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Substituent effects in π -hole regium bonding interactions between $\text{Au}(p\text{-X-Py})_2$ complexes and Lewis bases: an *ab initio* study

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Dedication ((optional))

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Abstract: For the first time, long range substituent effects in regium bonding interactions involving Au(I) linear complexes are investigated. The Au(I) atom is coordinated to two *para*-substituted pyridine ligands. The interaction energy (RI-MP2/def2-TZVP level of theory) of the π -hole regium bonding assemblies is affected by the pyridine substitution. The Hammett's plot representations for several sets of Lewis bases have been carried out and, in all cases, good regression plots have been obtained (interaction energies vs. Hammett's σ parameter). The Bader's theory of "atoms-in-molecules" has been used to evidence that the electron density computed at the bond critical point that connects the Au-atom to the electron donor can be used as a measure of bond order in regium bonding. Several X-ray structures retrieved from the Cambridge Structural Database (CSD) provide some experimental support to the existence of regium π -hole bonding in $[\text{Au}(\text{Py})_2]^+$ derivatives.

1. Introduction

A deep comprehension of noncovalent interactions is essential in modern chemistry.^[1-4] Well known forces are hydrogen bonds and those involving aromatic rings (π -stacking, ion- π , lone-pair- π , $\text{CH}\cdots\pi$, etc),^[5-11] which are extremely important in many fields including molecular recognition and sensors, crystal engineering and enzymatic mechanisms. In addition, elements of p-block covalently bound to electron withdrawing groups (EWG) are well known to favorably interact with Lewis bases, anions or even π -systems.^[12-25] These type of contacts are known as σ,π -hole interactions and the most studied ones are halogen^[26] and chalcogen bonds,^[27] where elements of groups 17 and 16 act as Lewis acids, respectively. Moreover, pnictogens (group 15)^[28-30] and tetrels (group 14)^[31,32] are also attracting increasing attention by the scientific literature. Apart from the p-block, other elements of the periodic table have been also proposed as good σ,π -hole donors, like group 12 (spodium bonding)^[33-35] or group 8 (osme bond).^[36]

The terms regium bond (RgB) and coinage bond (CiB) have been used indistinctly in the literature to describe noncovalent interactions involving elements belonging group 11 (Cu, Ag and

Au).^[37,38] Both theoretical and experimental studies have been reported^[39-46] that illustrate the ability of group 11 of elements to participate in σ -hole interactions. In addition, the interplay between RgBs and other noncovalent interactions like has been also analyzed theoretically.^[47-49] Finally, it has been recently demonstrated the potential applications of π -hole regium bonds in protein-ligand chemistry, crystal engineering and surface absorption mechanisms.^[50-54]

The aim of the present study is to investigate the geometric and energetic features of regium bonds established between Lewis bases and linear Au(I) coordination complexes. In the model systems used herein, the gold is coordinated to two *para*-substituted pyridine rings. This allows the analysis of substituent effects, which have been studied using *ab initio* calculations (RI-MP2/def2-TZVP level of theory). As far as our knowledge extends, no previous work has been reported before in the literature analyzing long range substituent effects in π -hole^[55] regium bonds (Figure 1). We have obtained good relationships for the Hammett's plots for each series of complexes. In addition, the quantum theory of "atoms in molecules" (QTAIM)^[56] analysis allows us to demonstrate that the electron density at the bond critical points that connect the gold atom to the electron rich atom of the Lewis base can be used as a measure of bond order.

