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DFT mechanistic investigation of Wacker-type oxidation of olefins catalyzed by a Pd(II) quinoline-2-oxazoline complex: the effect of electronic asymmetry of the ligand

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This study investigates the mechanism of Wacker-type oxidation of olefins mediated by the Pd–Quinox catalyst, which incorporates an electronically asymmetric quinoline-2-oxazoline (Quinox) ligand, utilizing density functional theory (DFT) calculations. The results demonstrate that oxidation proceeds *via* syn-peroxypalladation, followed by ring expansion and a 1,2-hydride shift, which is in agreement with the experimental results reported earlier. The 1,2-hydride shift is identified as the rate-limiting step. To evaluate the effects of ligand modification, a series of Pd(II) catalysts bearing Quinox ligands with various substituents on the quinoline moiety are examined. Furthermore, a series of *para*-substituted styrene derivatives are employed to examine the effects of substrate variation. We also investigate the effect of the electronic asymmetry of Quinox, pyridyl oxazoline (Pyrox), 2-(pyridin-2-yl)benzoxazole (PBO), and imidazolin-2-imine (AmIm) ligands on the stability of catalytic intermediates in palladium-catalyzed Wacker-type oxidation, utilizing DFT and natural bond orbital (NBO) analyses. The findings indicate that these ligands influence the overall reaction pathway by controlling the arrangement of reactants on the metal center within the catalytic intermediates. The Pyrox ligand displays behavior similar to that of Quinox, whereas the AmIm ligand exhibits a stronger σ-donating and π-accepting character compared to the structurally related β-diketiminate (BDK) ligands. A detailed structural analysis of the optimized geometries of intermediates with these ligands, along with an in-depth discussion of second-order perturbation energies associated with various donor–acceptor interactions, is presented.

Introduction

The electronically asymmetric ligands are bidentate ligands whose two donor units possess distinct electronic properties, resulting in variations in the strength of σ-donor and/or π back-bonding interactions with the metal center.[1] This electronic dissimilarity of the donor components plays an important role in controlling the coordination sphere of transition metal complexes, which has been utilized to stabilize transient metal species,[2] and enhancing catalytic efficiency.[3] For instance, an electronically asymmetric pyridyl oxazoline ligand (Pyrox-A) (Scheme 1a) has been demonstrated to stabilize low-valent Co(I) intermediates.[2] Similarly, electronically asymmetric ligands have been shown to control site selectivity in palladium-catalyzed reactions.[4] In the case of 1,4-difunctionalization of isoprene to generate polyenes, the Pyrox B ligand (Scheme 1a) was found to be important in directing the regioselectivity of the reaction, owing to the interplay of its electronic asymmetry and steric properties.[4] In addition to their influence on regioselectivity, electronically asymmetric ligands also play a role in enantioselective catalysis by modulating chiral induction.[5–7] For example, in the enantioselective intramolecular oxidative amidation of alkenes using molecular oxygen as an oxidant, a catalyst bearing an electronically asymmetric ligand Pyrox-C (Scheme 1a) was employed to control the stereochemical outcome.[5] DFT studies indicated that the Pyrox-C ligand contributed to the stereochemical selectivity by complementing steric effects with its electronic asymmetry, thereby influencing the amidopalladation step.

The use of electronically asymmetric ligands to stabilize transition metal catalysts is particularly useful when two reactants with different electronic characteristics bind the metal center simultaneously in the catalytic cycle.[1] The controlled spatial arrangement of reactants within a catalytic intermediate, facilitated by the distinct donor units of the ligand, can enhance both catalytic efficiency and selectivity.[8] A notable example is the catalyst-controlled Wacker-type oxidation for the conversion of terminal olefins to methyl ketones, which is

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