perpendicular orientation of the linear L-Au-Cl monomeric units.²⁶ However, the global minima on the potential energy surface are almost always characterized by an antiparallel orientation of the monomeric units, evidenced also by the existing crystal structures (for example, in refs 31c and 55) and as found for our clusters as well (Figure S12). We have constrained the perpendicular orientation of the monomers only for a few model dimers in order to estimate "pure" aurophilic interactions (Table 2, bottom). The reader interested in a detailed computational investigation of the orientational dependence of the interacting closed-shell metal dimers is referred to the work of Straka and Pyykkö.⁵⁶

The calculated interaction energies (Table 2) show that in all cases the SCS-MP2 values quantitatively agree with the reference CCSD(T) values (the mean absolute deviation is 0.6 kJ mol⁻¹, whereas maximum absolute deviation is 1.4 kJ mol⁻¹), both in the aug-cc-pVDZ (all model systems) and in the aug-cc-pVTZ (for $X/Y = PH_{3}$, :CN₂) basis sets. This allowed us to conveniently investigate the convergence with respect to the basis set employing the much cheaper SCS-MP2 method and aug-cc-pVXZ basis sets (X = D, T, Q; cf. eqs 2a and 2b). It can be seen that the SCS-MP2/CBS[T:Q] values are 2-3 kJ mol⁻¹ more negative than SCS-MP2/CBS[D:T] values (that are affordable for the target systems), and thus we may conclude that the latter values used throughout this work will very slightly underestimate the interaction between [(L)AuCl] and [(L')AuCl] monomers. Surprisingly, the opposite is true for the HCl dissociation channel (these are BSSE-uncorrected values for the two model systems, and expectedly, the convergence with the basis set might be slower). Finally, the SCS-MP2/CBS[T:Q] and SCS-MP2/CBS[D:T] values for the interaction energies of the [(L)AuCl] and [(L')AuCl] monomers in the perpendicular orientation of the L-Au-Cl and L'-Au-Cl bonds differ by only 1 kJ mol^{-1} (last

Table 2. Calculated BSSE-Corrected Interaction Energies	(ΔE_{int})) for the Model	[(L)AuCl]	[(L')AuCl] Dimers [*]	
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$L\cdots L'$	$\begin{array}{c} \operatorname{CCSD}(\mathrm{T}) \\ \left(\mathrm{aDZ}\right)^{b} \end{array}$	SCS-MP2 (aDZ)	ΔCC_{aDZ}^{c}	$\begin{array}{c} \operatorname{CCSD}(\mathrm{T}) \\ \left(\mathrm{aTZ}\right)^{b} \end{array}$	SCS-MP2 (aTZ)	ΔCC_{aTZ}	SCS-MP2 CBS[D:T]	SCS-MP2 CBS[T:Q]
$N_2C\cdots N_2C$	-39.2	-39.7	-0.5	-49.3	-48.3	1.0	-52.4	-55.9
$N_2C\cdots H_3P$	-52.6	-53.2	-0.6	-61.2	-60.2	1.0	-63.8	-66.8
N ₂ C…NHC	-81.6	-80.2	1.4				-94.7	-98.0
NHC…H ₃ P	-88.6	-87.5	1.1				-99.0	-101.1
$\rm NHC^{CT} \cdots N_2 C^d$	-85.3	-85.6	-0.3				-96.4	-99.2
NHC ^{CT} ····H ₃ P	-105.4	-105.0	0.4				-115.5	-118.1
$\begin{array}{c} \text{NHC}^{\text{CT}} \cdots \text{N}_2\text{C} \\ (\text{HCl}_{\text{assoc}})^e \end{array}$	-26.4	-26.5	-0.1		-20.0		-21.7	-15.5
$NHC^{CT} \cdots H_3P$ (HCl_{assoc})	-20.9	-20.5	0.4		-15.5		-17.1	-9.9
$H_3P \cdots H_3P$	-64.4	-65.4	-1.0	-71.8	-71.2	0.6	-74.4	-77.0
$N_2C\cdots N_2C^{90\circ f}$							-22.1	-23.1
$N_2C\cdots H_3P^{90\circ}$							-28.0	-29.3
$H_3P\cdots H_3P^{90\circ}$							-29.3	-30.6

^{*a*}All values are in kJ mol⁻¹. ^{*b*}aDZ/aTZ stands for the aug-cc-pVDZ/aug-cc-pVTZ basis sets, respectively. ^{*c*}Difference from the CCSD(T) level. ^{*d*}NHC^{CT} = charge-tagged ligand (4-NH₃⁺CH₂)NHC. ^{*c*}BSSE-uncorrected interaction energy for the $[(NHC^{CT})Au_2Cl]^+ + HCl \rightarrow [(NHC^{CT})AuCl]^+...[(L')AuCl]$ dissociation channel; the sign of ΔE_{int} corresponds to an association as exemplified by the above equation. ^{*f*}Interaction energy for the perpendicular orientation of the L-Au-Cl···L'-Au-Cl units.