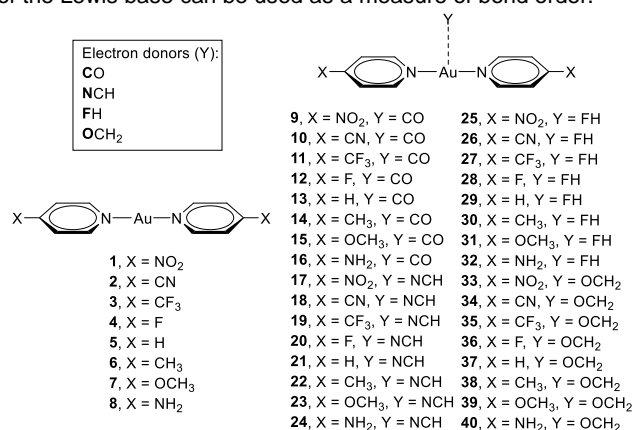


Figure 1 Gold(I) coordination complexes (1–8), electron donors and π -hole complexes 9–40 used in this work.

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2. Results and Discussion

2.1 CSD study

Prior to the theoretical study, the CSD has been examined to provide some experimental support to the existence of regium bonding interactions in X-ray structures. A simple search for dicoordinated linear Au(I) complexes incorporating two N-donor ligands afford a total of 249 structures. If the search is limited to pyridine derivatives, the hit list is drastically reduced to 21 structures. Three of them have been selected as examples to illustrate the ability of this type of complexes to establish π -hole regium bonding, which are represented in Figure 2. The refcode ZINTIB^[57] corresponds to *bis*(4-picoline)-gold(I) complex where the gold atom establishes two noncovalent Au...Br contacts with the electron rich dibromidoaurate counterions (see Figure 2a). The distance (3.650 Å) is clearly too long to be considered a coordination bond. Similarly, in refcode BUVTUI^[58] the *bis*(2,6-dimethylpyridine)-gold(I) complex establishes two symmetrically equivalent regium bonds with the dichloridoaurate counterions. IN this case the closest atom is the central Au-atom of the anionic moiety.

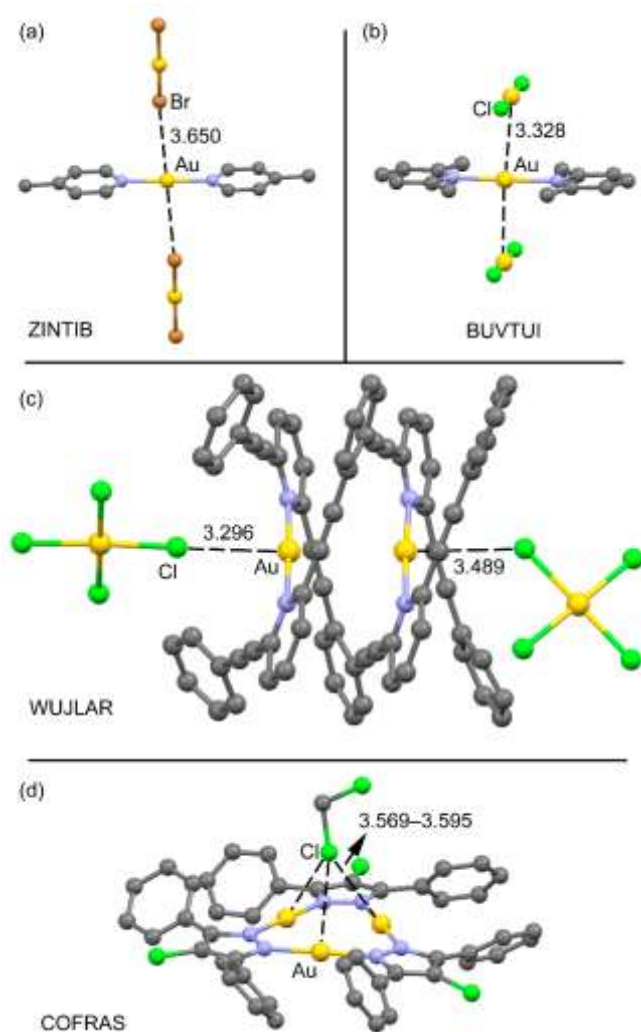


Figure 2. Partial views of the X-ray solid state structures of CSD refcodes ZINTIB (a), BUVTUI (b), WUJLAR (c) and COFRAS (d). H-atoms omitted for clarity. Distances in Å.

