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2-Hydroxyarylphosphines: Ligand Tayloring for Homogenous Nickel Catalyzed Poly- and Oligomerization of Ethene

J. Heinicke^a; M. Köhler^{ab}; M. He^a; E. Mousina^{ab}; W. Keim^b

^a Universität Greifswald, Germany ^b Institut für Technische Chemie, Rwth Aachen, Germany

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2-HYDROXYARYLPHOSPHINES: LIGAND TAYLORING FOR HOMOGENOUS NICKEL CATALYZED POLY-AND OLIGOMERIZATION OF ETHENE

J. Heinicke, ^a M. Köhler, ^{a,b} M. He, ^a E. Mousina, ^{a,c} and W. Keim^b Universität Greifswald, Germany; ^a Institut für Technische Chemie, Rwth Aachen, Germany; ^b and Russian Academy of Science, Russia^c

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 $Ni(COD)_2$ reacts with tertiary, secondary, and even some primary 2-hydroxyarylphosphines to form catalysts for the polymerization of ethene. The conversion and molecular weight distribution depend strongly on steric and electronic effects, particularly on the other substituents at phosphorus (Table I) as well as on solvents and auxiliaries. Increasing P-basicity favors, increasing steric demand of P-substituents

TABLE I

PR ₂					
~ 0	Су	iPr	Et	tBu	Ph
Conversion (%) ^a	72	40	84	94	66
M _w (g/mol)	58,930	25,840	21,810	14,020	5,510
M _n (g/mol)	26,500	6,230	7,943	2,330	4,430
Conversion $(\%)^b$	50.4	59	98*	25	
M _w (g/mol)	97,490	38,400	25,140*	29,920	
M_n (g/mol)	32,040	13,100	9,226*	$7,\!274$	

^a50 bar/100°C.

Address correspondence to J. Heinicke, Institut für Chemie und Biochemie, Universität, Greifswald, Greifswald, 17487 Germany. E-mail: heinicke@uni-greifswald.de

^b30 bar/70°C.

diminishes the chain growth as compared to chain transfer or termination. P-primary derivatives give catalysts when the ligands are activated/protected by 4-OMe or 4,6-tBu $_2$ substituents. Addition of suitable R_3P to the $Ph_2PC_6H_4/O^-/Ni$ catalysts causes oligomerization of C_2H_4 in high yield.