Preparation of Linear α-Olefins Using Cationic Nickel(II) α-Diimine Catalysts

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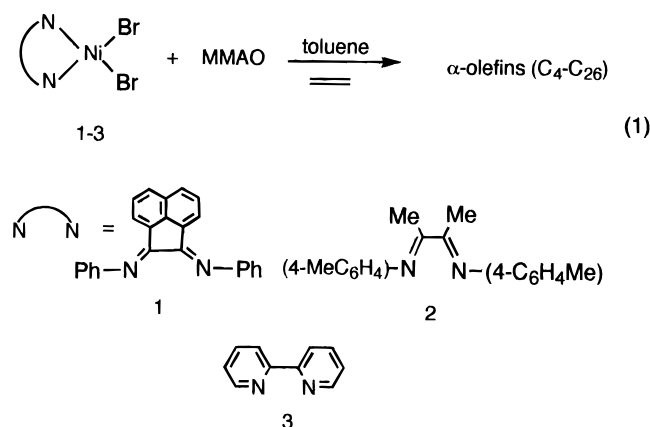*Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290*

Summary: Nickel(II) dibromide complexes containing para- and unsubstituted aryl α-diimine ligands in combination with modified methylaluminoxane (MMAO) are highly active and efficient catalysts for the oligomerization of ethylene to linear α-olefins. α-Olefins in the C_4–C_{26} range have been prepared with selectivities as high as 94%. The Schulz–Flory product distributions and selectivities for α-olefins are a sensitive function of catalyst structure and reaction conditions. Details of this catalyst system are described, including the synthesis of initiators, catalyst activities, and α-olefin product distributions.

The transition-metal-catalyzed oligomerization of ethylene provides α-olefins in the C_6–C_{20} range.[1] These olefins are feedstocks for the preparation of detergents, plasticizers, and many fine chemicals, as well as co-monomers for the synthesis of linear low density polyethylene (LLDPE). The pioneering work of Keim in the development of soluble Ni(II)-based catalysts for the oligomerization of ethylene is the basis for the commercially practiced Shell Higher Olefin Process (SHOP).[2,3] These soluble *neutral* Ni(II) catalysts contain bidentate phosphorus/oxygen chelate ligands and show exceptionally high selectivity for linear α-olefins (98%).[3] Keim and others have demonstrated the influence of catalyst structure on catalyst activity and selectivity.[4] Notably, Murray has reported new organophosphorus–sulfonate nickel catalysts for the oligomerization of ethylene that show increased activity relative the classical SHOP systems.[4e–g]

We have recently described the development of a new class of cationic Ni(II) and Pd(II) complexes of bulky aryl-substituted α-diimines that catalyze the polymerization of ethylene and α-olefins.[5] The catalytic cycle is shown in Scheme 1. The fact that these complexes produce high molecular weight polymer is a consequence of slow chain transfer relative to chain propagation. In these d[8] square planar systems, chain transfer is proposed to occur by *associative* olefin displacement (Scheme 1) and is hindered by the axial bulk provided by the *ortho*-substituents of the aryl rings. We reasoned that by eliminating the steric bulk of the *ortho*-substituents, rates of associative chain transfer should be substantially increased, resulting in oligomerization rather than polymerization reactions. This has proved to be the case, and we report here new highly active cationic Ni(II) catalysts based on unhindered α-diimine ligands for the oligomerization of ethylene.

The catalyst systems described in eq 1 were examined for ethylene oligomerization. Catalysts **1** and **2** are

$$\text{(complex 1-3)} + \text{MMAO} \xrightarrow[\equiv]{\text{toluene}} \alpha\text{-olefins (C}_4\text{-C}_{26})$$

(1)

based on aryl-substituted α-diimines that lack *ortho*-aryl substituents, and catalyst **3** contains the unsubstituted 2,2′-bipyridine ligand.

The complexes were synthesized by the reaction of (dimethoxyethane)NiBr$_2$ with the bidentate nitrogen ligands[6] in CH$_2$Cl$_2$ at 25 °C (see Supporting Information). A typical ethylene oligomerization involves the addition of modified MAO[7] (MMAO, 100 equiv) to a rapidly stirred suspension of the nickel dibromide precursor (*ca.* 0.022 mmol) in 200 mL of toluene in a

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(2) (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978,** *17,* 466. (b) Keim, W.; Hoffmann, B.; Lodewick, R.; Peuckert, M.; Schmitt, G. *J. Mol. Catal.* **1979,** *6,* 79–97.