Figure 2c shows the interesting structure of WUJLAR^[59] where two pyridine based ligands form a dimeric helix incorporating two coordinated Au-atoms. Each Au-atom establishes a regium bond with the tetrachloro-gold(III) counterions (Au...Cl contacts). Finally, we have also selected one hit from the general search also involving an aromatic N-donor ligand. It corresponds to the refcode COFRAS^[60] (Figure 2d) that consists of tris(μ_2 -4-Chloro-3,5-diphenylpyrazolato)-tri-gold complex that co-crystallizes with a solvent dichloromethane molecule. Quite remarkably, one chlorine atom of dichloromethane is approximately equidistant with respect to the three gold(I) metal centers, establishing three concurrent regium bonding interactions with distances that range 3.569 to 3.595 Å. Though it is not the main purpose of this manuscript, it is worth mentioning that similar RgB interactions also exist in dicoordinated X-ray structures of the other elements of group 11, silver(I) and copper(I). Two examples exhibiting Ag...F and Cu...O RgBs are highlighted in the ESI (see Figure S1)

2.2 Molecular electrostatic potential (MEP)

The Molecular Electrostatic Potential (MEP) values at the Au-atom perpendicular to the molecular plane for the regium bond donors **1–8** (pyridine derivatives, see Figure 1) have been calculated and summarized in Table 1 in order to analyze the influence of the substituents on the Lewis basicity of Au. The values are gathered in Table 1 and it can be observed that the MEP energies are large and positive due to the cationic nature of the $[\text{Au}(p\text{-X-py})_2]^+$ electron acceptor. Moreover, they are significantly influenced by the pyridine substituent (up to 25 kcal/mol difference between $\text{X} = \text{NO}_2$ and $\text{X} = \text{NH}_2$). Two prototypical MEP representations are shown in Figure 3 corresponding to most polarized compounds **1** ($\text{X} = \text{NO}_2$) and **8** ($\text{X} = \text{NH}_2$). In case of compound **1** (EWG substituent), the MEP maximum (105.4 kcal·mol⁻¹) is located at the aromatic H-atoms adjacent to the coordinated N-atom. The MEP is also large and positive over the ring center (+92.8 kcal·mol⁻¹).

Table 1 MEP energies in the gas-phase (MEP, kcal mol⁻¹) for regium bond donors **1–8** at the RI-MP2/def2-TZVP level of theory. The Hammett's σ_p values retrieved from ref [61] are also indicated.

Complex	$V_{s,\text{Au}}$	σ_p (X)
1 , X = NO ₂	+80.9	+0.778
2 , X = CN	+79.7	+0.660
3 , X = CF ₃	+76.6	+0.540
4 , X = F	+72.5	+0.062
5 , X = H	+69.0	0.00
6 , X = CH ₃	+64.3	-0.170
7 , X = C(CH ₃) ₃	+62.5	-0.200
8 , X = NH ₂	+55.8	-0.660

Compound **8** (EDG substituent), exhibits four equivalent maxima located at the H-atoms of the amino groups (102.9 kcal·mol⁻¹). The MEP is also positive at the Au-atom (+55.8) and over the

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center of the ring (+63.4 kcal/mol). The fact that the MEP values at the Au-atoms does not correspond to the MEP maximum in the whole series, that is likely related to the d^{10} configuration of the Au(I) atom. As a matter of fact, some degree of nucleophilicity (gold as electron donor) has been recently described for neutral Au(I) complexes^[62] and previously demonstrated by Esterhuysen *et al* for H-bonding and halogen bonding interactions, where the Au(I) acts as electron donor.^[63]

