

Electronic Asymmetry of an Annelated Pyridyl–Mesoionic Carbene Scaffold: Application in Pd(II)-Catalyzed Wacker-Type Oxidation of Olefins

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ABSTRACT: The two donor modules of an annelated pyridyl–mesoionic carbene ligand (aPmic) have different σ - and π -bonding characteristics leading to its electronic asymmetry. A Pd(II) complex **1** featuring aPmic catalyzes the oxidation of a wide range of terminal olefins to the corresponding methyl ketones in good to excellent yields in acetonitrile. The catalytic reaction is proposed to proceed via *syn*-peroxypalladation and a subsequent rate-limiting 1,2-hydride shift, which is supported by kinetic studies. The electronic asymmetry of aPmic renders a well-defined coordination sphere at Pd. The favored arrangement of reactants on the metal center features an olefin trans to the pyridyl module and a ^tbutylperoxide trans to the carbene. This arrangement gains added stability by the π -delocalization paved by the compatible orbitals on Pd, the pyridyl module, and the olefin that is perpendicular to the Pd(aPmic) plane. The π -interactions are absent in an alternate arrangement wherein the olefin is trans to the carbene. Density functional theory studies reveal the matching orbital overlaps responsible for the preferred arrangement over the other. This work provides an orbital description for the electronic asymmetry of aPmic.

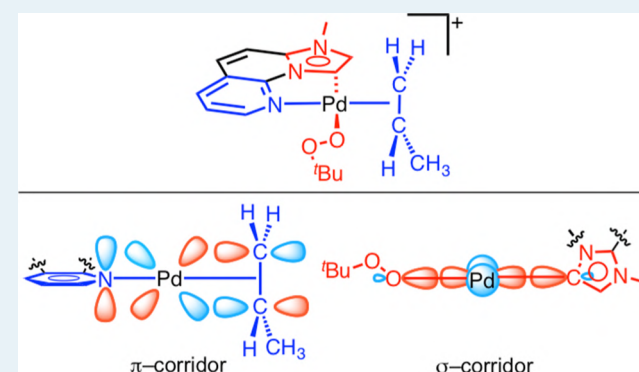
KEYWORDS: electronically asymmetric ligands, annelated carbenes, mesoionic carbenes, Wacker-type oxidation, catalysis

INTRODUCTION

Electronically asymmetric ligands wherein the donor modules differ in their electronic characteristics have received significant attention in recent years.¹ The difference in electronic characteristics of the donor modules results in significant variation in the nature and strength of metal–ligand interactions. Electronic asymmetry of the pyridine–oxazoline ligand (Pyrox-A) (Scheme 1a) has been implicated in stabilizing low-valent Co(I) intermediates.² The electronic disparity also plays a key role in many transformations catalyzed by transition metal compounds by controlling the catalyst coordination sphere. For example, Pyrox-B (Scheme 1a) imparts site selectivity in palladium-catalyzed 1,4-difunctionalization of isoprene by controlling the migratory insertion of alkene into the Pd–alkenyl bond.³ Mechanistic studies suggested that the directed insertion is the result of the unique electronic asymmetry and steric properties of the ligand. Electronic asymmetry has also been found to influence the chiral induction in enantioselective transformations.⁴ Based on density functional theory (DFT) calculations, Stahl and co-workers suggested that the electronic asymmetry of Pyrox-C (Scheme 1b) complements the steric asymmetry and thereby

controls the stereochemical outcome of the amidopalladation step in the Pd(II)-catalyzed enantioselective oxidative amidation of alkenes.^{4a}

Catalytic transformations that involve two electronically different reactants are the best suited to evaluate the effects of electronic asymmetry of a ligand. In such transformations, the electronically asymmetric ligand directs the binding of the reactants (inner sphere) in a specific arrangement. The most well-studied example is the catalyst-controlled Wacker-type oxidation, which involves the coordination of an olefin and a ^tbutylperoxide to a Pd center. The Wacker oxidation is a synthetically important process for converting a terminal olefin to a methyl ketone.^{5–7} Under Tsuji–Wacker conditions, this reaction is substrate-controlled, which can result in a mixture of aldehyde and ketone products, especially when the alkene



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