(3) Keim, W. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 235–244.

(4) (a) Keim, W.; Schulz, R. P. *J. Mol. Catal.* **1994,** *92,* 21–33. (b) Kissin, Y. V. *J. Polym. Sci., Polym. Chem. Ed.* **1989,** *27,* 147–155. (c) Cavell, K. J.; Masters, A. F. *J. Aust. J. Chem.* **1986,** *39,* 1129–1134. (d) Brown, S. J.; Masters, A. F. *J. Organomet. Chem.* **1989,** *367,* 371–374. (e) Murray, R. E. U.S. Patent 4 689 437, 1987. (f) Murray, R. E. U.S. Patent 4 716 138, 1987. (g) Murray, R. E.; Wenzel, T. M. Novel Preparation and Conversion of Light Olefins. *Abstracts of Papers,* National Meeting of the American Chemical Society, Miami, FL, 1989; American Chemical Society: Washington, DC, 1989. (h) Comparison of cationic and neutral Ni(II) catalysts for ethylene oligomerization has been described, see: Bonnet, M. C.; Francoise, D.; Ecke, A.; Keim, W.; Schulz, R. P.; Tkatchenko, I. *J. Chem. Soc., Chem. Commun.* **1994,** 615.

(5) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995,** *117,* 6414–6415.

(6) For extensive studies of the chemistry of d[8] α-diimine complexes, see: (a) van Asselt, R.; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994,** *13,* 706–720. (b) van Asselt, R.; Gielens, E. E. C. G.; Rülke, R. E.; Vrieze, K.; Elsevier, C. J. *J. Am. Chem. Soc.* **1994,** *116,* 977–985. (c) van Asselt, R. Ph.D. Thesis, Universiteit van Amsterdam, Amsterdam, The Netherlands, 1993. (d) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; Benedix, R. *Recl. Trav. Chim. Pays-Bas* **1994,** *113,* 88–98.

(7) MMAO is a modified methylaluminoxane activator containing 25% isobutyl aluminoxane. MMAO has the advantage of an improved shelf life, while no difference in reactivity with respect to MAO is observed for these oligomerizations.

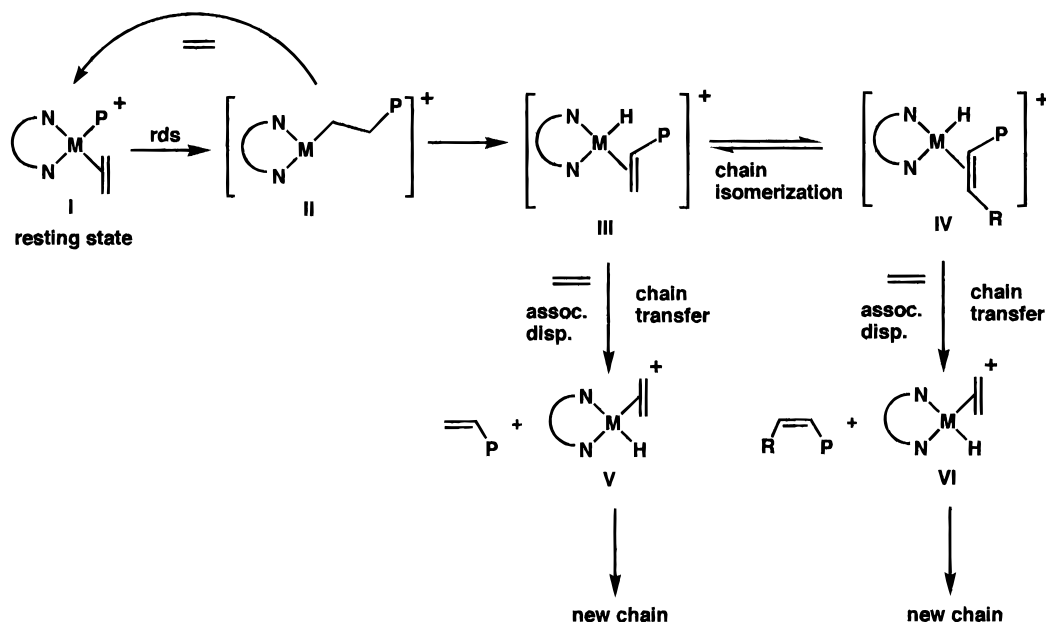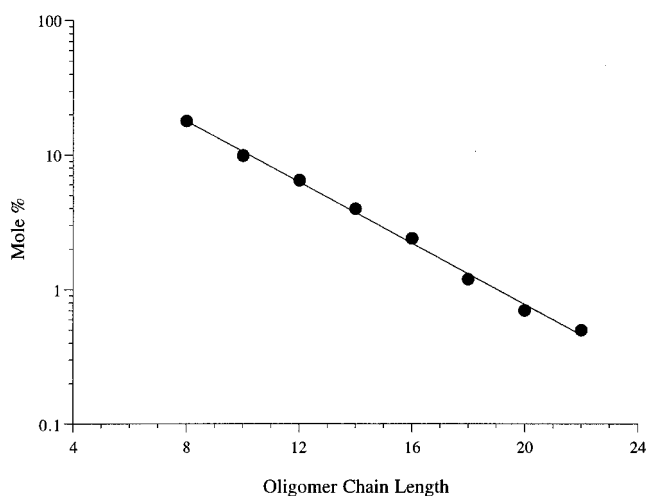**Scheme 1. Mechanism for Olefin Polymerization/Oligomerization**

