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Theoretical Study of the Structure of Acyclic Diaminocarbene Ligands in Pd(II) Complexes

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Abstract—The electronic and steric features of acyclic aminohydrazinocarbene ligands in palladium(II) complexes are studied by the DFT method. It was found that most of the studied complexes prefer an *amphi*-2 conformation over all the other possible conformations. At the same time, in the ligand containing a hydrazide fragment more stable is a *syn* conformation. The basicity and nucleophilicity of the title ligands are much higher compared to the respective characteristics of the triphenylphosphine ligand and close to those of bis-(diisopropylamino)carbene.

Keywords: palladium carbene complexes, quantum-chemical calculations, acyclic diaminocarbenes

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At present palladium complexes with heterocyclic (Pd-NHC) [1] and acyclic (Pd-ADC) [2, 3] diaminocarbene ligands are one of the most effective catalysts of organic cross-coupling reactions. Qwing to the donor properties of the carbine ligand, such complexes are quite active in reactions of oxidative addition of aryl halides, which makes them highly effective catalysts for a variety of aryl halide reactions involving carbon–carbon bond formation. The other important feature of such complexes, which sets them apart from classical cross-coupling catalysts (palladium phosphine systems), is a large conical angle. Bulkier ligands favor higher rates of the final stage of cross-coupling reactions, specifically, reductive elimination. Moreover, they enhance stability of the palladium catalyst. Therewith, acyclic ligands occupy more place in the coordination sphere than cyclic. This is explained by a larger N–C–N bond angle (121° and 105° for acyclic and cyclic diaminocarbene ligands, respectively [2, 4, 5]).

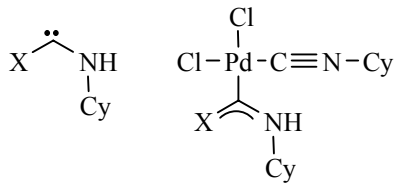
One more important feature of acyclic ligands is a possible, even though hindered, rotation about the C–N bond. By experimental [5] and theoretical [6] estimates, the barrier to rotation about these bonds is no higher than 13 kcal/mol. This imparts flexibility to the ligand sphere of the catalysts and allows them to adapt to contradictory steric demands of different stages of the catalytic cycle [2].

The highest catalytic activity among Pd-ADC was found to be characteristic of compounds containing a hydrazine fragment in the carbene ligand [7–13]. The reasons for this phenomenon are still unclear, and, therefore, we decided to study the electronic and steric features of the carbene ligands in such catalysts (Scheme 1, complexes **I–VI**) by the DFT method (GAUSSIAN 03 [14]).

Such ligands (free or coordinated with transition metals) can exist in four different conformations: *syn*, *anti,* and two *amphi* (Scheme 2). Therewith, the plane of the diaminocarbene fragment is perpendicular to the plane of the complex.

We studied the stereochemistry of the carbene ligands in complexes **I–VI**. The example of complex

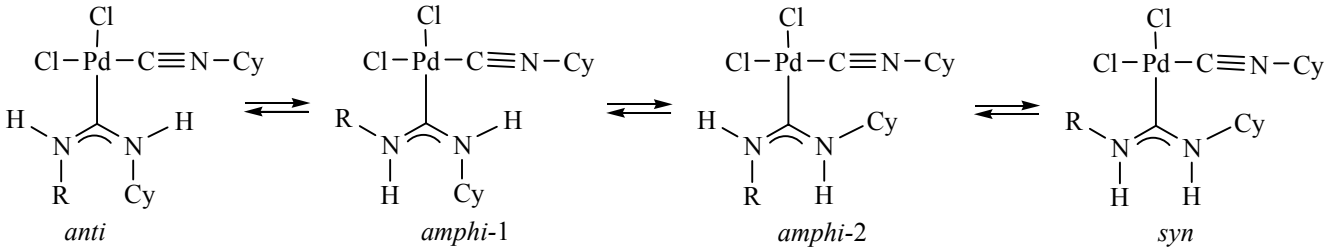
Scheme 1.



L^I–L^{VI} **I–VI**

X = 4-$NO_2C_6H_4CONHNH$ (**I**), 4-$NO_2C_6H_4NHNH$ (**II**), Me_2NNH (**III**), Ph_2NNH (**IV**), $Ph_2C{=}NNH$ (**V**), $(4\text{-}MeOC_6H_4)_2C{=}NNH$ (**VI**).

Scheme 2.



II which has found wide use as a catalyst [8−11] was used to show that the most stable conformation is *amphi*-2 (Fig. 1). The other conformations all have much appreciably energies, including the *anti* conformation which is the most stable in some Ir(I) complexes [15]. The *syn* conformation of complex **II** is destabilized by 26 kJ/mol (compared to *amphi*-2), *anti* by 23 kJ/mol, and *amphi-1* by 40 kJ/mol.

