New Ni(II)-Ni(II) dinuclear complex, a resting state of (α-diimine)$NiBr_2$/$AlMe_3$ catalyst system of ethylene polymerization

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Electronic Supplementary Information

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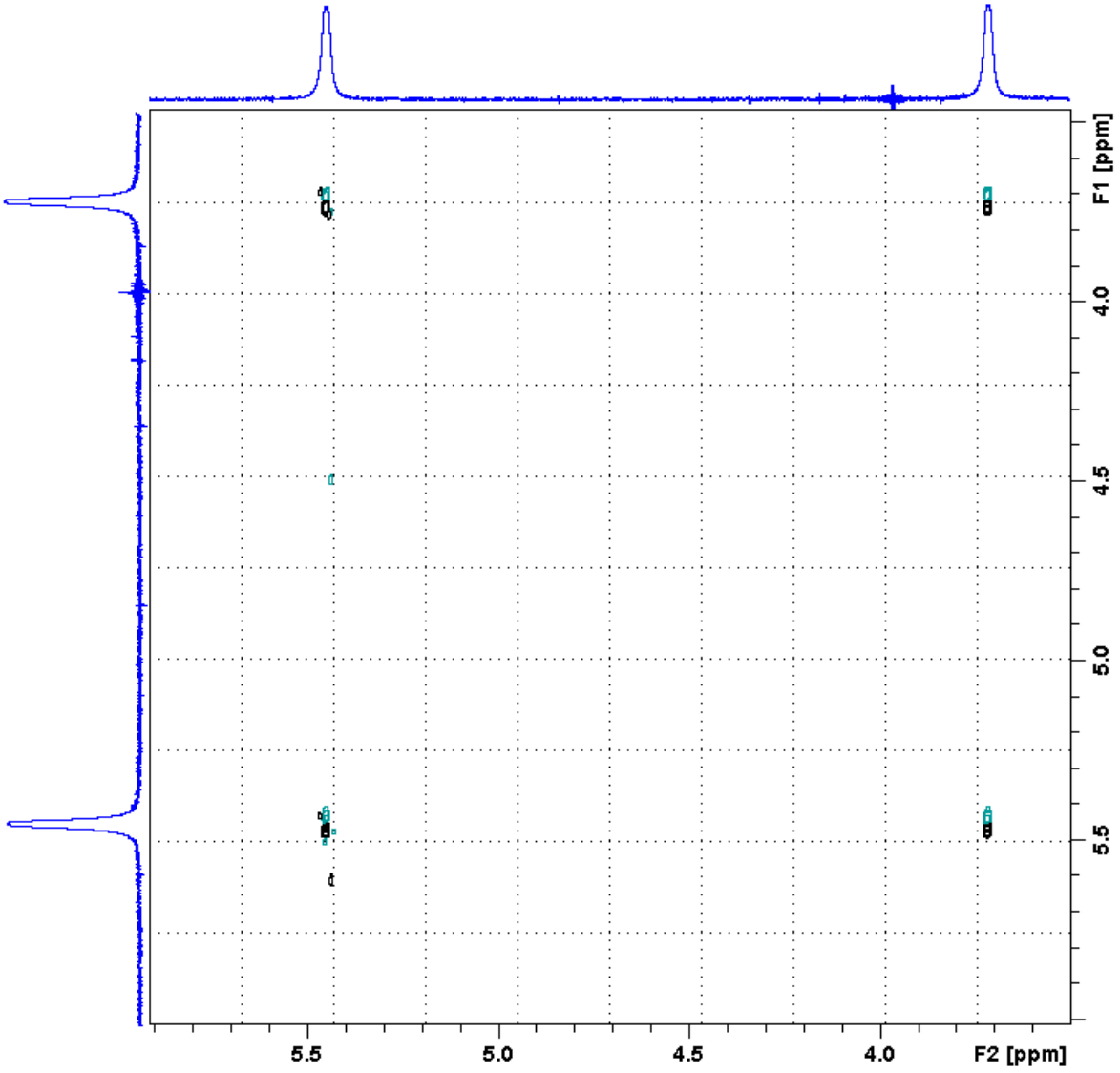


Figure S1. ^{1}H-^{1}H cosydfph NMR spectrum of the sample **1**/AlMe$_3$ (toluene-d$_8$, [Al]/[Ni] = 10/1, C_{Ni} = 5 mM), recorded at 0 °C.