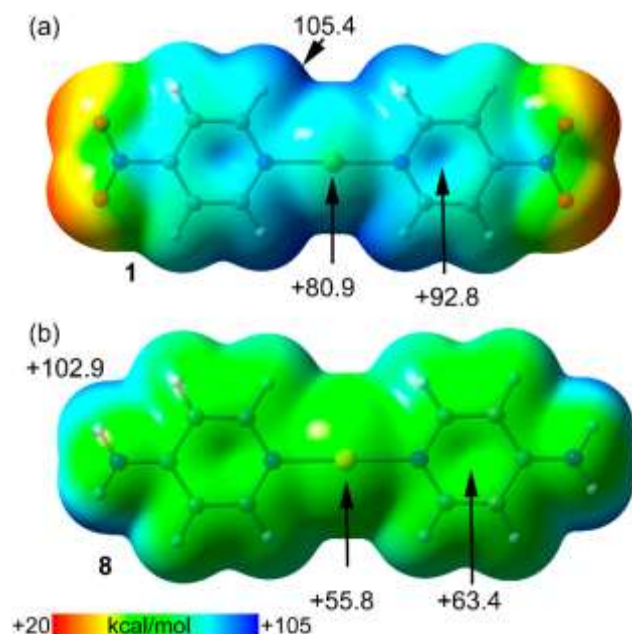


Figure 3 MEP surfaces of compounds **1** (a) and **8** (b). Blue and red regions represent positive and negative MEP values, respectively. The MEP values at selected points are indicated in kcal mol⁻¹.

2.3 Energetic study

Table 2 summarizes the binding energies with the basis set superposition error (BSSE) correction and equilibrium distances (R_e) for complexes **9–40** (see Figure 1) at the RI-MP2/def2-TZVP level of theory. The interaction energies are small, ranging from –5.69 to –1.00 kcal mol⁻¹ in line with the modest Lewis basicity of the interacting molecules. Such weak electron donors have been selected to avoid the formation of coordination bonds and/or ligand substitution reaction. On the contrary, they have been used to promote the formation of noncovalent regium bonds. Moreover, such selection of Lewis bases allows the utilization of four different donor atoms (C, N, F and O). As expected, the most favorable complex is formed by the interaction of strongest Lewis base (NCH) and the π -hole donor molecule with *p*-nitropyridine as ligand (complex **17**, –6.61 kcal/mol). The contrary is observed for the combination of the weakest Lewis base (CO) and the most electron donor substituent ($X = \text{NH}_2$), complex **16**. In line with the binding energies, the equilibrium distances for the $Y = \text{CO}$ complexes are the longest ones of the four series (3.5 – 3.7 Å), see Table 2. Such long distances are in line with the experimental observations (*vide supra*, section 2.1). For the $Y = \text{HCN}$ series, the complexes have been also optimized using diffuse functions (def2-TZVP basis set) in order to discard a possible anomalous effect of the def2-TZVP basis set in the calculation of the BSSE energies. The values are given in parenthesis in Table 2 and, satisfyingly, it can be observed a quite good agreement between

both levels of theory (with and without diffuse functions). The energetic differences are lesser than 0.4 kcal/mol in all cases.

Table 2 Interaction energies with the BSSE correction (E_{BSSE} , kcal mol⁻¹), equilibrium distances (R_e , Å), and the charge density at the bond CP (ρ , a.u.) at the RI-MP2/def2-TZVP level of theory for complexes **9–40**. Values in parenthesis correspond to the RI-MP2/def2-TZVPD level of theory.

