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Investigating Cooperativity Between Pd (0) and Sb (V) in Bis(2-Picolyl)-Pd-$SbCl_3$ Using Lewis Bases: A Case Study Using DFT

Arjun C. Bhowmick[1,2,3,*], Julia M. Fitzgerald[1], Alexandra Z. Chafetz[1]

[1]Department of Chemistry and Biochemistry, Kalamazoo College, Kalamazoo, Michigan, USA
[2]Department of Chemistry, University of South Dakota, Vermillion, South Dakota, USA
[3]Department of Chemistry, Mawlana Bhashani Science and Technology University, Santosh, Tangail, Bangladesh

Abstract Model complexes **1-4** have been studied using the method density functional theory (DFT). The cooperativity between Pd-Sb is noted while binding Lewis bases. NBO analysis is applied to understand the metal contribution, electron occupancy in orbitals, and types of bonds formed in Pd-Sb. Although the theoretical study suggests that the bond is partially covalent in nature as we see the Wiberg bond order index 0.6 (model complex **2-4**), the net Pd-Sb bonding interaction is repulsive. The study clearly illustrates the future development of 2-picolyl-based metal complexes and assesses their suitability as a catalyst.

Keywords Lewis Acid, Lewis Base, Metal complex, DFT, NBO

1. Introduction

Metal complexes are being used as a catalyst over a long period as they are catalyzing various reactions involving organic synthesis [1-5]. The superiority of one metal complex over another plays a vital role while choosing metal complexes and in this continuous effort, researchers are developing metal complexes having low-cost earth-abundant metals to replace precious metals [6]. In the last couple of years, monometallic, homo-bimetallic, hetero-bimetallic, and multi-metallic complexes have been developed a lot and additionally, researchers successfully assessed their catalytic performance [7,8]. It was observed that the synergistic effect of the hetero-multi metallic system plays a vital role [9] over their mono or homo metallic systems. The recent discovery by Stephan and coworkers [10] of metal-free LA-LB (Lewis's acid-Lewis's base) pairs for activating H_2 revolutionized a new pathway of research. Now, researchers are concentrating on LA-LB homo or heterobimetallic systems for activating small molecules [11,12] and synthesizing various value-added products in the development of metal catalysts [13-17]. The novelty of the method is that the nearby Lewis acidic metal center helps in catalyzing reactions over other metals taking some electron density and this is known as cooperativity [18-20]. Putting an electron-withdrawing group on a Lewis basic metal center or oxidizing it makes the Lewis base metal further electron deficient in nature. The Lewis basic metal now helps in withdrawing electron density from the nearest metal, which is the key concept in catalysis [21-25] by this LA-LB system. Here we are trying to assess the cooperativity between the Sb-Pd system for binding Lewis bases [26] using the method DFT. We choose a model complex bis(2-picolyl)-Pd(0)-Sb(v)-Cl_3 (**1**) and it is not available in the literature. We believe the research may attract the experimental research groups to design and synthesize the complexes of similar or different systems by investigating their catalytic application, as we see from the theoretical study the complexes show a positive effect for cooperativity between two metals while binding Lewis bases.

* Corresponding author:
bhowmick_mbstu@yahoo.com (Arjun C. Bhowmick)
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2. Quantum Chemical Calculations

2.1. Computational Details

We used density functional theory (DFT) to investigate the geometry and electronic structures of the complexes. The complexes were optimized in gaussian 16. M06-L functional [27] was selected with def2-TZVP [28,29] basis set for Pd and Sb and def2-SVP [30] was used for C, H, N, P, and Cl. All calculations were done in the solvent phase using the method PCM [31] and the solvent was used tetrahydrofuran. Molecular orbitals were drawn by the chem craft software (free version) choosing isosurface 0.03. Harmonic vibrational analysis was performed at the same level to

verify the nature of the stationary point. In addition, NBO analysis was done using the same basis set and functionals as stated above for localizing the orbitals of interest [32].