Figure 4. Equilibrium geometries of several representative structures studied in this work. The numbers given are internuclear distances in angstroms. (a) Neutral $[(L^1)AuCl]...[(L^1)AuCl]$ species, the typical arrangement also observed in the crystal structures. (b) $[(L^1)AuCl]...[(L^1)AuCl]...[(L^1)AuCl]...[(L^1)AuCl]]$. (c) $[(L^1H)AuCl]^+...[(L^1)AuCl]$ charge-tagged (protonated) complex; internal rotation of the substituted phenyl ring leads to formation of a Cl…H⁺ hydrogen bond. (d) $[(L^1H)AuCl]^+...[(L^3)AuCl]$; HCl dissociated. (e) $[(L^1H)AuCl]^+...[(L^3)AuCl]$ with 1,2- μ -Cl arrangement, by ~25 kJ mol⁻¹ less stable than (d). (f) $[(L^1H)AuCl]^+...[(L^1)AuCl]$ with the Au(I)...H(+) interaction (cf. Figure 1d). Full set of equilibrium geometries can be found in the Supporting Information.

three rows in Table 2). The perpendicular orientation of the units decreases the interaction energy in the dimer $(23-30 \text{ kJ} \text{ mol}^{-1} \text{ vs } 56-118 \text{ kJ mol}^{-1})$, and therefore also these deviations are smaller than for the fully optimized structures.

On the other hand, all tested DFT(-D3) and MP2 (including SOS-MP2) methods failed to quantitatively agree with the benchmark CCSD(T) calculations. They tended to overestimate the aurophilic interactions by 15-45%.⁵⁷ It can thus be concluded that from all the studied methods, SCS-MP2 is apparently the only method that may be capable of providing quantitatively accurate results for the target systems which are way beyond the computational feasibility of the CCSD(T) method and likely also beyond its DLPNO(TightPNO) variant,⁵⁸ if we consider the CCSD(T) values as solid reference values.

Hence, we employed SCS-MP2/aug-cc-pVDZ and SCS-MP2/aug-cc-pVTZ levels and the extrapolation to the CBS for

the calculations of the interaction and association (dissociation) energies of the target systems. Because of the size of the systems, we had to use the RI-JK/HF approximation to obtain the reference Hartree–Fock wave functions. We verified this approach on the smallest target systems: $[(L^1H)AuCl]^+...$ $[(L^5)AuCl]$ and $[(L^1)AuCl]...[(L^5)AuCl]$. The errors introduced by the RI-JK/HF approximation on the final SCS-MP2 dissociation energies are negligible $(0.1-0.2 \text{ kJ mol}^{-1})$.

4.3. Interaction Energies and Enthalpies of the $[(L^1H)AuCI]^+...[(L^n)AuCI]$ and $[(L^1)AuCI]...[(L^n)AuCI]$ Dimers. Neutral dimers $[(L^1)AuCI]^+...[(L^n)AuCI]$ almost exclusively adopt the expected antiparallel orientation of the linear L-Au-Cl units (Figures 4 and S12). On the contrary, protonated dimers $[(L^1H)AuCI]^+...[(L^n)AuCI]$ and the products of the HCl elimination exist in a multitude of conformations. Therefore, we started with several (5–15) conformations and geometrical arrangements for each of the

