

supporting information for

Nickel and Palladium Complexes of Pyridine-Phosphine Ligands as Ethene Oligomerization Catalysts

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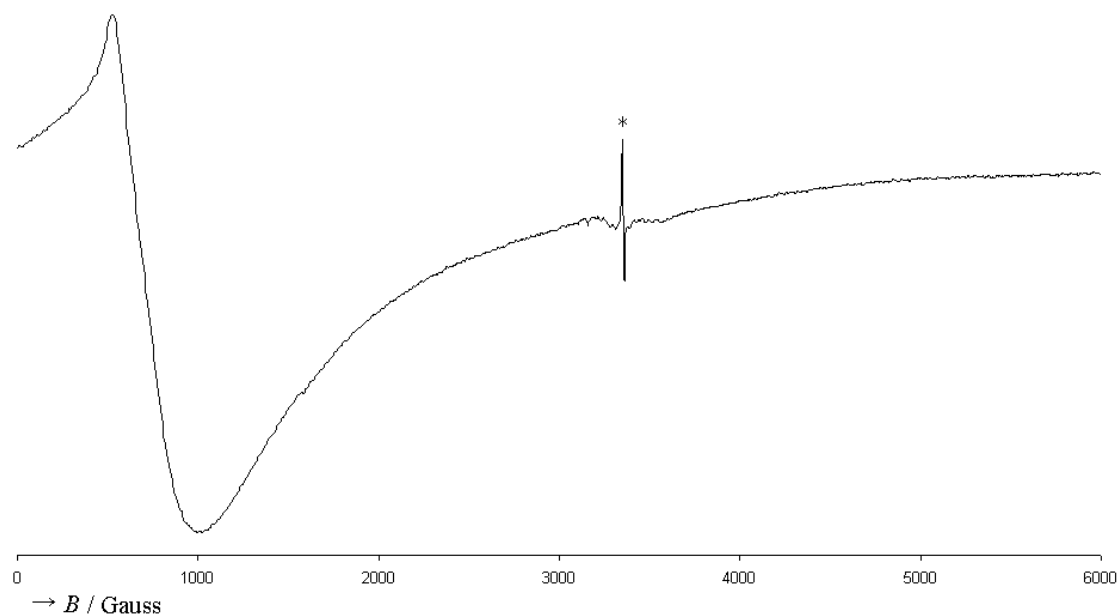


Figure S1. EPR spectrum of compound **10**. The signal marked with * is the results of a small amount of paramagnetic impurities in the cryostat Dewar.