3. Results and Discussions

The theoretical study (DFT) suggests that the singlet is the lowest energy ground state for model complex **1**. The singlet and triplet energies are found at 0 $kcalmol^{-1}$ and -10.7 $kcalmol^{-1}$. The model complex bis(2-picolyl)-Pd(0)-Sb(V)-Cl_3 (**1**) is shown in Figure 1. The oxidation state of the palladium is zero and the oxidation state of Sb is +5. We hypothesize that the electron-filled d orbital of Pd should interact with Sb empty orbital and transfer some electron density to Sb. In this way, Sb will act as a Lewis basic center. When Pd will donate electron density, the Pd center will be deficient in an electron, and it should now act as Lewis acidic in nature for incoming Lewis bases. Pd should have empty orbitals (5s, 5P) to accept any electron density from Lewis bases in close contact with Pd.

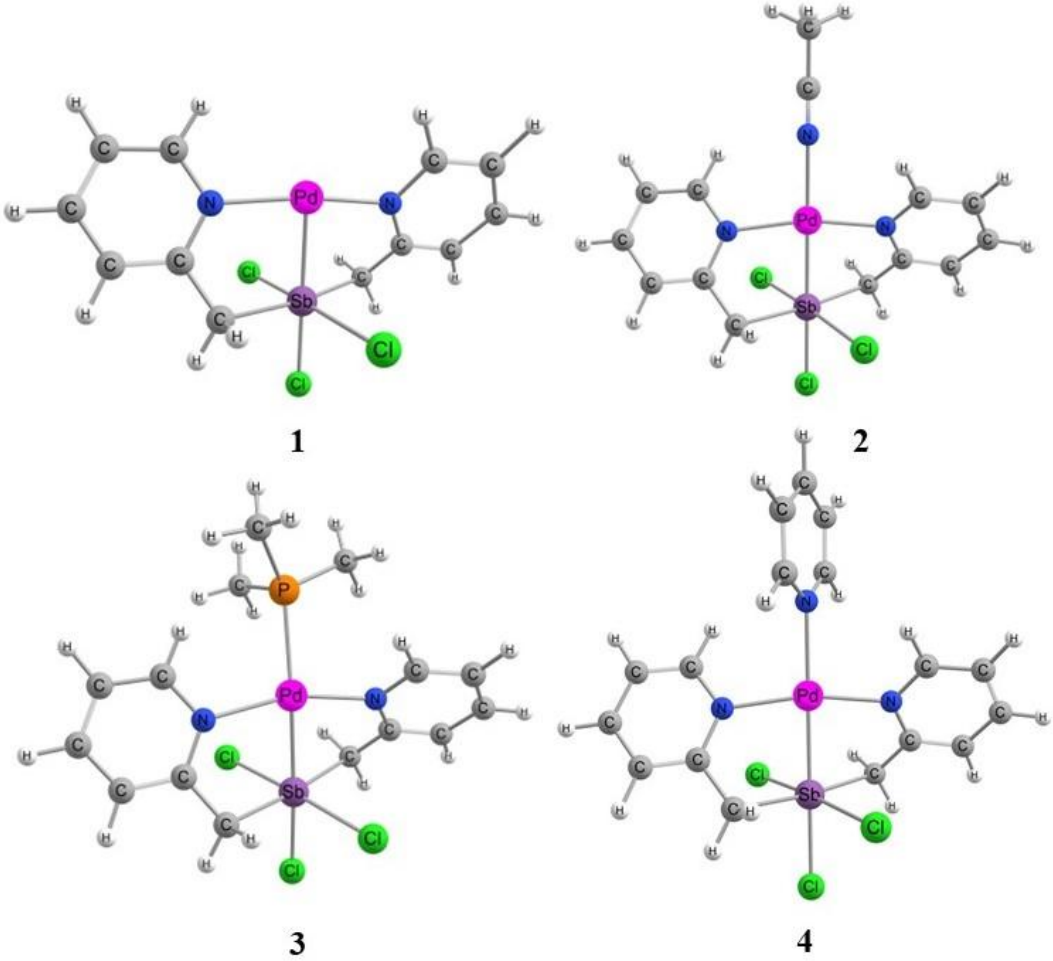

Figure 1. The structure of model complexes

Table 1. Calculated structural parameters of the complexes **1-4**

Complex	Atom	Charge	% M	Bonds	Distance	Sum of covalent Radii	Weiberg Bond order
Pd-Sb	Pd	0.19516	81.15	Pd-Sb	2.552	2.78	0.3
	Sb	1.67695	18.85	-	-	-	-
MeCN-Pd-Sb	Pd	0.13171	77.91	Pd-Sb	2.548	2.78	0.6
	Sb	1.66618	22.09	Pd-N	2.293	2.10	0.3
PMe_3-Pd-Sb	Pd	0.04204	69.32	Pd-Sb	2.579	2.78	0.7
	Sb	1.63346	30.68	Pd-P	2.524	2.46	-0.6
Py-Pd-Sb	Pd	0.18801	76.83	Pd-Sb	2.544	2.78	0.6
	Sb	1.64072	23.17	Pd-N	2.328	2.10	0.2

Table 2. Metals orbital contributions and occupancies for the bond Pd-Sb

Complex	Orbitals	Orbital contributions % Pd	Orbital e occupancy (Pd)	Orbital contributions % Sb	Orbital e occupancy (Sb)
Pd-Sb	s	12.77	none	30.11	none
	P	1.00	0.08	38.90	1.29
	d	86.23	6.75	30.83	1.02
	f	0.00	0.00	0.16	0.01
MeCN-Pd-Sb	s	9.62	none	28.79	none
	p	4.07	0.42	39.16	1.36
	d	86.3	8.97	31.91	1.11
	f	0.00	0.00	0.13	0.00
PMe_3-Pd-Sb	s	9.51	none	15.17	none
	p	3.39	0.36	83.50	5.50
	d	87.09	9.15	1.19	0.08
	f	0.00	0.00	0.13	0.01
Py-Pd-Sb	s	9.85	none	31.2	none
	p	2.80	0.28	38.03	1.22
	d	87.34	8.86	30.66	0.98
	f	0.01	0.00	0.11	0.00

