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LINEAR RELATIONSHIP BETWEEN ^{13}C NMR CHEMICAL SHIFTS AND ELECTRONIC CHEMICAL POTENTIAL, CHEMICAL HARDNESS AND ELECTROPHILICITY INDEX OF ALLYLIC Pd(II) COMPLEXES

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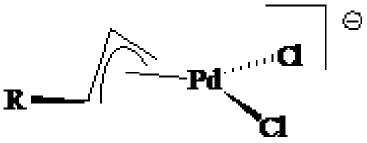
In the frame of conceptual density functional theory the chemical shifts values (δ) of signals in ^{13}C NMR spectra of substituted allylic Pd(II) complexes were calculated considering equilibrium population of conformers in aqueous solution. On the basis that δ values of signals of unsubstituted terminal carbons C3 are in linear relationship with charge on C3, Pd-C3 bond length, electron chemical potential μ, hardness η and electrophilicity index ω as well, ^{13}C NMR chemical shifts for C3 can be used as descriptors of chemical reactivity of anionic allylic Pd(II) complexes.

Key words: *allylic complexes of palladium(II), conceptual density functional theory, ^{13}C NMR, electronic chemical potential, chemical hardness, electrophilicity index.*

Introduction

NMR ^{13}C chemical shifts are commonly used for assessment of both electronic and steric effects of substituents in η^3-allylic palladium complexes. Variety of one-, two- and three-parameter correlation equations connecting ^{13}C and ^{31}P NMR chemical shifts of ligands with Hammett constants, Swain-Lupton parameters and polarization constants exists and are useful for prediction reactivity [1, 2]. Notably that both experimental and theoretical value of ^{13}C chemical shifts calculated in the frame of density functional theory (DFT) can be used in such relationships interchangeably [3].



In particular, chemical shifts in ^{13}C NMR spectra of $[R\text{-}\eta^3\text{-}C_3H_4)PdCl_2]^-$ (R = H, Me, Ph, CH_2OH, CH_2OMe, CO_2H, COMe, CO_2Me, CHO) calculated for single most stable conformer in PCM-B3LYP/LANL2DZ(Pd)+6-31+G*(H,C,O,Cl) approximation, are in good accordance with observed values (eq. 1) [4]:

$$\delta^{calc.} = 3.75 \pm 1.61 + (0.96 \pm 0.02)\delta^{exp.}, \quad r = 0.9956,\ s = 4.05, n = 33 \qquad (1)$$

lso the linear relationship between frontier molecular orbital (MO) energies and substituent constants was found [4, 5]:

$$\varepsilon_{MO} = Const + \rho_{R^-} R^- + \rho_F F + \rho_\alpha \sigma_\alpha, \qquad (2)$$

where F and R^- are Swain-Lupton field and resonance parameters, σ_α is a polarization constant.

Assuming that frontier MOs energies are connected, according to Koopmans theorem, with ionization potential (PI) and with electron affinity (EA) by relationships PI = $-\varepsilon_{HOMO}$, EA = $-\varepsilon_{LUMO}$, one can suggest that global indexes of reactivity in the frame of conceptual DFT [6] also can follow three-parameter equation similar to (2).

Electonic chemical potential μ that measures escaping tendency of an electronic cloud, chemical hardness η that measures the resistance to deformation or change and global electrophilicity index ω that measures the energy change of an electrophile when it becomes saturated with electrons, can be easily found by formulas (3 – 5) [7].

$$\mu = -\frac{(IP + EA)}{2} \qquad (3)$$

$$\eta = \frac{(IP - EA)}{2} \qquad (4)$$

$$\omega = \frac{\mu^2}{2\eta} \qquad (5)$$

The object of the study is the calculation of adjusted ^{13}C nuclear shielding constants in anions $[R\text{-}\eta^3\text{-}C_3H_4)PdCl_2]^-$ based on all conformers content and the comparison of obtained values with descriptors of chemical reactivity of conceptual DFT – electron chemical potential μ, hardness η and global electrophilicity index ω.

Experimental

Calculations were made with GAUSSIAN-09 software [8] in the frame of DFT (approximation PCM-B3LYP [9, 10]). Equilibrium geometry and nuclear shielding constants by method of gauge including atomic orbitals (GIAO) were calculated with Gen1=LANL2DZ(Pd)+6-31+G*(H,C,O,Cl) basis set. No imaginary frequencies were found, all structures correspond to minima on potential energy surface. Atomic charges by method of natural population analysis (NPA) were calculated with Gen2=LANL2DZ(Pd)+6-31G*(H, C, O, Cl) basis set.

