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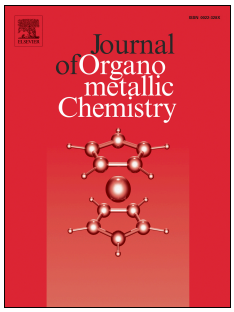

Synthesis and structure elucidation of allyl Pd(II) complexes of NHC ligands derived from substituted imidazo[1,5-*a*]quinolin-1(2H)-ylidene

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Synthesis and Structure elucidation of Allyl Pd(II) Complexes of NHC Ligands Derived from Substituted Imidazo[1,5-a]quinolin-1(2H)-ylidene

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ABSTRACT: Nine Pd(II) complexes involving N-heterocyclic carbenes (NHCs) derived from 2-substituted and 2- and 7-substituted imidazo[1,5-a]quinolin-1(2H)-ylidene with auxiliary allylic ligands were synthesized and characterized. The structure and configuration of the complexes were elucidated on the basis of combination of dynamic NMR and DFT studies. Conformational studies in respect of hindered rotation around Pd-C bond and η^3-η^1-η^3 pseudo allyl rotation were performed. The results from dynamic NMR and DFT studies confirmed the mechanism of selective η^3-η^1-η^3 isomerization**,** whose energy barriers are affected by steric hindrance of substituents at nitrogen atom. Energy barriers of isomerization (16.7 – 18.8 kcal/mol) are slightly influenced by the electronic nature of substituents at seventh position in imidazo[1,5-a]quinolin-1(2H)-ylidene moiety. The results from DFT calculations were in good agreement with the experimental energy barriers.

Keywords: NHC, Palladium, Allyl Complexes, Dynamic NMR Spectroscopy, DFT calculations

1. Introduction

N-heterocyclic carbenes (NHC) are state of the art ligands in organometallic chemistry [1-6] and catalysis [7-11]. The nitrogen atoms in the heterocycle offer possibilities for tuning of the ligand structure; through change in the N substituents, steric demands and electronic properties of the ligand can be modified to provide complexes with enhanced catalytic performances [12-15]. The extension of aromatic system by annulation of imidazole-2-yliden moiety provides another possibility for tuning of electronic and steric properties of NHC ligands. Polyaromatic-fused NHCs derivative of phenanthrene [16], acenaphtene [17], pyrene [18], heterocycles [19-21] demonstrate fertile catalytic properties and interesting photophysical features [22-24]. Various functional groups can be introduced, resulting in complexes with wider applications [25, 26]. The introduction of a suitable donor group can lead to versatile structures in ditopic complexes or enhanced catalytic

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