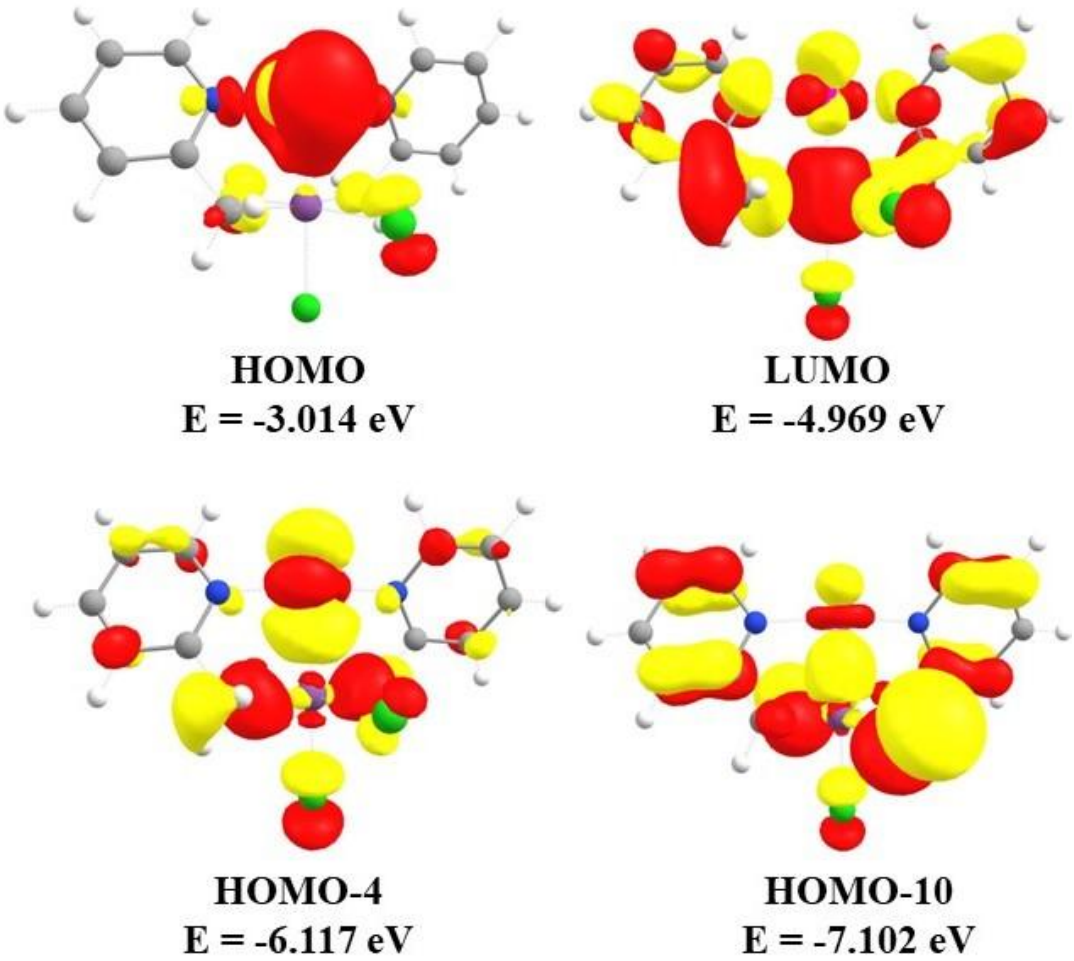

Figure 2. Molecular orbitals of bis(2-picolyl)-Pd(0)-Sb(v)Cl_3 (1)

Table 3. The d-orbitals and electron occupancies of metal Pd

Pd	Pd-Sn	MeCN-Pd-Sb	PMe_3-Pd-Sb	Py-Pd-Sb
Orbitals	**e occupancy**	**e occupancy**	**e occupancy**	**e occupancy**
4dxy	1.9642	1.95162	1.81498	1.95242
4dyz	1.97526	1.96481	1.923	1.91081
4dxz	1.88365	1.90609	1.96443	1.97471
$4dx^2$-y^2	1.49315	1.45074	1.61035	1.43315
$4dz^2$	1.93797	1.94183	1.95161	1.93958
5s	0.44045	0.39727	0.40612	0.39339
5px	0.03656	0.06827	0.14961	0.08978
5py	0.03695	0.13825	0.078	0.0607
5pz	0.03274	0.04185	0.05015	0.04428

Table 4. The d-orbitals and electron occupancies of metal Sb

Sb	Pd-Sn	MeCN-Pd-Sb	PMe_3-Pd-Sb	Py-Pd-Sb
Orbitals	**e occupancy**	**e occupancy**	**e occupancy**	**e occupancy**
4dxy	1.99954	1.9995	1.99952	1.99953
4dyz	1.99977	1.99969	1.99852	1.99846
4dxz	1.99842	1.9984	1.99967	1.99973
$4dx^2$-y^2	1.99904	1.99925	1.99927	1.99932
$4dz^2$	1.9996	1.99957	1.99961	1.99959
5s	1.33383	1.33947	1.36199	1.34901
5px	0.59561	0.59173	0.73516	0.76879
5py	0.7314	0.75051	0.60888	0.5908
5pz	0.58789	0.58235	0.59137	0.58083

In this way, the Pd center will be a suitable catalytic center and the neighboring Sb atom will cooperate with Pd through electronic effect to pull electron density from Pd so that Pd acts as Lewis acidic center for incoming bases. So, the dual role of Pd helps us to claim Pd center is behaving as