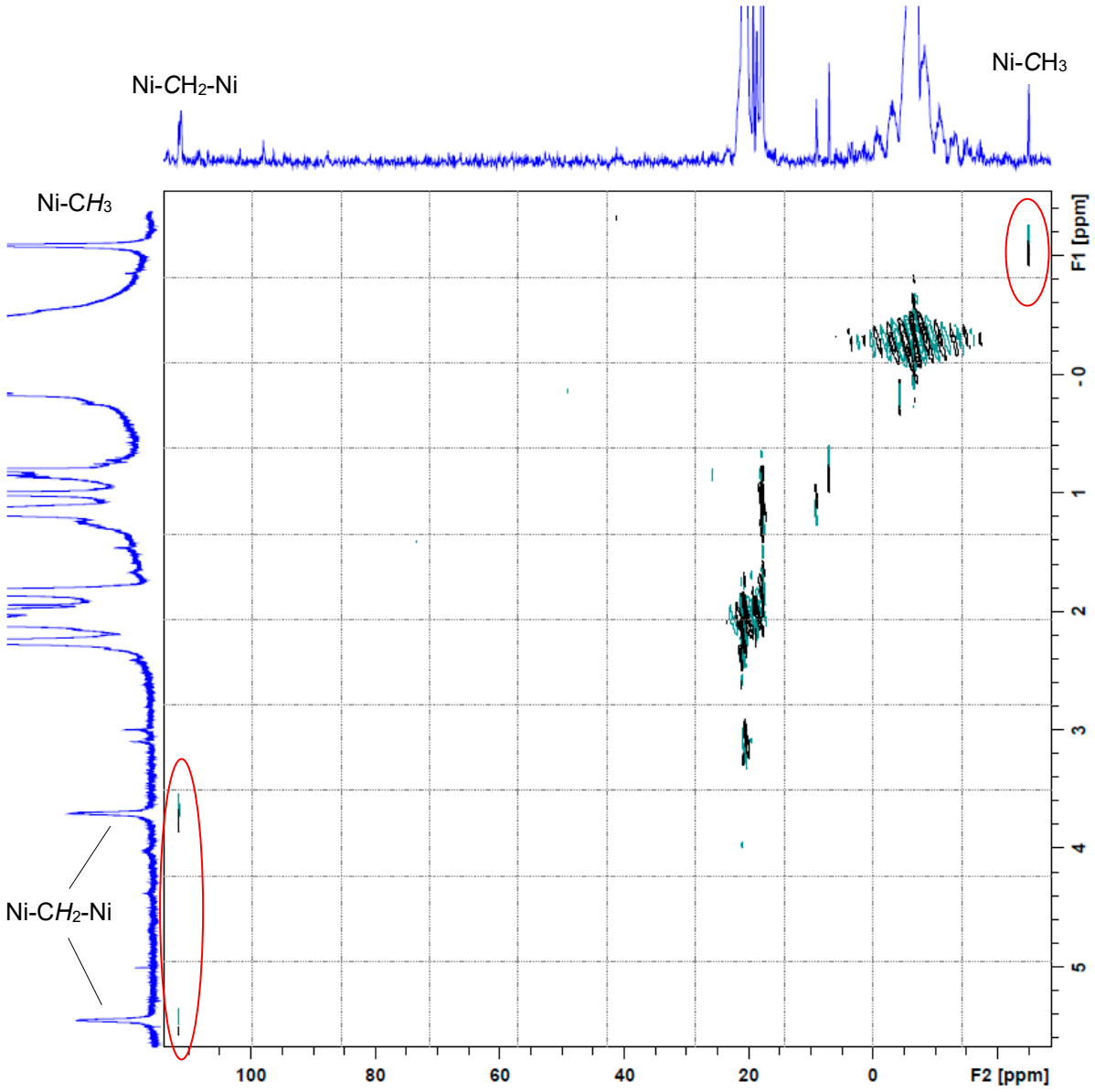


Figure S2. ^{1}H-^{13}C hxdeptbiqf NMR spectrum of the sample **1**/AlMe$_3$ (toluene-d$_8$ (0.5 ml) + 1.2-difluorobenene (0.2 ml), [Al]/[Ni] = 10/1, C_{Ni} = 30 mM), recorded at 0 °C. To increase the solubility of **2** at 0 °C, ca. 0.2 ml of 1.2-difluorobenene was added to the **1**/AlMe$_3$ sample.