	[(L ¹)AuCl]	$.[(L^n)AuCl]$	$[(L^1H)AuCl]^+[(L^n)AuCl]$		[(L ¹ H)AuCl] ⁺ [(L ⁿ)AuCl]; HCl ass		
L'	$D_{\rm e}$	ΔH_0	$D_{\rm e}$	$\Delta H_0 \left(A E_{\rm exp} \right)^{b}$	$D_{\rm e}$	ΔH_0	
L^1	-104.8	-102.3	-123.5	$-117.4 (134 \pm 5)$	-83.8	-67.7	
L^2	-109.3	-107.3	-131.0	$-126.5 (132 \pm 5)$	-78.6	-62.8	
L^3	-85.5	-84.0	-140.7	$-134.1 (147 \pm 7)$	-107.6	-90.5	
L^4	-91.7	-87.5	-138.5	$-133.1 (144 \pm 7)$	-107.6	-94.3	
L^5	-86.7	-84.6	-106.2	$-102.3 (102 \pm 11)$	-113.2	-95.9	
L^{6}	-90.5	-88.9	-112.4	$-108.1 (123 \pm 7)$	-104.5	-88.6	
L ⁷ ·AuCl ^c	-76.8	-74.4	-154.5	$-149.2 (154 \pm 6)$	-110.3	-93.0	
a All values are in lt n	$aal^{-1} b_{AE} \sim AE$	J Note that 17 f	arms a complay with	two gold stoms (see shows).	i a sura alturationa improve	tigata tha cluster	

Table 3. Calculated SCS-MP2/CBS Interaction (Association) Energies (ΔE_{int} , D_e) and Enthalpies (ΔH_0) for the $[(L^1H)AuCl]^+...[(L^n)AuCl]$ and $[(L^1)AuCl]...[(L^n)AuCl]$ Dimers^{*a*}

"All values are in kJ mol⁻¹. ${}^{b}AE_{exp} \approx -\Delta H_0$. "Note that L⁷ forms a complex with two gold atoms (see above); i.e., we always investigate the cluster $[(L^1H)AuCl]^+...[(L^7AuCl)AuCl]]$.

protonated dimeric structures. Moreover, we ran 500 ps molecular dynamics trajectories at 500 K (employing the CUBY program and PM6-D3H4 semiempirical potential) for each dimer and submitted 50 snapshots from each trajectory to the quantum chemical calculations.⁵⁹ All the equilibrium geometries are deposited in Supporting Information, and only several representative systems are depicted in Figure 4. These structural motifs are consistent with the experimental IR spectra of $[(L^1H)AuCl]^+...[(L^1)AuCl]$ dimer (Figure 1) and most of them are verified *a posteriori* by comparison of the computed interaction energies with the experimental data.

The calculated interaction energies/enthalpies are systematically larger for the protonated dimers $[(L^1H)AuCl]^+...[(L^n)-$ AuCl] than for their neutral counterparts (D_e and $\Delta H_{0 \text{ K}}$ in Table 3; $\Delta H_{298 \text{ K}}$ and $\Delta G_{298 \text{ K}}$ are in Table S3). Somewhat surprisingly, we did not observe a strong correlation between the corresponding interaction energies obtained for the neutral and the protonated clusters. We attribute this to the difference in structural arrangements between the neutral and protonated dimers. In accordance with the experimental data, the calculations clearly show that the HCl dissociation channel (forming HCl and $[(L^1)(L^n)Au_2Cl]^+$) was thermodynamically preferred in all cases by 6-64 kJ mol⁻¹ to the cluster cleavage. We attempted to localize the corresponding transition structures for the elimination of the HCl and calculated activation enthalpies, ΔH_0^{\ddagger} , but the obtained values (Table S3) are considerably larger than the experimental AEs for the HCl elimination. The character of these transition states suggests that the HCl elimination may have a loose transition state (it is associated with an imaginary frequency of about $i100 \text{ cm}^{-1}$). Location of the correct transition states turned out to be too complicated and because it was not in the focus of this study, it was not pursued further.

5. DISCUSSION

The agreement between computed and experimental values is crucial for further discussion. The calculated interaction enthalpies between the monomers in the $[(L^1H)AuCl]^+...$ $[(L^n)AuCl]$ clusters are on average 10 kJ mol⁻¹ (precisely 9.3 kJ mol⁻¹) smaller than their experimental counterparts (Figure 5). As shown in Table 2, part of this systematic shift can be likely attributed to slight underestimation of the interaction energies at the SCS-MP2/CBS[D:T] level (3–5 kJ mol⁻¹) or due to a small systematic shift in the experimental CID energies. Alternatively, one other reason for this small underestimation of the interaction energies, sometimes seen in the supramolecular systems, could be the use of counterpoise-corrected energies, as pointed out by Mentel and Baerends.⁶⁰ Apart from



