

# Communications to the Editor

## Ethylene Polymerization by Novel, Easily Accessible Catalysts Based on Nickel(II) Diazene Complexes

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The vast economic importance of polyolefins is reflected by an annual production of more than 70 million tons of polyethylene and polypropylene. The major portion of these materials is produced by catalytic polymerization, employing Ziegler or Phillips catalysts based on early transition metals (Ti, Zr, Cr, V). Over the past decade, olefin polymerization by complexes of late transition metals has received increasing attention.<sup>1</sup> By comparison to early transition metal complexes, they are much less oxophilic and more tolerant toward polar reagents. In addition, polyolefins with novel microstructures are accessible. Neutral nickel(II) complexes with bidentate  $\kappa^2$ -P,O ligands [(P<sup>^</sup>O)Ni<sup>II</sup>R(L)] are the basis for the Shell higher olefin process (SHOP) for ethylene oligomerization to linear 1-olefins, developed in the 1960s.<sup>2</sup> By suitable variation of the ligands, linear polyethylene can also be obtained instead of low-molecular-weight oligomers.<sup>3</sup> In 1995, Brookhart reported on ethylene and 1-olefin polymerization by cationic Ni<sup>III</sup> or Pd<sup>II</sup> complexes with diimine ligands.<sup>4</sup> Ethylene homopolymers with various microstructures<sup>5</sup> can be obtained with high activities, and the cationic Pd<sup>II</sup> complexes can copolymerize ethylene and 1-olefins with simple polar-functionalized olefins such as acry-

lates.<sup>4</sup> Recently, neutral Ni<sup>II</sup> complexes have received renewed interest, as they are expected to be more functional group tolerant than their cationic Ni<sup>II</sup> counterparts.<sup>6,7</sup> For example, such neutral complexes can polymerize ethylene in aqueous emulsion, affording stable polymer latices.<sup>8</sup>

The quest for novel polymerization catalysts involves the search for new ligand structures with other donor functions. To date, this search is empirical to a large extent; albeit recent developments have provided somewhat more comprehensive guidelines for catalyst design. The known well-defined late transition metal systems for ethylene polymerization affording polymers of reasonably high molecular weight with good activities are based on a relatively limited number of donor functions, most prominently phosphine Ar<sub>2</sub>RP, imine R<sup>1</sup>R<sup>2</sup>C=NR<sup>3</sup>, pyridine, and alkoxide or phenolate RO<sup>-</sup> (R = alkyl, enyl, aryl) moieties. We now report on ethylene polymerization by neutral nickel(II) complexes of bidentate ligands comprising a diazene function -N=N- as a donor and the properties of the polymers obtained.

The ligands **1a–c** were prepared from anilines and 2-naphthol by azo coupling.<sup>9</sup> Isoamyl nitrite was employed as a reagent for generation of the diazene moiety. The intermediate diazonium salts were briefly isolated and reacted with 2-naphthol to afford **1a–c** in good yields. (For experimental details and analytical data cf. Supporting Information. **1c** is also commercially available as a dye.)

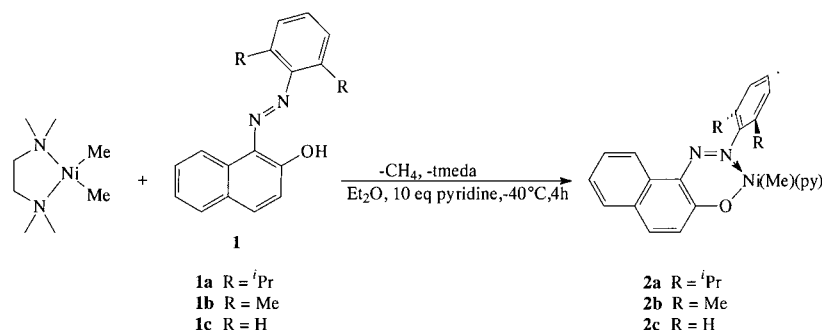
Nickel(II) complexes **2a–c** were obtained by reaction of the ligand with 1 equiv of [(tmeda)NiMe<sub>2</sub>]<sup>10</sup> in the presence of excess pyridine at low temperature (Scheme 1). The complexes were isolated as air-sensitive microcrystalline solids. In the <sup>1</sup>H NMR spectra of **2a–c**, the characteristic resonance of the Ni–Me group occurs at ca. -0.3 ppm. For complex **2a**, coordination of the diazene moiety to the nickel center results in inequivalence of the isopropyl substituents CH<sub>3</sub> groups, as evidenced by the observation of two doublets (cf. Supporting Information). To date, we have not obtained crystals suitable for an X-ray structure determination.