Complex	X	Y	E_{BSSE}	R_e	ρ
9	NO ₂	CO	–1.60	3.579	0.0070
10	CN	CO	–1.62	3.679	0.0055
11	CF ₃	CO	–1.45	3.597	0.0064
12	F	CO	–1.30	3.621	0.0061
13	H	CO	–1.19	3.630	0.0060
14	CH ₃	CO	–1.10	3.656	0.0057
15	C(CH ₃) ₃	CO	–1.16	3.754	0.0053
16	NH ₂	CO	–1.00	3.702	0.0047
17	NO ₂	NCH	–6.61 (–7.01)	3.171 (3.087)	0.0119
18	CN	NCH	–6.54 (–6.76)	3.183 (3.093)	0.0117
19	CF ₃	NCH	–6.16 (–6.42)	3.181 (3.108)	0.0117
20	F	NCH	–5.58 (–5.80)	3.226 (3.129)	0.0107
21	H	NCH	–5.18 (–5.45)	3.231 (3.147)	0.0106
22	CH ₃	NCH	–4.74 (–4.92)	3.269 (3.162)	0.0099
23	C(CH ₃) ₃	NCH	–4.40 (–4.68)	3.219 (3.160)	0.0109
24	NH ₂	NCH	–3.88 (–4.10)	3.311 (3.206)	0.0091
25	NO ₂	FH	–3.93	3.184	0.0077
26	CN	FH	–3.85	3.191	0.0076
27	CF ₃	FH	–3.64	3.197	0.0075
28	F	FH	–3.30	3.233	0.0070
29	H	FH	–3.04	3.239	0.0069
30	CH ₃	FH	–2.75	3.276	0.0064
31	C(CH ₃) ₃	FH	–2.62	3.310	0.0062
32	NH ₂	FH	–2.20	3.323	0.0059
33	NO ₂	OCH ₂	–5.69	3.079	0.0115
34	CN	OCH ₂	–5.61	3.115	0.0107
35	CF ₃	OCH ₂	–5.24	3.096	0.0111
36	F	OCH ₂	–4.74	3.115	0.0107
37	H	OCH ₂	–4.40	3.119	0.0106
38	CH ₃	OCH ₂	–4.02	3.197	0.0090
39	C(CH ₃) ₃	OCH ₂	–3.80	3.179	0.0093
40	NH ₂	OCH ₂	–3.18	3.183	0.0083

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The Hammett's plots for the four series of regium π -hole complexes studied here are represented in Figure 4, where the interaction energies (BSSE corrected) vs. the aromatic substituent constant (σ) for the pyridine complexes are plotted. For all representations, a good degree of correlation is observed (regression coefficient $r > 0.97$), even for the CO series where the range of binding energies is very small (only 0.62 kcal/mol difference between the strongest and weakest complexes). In fact, the worst correlation is found for this series. From these plots, it can be concluded that the aromatic substituent constant (σ) can be used as a general predictor of trends in regium π -bonding. Moreover, in the Hammett's plots both EWGs and EDGs are included in the same representation and they correlate well with the standard σ values.^[62]

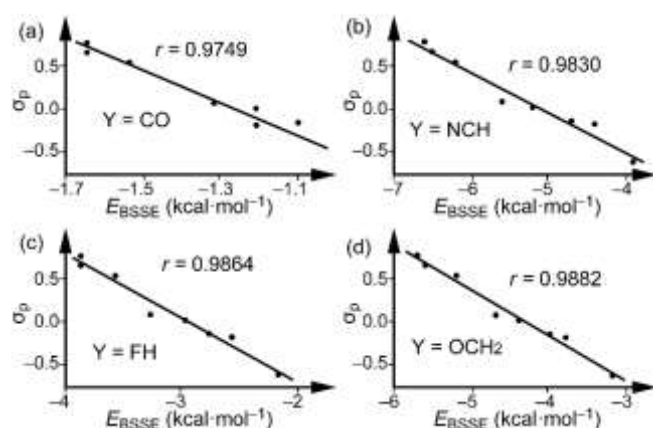


Figure 4 Hammett's plots of CO (a), NCH (b), HF (c) and OCH₂ (d) series of complexes.

