

Supporting Information for

Phosphine-Phenoxide Nickel Catalysts for Ethylene/Acrylate

Copolymerization: Olefin Coordination and Complex Isomerisation Studies

Relevant to the Mechanism of Catalysis

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7. Computational Details

DFT energy calculations and geometry optimizations in the gas phase are carried out with Gaussian software.⁵ The hybrid meta-generalized gradient approximation (hybrid meta-GGA) functional M06⁶ was used with the Karlsruhe-family double- ζ valence basis set def2-SVP.⁷ M06 was chosen for its extensive benchmarking with organometallic systems⁸ and from prior use in related systems.² When available, the initial guess for geometry optimization was the experimental X-ray crystal structure. Conformational sampling was performed using Entos Qcore software⁹ by running an annealing MD trajectory for a given structure using the GFN-xTB1¹⁰ potential energy surface, followed by optimization at the XTB level, and finally DFT optimization using the M06 functional. The critical points on the potential energy surface are confirmed with harmonic frequency analysis, where exactly zero imaginary frequencies are seen for ground-state structures. Single point corrections are performed using the M06 functional and the triple- ζ def2-TZVP basis set. Implicit solvation effects by toluene solvent are considered by using the SMD continuum solvation model¹¹ as an additional single point correction with the ORCA software package.¹³ Gibbs free energies are taken at 298.15 K. Natural charges at the nickel metal center were taken using natural bond orbital (NBO) analysis.¹³

In Figure 10, the following ligands bound to the Ni center were considered for each catalyst **2L** (R = silane), **2L-Me** (R = Me), and **2L-CCO** (R = ester): pyridine, 1,5-dimethylpyridine, 5-fluoropyridine, ethene, butene, hexene, methyl vinyl ether (binding at alkene), methyl vinyl ether (binding at O), vinyl acetate (binding at alkene), vinyl acetate (binding at O), *t*-butyl acrylate (binding at alkene), *t*-butyl acrylate (binding at O),

acrylonitrile (binding at alkene), acrylonitrile (binding at N), methyl vinyl ketone (binding at alkene), and methyl vinyl ketone (binding at O).

Regression analysis was performed on the data in Figure 10. The lines of regression for the catalyst systems **2L** (R = silane) and **2L-Me** (R = Me) are $y = 0.98x + 3.07$ kcal/mol ($R^2 = 0.82$) and $y = 1.00x + 2.25$ kcal/mol ($R^2 = 0.79$), respectively.

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