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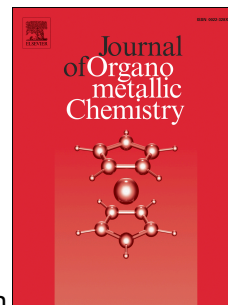
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Structure and Vibrational Spectroscopic Study of Phthalimido-functionalized N-heterocyclic Palladium Complexes. Correlations between Structure and Catalytic Activity.

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Abstract

New complexes of Pd(II) with cationic phthalimido-functionalized N-heterocyclic carbene (NHC), the *cis*-Diacyetonitrile(chloro)[1-(2_-phthalamidoethyl)-3-methylimidazolinyldene]palladium(II) Hexafluorophosphate (and its CD₃CN derivative) had been successfully used as catalyst in the Suzuki–Miyaura cross-coupling reaction. This complex have been studied by structural (XRD), spectroscopic (infrared, far-infrared and Raman) and theoretical (DFT and normal coordinate calculations) methods. Palladium is bound to two acetonitrile ligands and one-one chloride ion and phthalimido-functionalized imidazolium salt, [3-methyl-1-(2_-phthalimidoethyl) imidazolium] (L=ligand) in a square–planar *cis* arrangement. The molecular structure of the [PdCl(NCCH₃)₂L]⁺ was obtained by XRD and DFT geometry optimization. The two acetonitrile ligands exhibited two different Pd–N bonds a shorter one 2.080 Å (opposite to Cl ion) and a longer one 2.120 Å (*trans* to heterocyclic ligand). The cationic [PdCl(NCCH₃)₂L]⁺ complex has as much as 132 fundamental modes and practically all of them have been assigned. The complex has no symmetry elements, but interpretation has been performed on the basis of local symmetries of its fragments. *Tans*-conformation of the bridging –CH₂–CH₂– group has been established from vibrational spectra, and this local structure avoided interaction of phthalimido moiety with the palladium center. Special attention has been paid for understanding and interpretation of the characteristic imidazolium ring vibrations connected to the strong electron donor phthalimido ring at 1553, 1397, 1347, 1218, 1149, 1118, 845, 748, 666, 629, 471, 245, 212, 124 and 104 cm⁻¹ which bands are up shifted comparing to those of 2,3-dialkyl substituted ring modes. Clear differences were established between the fundamentals and force constants of the two differently coordinated acetonitrile. The more strongly coordinated CH₃CN(1) has Raman bands at 2336, 958 and 279 cm⁻¹ while the other CH₃CN(2) has at 2321, 936 and 266cm⁻¹ like antisymmetric CN, CC and Pd–N stretching modes, respectively. The Pd–N stretching modes were assigned with the help of spectral and calculated data of CD₃CN complex. For acetonitrile (1) the light and heavy stretching modes were 279 and 275 cm⁻¹, respectively exhibiting 4 cm⁻¹ isotope shift whyle those for acetonitrile (2) were as 266 and 264 cm⁻¹ with less isotope shift. Rather small but different 1.630 and 1.493 Ncm⁻¹ Pd–N stretching force constants were fitted for stronger and weaker bonded acetonitrile as compared to those of 3.931 Ncm⁻¹ for [Pd(NCCH₃)₂]²⁺, and 4.050 Ncm⁻¹ for *cis*-PtCl₂(NCCH₃)₂. In contrast, the strongly weakened Pd–N bonds the

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