both Lewis acidic (LA) and Lewis basic (LB) in nature under suitable reaction conditions as it donates electron density to Sb and simultaneously it accepts electron density from Lewis bases. Here, the Sb atom is acting as Lewis acidic in nature helping Pd for playing LA-LB dualism in reaction. From the theoretical study, we see that electron-filled $4dx^2$-y^2 of Pd is available for bonding with empty 5s (Figure 2) of Sb (Figure 2, LUMO, HOMO, HOMO-4). There is also a repulsive interaction between the electron-filled $4dx^2$-y^2 orbital of Pd and the $4dx^2$-y^2 orbital of Sb (HOMO-10, Figure 2). The Pd-Sb bond order is measured at 0.3 (Wiberg bond index) using NPA (Natural population analysis) analysis suggesting a noncovalent or electrostatic type interaction (for covalent bond Wiberg bond index = 1) [33,34]. The analysis further predicts that the Pd and Sb contribution in this bond is 81.15 (%) and 18.85 (%), respectively (Table 1). The calculated Pd-Sb bond distance is found 2.55 Å and this bond is stronger as it is smaller than the sum of their covalent radii 2.78 Å (Table 1). The NPA analysis further suggests that the contribution from the d orbital of Pd is higher than others s, p, and f orbitals for forming the Pd-Sb (Table-2). Conversely, the s, p, and d orbitals of Sb contribute equally to forming the Pd-Sb (Table 2). The occupancy of electrons in the orbitals is shown in Table 3 and Table 4.