We also calculated the relative free energies of the *syn* and *amphi*-2 conformers of complexes **I–VI** ($\Delta G_{rel} = \Delta G_{syn} - \Delta G_{amphi\text{-}2}$, kJ/mol), which, along with selected geometric parameters are listed in Table 1.

It was found that complexes **III–VI** prefer the *amphi*-2 conformation over the *syn* conformation (like complex **II**). Obviously, the reason for the enhanced stability of the *amphi*-2 conformation in these cases is that in this conformation the possible steric effects associated with the restricted mobility of the cyclohexyl and hydrazine substituents in the carbene ligand are minimized. The N^1CN^2 bond angle in the carbene ligand in complexes **III** and **IV** is 116.5°–125.4°, and, therewith, this angle in the *amphi* conformation is larger and has more asymmetric C–N bonds than the *syn* conformation.

At the same time, complex **I** prefers the structure with a *syn* conformation of the carbene fragment. This fact is probably explained by hydrogen bonding between the fairly acidic proton –CONH– in the arylhydrazide substituent with one of the chlorine atoms. Evidence for such bonding comes from the fact that the distance between the –CONH– proton and the chlorine atom in the complex with an optimized geometry is much shorter than the sum of the van der Waals radii of these atoms [16] (Fig. 2). Further evidence for the presence of this hydrogen bond is provided by its Wiberg index (0.09).

To reveal the electronic features of complexes **I−VI**, we determined the basicity and nucleophilicity of the carbene ligands. The basicity of carbene ligands $\mathbf{L^I–L^{VI}}$ was measured by their proton affinity [17]. The calculation results are listed in Table 2.

The resulting data suggest that the conformers do not much differ from each other in basicity (≤5 kcal/mol. All the studied acyclic diaminocarbene ligands containing a hydrazine fragment are fairly strong bases as compared to phosphine ligands [17]). At the same time, they are lower in basicity than bis(diisopropylamino)carbene [PA = 287 kcal/mol, DFT B3LYP/6-31+G(dp) calculation].

The reactivity of the complexes is also dependent on the nucleophilicity of the carbene ligands, i.e. on the ability of the latter to transfer the electron density to a soft reaction center (in our case, palladium). To estimate this parameter, we calculated natural atomic charges (NBO). The natural atomic charge on Pd in

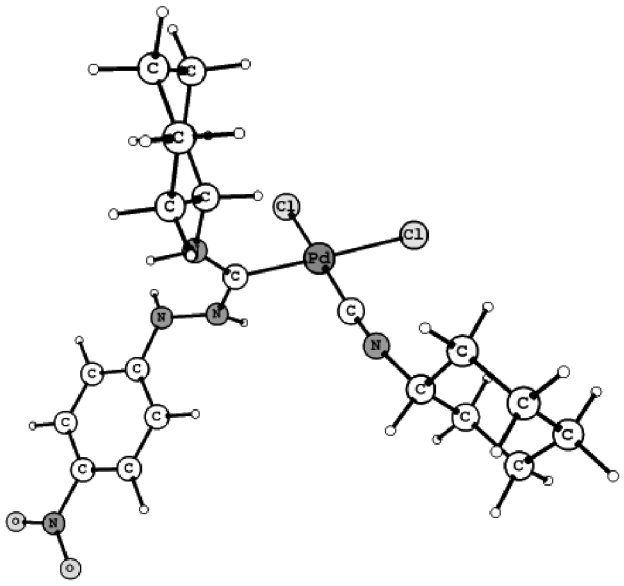


Fig. 1. Spatial arrangement of complex **II** (*amphi*-2 conformation).

Table 1. Selected energy and structure parameters of complexes **I–VI** [DFT B3LYP/CEP 121, 6-31+G(dp)][a]

Complex	ΔG_{rel}	Bond lengths, Å				Angles, deg		
		Pd–C_{carb}	Pd–C_{iso}	C–N^1	C–N^2	N^1CN^2	$C_{carb}PdC_{iso}$	θ[b]
I-*syn*	–24.5	2.042	1.952	1.334	1.336	116.5	94.9	73.2
I-*amphi*-2	0	2.028	1.956	1.331	1.358	117.7	96.3	82.4
II-*syn*	25.7	2.029	1.953	1.327	1.352	123.5	97.1	78.6
II-*amphi*-2	0	2.025	1.955	1.319	1.357	117.7	97.4	86.0
III-*syn*	29.6	2.030	1.949	1.331	1.343	116.5	96.1	85.9
III-*amphi*-2	0	2.025	1.952	1.323	1.348	117.4	96.5	88.0
IV-*syn*	30.1	2.035	1.953	1.330	1.349	122.4	96.2	80.8
IV-*amphi*-2	0	2.028	1.952	1.321	1.351	124.6	96.3	87.9
V-*syn*	28.5	2.027	1.951	1.330	1.349	124.0	96.2	84.8
V-*amphi*-2	0	2.026	1.952	1.323	1.350	125.4	96.1	89.2
VI-*syn*	29.2	2.028	1.950	1.332	1.347	123.8	95.9	85.0
VI-*amphi*-2	0	2.026	1.951	1.325	1.347	125.2	95.6	81.6