Figure 5. Correlation of the experimental appearance energies and SCS-MP2/CBS dissociation energies $(-\Delta H_{0K})$ of the $[(L^1H)AuCl]^+...$ $[(L^n)AuCl]$ dimers to monomers. The lines shows the linear dependence with an offset of 10 kJ mol⁻¹ (red) or 0 kJ mol⁻¹ (blue). The data can be found in Tables 1 and 3.

the systematic shift of 10 kJ mol⁻¹, we consider the agreement between the computed and experimental data as excellent with maximum deviations within the experimental error bounds (Figure 5, red line). For neutral species, the SCS-MP2/CBS calculated values of interaction energies range between 71 and 105 kJ mol⁻¹ (ΔH_0). The reported ΔH_0 values can be viewed as experimentally and computationally calibrated interaction enthalpies (to within 10 kJ mol⁻¹) for the prototypical Au···Au dimers and may represent benchmarks for experimental and computational studies dealing with aurophilic interactions.

En route to singling out "pure" metallophilic interactions from the overall interaction enthalpies, we compared the protonated systems with their neutral counterparts. An expected difference of 15-75 kJ mol⁻¹ was attributed to the charge-dipole term in the overall interaction energy. The interaction enthalpies for neutral systems can then be compared with the values calculated for model systems with the corresponding NHC and PH₃ ligands (cf. Figure 6), at the geometries of the parent [(L¹)AuCl]...[(Lⁿ)AuCl] complexes, denoted as ΔE_{int} (core) and listed in Table 4. The values obtained for the D_e values of $[(L^1)AuCl]...[(L^n)AuCl], n = 1-$ 6, are 21-37 kJ mol⁻¹ more negative than those in the corresponding model complex. This additional interaction can originate either from the mutual interaction of the bulky ligands or from the electronic effects of the substituents on the $ClAu(NHC)/(PH_3)$ core.

We further evaluated the inter-ligand interactions in the studied dimers by calculations, in which we removed the core $(NHC)/(PH_3)AuCl$ units from the $[(L^1)AuCl]...[(L^n)AuCl]$ systems in the equilibrium geometry and capped the resulting



Figure 6. Geometry used to calculate the $L \cdots L'$ inter-ligand interaction energy between the substituents on the respective (NHC)AuCl "cores" of the dimer. The substituents on the left side are considered as subsystem 1, whereas the substituents on the right side (originally on the second monomer) form subsystem 2.

valence vacancies by hydrogens (see Figure 6). The computed interaction energies are summarized in Table 4. The mutual interactions between the ligands are predicted to be attractive by 6–26 kJ mol⁻¹. Under the assumption of the additivity of these nonbonding ligand interactions with the interactions between the ClAu(NHC)/(PH₃) cores, the estimated interaction energies: $\Delta E_{int}(L\cdots L') + \Delta E_{int}(core)_{est}$ are compared with the values calculated for the full system. Intuitively, the difference between the two can be attributed to the "electronic" effect of the bulky substituents on the strength of the interaction of the (NHC)/(PH₃)AuCl cores of the monomers. The electronic effects, estimated as $\Delta E_{\rm int}({
m el})$ = $\Delta E_{\rm int}$ – $(\Delta E_{int}(L \cdots L') + \Delta E_{int}(core))$, are in all cases except one (L^3) by 11-18 kJ mol⁻¹ stabilizing. For L³ ligand, these are close to neutral (3 kJ mol⁻¹ destabilizing). An in-depth analysis of the observed effect is beyond the scope of this work.

Another simple computational experiment—inspired by the work of Straka and Pyykkö⁵⁵—was the rotation of the monomers in the model systems by 90° around the Au–Au axis (L–Au···Au and Au···Au–L' bond angles and L–Au···Au–L' torsion angle were constrained to 90°; all other structural parameters were optimized). The perpendicular arrangement of the units cancels the leading dipole–dipole term. The investigated three model systems included only ([(N₂C)-AuCl]₂, [(N₂C)AuCl]...[(H₃P)AuCl], and [(H₃P)AuCl]₂), because the bulky ligands in the [(L¹)AuCl]...[(Lⁿ)AuCl] structures do not allow for the 90° rotation. The computed SCS-MP2/CBS[D:T, T:Q] interaction energies are -23 to -30 kJ mol⁻¹ (Table 2). These values include the higher multipoles and dispersion interactions and in our opinion

represent "pure" metallophilic interactions. These computed values may, in fact, slightly differ for the studied $[(L^1)AuCl]...$ $[(L^n)AuCl]$ systems depending on the actual Au–Au distance which varies from system to system, but the above values may serves as good (semi)quantitative estimates. Therefore, it can be concluded that the metallophilic interactions are expected to be 20–30 kJ mol⁻¹, and they account for ~30% of the overall interaction energy in the neutral $[(L^1)AuCl]...[(L^n)AuCl]$ dimers.

