

SIDE-BOUND C=O AND C=N BONDS AS COOPERATIVE LIGANDS IN NICKEL CATALYSIS

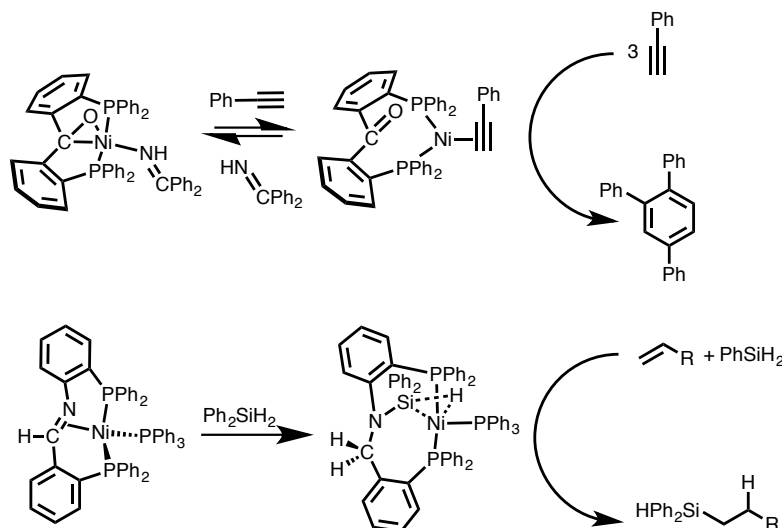
Dide G. A. Verhoeven,[†] Alessio Orsino,[†] Martin Lutz,[‡] Marc-Etienne Moret,^{†,*}

[†]*Organic Chemistry & Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG, Utrecht, The Netherlands.*

[‡]*Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Faculty of Science, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

e-mail: m.moret@uu.nl

The development of greener and cheaper chemical processes motivates a widespread investigation of complexes of first-row transition metals as potential homogeneous catalysts to replace or, better, improve on traditional systems that are widely based on noble metals.^[1] Progress in this area has been intimately related to the development of tailored ligands, such as cooperative ligands that actively participate in chemical reactions.^[2]



In this contribution, we investigate the use of side-bound C=O and C=N π -ligands^[3,4,5] tethered by phosphine side-arms as cooperative ligands in base-metal catalysis. In particular, a hemilabile P(CO)P ligands afford selective Ni(0) alkyne cyclotrimerization catalysts (top), and Ni(0) complexes of P(CN)P ligands activate Ph₂SiH₂ over the C=N bond and function as olefin hydrosilylation catalysts (bottom). Insights into the mechanism of these transformations are provided by both experiment and computations.

References:

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