

## Electronically flexible pyridylidene amide ligands for palladium-catalyzed $\alpha$ -arylation of ketones

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Electronically flexible ligands such as pyridylideneamides (PYAs, Fig. 1A) can vary their degree of donor ability and may stabilize several intermediates of a catalytic cycle.<sup>[1]</sup> This ligand flexibility is a highly desirable feature in catalytic processes, especially when different oxidation states are involved.<sup>[2]</sup> In their zwitterionic form, these ligands exhibit strongly donating properties that facilitate oxidative additions on the coordinated metal center. Furthermore, their ease of production, low-cost synthesis and high tunability make them efficient alternatives to carbenes and phosphines. Surprisingly, the potential of such donor-flexible PYA ligands has been poorly investigated in palladium-catalyzed cross-coupling processes. Here we introduce different bidentate pyridyl-PYA ligands coordinated to palladium(II), which afford highly active and robust ketone  $\alpha$ -arylation catalysts with unprecedented turnover numbers (TONs) for N-based ligands in this transformation (Fig. 1B).<sup>[3]</sup> Moreover, we will discuss mechanistic details that emerged from using these well-defined precatalysts.

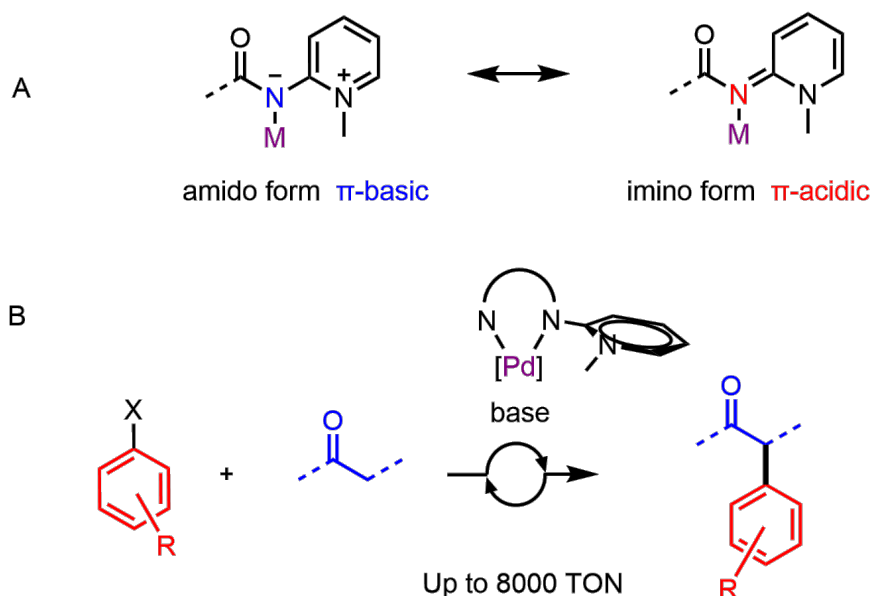


Figure 1. A: Resonance forms of the PYA ligand. B: Schematic representation of a palladium complex containing a pyridyl-pyridylidene amide ligand that is active in the  $\alpha$ -arylation of ketones.

[1] M. Navarro, L. Mo, H. Müller-Bunz, S. Bernhard, M. Albrecht. *Chem. Eur. J.*, **2016**, 22, 6740-6745.

[2] P. D. W. Boyd, L. J. Wright, M. N. Zafar, *Inorg. Chem.*, **2011**, 50, 10522-10524.

[3] P. Novák, R. Martin, *Curr. Org. Chem.*, **2011**, 15, 3233-3262.