Since in all compounds the MEP value at the region under the influence of the *ortho* C–H bonds (in the molecular plane, see Figure 3a) is more positive than that at the Au-atom, the H-bonding complexes for one series (Y = HCN) have been also computed for comparison purposes. The energies and optimized geometries are given in Table S1 and Figure S2 in the ESI). The interaction energies range from –9.4 kcal/mol for X = CN to –6.4 kcal/mol for X = NH₂. Therefore the formation of bifurcated N...H,H interactions is around 3 kcal/mol more favored than the RgB interaction.

2.4 QTAIM analysis

The QTAIM analysis of all RgB complexes included in this study has been also performed. The distribution of intermolecular bond critical points (CPs) and bond paths of some representative complexes are given in Figure 5. The regium bond is characterized by a bond critical point and a bond path connecting the Au atom with the electron donor. In fact, this is the only intermolecular CP found in all complexes. The values of ρ at the bond CPs are also indicated in Figure 5 (values in italics next to the bond CPs), showing that they correlate with the interaction energies of the complexes, indicated in red. At this point, it should be mentioned that the density at the bond critical point (ρ) has been used before as a measure of bond strength in a variety of noncovalent interactions.^[64–66] We have examined if these values can be also used as a measure of bond order in the complexes

studied here. Satisfyingly, a linear relationship ($r = 0.95$, see Figure 5) between the BSSE corrected interaction energies and the ρ values (gathered in Table 2) has been found. It should be emphasized that in the same plot we have combined N, C, F and O-donor atoms. Therefore, this relevant representation allows for dealing simultaneously with a variety of regium π -hole complexes. It is also worthy to comment that this correlation evidences that in the complexes with strong EWGs the density value at the bond CP is greater than that for the complexes with EDGs. This seems counterintuitive since the density is expected to increase instead of decrease when using EDGs. A likely explanation is that the Au...Y distance is shorter for those complexes with EWGs, thus increasing the density at the bond CP.

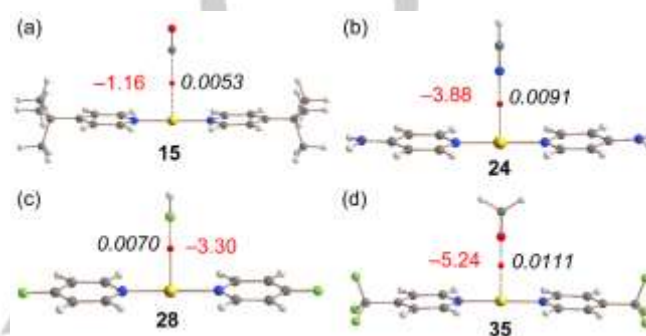


Figure 5 QTAIM distribution of bond critical points (red spheres) and bond paths for one representative complex of each series: **15** (a), **24** (b), **28** (c) and **35** (d). The values of ρ at the bond CPs are indicated in italics. The interaction energies in kcal·mol^{–1} are indicated in red.

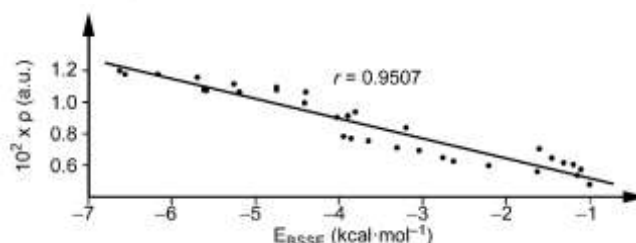


Figure 6 Regression plot of the density at the bond CP versus the interaction energy (BSSE corrected) for complexes **9–40** at the RI-MP2/def2-TZVP level of theory.

2.5 Physical nature

We have further analyzed the interaction using an orbital point of view by means of the natural bond orbital (NBO) methodology, however we have not found any remarkable contribution from orbital donor-acceptor interactions. Therefore, the regium bonding interaction and the substituent effects are likely dominated by electrostatic effects. With the purpose to confirm this assumption, we have represented the MEP values summarized in Table 1 for compounds **1–8** versus the interaction energies of the four series of complexes. For all series, we have obtained strong relationships (up to $r = 0.9984$) between the interaction energies of the complexes and the MEP values. These results clearly demonstrate that the changes observed in interaction energies of the complexes due to the different substituents are primarily caused by electrostatic effects.

