Trapping the Short-Chain Odd Carbon Number Olefins Using Nickel(II)-catalyzed Tandem Ethylene Oligomerization and Friedel-Crafts Alkylation of Toluene

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Abstract

Nickel(II) complexes with pyrazole-based ligands are widely employed in catalysis of ethylene oligomerization and subsequent Friedel-Crafts alkylation of toluene. We have prepared ten new nickel(II) dibromide complexes with various substituted bis(azolyl)methanes. They have been characterized using 1H NMR, IR, high resolution mass spectrometry and elemental analysis. The structures of three complexes have been unambiguously established using X-ray diffraction. It was found that these complexes in the presence of Et2AlCl or Et3Al2Cl3 are active both in ethylene oligomerization and Friedel-Crafts alkylation processes (activity up to 3720 kgoligomer·mol[Ni]-1*h-1). The use of Et3Al2Cl3 results in the higher share of alkylated products (up to 60%). Moreover, catalytic systems activated with Et3Al2Cl3 produced small amounts of odd carbon number olefins (up to 0.8%). The Friedel-Crafts alkylation was used as a trap for previously undetected short-chain odd carbon number olefins (C3 and C5).

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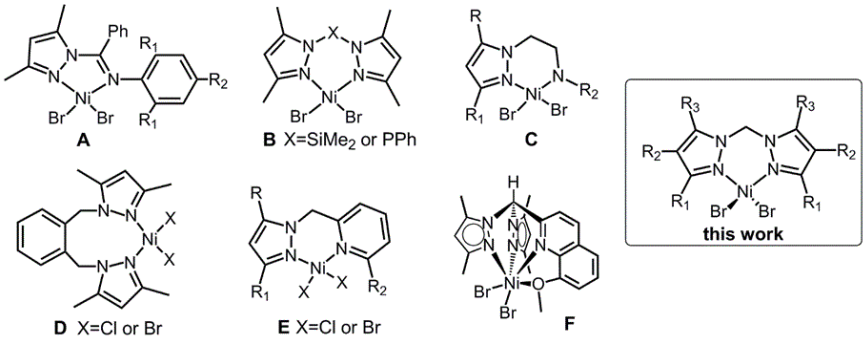
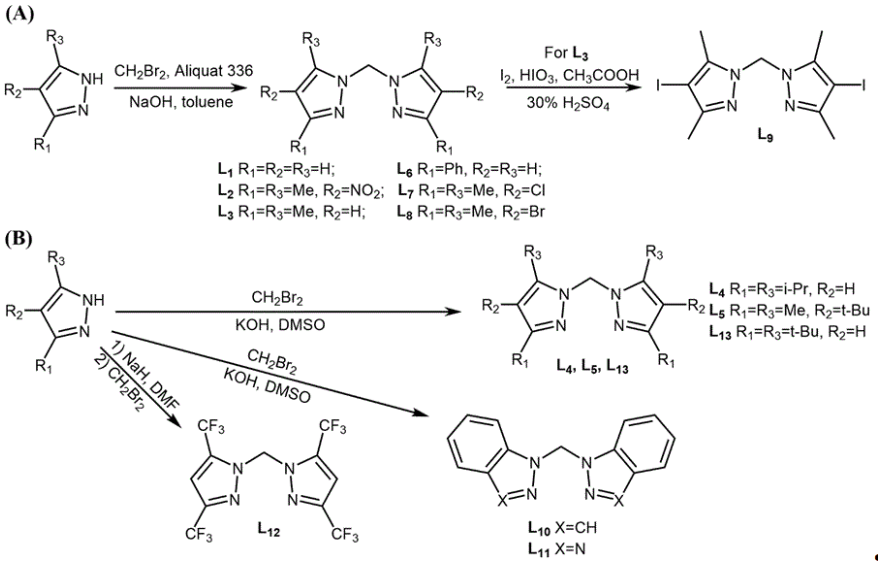
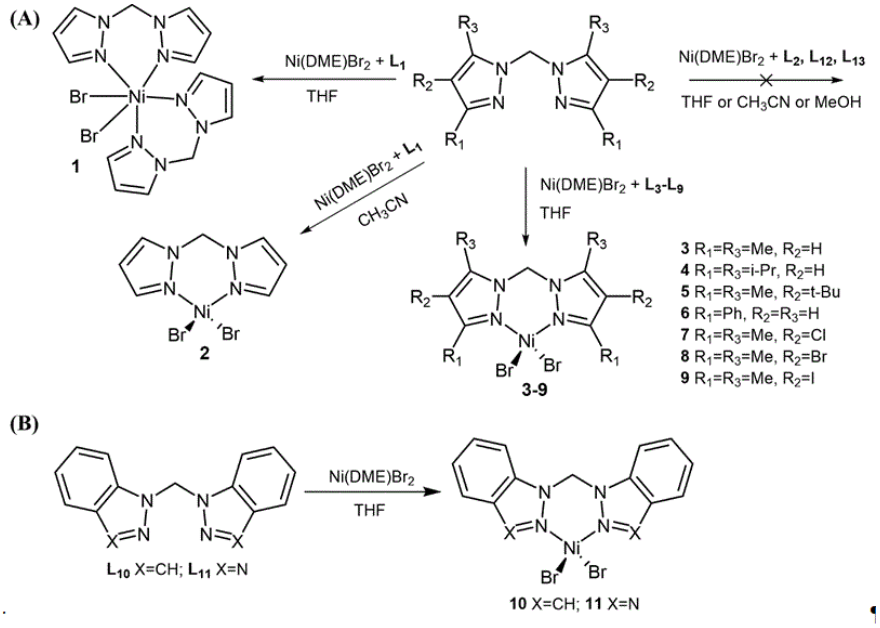