6. CONCLUDING REMARKS

We present the first experimental assessment of the magnitude of the aurophilic interactions. The binding energies between the monomers in the $[(L^{1}H)AuCl]^{+}...[(L^{n})AuCl]$ dimers were determined by collision induced dissociation experiments. The data were complemented by quantum chemical calculations calibrated against the CCSD(T) level with corrections for basis set incompleteness effects. The experimental binding energies show a systematic shift of approximately 10 kJ mol⁻¹ with respect to the theoretical values. Allowing for this shift, partially attributed to the ~3-5 kJ mol-1 underestimated SCS-MP2/ CBS[D:T] values, the agreement between the two enables us to quantify the metallophilicity and to discuss its role in the structure of gold(I) clusters. Our experimental and theoretical findings confirm the overall importance of the aurophilic interactions accounting for $\sim 25-30$ kJ mol⁻¹ in the overall interaction energies of the real gold(I) dimers. This value is comparable or even greater than strong hydrogen bonds. However, structures of polynuclear gold(I) complexes may be determined also by other factors as suggested by "switching off" the metallophilicity in the model Hartree-Fock calculations of the compounds studied which led to expected elongations of the Au-Au distances, but not to the dissociation of the dimers (data not shown). Borrowing a certain amount of licentia poetica for the gold(I) dimers studied, we conclude that "all that glitters is not gold, but it matters once they hold."

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b12509.

Further experimental details; Figure S1, energy resolution; Figure S2, zero-pressure extrapolation; Figure S3, ion preparation; Figures S4–S11 and Tables S1 and S2, L-CID modeling of all data; Figure S12, representative structures of the model compounds; Figures S13–S17 and Tables S3–S6, details of the modification of the L-CID program (PDF)

Equilibrium geometries of the compounds studied (TXT)

Table 4. Calculated Intra-ligand Interaction Energies ($D_e = \Delta E_{int}$; SCS-MP2/CBS, BSSE-corrected) for the [(L¹)AuCl]... [(Lⁿ)AuCl] Dimers (n = 1-6) Studied^a

	$\Delta E_{ m int}$	$\Delta E_{\rm int}({ m core})$	$\Delta E_{\rm int}(L^1\cdots L^n)$	$\Delta E_{\rm int}(L^1L^n) + \Delta E_{\rm int}({\rm core})$	$\Delta E_{\text{int}} - \left[\Delta E_{\text{int}}(L^1L^n) + \Delta E_{\text{int}}(\text{core})\right]$
L^1	-104.8	-74.2	-16.6	-90.8	-14.0
L^2	-109.3	-74.2	-17.5	-91.7	-17.6
L^3	-85.5	-62.9	-26.3	-89.2	3.7
L^4	-91.7	-59.0	-22.0	-81.0	-10.7
L ⁵	-86.7	-65.8	-6.3	-72.1	-14.6
L^6	-90.5	-53.6	-18.8	-72.4	-18.1

^aAll values are in kJ mol⁻¹ (negative values indicate an attractive interaction).

All computed primary energetic data (XLSX)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Sculfort, S.; Braunstein, P. Chem. Soc. Rev. 2011, 40, 2741–2760.
 Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.;
- Hwang, W. S.; Lin, I. J. B. Chem. Rev. 2009, 109, 3561–3598.
 (3) Schmidbaur, H.; Graf, W.; Müller, G. Angew. Chem., Int. Ed. Engl. 1988, 27, 417–419.
- (4) Schmidbaur, H.; Scherbaum, F.; Huber, B.; Müller, G. Angew. Chem., Int. Ed. Engl. 1988, 27, 419–421.
- (5) Scherbaum, F.; Grohmann, A.; Huber, B.; Krueger, C.; Schmidbaur, H. Angew. Chem., Int. Ed. Engl. 1988, 27, 1544–1546.

(6) Schmidbaur, H.; Schier, A. Chem. Soc. Rev. 2008, 37, 1931-1951.

(7) Schmidbaur, H.; Schier, A. Chem. Soc. Rev. 2012, 41, 370-412.