Results and Discussion

As mentioned above, values of δ used in (1) were obtained for equilibrium geometries of the most stable conformers of *syn*-substituted anions $[R\text{-}\eta^3\text{-}C_3H_4)PdCl_2]^-$ [4]. To reduce standard deviation s and to make the slope in (1) more close to unit, incorporation of each conformer into σ was taken into account by means of Boltzman formulas (6, 7):

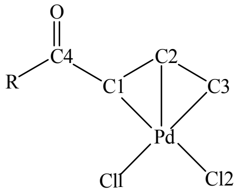
$$\frac{P_i}{P_j} = e^{-(G_i - G_j)/k_B T}, \qquad (6)$$

$$\sigma = \sum_i \frac{\sigma_i e^{-G_i/RT}}{\sum_j e^{-G_j/RT}}, \qquad (7)$$

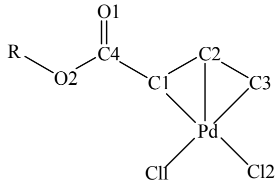
were P_i, P_j – content and G_i, G_j – Gibbs free energy of *i*–th and *j*–th conformers in equilibrium mixture at temperature T, σ_i – isotropic nuclear shielding constant for given C carbon of *i*–th conformer, σ – isotropic nuclear shielding constant for given C carbon based on each conformer contribution.

Relative equilibrium content of conformers was determined according to (6) after thermochemistry calculations. Data for conformers with equilibrium content <0.5 % were not considered for (7).

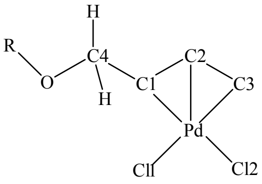
For methyl- and phenyl-substituted anions (R = Me, Ph) the single stable conformation was found on potential energy surface. Calculation results for anions **1** – **6** are presented in Tables 1 – 3.



1 (R = H), **2** (R = Me)



3 (R = H), **4** (R = Me)



5 (R = H), **6** (R = Me)

Most stable conformers of formyl- and acetyl-substituted complexes **1** and **2** differ in dihedral angle $\angle C_2C_1C_4O$ (Table 1).

Table 1. Relative free energies, equilibrium content and shielding constants of conformers of complexes **1** and **2** at 298 K

Conformer	$\angle C_2C_1C_4O$,°	G_{298}, kcal/mole	Content, %	σ_i, ppm				
				C_1	C_2	C_3	C_4	C_5
1.1	169.1	0	89.0	101.8	62.1	108.0	-25.5	–
1.2	1.5	1.2	11.0	108.6	69.9	107.2	-27.0	–
			σ according to eq. 4:	102.6	63.0	107.9	-25.7	–
2.1	-2.6	0	82.0	107.1	67.2	109.0	-33.5	148.7
2.2	167.4	0.9	18.0	102.0	64.3	108.5	-34.4	154.3
			σ according to eq. 4:	106.2	66.7	108.9	-33.7	149.6

Table 2. Relative free energies, equilibrium content and shielding constants of conformers of anions **3** – **5** at 298 K

Conformer	Dihedral angle, °		G_{298}, kcal/mole	Content, %	σ_i, ppm			
	$\angle C_2C_1C_4O_1$	$\angle C_1C_4O_2H(C_5)$			C_1	C_2	C_3	C_4
3.1.1	167.9	-179.5	0.5	24.5	112.9	63.6	108.9	3.1
3.1.2	148.9	-10.3	4.1	< 0.1	–	–	–	–
3.2.1	-9.3	178.8	0	61.2	114.6	63.4	109.0	2.5
3.2.2	39.2	19.2	0.8	14.3	104.5	64.2	109.7	2.3
				σ according to eq. 4:	112.7	63.6	109.1	2.6
4.1.1	167.3	179.7	0.5	29.6	109.9	64.0	110.1	2.4
4.1.2	145.2	-8.4	9.8	< 0.1	–	–	–	–
4.2.1	-10.1	179.5	0	70.4	110.6	63.9	111.0	1.4
4.2.2	-3.5	2.3	5.2	< 0.1	–	–	–	–
				σ according to eq. 4:	110.4	63.9	110.7	1.7
5.1.1	101.7	-64.9	2.0	2.4	92.2	65.0	114.5	113.3
5.1.2	90.5	70.1	2.1	2.0	92.9	63.7	113.6	113.8
5.1.3	97.3	170.4	1.6	5.0	94.0	63.5	114.0	114.0
5.2.1	-45.3	-65.2	0.8	18.3	82.3	69.1	116.3	119.4
5.2.2	-21.5	80.3	3.1	0.4	85.9	72.4	116.8	116.5
5.2.3	-22.5	179.7	2.7	0.7	89.2	71.5	116.3	117.3
5.3.1	178.4	-70.6	4.1	< 0.1	–	–	–	–
5.3.2	-153.1	56.5	0	71.0	84.1	67.8	115.7	114.2
5.3.3	176.8	180.0	4.1	< 0.1	–	–	–	–
				σ according to eq. 4:	87.5	68.6	115.6	115.1

* Since equilibrium content of the conformer was less then 0.1%, σ values were not calculated.