Next, we studied model complex **1** for binding Lewis bases (MeCN (**2**), PMe_3 (**3**), Pyridine (**4**)) and model structures are shown in Figure 1. The Pd-Sn bond order is increased to 0.6 and looks weakly covalent in nature, although in model complex **1** we see the bond is electrostatic type. The contribution of Pd 77.91(%) is smaller than the model complex **1** (81.15). The contribution of Sb is 22.09 which is higher than the model complex **1** (18.85) (Table 1). The result suggests that there is electronic communication in the bond Pd-Sb while binding MeCN with the Pd center. But the bond between Pd-N is very weak and Wiberg bond order we see 0.3. It is signifying that the Pd-N bond is ionic in nature (Table 1). The calculated bond distance of 2.293 Å is higher than the sum of covalent radii 2.10 Å. As we expect when the interaction of MeCN with the Pd center, the Pd electron filled $4dx^2$-y^2 orbital should donate electron density to empty 5s orbital of Sb. We see there is a change in electron occupancy in the orbital with increasing electron density in the 5s orbital of model complex **2** than **1** (Table 4). As palladium $4dx^2$-y^2 orbital is donating to 5s orbital of Sb, the electron density of $4dx^2$-y^2 orbital of Pd in **2** is decreased than **1** (Table 3). Here, we also see that d orbital contribution is higher for Pd when it is interacting with Sb than other orbitals s, p, and f. Alternately, in Sb, the orbitals contributions remain the same as **1** with the highest bonding

contribution noted from s, p, and d orbitals (Table 4).

We see that the bonding of PMe_3 with Pd (Model complex **3,** Figure 1) has given some unusual results such as the occupancy of the electron of $4dx^2$-y^2 orbital in Pd has increased where our expectation it may not increase and the Wiberg bond order index in negative, this signifying that the steric factor playing a vital role for explaining this deviation from the normal trend with other Lewis base binding (MeCN, Pyridine). Our final model structure **4** (Figure 1) has almost a similar trend to model complex **2**. Here we also see the electron density of the $4dx^2$-y^2 orbital of Pd has decreased from **1 (**Table 3**)** with increasing electron density in the 5s orbital of Sb (Table 4). We see Wiberg bond order index for Pd-Sb is 0.6 and Pd-N is 0.2 feasible with increasing electronic communication. But it also clearly, indicates that the Pd-N bond for binding pyridine is ionic in nature and that is weak interaction, while the Pd-Sb bond is slightly covalent in nature. We have also observed that the charges of Pd and Sb in model complexes **2-4** do not change much while interacting with Lewis bases from model complex **1**.

The theoretical study of the model complexes **1-4** suggests that the Pd center is acting as a weak nucleophilic center for incoming Lewis bases. The electronic structure, NBO, and NPA suggest that the net interaction in the bond Pd-Sb is repulsive anti-bonding types as both d orbitals are filled by electrons (Table 3 and Table 4, Figure 2). The attractive interaction between $4dx^2$-y^2 (Pd) with 5s (Sb) is very weak as the two orbitals are different in energy.

4. Conclusions

In conclusion, we say that the model bimetallic bis(2-picolyl)-Pd(0)-Sb(v)-Cl_3 complex shows some agreement with our hypothesis. We can say that the complex may be suitable as a catalyst in organic synthesis as the theoretical study suggests an electronic communication exists while binding Lewis bases. The Pd is playing a dual role such as Lewis's base and Lewis acidic center while binding Lewis bases and the nearest Sb is acting as Lewis's basic center. Additionally, NBO analysis predicts that the interaction between Pd-Sb is partially covalent while interacting with Lewis bases. We believe our findings will be helpful to develop and tune better catalysts in the future.

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Conflicts of Interest

The authors declare no competing financial interest.

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