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Scheme 1

Table 1. Polymerization and Oligomerization of Ethylene by Complexes 2a–c<sup>a</sup>

entry no.	reaction conditions				product	results			
	catalyst precursor	reaction temp/°C	ethylene press./bar	reaction time/h		productivity/ (mol(ethylene) mol (Ni) <sup>-1</sup> )	av activity/ (mol (ethylene) mol (Ni) <sup>-1</sup> h <sup>-1</sup> )	<i>M<sub>w</sub></i> <sup>b</sup> (g mol <sup>-1</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>b</sup>
1	<b>2a</b>	50	50	2	PE	3180	1590	4.5 × 10 <sup>4</sup>	2.3
2	<b>2b</b>	50	50	1	oligomers	940	940		
3	<b>2b</b>	50	50	2	oligomers	1790	900		
4	<b>2b</b>	50	50	4	oligomers	2820	710		
5	<b>2b</b>	50	50	8	oligomers	2870	360		
6	<b>2c</b>	50	50	2	oligomers, <i>C<sub>max</sub></i> 10	2550	1280		
7	<b>2a</b>	25	5	2	PE	<10	<10		
8	<b>2a</b>	25	20	2	PE	360	180	2.3 × 10 <sup>4</sup>	1.8
9	<b>2a</b>	25	50	2	PE	840	420	4.6 × 10 <sup>4</sup>	2.3
10	<b>2a</b>	70	50	2	PE	5710	2860	5.2 × 10 <sup>4</sup>	1.9

<sup>a</sup> Conditions: 50 μmol of Ni<sup>II</sup>; total volume of toluene: 20 mL; PE = polyethylene. <sup>b</sup> Determined by GPC, referenced to linear polyethylene.

However, the spectroscopic properties of **2a–c** are in accordance with a square-planar structure with  $\kappa^1$ -N  $\sigma$ -bonding of the diazene moiety (Scheme 1), as in other comparable nickel(II) diazene complexes.<sup>11</sup>

All complexes **2a–c** are catalytically active toward ethylene (Table 1).<sup>12</sup> With **2a**, comprising a bulky substituted aryl group (R = <sup>i</sup>Pr) bound to the diazene function, polymeric materials are obtained. A reduction in steric bulk (complex **2b**, R = Me) results in a marked decrease in product molecular weight, as with known cationic diimine-substituted polymerization catalysts. The major portion of the products consists of oligomers detectable by gas chromatography (degree of oligomerization less than 13). For R = H (complex **2c**), olefins with a maximum degree of oligomerization of *n* = 5 are obtained. This different catalytic behavior depending on the ligand substitution pattern clearly demonstrates coordination of the diazene moiety to the metal center throughout the catalytic reaction.

Polymerization and oligomerization require somewhat elevated temperatures. For R = <sup>i</sup>Pr (**2a**) 70–80 °C represents the optimum (entry 10). At higher temperatures the initial activity increases further; however, catalyst deactivation is evidenced by formation of elemental nickel. The temperature stability appears to be increased by bulky substituents, the catalyst with the less sterically demanding R = H decomposing to a significant extent already at temperatures above 50 °C. As an indication of catalyst stability over time, experiments with different reaction times revealed a nearly constant rate of oligomerization over 4 h; at higher reaction times a significant drop in activity occurred (R = Me, 50 °C; entries 2–5). The polymerization rate is strongly dependent on ethylene concentration (entries 7–9; R = <sup>i</sup>Pr).

With several thousand turnovers per hour, observed activities of **2a–c** in ethylene polymerization and oli-

gomerization can be regarded as moderate. For related nickel(II) complexes with a chelating  $\kappa^2$ -N,O salicylaldiminato ligand, activities of up to 10<sup>5</sup> TO h<sup>-1</sup> have been reported upon tailoring of the substitution pattern, i.e., introduction of bulky groups in ortho position of the phenolate moiety and introduction of electron-withdrawing substituents in a remote position of the phenolate function. This can be taken as an indication that a variation of the structure of the diazene ligand beyond the basic examples investigated in this work may allow for significant increases in catalyst performance.

GPC analysis of the polyethylenes obtained employing complex **2a** with the bulky substituted diazene ligand reveals molecular weights of typically *M<sub>w</sub>* = 5 × 10<sup>4</sup> g mol<sup>-1</sup>. The relatively narrow molecular weight distributions of 1.8–2.3 are indicative of a well-behaved single site catalyst. High-temperature <sup>13</sup>C NMR shows that the polymers are moderately branched (cf. Supporting Information).<sup>13</sup> Methyl branches predominate, with ca. 10 Me branches per 1000 carbon atoms. Additional weak signals suggest that higher branches are also present in smaller amounts. This polymer microstructure is similar to that obtained with nickel(II) salicylaldiminato complexes 6a–c. Polymer crystallinity amounts to ca. 45%, as determined by DSC. The melt peak, determined by DSC, occurs at ca. 115–120 °C. Gas chromatographic analysis of the low-molecular-weight products obtained employing complexes **2c** (R = H) and **2b** (R = Me) show that linearity and 1-olefin content decrease with increasing reaction temperature, as expected.

In summary, neutral nickel(II) complexes with chelating diazene ligands represent a novel class of ethylene polymerization catalysts. Well-defined complexes are available as precursors to activator-free catalysts. High-molecular-weight, moderately branched polymers are accessible at reasonable rates employing bulky substituted ligands. The versatility of the ligand synthesis,

which can employ a large variety of commercially available anilines and also substituted naphthols and phenols, makes this catalyst system amenable to a considerable range of structural variations.

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**Supporting Information Available:** Synthesis and analytical data for ligands and metal complexes, details of the polymerization procedure, and a  $^{13}\text{C}$  NMR spectrum of a polyethylene prepared. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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