

Organometallics 2015 vol.34 N16, pages 3998-4010

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## Pyrazole-Based PCN Pincer Complexes of Palladium(II): Mono- and Dinuclear Hydroxide Complexes and Ligand Rollover C-H Activation

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### Abstract

© 2015 American Chemical Society. Palladium complexes of the novel unsymmetrical phosphine pyrazole-containing pincer ligands PCN<sup>H</sup> (PCN<sup>H</sup> = 1-[3-[(di-*t*-*rt*-butylphosphino)methyl]phenyl]-1H-pyrazole) and PCN<sup>Me</sup> (PCN<sup>Me</sup> = 1-[3-[(di-*t*-*rt*-butylphosphino)methyl]phenyl]-5-methyl-1H-pyrazole) have been prepared and characterized through single-crystal X-ray diffraction and multinuclear <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. In preparations of the monomeric hydroxide species (PCN<sup>H</sup>)Pd(OH), an unexpected N detachment followed by C-H activation on the heterocycle 5-position took place resulting in conversion of the monoanionic {P,C,N} framework into a dianionic {P,C,C} ligand set. The dinuclear hydroxide-bridged species (PCN<sup>H</sup>)Pd(μ-OH)Pd(PCC) was the final product obtained under ambient conditions. The "rollover" activation was followed via <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, and dinuclear cationic μ-OH and monomeric Pd<sup>II</sup> hydroxide intermediates were identified. DFT computational analysis of the process (M06//6-31G\*, THF) showed that the energy barriers for the pyrazolyl rollover and for C-H activation through a σ-bond metathesis reaction are low enough to be overcome under ambient-temperature conditions, in line with the experimental findings. In contrast to the PCN<sup>H</sup> system, no "rollover" reactivity was observed in the PCN<sup>Me</sup> system, and the terminal hydroxide complex (PCN<sup>Me</sup>)Pd(OH) could be readily isolated and fully characterized. (Chemical Equation Presented).

<http://dx.doi.org/10.1021/acs.organomet.5b00355>

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