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Homogeneous Catalysis

Nickel α-Keto-β-Diimine Initiators for Olefin Polymerization**

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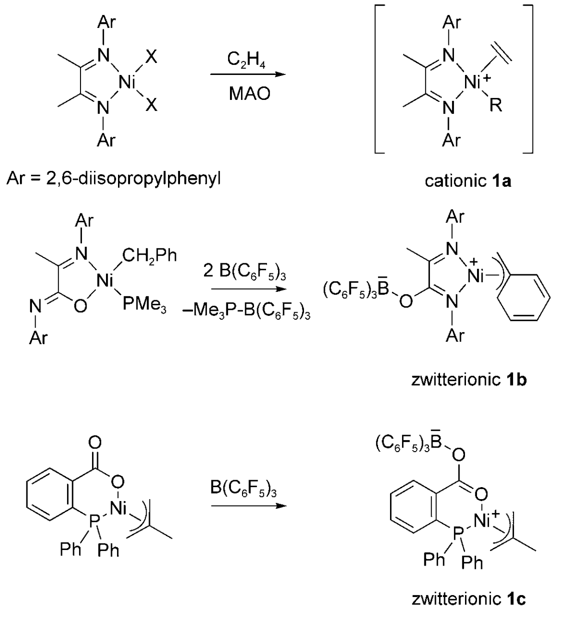
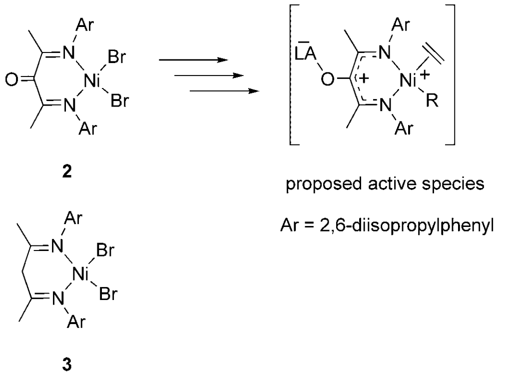
Late transition metal initiators for olefin polymerization and oligomerization are of interest owing to their low oxophilicity and high functional group tolerance.[1] Nickel- and palladium-based initiators provide several benefits. These include control over molecular weight characterisitics,[2] backbone stereochemistry,[3] and comonomer incorporation.[1,4] "Chain walking" reactions, in which the metal center migrates along the growing polymer chain through a series of β-hydride eliminations and reinsertions, allow for the generation of a wide variety of novel materials.[5] New ligand structures continue to appear and offer further optimization of reactivity and polymer properties.[1d,e,4b,5c,6]



Scheme 1. Examples of cationic and zwitterionic polymerization/oligomerization active sites. R = alkyl.

Scheme 1 shows representative cationic and zwitterionic nickel active sites. Example **1a** (charge compensating anion is not shown) corresponds to the broadly studied class of α-diimine complexes, for which the resting state is a cationic alkyl olefin species.[7] These species can be generated from a dihalide precursor in the presence of olefin and an appropriate activator, such as methylaluminoxane (MAO).[7] Also shown are two prototypical zwitterionic initiators (**1b** and **1c**; important resonance contributions are not shown).[8] A relevant perspective for understanding the reactivity of zwitterionic species is that Lewis acid complexation onto a basic ligand site reduces the electron density of the metal center in a neutral complex.[4c,8,9] This concept is more easily appreciated by examination of **1c**. Bulky substituents that occupy axial sites are important structural components for minimizing chain-growth termination in both cationic and zwitterionic systems: for example, **1b** produces high-molecular-weight polyethylene (PE), whereas **1c** yields a distribution of 1-alkenes.[8]

Herein, we report on the synthesis, characterization, and reactivity of a ligand–metal combination that was designed to be cationic and also to benefit from removal of electron density from the metal center by the action of a Lewis acid on the ligand framework. We targeted a nickel complex containing a bulky α-keto-β-diimine ligand with 2,6-diisopropylphenyl substituents (**2**, Scheme 2). The exocyclic carbonyl functionality was anticipated to provide an electronically delocalized conduit extending from the potentially cationic metal center to a site of Lewis acid interaction through the oxygen lone pairs. The previously reported β-diimine complex



Scheme 2. Complexes **2** and **3** and the proposed active species derived from activation of **2**. LA = Lewis acid, R = alkyl.