Figure 1. Structures of nickel(II) halide complexes with pyrazole containing ligands active in ethylene oligomerization.¶



Scheme 1. Synthesis of bis(azolyl)methane ligands L_1-L_{13}.¶



Scheme 2. Synthesis of nickel(II) complexes **1**-**11**.¶

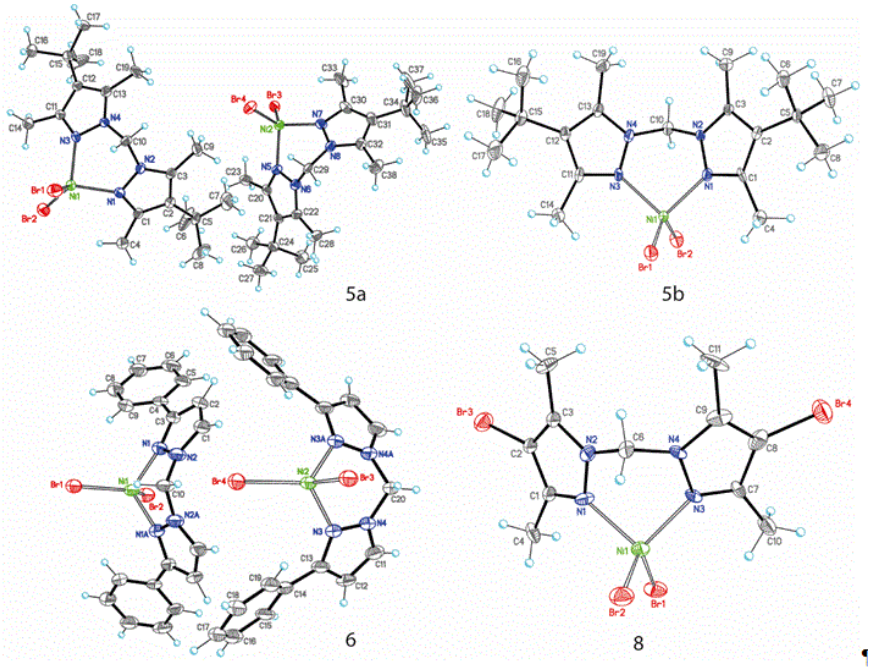


Figure 2. Molecular structures of complexes **5a**, **5b**, **6** and **8**. Thermal ellipsoids are shown at the 50% probability level.¶