(8) Pyykkö, P. Chem. Soc. Rev. 2008, 37, 1967–1997.

(9) Xiong, X. G.; Xu, W. H.; Li, J.; Pyykkö, P. Int. J. Mass Spectrom. 2013, 354, 15–18.

(10) See, e.g.: Kishimura, A.; Yamashita, T.; Aida, T. J. Am. Chem. Soc. **2005**, 127, 179–183.

(11) Weaver, J.; Gaillard, S.; Toye, C.; Macpherson, S.; Nolan, S. P.; Riches, A. *Chem. - Eur. J.* **2011**, *17*, 6620–6624.

(12) Rubbiani, R.; Can, S.; Kitanovic, I.; Alborzinia, H.; Stefanopoulou, M.; Kokoschka, M.; Mönchgesang, S.; Sheldrick, W. S.; Wölfl, S.; Ott, I. *J. Med. Chem.* **2011**, *54*, 8646–8657.

(13) Oehninger, L.; Rubbiani, R.; Ott, I. Dalton Trans. 2013, 42,

3269–3284. (14) Turek, J.; Růžičková, Z.; Tloušťová, E.; Mertlíková-Kaiserová,

H.; Günterová, J.; Rulíšek, L.; Růžička, A. Appl. Organomet. Chem. 2016, 30, 318-322.

(15) Echavarren, A. M.; Hashmi, A. S. K.; Toste, F. D. Adv. Synth. Catal. 2016, 358, 1347–1347.

(16) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* 2008, 37, 1776–1782.
(17) Roithová, J.; Janková, Š.; Jašíková, L.; Váňa, J.; Hybelbauerová, S. *Angew. Chem., Int. Ed.* 2012, *51*, 8378–8382.

(18) Shu, X.-Z.; Nguyen, S. C.; He, Y.; Oba, F.; Zhang, Q.; Canlas, C.; Somorjai, G. A.; Alivisatos, A. P.; Toste, F. D. J. Am. Chem. Soc. **2015**, 137, 7083–7086.

(19) Tkatchouk, E.; Mankad, N. P.; Benitez, D.; Goddard, W. A.; Toste, F. D. J. Am. Chem. Soc. **2011**, 133, 14293-14300.

(20) Larsen, M. H.; Houk, K. N.; Hashmi, A. S. K. J. Am. Chem. Soc. 2015, 137, 10668–10676.

- (21) Zheng, Z.; Wang, Z.; Wang, Y.; Zhang, L. Chem. Soc. Rev. 2016, 45, 4448-4458.
- (22) Asiri, A. M.; Hashmi, A. S. K. Chem. Soc. Rev. **2016**, 45, 4471–4503.
- (23) Harris, R. J.; Widenhoefer, R. A. Chem. Soc. Rev. 2016, 45, 4533-4551.
- (24) Obradors, C.; Echavarren, A. M. Chem. Commun. 2014, 50, 16–28.

(25) Pyykkö, P.; Runeberg, N.; Mendizabal, F. Chem. - Eur. J. 1997, 3, 1451–1457.

(26) Muñiz, J.; Wang, C.; Pyykkö, P. Chem. - Eur. J. 2011, 17, 368–377.

(27) Andrejić, M.; Mata, R. A. Phys. Chem. Chem. Phys. 2013, 15, 18115-18122.

(28) Pinter, B.; Broeckaert, L.; Turek, J.; Růžička, A.; De Proft, F. Chem. - Eur. J. 2014, 20, 734-744.

(29) (a) Armentrout, P. B.; Ervin, K. M.; Rodgers, M. T. J. Phys. Chem. A 2008, 112, 10071–10085. (b) Amicangelo, J. C.; Armentrout, P. B. Int. J. Mass Spectrom. 2011, 301, 45–54.

(30) Narancic, S.; Bach, A.; Chen, P. J. Phys. Chem. A 2007, 111, 7006-7013.

(31) (a) Turek, J.; Panov, I.; Horáček, M.; Černošek, Z.; Padělková, Z.; Růžička, A. Organometallics 2013, 32, 7234–7240. (b) Turek, J.; Panov, I.; Semler, M.; Štěpnička, P.; De Proft, F.; Padělková, Z.; Růžička, A. Organometallics 2014, 33, 3108–3118. (c) Turek, J.; Panov, I.; Švec, P.; Růžičková, Z.; Růžička, A. Dalton Trans. 2014, 43, 15465–15474.