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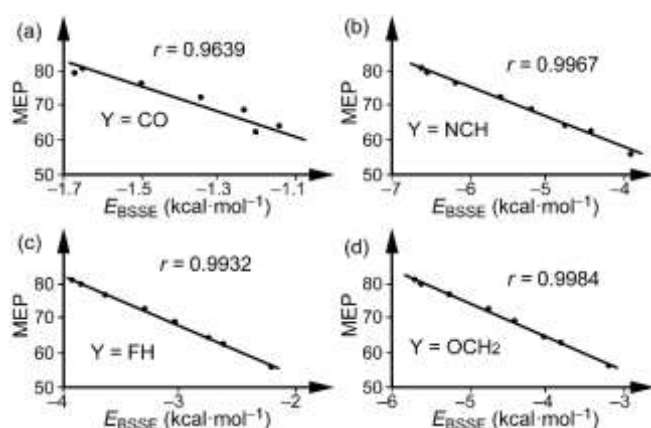


Figure 6 MEP (kcal·mol⁻¹) vs E_{BSSE} regression plots of CO (a), NCH (b), HF (c) and OCH₂ (d) complexes.

Conclusions

The analysis of the results presented in this manuscript offers some interesting conclusions:

1. The CSD search reveals that regium π -hole bonding interactions are common in Au(I) linear complexes with N-donor ligands.
2. Linear relationships have been found between the π -hole interaction energies (BSSE corrected) and the Hammett's σ constant of the substituents for the four series of complexes, indicating that this parameter can be used as a general predictor of trends in regium bonding stability.
3. The density at the bond critical point that connects the Au-atom to the electron rich molecule can be used as a measure of bond order of the regium bond and it linearly correlates with the interaction energy.
4. It has been demonstrated that the MEP values at the Au-atoms computed for [Au(p-X-py)₂]⁺ derivatives strongly correlate with the interaction energies of the complexes, disclosing that the physical nature of the regium bond interaction is basically electrostatic.

Computational details

The geometries and energies of the regium- π complexes included in this study were computed at the RI-MP2^[67]/def2-TZVP^[68] level of theory by means of the TURBOMOLE 7.2 software.^[69] The verification of true minima was ascertained by the analysis of vibrational frequencies of normal modes which showed no imaginary frequencies. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.^[70] The MEP (Molecular Electrostatic Potential) surface analyses were carried out at the MP2/def2-TZVP level of theory by means of the Gaussian 16 calculation package using the 0.001 a.u. isosurface.^[71] The calculations for the wavefunction analysis were performed at the MP2/def2-TZVP level of theory also using Gaussian-16 software. The Bader's "Atoms in molecules" theory^[72-74] has been used to study the interactions discussed herein by means of the AIMAll calculation package.^[75]

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Keywords: regium bond • noncovalent interaction • gold • ab initio • QTAIM

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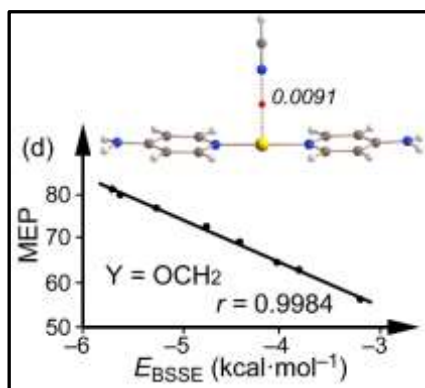
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Substituent effects in π -hole region bonding interactions between Au(p-X-Py)₂ complexes and Lewis bases are analyzed and demonstrated using *ab initio* calculation.

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