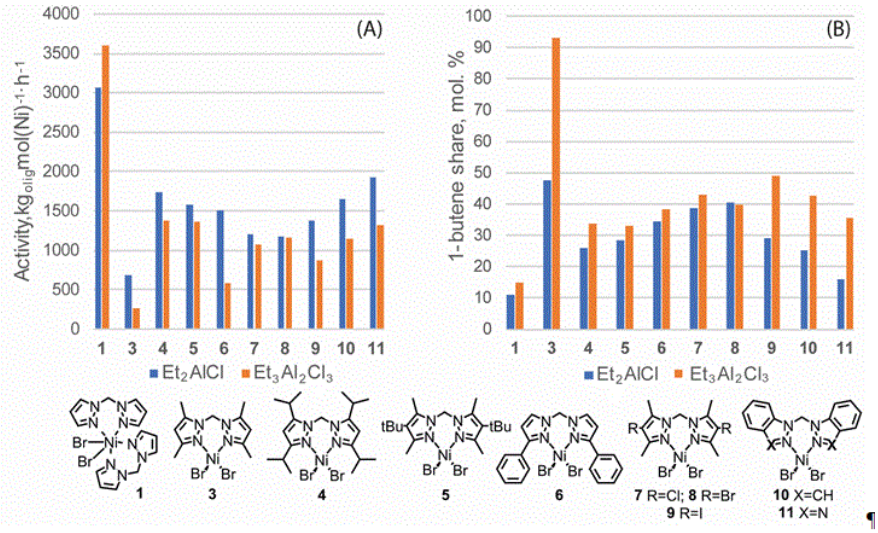


Figure 3. Dependencies of catalytic activity **(A)** and 1-butene share **(B)** on the composition of catalytic system.

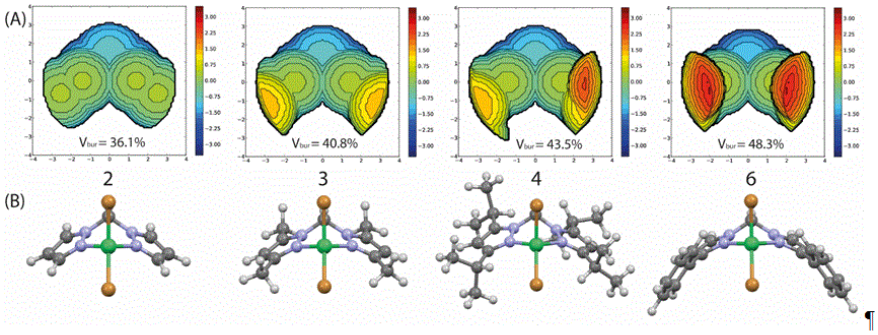


Figure 4. (A): Topographic steric maps of the nickel complexes **2**, **3**, **4** and **6**. Only bispyrazolylmethane ligands have been considered for calculations of %V$_{bur}$. Ni atom was placed as the center of the sphere and xz-plane was defined by Ni and 2 coordinated nitrogen atoms; the z-axis bisects N-Ni-N angle. **(B):** Structures of nickel complexes **2**, **3**, **4** and **6** optimized using DFT calculation and oriented the same way as topographic steric maps.