Table 3. Relative free energies, equilibrium content and shielding constants of conformers of anions **6** at 298 K

Confor mer	Dihedral angle, °		G_{298}, kcal/ mole	Content, %	σ_i, ppm				
	$\angle C_2C_1C_4O$, °	$\angle C_1C_4OC_5$, °			C_1	C_2	C_3	C_4	C_5
6.1.1	103.8	-73.3	0.7	14.5	96.1	63.7	114.7	106.1	125.1
6.1.2	92.9	79.8	1.2	6.7	96.9	63.2	113.5	106.4	124.0
6.1.3	97.2	75.8	0	47.7	95.0	63.4	114.1	105.7	121.4
6.2.1	13.1	-88.3	2.1	1.3	90.0	71.0	116.4	109.1	121.3
6.2.2	-10.0	92.1	2.1	1.5	87.0	71.6	118.8	109	121.5
6.2.3	-23.1	179.5	0.4	24.4	89.0	71.1	117.2	109.2	122.1
6.3.3	178.8	-179.0	1.5	3.8	86.1	70.3	116.8	107.1	122.1
				σ according to eq. 4:	93.3	65.8	115.1	106.8	122.3

As expected, the change in shielding constants is more pronounced (from 5 to 10 ppm) for C1 atoms directly connected with terminal substituent R. Inclusion of *σ* values for all stable conformers improves regression parameters *r* and *s* comparing to parameters of equation (1) and leads to excellent linear correlation with experimental data (Fig. 1). The biggest deviations were observed for *σ*(C1) in Ph, Me and CH_2OH-substituted complexes. Exclusion of these values improves both *s* and *r* (eq. 8).

$$\sigma^{calc.} = 178.91 \pm 0.88 + (1.02 \pm 0.01)\delta^{exp.}, \ r = 0.9990, \ s = 2.19, \ n = 31 \quad (8)$$

(CCfor Me, Ph, CH_2OH are not included)

Shielding constants for C3 atoms of 13 most stable conformers of complexes investigated correlate with Swain-Lupton field and resonance parameters (eq. 10) [11]:

$$\sigma^{calc.}(C3) = 116.8 \pm 0.3 - (8.0 \pm 0.8)R^{-} - (11.7 \pm 1.7)F; \ r = 0.9948, \ s = 0.14, \ n = 13 \quad (9)$$

Shielding constants for C3 atoms are also in good linear relationship with Pd-C3 bond length (Fig. 2) and NPA charge on C3 atoms (eq. 10). Such correlations are common for organometallic compounds and some of them were observed recently for Rh and Ir complexes [12].

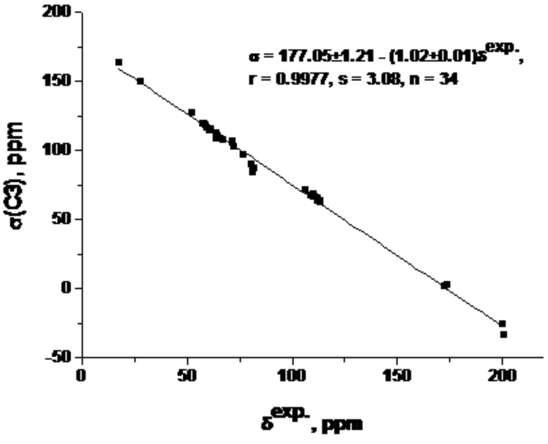


Fig. 1. Linear correlation between calculated σ(C3) and experimental δ(C3) values.

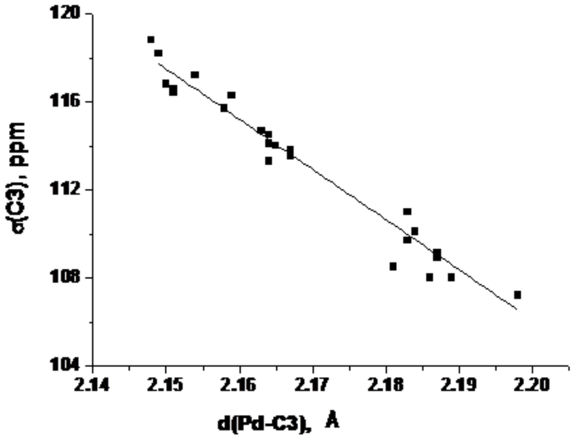
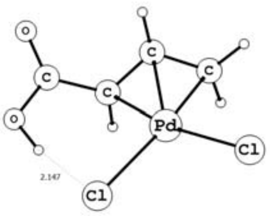
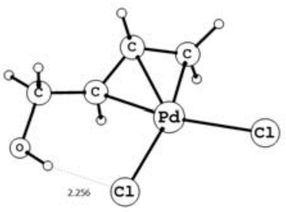


Fig. 2. Linear correlation between calculated σ(C3) and Pd-C3 bond length.