[a] N^1 – NHCy, N^2 – NHN. [b] Dihedral angles between the plane of the carbene ligand and the $C_{iso}PdCN$ coordination plane.

different conformers of complexes **I–VI** varies within a narrow range (0.55–0.57 *e*), and charge on the carbene carbon atom is 0.33–0.36 *e*. The ligand-to-metal charge transfer (estimated as the difference in the natural charge of carbon in the complex and the corresponding free carbene), which is a measure of the nucleophilicy of the ligand, is 0.15–0.18 *e*. This value is close to the respective value for bis(diisopropylamino)carbene (0.180 *e* [17]) and higher than in bis(dimethylamino)carbene (0.139 *e* [17]).

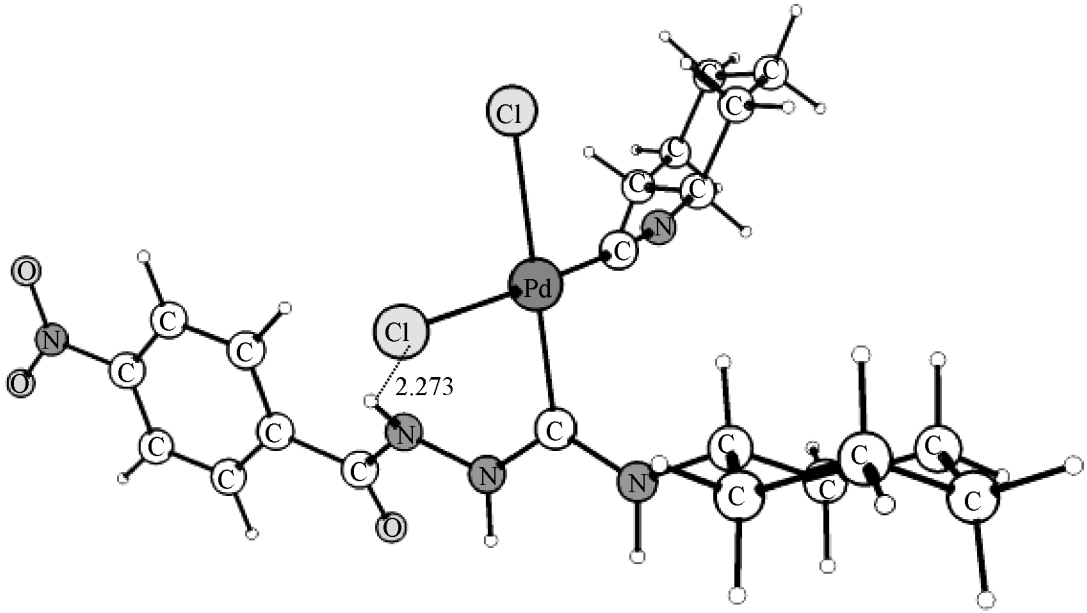


Fig. 2. Spatial arrangement of complex I (*syn* conformation).

Table 2. Proton affinities (PA, kcal /mol) of acyclic diaminocarbene ligands in different conformations [DFT B3LYP/6-31+G(dp)]

Ligand	*anti*	*amphi*-1	*amphi*-2	*syn*
$\mathbf{L^{I}}$	266	263	265	262
$\mathbf{L^{II}}$	263	260	262	258
$\mathbf{L^{III}}$	276	278	274	275
$\mathbf{L^{IV}}$	274	275	272	272
$\mathbf{L^{V}}$	280	282	278	278
$\mathbf{L^{VI}}$	285	286	283	283

Thus, we showed that aminohydrazinocarbene palladium(II) complexes **I–VI** are characteristically present in *amphi-2* or *syn* conformations, which have a larger conical angle than that in the *anti* conformation (characteristic of diaminocarbene complexes). The ligands studied in the present work are much more basic that the triphenylphosphine ligand and compare in basicity with bis(diisopropylamino)carbene. Such combination of stereochemical and electronic features is likely to explain the high catalytic activity of aminohydrazinocarbene palladium(II) complexes in cross-coupling reactions involving aryl halides.

Geometry optimization of the structures of free carbenes $\mathbf{L^{I}}$–$\mathbf{L^{VI}}$ and bis(diisopropylamino)carbene was performed a B3LYP DFT method with Becke's three-parameter exchange potential [18] and a gradient-corrected correlation functional [19, 20] in a standard 6-31+G(dp) basis set including polarization and diffuse functions. The structures of complexes **I–VI** were calculated in terms of the effective core potential model with the CEP121G split-valence basis set for Pd and the 6-31+G(dp) basis set for the other atoms. The charge distributions and bond orders were estimated by natural bond orbital (NBO) analysis.

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