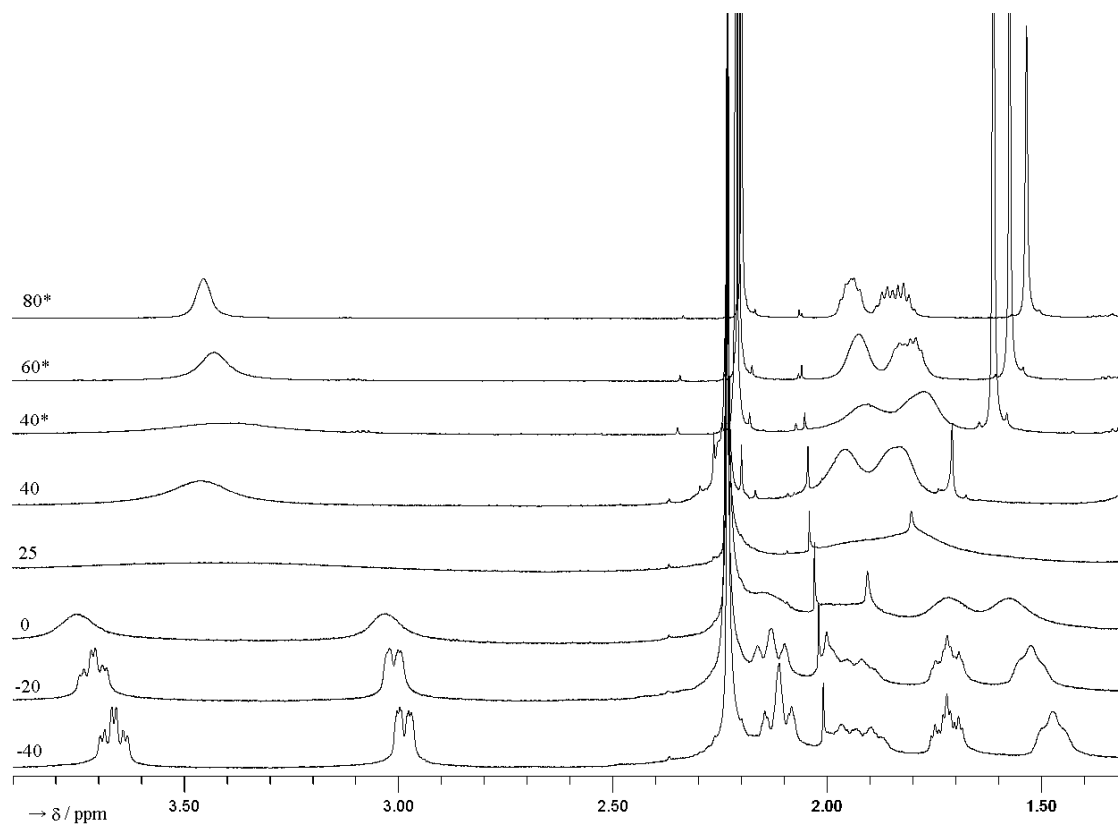


Figure S2. Methylene region of the ^1H NMR spectra of compound **21** at different temperatures (in °C), recorded in CD_2Cl_2 except spectra marked with * which are recorded in $\text{Cl}_2\text{DCCDCl}_2$.

General experimental considerations

All reactions involving sensitive compounds were carried out under an atmosphere of purified dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and distilled under dinitrogen; acetonitrile, CH_2Cl_2 , CD_2Cl_2 , and CDCl_3 from CaH_2 , toluene from sodium, Et_2O and THF from sodium / benzophenone, and pentane and hexanes from sodium / benzophenone / triglyme. Toluene and heptane in toluene solution used for nickel catalyzed oligomerization were stored over sodium / potassium alloy. All other chemicals were purchased from commercial suppliers and used as received. Silica 60 was used for column chromatography unless stated otherwise. Elemental analyses were carried out by Kolbe Mikroanalytisch Laboratorium, Mülheim an der Ruhr (Germany). Electron Ionization (EI) mass spectrometry (MS) was carried out on an Agilent Technologies 6890N/5973N GC-MS using an ionizing energy of 70 eV. Samples were dissolved in Et_2O or CH_2Cl_2 . Fast Atom Bombardment (FAB) and Field Desorption (FD) high resolution mass spectrometry (HRMS) were carried out at the Department of Mass Spectrometry at the University of Amsterdam using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. For FAB, samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3KeV. During the high resolution FAB-MS measurements a resolving power of 10000 (10% valley definition) was used. For FD, 10 μm tungsten wire FD emitters containing carbon microneedles with an average length of 30 μm were used. The samples were dissolved in CH_2Cl_2 and then loaded onto the emitters with the dipping technique. An emittercurrent of 0–30 mA was used to desorb the samples. The ion source was generally at room temperature. NMR spectra were recorded on a Varian Mercury 300 operating at 300.1 (^1H), 75.5 (^{13}C), 121.5 (^{31}P), and 282.4 (^{19}F) MHz or a Varian Inova 500 operating at 499.8 (^1H) and 125.7 (^{13}C) MHz, at ambient temperature unless stated otherwise. Signals are referenced to TMS (^1H and ^{13}C), 85% H_3PO_4 (^{31}P), and CCl_2F_2 (^{19}F) as external standards at 0 ppm, except when $\text{Cl}_2\text{DCCDCl}_2$ was the solvent, in which case signals are referenced to residual solvent signal at 6.00 (^1H) and 73.78 (^{13}C) ppm. Magnetic moments were determined in CD_2Cl_2 solution with 5% cyclohexane as reference by the Evans NMR

method.¹ Experimental X-band EPR spectra were recorded on a Bruker EMX Plus spectrometer with a spectrometer frequency of 9.378347 GHz in CH₂Cl₂ at 20 K. The addition of ~0.1 M [*n*-Bu₄N]PF₆ to the solution improved the quality of the glass. Solution-phase GC analysis was performed on an Interscience Thermo Focus GC equipped with a flame ionization detector and a 10 m Restek RTX-5 column with a 0.18 mm internal diameter, using helium as carrier gas at 0.2 ml/min. Gas-phase GC analysis was performed on an Interscience Compact GC equipped with a thermal conductivity detector and a 10 m Porabond Q column with a 0.32 mm internal diameter operated isothermally at 60 °C, using helium as carrier gas at 60 kPa. Oligomerization reactions were performed in a stainless steel 180 mL autoclave, equipped with a glass liner, a thermocouple, an internal cooling spiral, a magnetic stirrer, and a gas inlet via a 40 mL injection chamber.

References

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