3.2.2



5.3.2

We note that stable conformers **3.2.2** and **5.3.2** of carboxy- and hydroxymethyl-substituted complexes are characterized by intramolecular hydrogen bond formation. Bond length d(H–Cl) in six-membered cycle stabilized by intramolecular hydrogen bond is equal to 2.147 Å in **3.2.2** and 2.256 Å in **5.3.2**. It is reasonable that these conformers are not participate in linear correlation between σ(C3) and charges on C3 atom (eq. 10)

$$\sigma^{calc.}(C3) = -124.7 \pm 11.5 - (714.7 \pm 34.8)q; \ r = 0.9884, \ s = 0.7, \ n = 12 \quad (10)$$

Shielding of unsubstituted carbon C3 were found to increase linearly with increase of electronic chemical potential μ (Fig. 3) and chemical hardness *η* (Fig. 4), but decrease with increase of electrophilicity index *ω* (Fig. 5). For Ph-substituted complex significant deviations from linearity were observed (Figs. 3 – 5), especially for correlation of σ(C3) with chemical hardness (Fig. 4). This is obviously caused by substantially higher HOMO energy of this complex than calculated by eq. (2) and consequently by smaller LUMO-HOMO energy gap [4]. Explanation of the observed phenomena is strong destabilizing polarization effect of the aromatic substituent which can not be compensated by small stabilizing effect of field [4]. It may be concluded that care should be taken when using *σ* value of unsubstituted carbon C(3) in unsaturated derivatives of allylic palladium complexes for spectral or computer-based reactivity prediction.

Conclusions

For the first time for η^3-allylic Pd(II) complexes, having flexible side-chain as a terminal substituent, the nuclear shielding constants *σ* were calculated based on fraction of all conformers. Each conformer contribution into observed *σ* values was assessed. This approach was shown to improve correspondence between calculated and experimental *σ* values. Further, linear correlations of *σ* for unsubstituted C3 carbon with Pd-C3 bond length, C3 charge, Swain-Lupton parameters and chemical reactivity descriptors of conceptual DFT were found. Therefore NMR ^{13}C chemical shifts for C3 can be used for prediction of chemical reactivity of anionic allylic Pd(II) complexes. As for C3 of Ph-substituted complex, its' *σ* value substantially deviates from the linearity observed in relationships with chemical reactivity descriptors testifying the importance of polarization effects.

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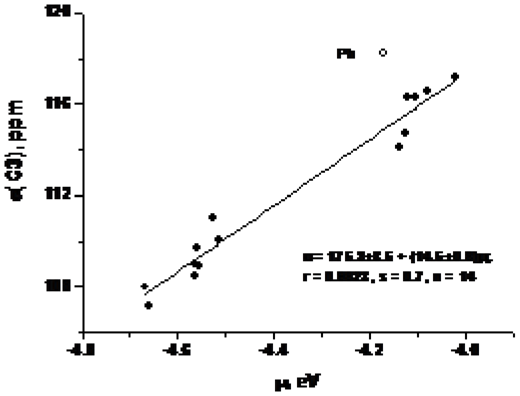

Fig. 3. Linear correlation between calculated σ(C3) and electronic chemical potential *μ*.

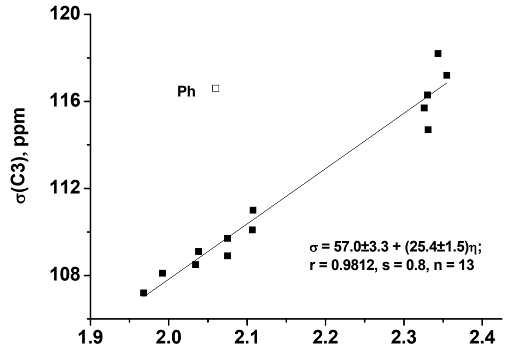

Fig. 4. Linear correlation between calculated σ(C3) and chemical hardness.

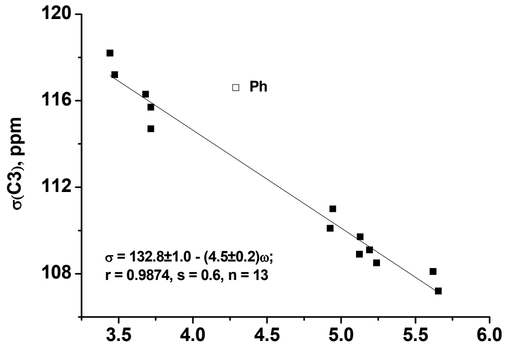

Fig. 5. Linear correlation between calculated σ(C3) and electrophility index *ω*.

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