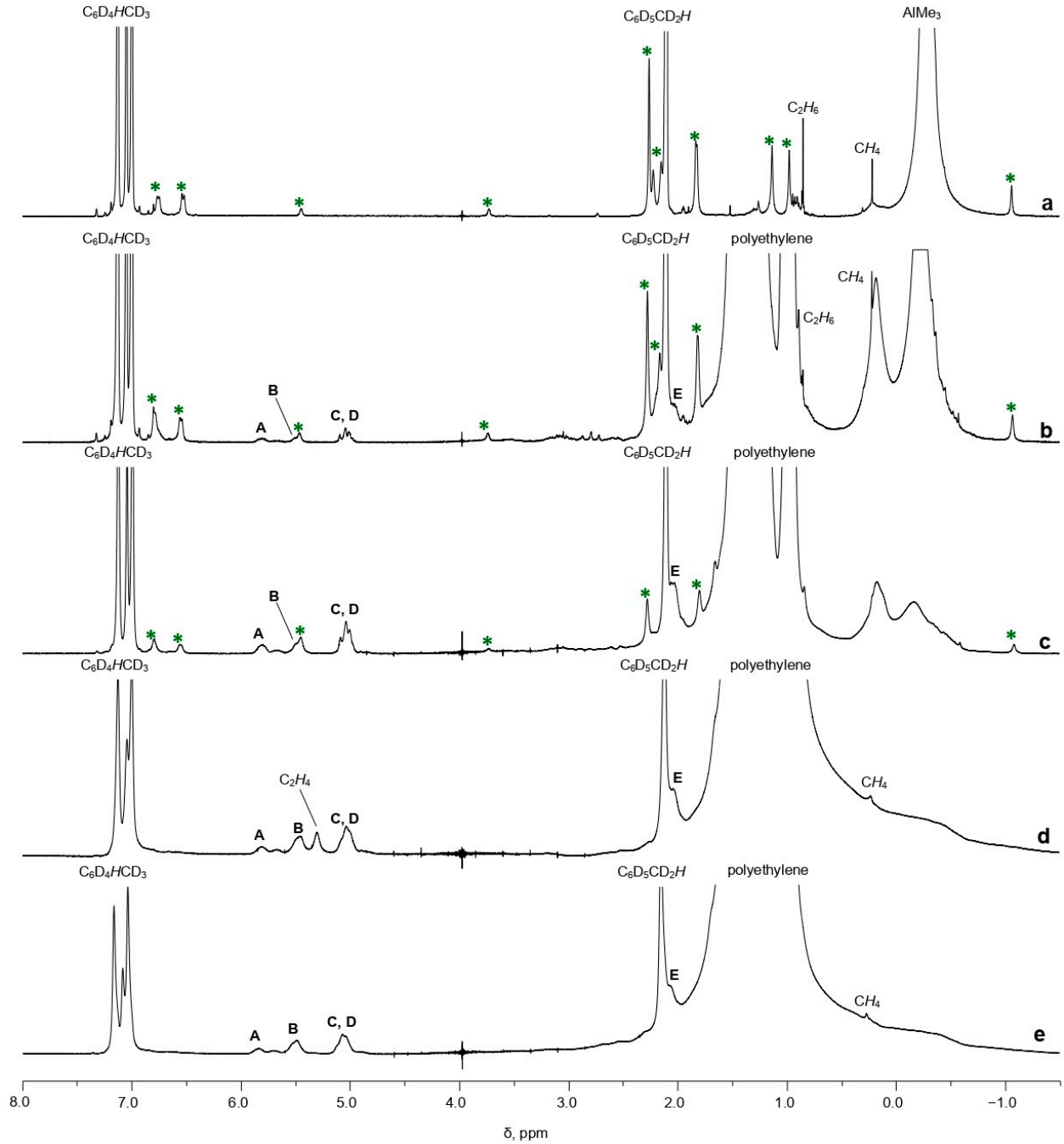


Figure S3. ^{1}H NMR spectra (toluene-d_8, 0 °C) of the samples:

a) **1**/$AlMe_3$ (Al/Ni = 10/1, C_{Ni} = 5 mM), mixed and stored during 1 h at 25 °C

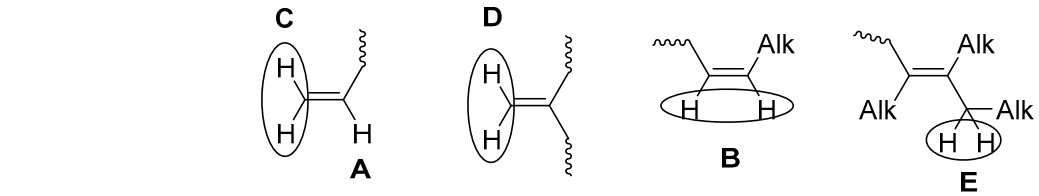
b) sample in (a) after bubbling ethylene for 30s at 25 °C

c) sample in (b) after bubbling ethylene for 30s at 25 °C

d) sample in (c) after bubbling ethylene for 30s at 25 °C

e) sample in (d) after storing for 10 min at 0 °C

Peaks marked by asterisks belong to the complex **2**. Peaks marked by **A**, **B**, **C**, **D**, and **E** correspond to the following protons of double-bond moieties of the polymer molecules:



Alk are linear or branched alkyl groups of various length

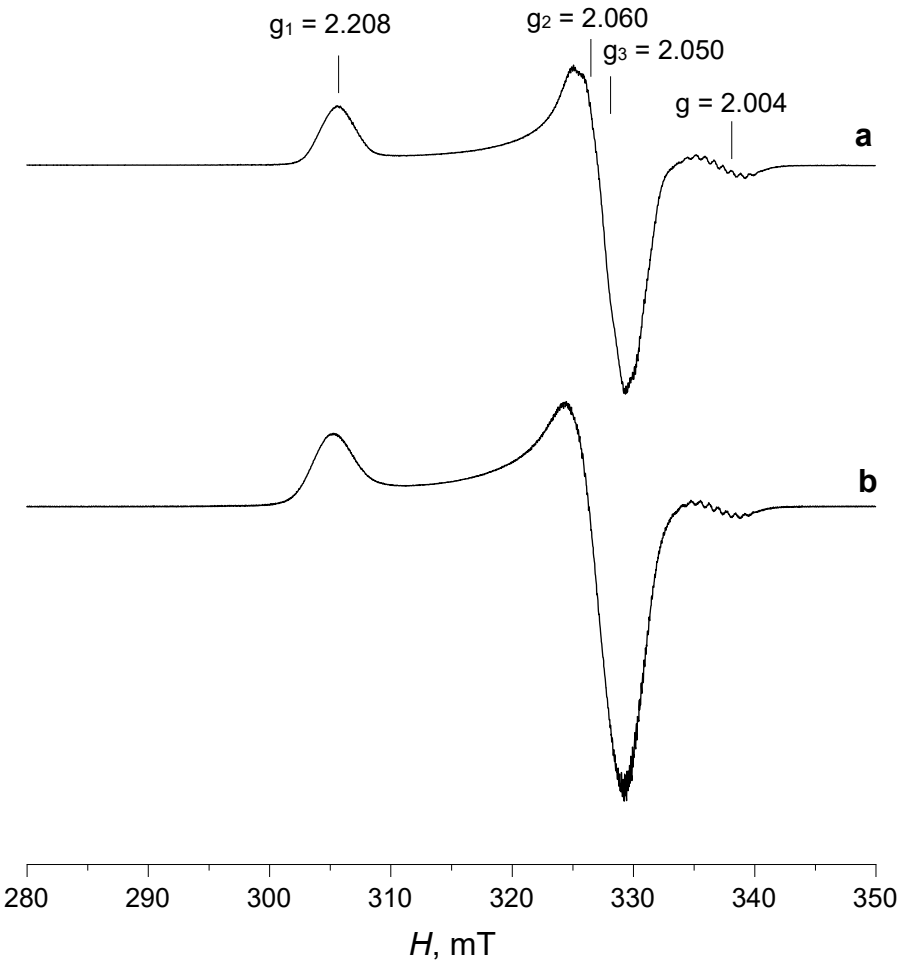


Figure S4. EPR spectra (toluene-d^8, −196 °C) of the samples:

a) **1**/$AlMe_3$ (Al/Ni = 10/1, C_{Ni} = 5 mM), mixed and stored during 1 h at 25 °C

b) sample in (a) ethylene bubbling (3×30s) at 25 °C

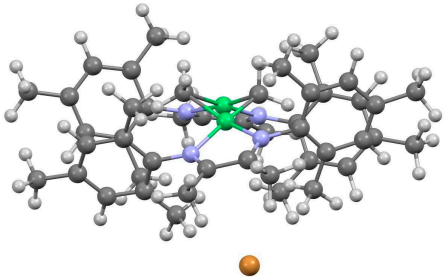
The resonances at g_1 = 2.208, g_2 = 2.060, and g_3 = 2.050 belong to the neutral heterobinuclear Ni(I) complex [$LNi^I(\mu\text{-}Me)_2AlMe_2$]. The multiplet at g = 2.004 corresponds to the radical $L^{(\bullet-)}AlMe_2$, formed via ligand transfer from Ni to Al.