Table 1. Ethylene Oligomerization in Toluene (200 mL)

entry no.	catalyst[a]	reaction conditions			TOF ($\times10^{-3}$/h)	% α-olefin[b]	α	β
		ethylene pressure (atm)	temp (°C)	time (min)				
1	**1**/MMAO	56	35	60	57	94	0.71	0.41
2	**1**/MMAO	56	35	120	53	94	0.69	0.45
3	**1**/MMAO	56	35	180	59	92	0.66	0.51
4	**1**/MMAO	56	55	60	74	94	0.66	0.51
5	**1**/MMAO	56	55	60	81	90	0.65	0.54
6	**1**/MMAO	56	75	60	94	90	0.62	0.61
7	**1**/MMAO	56	75	60	92	87	0.58	0.72
8	**1**/MMAO	28	35	60	60	90	0.64	0.56
9	**1**/MMAO	15	35	60	62	85	0.65	0.54
10	**2**/MMAO	56	55	60	87	85	0.59	0.69
11	**2**/MMAO	56	75	60	110	80	0.52	0.92
12	**3**/MMAO	56	35	60	73	64	0.58	0.72
13	**3**/MMAO	56	55	60	63	55	0.57	0.75
14	**3**/MMAO	56	75	60	43	49	0.45	1.2

[a] Entries 1−9, 2.2×10^{-5} mol Ni complex; entry 10, 2.9×10^{-5} mol Ni complex; entries 11−14, 2.1×10^{-5} mol Ni complex activated with 100 equiv of MMAO. [b] Percent α-olefin determined by ^{1}H NMR spectroscopy.

1000 mL stirred Parr high-pressure autoclave. The results of the oligomerization reactions are summarized in Table 1. These cationic nickel catalysts exhibit very high activities. For example, **1** + MMAO at 75 °C exhibits an apparent turnover (TO) frequency of 9.4×10^4 TO/h. In addition, the rate of oligomerization is independent of ethylene concentration at these pressures (compare entries 1, 8, and 9; Table 1). Comparison with neutral SHOP catalysts employing phosphine−carboxylate bidentate ligands suggests these cationic systems are *ca.* 15 times more active.[1b,3] Furthermore, no detectable loss of catalyst activity occurs over periods up to 3 h, indicating long catalyst lifetimes under these conditions (Table 1, entries 1−3).

The mechanism of oligomerization is assumed to be that shown in Scheme 1, where chain transfer is now competitive with chain propagation. A Schulz−Flory chain length distribution[8] of olefin oligomers (GC analysis) was observed in all catalytic runs. For example, a plot of the oligomer chain length versus the ln(mol % oligomer) in the product mixture shows the expected

(8) (a) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561−1565. (b) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1935**, *30*, 379−398. (c) Schulz, G. V. *Z. Phys. Chem., Abt. B* **1939**, *43*, 25−46.