(32) Ducháčková, L.; Roithová, J. Chem. - Eur. J. 2009, 15, 13399– 13405.

(33) Jašíková, L.; Roithová, J. Organometallics 2012, 31, 1935–1942.

(34) Note that the Lorentzian shape of the kinetic energy distribution is a consequence of the quadrupolar field that influences the ion transmission.

(35) Jašík, J.; Žabka, J.; Roithová, J.; Gerlich, D. Int. J. Mass Spectrom. **2013**, 354–355, 204–210.

(36) Roithová, J.; Gray, A.; Andris, E.; Jašík, J.; Gerlich, D. Acc. Chem. Res. **2016**, *49*, 223–230.

(37) *TURBOMOLE* V7.0 2015, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007; TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

(38) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.

(39) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. **2010**, 132, 154104. (b) Grimme, S.; Hansen, A.; Brandenburg, J. G.; Bannwarth, C. Chem. Rev. **2016**, 116, 5105–5154.

(40) Weigend, F.; Ahlrichs, R. Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.

(41) Schäfer, A.; Huber, C.; Ahlrichs, R. J. Chem. Phys. 1994, 100, 5829-5835.

(42) Tao, J. M.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. Phys. Rev. Lett. 2003, 91, 146401.

(43) (a) Becke, A. D. Phys. Rev. A: At., Mol., Opt. Phys. 1988, 38, 3098–3100. (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B: Condens. Matter Mater. Phys. 1988, 37, 785–789. (c) Becke, A. D. J. Chem. Phys. 1993, 98, 5648–5652. (d) Vosko, S. H.; Wilk, L.; Nusair, M. Can. J. Phys. 1980, 58, 1200–1211.

(44) Grimme, S. J. Chem. Phys. 2003, 118, 9095-9102.

(45) Woon, D. E.; Dunning, T. H., Jr. J. Chem. Phys. **1993**, 98, 1358–1371.

(46) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, 286, 243–252.

(47) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. J. Chem. Phys. **1992**, *96*, 6796–6806.

(48) Eichkorn, K.; Treutler, O.; Öhm, H.; Häser, M.; Ahlrichs, R. Chem. Phys. Lett. **1995**, 240, 283–290.

(49) Eichkorn, K.; Weigend, F.; Treutler, O.; Ahlrichs, R. Theor. Chem. Acc. 1997, 97, 119-124.

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(50) (a) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Theor. Chim. Acta **1990**, 77, 123–141. (b) Figgen, D.; Rauhut, G.; Dolg, M.; Stoll, H. Chem. Phys. **2005**, 311, 227–244.

(51) Jensen, F. Introduction to Computational Chemistry; John Wiley & Sons: New York, 1999.

(52) (a) Schulz, J.; Jašíková, L.; Škríba, A.; Roithová, J. J. Am. Chem. Soc. 2014, 136, 11513–11523. (b) Schulz, J.; Jašík, J.; Gray, A.; Roithová, J. Chem. - Eur. J. 2016, 22, 9827–9834.

(53) (a) Moret, M. E.; Serra, D.; Bach, A.; Chen, P. Angew. Chem., Int. Ed. 2010, 49, 2873–2877. (b) Serra, D.; Moret, M. E.; Chen, P. J. Am. Chem. Soc. 2011, 133, 8914–8926. (c) Oeschger, R. J.; Ringger, D. H.; Chen, P. Organometallics 2015, 34, 3888–3892. (d) Oeschger, R. J.; Chen, P. J. Am. Chem. Soc. 2017, 139, 1069–1072.

(54) Pollice, R.; Bot, M.; Kobylianskii, I. J.; Shenderovich, I.; Chen, P. J. Am. Chem. Soc. 2017, 139, 13126–13140.

(55) Ray, L.; Shaikh, M. M.; Ghosh, P. Inorg. Chem. 2008, 47, 230–240.

(56) Pyykkö, P.; Straka, M. Phys. Chem. Chem. Phys. 2000, 2, 2489–2493.

(57) The interested reader is referred to the Supporting Information, where the full set of energetic and structural data are available and can be used for calibration and testing of various popular DFT functionals (including several basis sets).

(58) Riplinger, C.; Neese, F. J. Chem. Phys. 2013, 138, 034106.

(59) Řezáč, J. J. Comput. Chem. 2016, 37, 1230–1237.

(60) Mentel, L. M.; Baerends, E. J. J. Chem. Theory Comput. 2014, 10, 252–267.