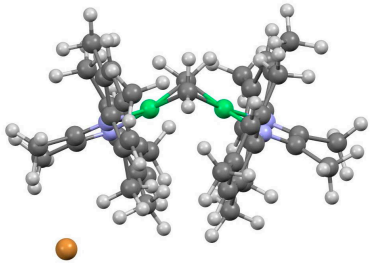
Table S1. The integral intensities of ^{1}H NMR resonances of 2 (toluene-d_8, recorded at 0 °C).

	Ar-H_o	Ar-C$H_{3\ p}$	Ar-C$H_{3\ o}$			CH_3-C=N		Ni-CH_3	Ni-CH_2	
δ, ppm	6.5-6.8	2.26	2.14, 2.21	1.83	1.82	0.98	1.14	−1.07	5.44	3.72
integral	4.00	5.98	5.84	5.90		3.13	2.96	1.51	1.02	1.05

DFT optimized Cartesian coordinates and potential energies (Ha) for the calculated structures

^{1}[LNi^{II}(μ-Me)(μ-CH$_2$)Ni^{II}L]$^{+}$Br^{-} in toluene (Ni green, N violet, Br orange, C grey)





Potential energy = -7600.3314761 Ha, Gibbs free energy = -7599.466929 Ha (0.0 kcal/mol)

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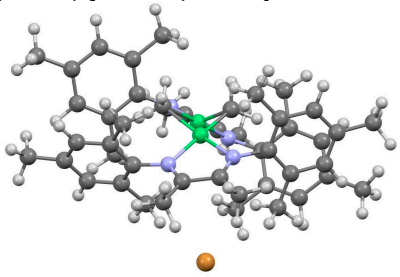
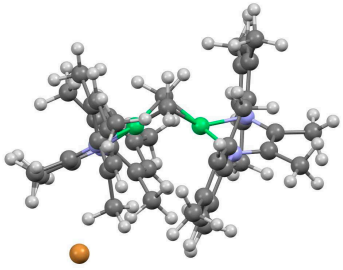
^{3}[LNi^{II}(μ-Me)(μ-CH$_2$)Ni^{II}L]$^{+}$Br^{-} in toluene (Ni green, N violet, Br orange, C grey)





Potential energy = -7600.3101345 Ha, Gibbs free energy = -7599.448161 Ha (+11.8 kcal/mol)

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