Figure 1. Schulz−Flory distribution of α-olefins. Ethylene oligomerization (Table 1, entry 5) at 55 °C and 56 atm.

linear decrease in ln(mol % oligomer) with increasing chain length (Figure 1).[1b] A Schulz−Flory distribution can be described by α, where α represents the probability of chain propagation:
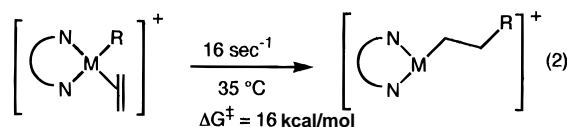
$$\alpha = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} = \frac{\text{moles of } C_{n+2}}{\text{moles of } C_n}$$

The probability of chain propagation (α) is then related to the ratio of the rate of chain transfer and chain propagation by the following expression:

$$\alpha = \frac{1}{1 + \beta} \text{ where } \beta = \frac{\text{rate of chain transfer}}{\text{rate of propagation}}$$

The α values for these systems are summarized in Table 1 and range from 0.71 for catalyst **1** at 35 °C and 56 atm of ethylene to 0.45 for catalyst **3** at 75 °C and 56 atm of ethylene. (For an α value of 0.7, the weight fraction is at a maximum at C_6; for an α value of 0.5, the maximum is at C_4.) The turnover frequency was shown to be independent of ethylene pressure and, thus, indicates that the alkyl olefin species is the catalyst resting state, with propagation rates controlled by the rate of the migratory insertion reaction.[5] Assuming that all of the nickel halide precursor **1** is converted to active catalyst, the rate of migratory insertion of the olefin alkyl species is *ca.* 16 s^{-1} at 35 °C, $\Delta G^{\ddagger} = 16$ kcal/mol (eq 2).

The data presented illustrates several trends regarding α-olefin chain length distribution and selectivity. First, the relative rate of chain propagation versus chain transfer, as reflected in α, is sensitive to both catalyst structure and reaction conditions. In general, as the reaction temperature increases, the relative rate of chain transfer increases with respect to the rate of chain propagation. For example, the value of α changes from 0.7 to 0.6 when the reaction temperature is increased from 35 to 75 °C using **1/MMAO**. In addition, selectivity for α-olefins is dependent on ethylene concentration, as illustrated by a 10% loss in selectivity with reduction in ethylene pressure from 56 to 15 atm (Table 1, entry 1 vs 9). The influence of ethylene concentration on α-olefin selectivity is believed to be due to a competition between chain transfer from the proposed α-olefin hydride intermediate **III** (Scheme 1) and chain isomerization (β-hydride elimination reinsertion), followed by chain transfer from the internal olefin hydride species

IV.[5] Higher ethylene concentration thus favors the formation of α-olefin products due to rapid chain transfer from species **III**, as opposed to chain isomerization. Finally, catalyst structure has a substantial effect on α-olefin selectivity and chain length distribution (compare entries 1−9 with 10−14). In the case of the bipyridine catalyst, α values as low as 0.45 have been seen with low selectivity for linear α-olefins in the range of 50−65%. This is in direct contrast to the high α-olefin selectivity observed for catalysts **1** and **2**. A control experiment was run in which 1-nonene was added to an oligomerization reaction to determine if the bipyridine catalyst exhibited a lower selectivity for α-olefin production as a result of partial isomerization of the α-olefin products during the course of the oligomerization. The oligomer mixture that resulted showed no detectable (GC analysis) isomerization of C_9 linear α-olefin, indicating rapid isomerization of the α-olefin products was not occurring to an appreciable extent during the oligomerization. Thus, the poor selectivity in the bipyridine system is likely due to an increased occurrence of chain transfer from an internal olefin hydride nickel complex relative to chain transfer from an α-olefin hydride species.

In summary, the α-diimine nickel complexes described here represent a new class of highly active Ni-(II) catalysts for the preparation of α-olefins ranging from C_4–C_{26}, with selectivity for linear α-olefins as high as 94%. In addition, variation in catalyst structure and reaction conditions has a significant influence on α-olefin selectivity and chain length distribution. Finally, the increased rate of chain transfer relative to propagation observed for these oligomerization catalysts relative to the previously described polymerization analogs[5] supports the premise that the control of the associative olefin exchange through variation in axial sterics represents a general methodology for the design of other late metal catalysts for olefin oligomerization or polymerization.

Supporting Information Available: Text giving details of catalyst and oligomer synthesis and ^{1}H NMR spectra and GC traces of the oligomers (10 pages). Ordering information is given on any current masthead page.

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