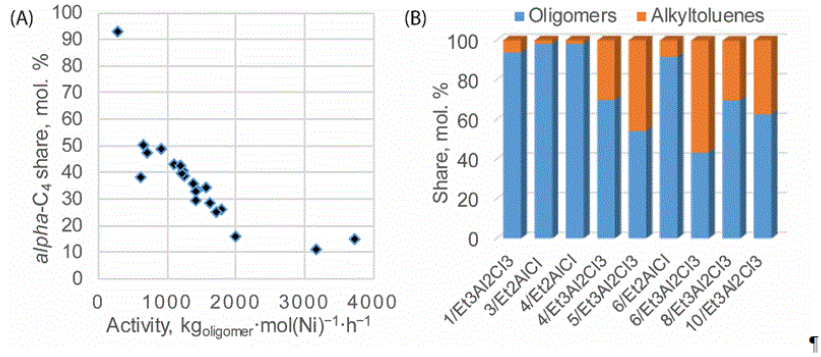
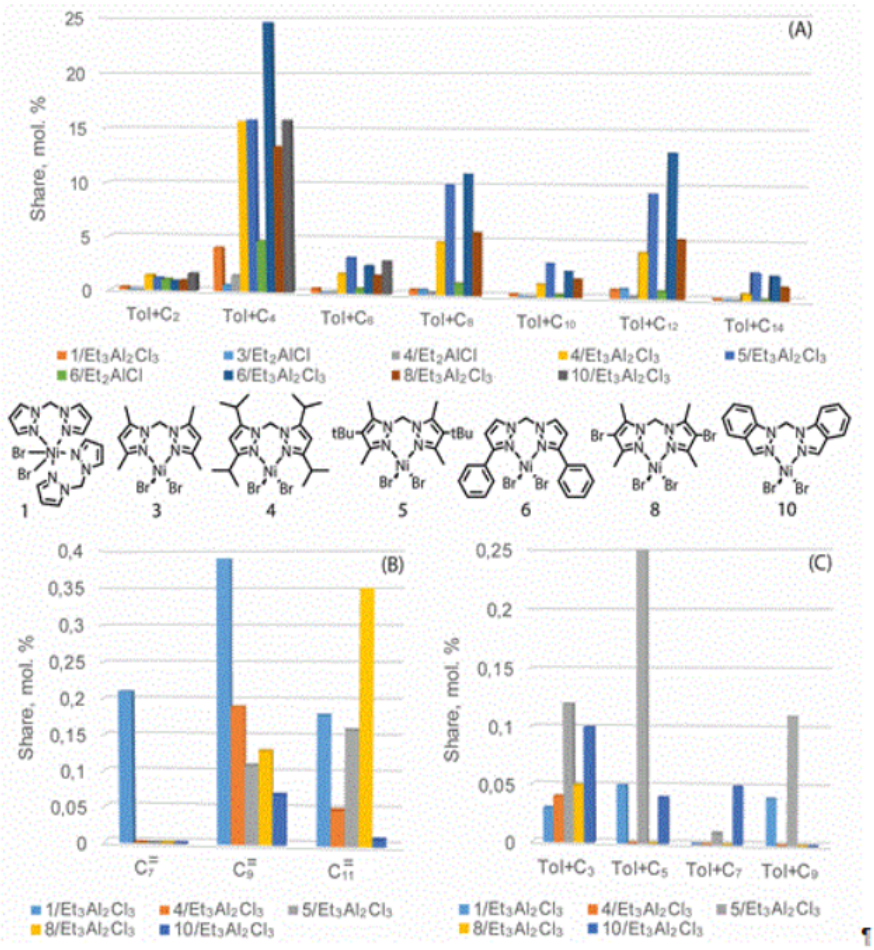


Figure 5. (A) Dependence of 1-butene share on catalytic activity; **(B)** shares of oligomers and alkyltoluenes for catalytic systems based on complexes **1**, **3**-**6**, **8**, **10** (determined using GC-MS).



Figure·6.·Shares·of·alkyltoluenes·**(A)**,·odd·carbon·number·olefins·**(B)**·and·toluene·alkylated·with·different·odd·carbon·number·olefins·**(C)**·in·the·reaction·mixtures·produced·with·catalytic·systems·based·on·complexes·**1,·3-6,·8,·10**·(determined·using·GC-MS).¶