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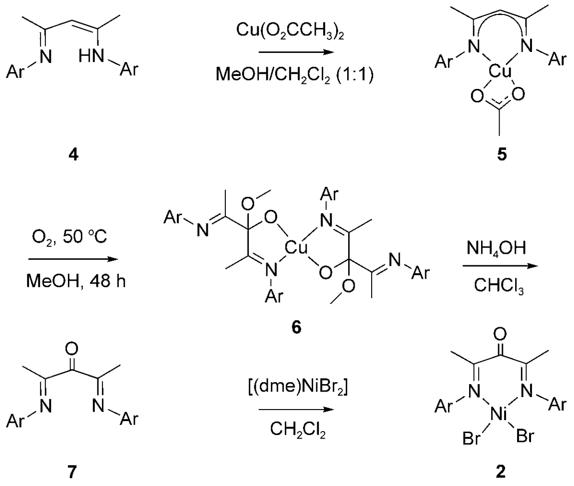
3[10] (Scheme 2) is a close structural analogue of **2**, differing only with respect to the presence of the carbonyl group at the α-site, and will be used for comparative purposes. Complex **3** is a precursor for ethylene polymerization that differs from the analogous α-diimine counterpart **1a** in two significant ways: lower activities are observed, and the PE produced is more crystalline upon activation with modified methylaluminoxane (MMAO).[10,11]

Scheme 3 shows the synthesis of **2**. The preparation of the ligand, 2,4-bis(2,6-diisopropylphenylimino)pentan-3-one, proceeds in good overall yield starting from 4-(2,6-diisopropylphenyl)iminopent-2-en-2-(2,6-diisopropylaniline)amine **4**.[10,12] Addition of **4** to a stirring solution of $Cu(O_2CCH_3)_2$ in CH_3OH/CH_2Cl_2 (1:1) at room temperature led to the formation of **5** in 88 % yield. X-ray crystallographic studies (see the Supporting Information) confirmed that **5** is a mononuclear complex with a distorted square-planar geometry around the copper center. Treatment of **5** with oxygen in methanol led to the nearly quantitative formation of complex **6**, in which copper exhibits N,N′,O,O′ coordination within a square-planar environment (see the Supporting Information). Treatment of **6** with aqueous ammonia gave 2,4-bis(2,6-diisopropylphenylimino)-pentan-3-one **7** in nearly quantitative yield.



Scheme 3. Synthesis of **2**. dme = 1,2-dimethoxyethane.

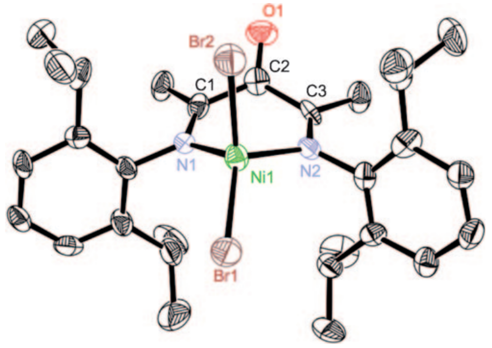


Figure 1. ORTEP drawing of **2**. Thermal ellipsoids are set at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Compound **2** is obtained in 49 % yield by the addition of **7** to a stirring suspension of $[(dme)NiBr_2]$ in CH_2Cl_2 at room temperature (Scheme 3). Single crystals suitable for X-ray crystallographic examination were obtained from a concentrated CH_2Cl_2 solution at −35 °C. The molecular connectivity (Figure 1) is consistent with a neutral N,N-bound 2,4-bis(2,6-diisopropylphenylimino)pentan-3-one ligand. Bond lengths within the six-membered chelate ring are consistent with the proposed structure (C3–N2: 1.292(10), C2–C3: 1.518(12), C1–N1: 1.287(11), C1–C2: 1.511(12), and C2–O1: 1.223(10) Å).[13] The Ni atom displays a pseudo-tetrahedral coordination geometry , and the chelate ring adopts a boat-like conformation similar to that observed in **3**.[10] Bond lengths for **2** and **3** are in close agreement; the main structural difference stems from the presence of the exocyclic carbonyl functionality on C2 in **2**.

A series of ethylene polymerizations were carried out using **2** under various reaction conditions and in the presence of different activators (Table 1). Polymerizations were initiated by the introduction of a stock solution of **2** into a stirring solution of activator in a specified volume of toluene in the presence of ethylene. In all cases, the formation of high-molecular-weight polyethylene (PE) is observed. Table 1, entry 1 illustrates that $AlMe_3$ can be used as an activator to

Table 1: Selected ethylene polymerization reactions.

Entry[a]	Conditions[b]	TOF × 10^{-3} [h^{-1}]	$M_n \times 10^{-3}$ [c]	PDI	Branches[d]	T_m[e] [°C]
1/5	250 $AlMe_3$, 32 °C, 300 psig, 10 min	64	956	1.7	28	$T_{m1} = 95$ $T_{m2} = 110$
2/5	250 MAO, 10 °C, 300 psig, 10 min	9.6	260	1.1	19	117
3/5	250 MAO, 32 °C, 100 psig, 10 min	62	1112	1.3	47	$T_{m1} = 72$ $T_{m2} = 114$
4/2.5	250 MAO, 32 °C, 300 psig, 10 min	125	1121	1.4	30	$T_{m1} = 88$ $T_{m2} = 114$
5/2.5	250 MAO, 32 °C, 500 psig, 10 min	125	1190	1.3	25	116
6/2.5	250 MAO, 32 °C, 800 psig, 10 min	127	1306	1.8	23	117
7/10	500 MMAO, 32 °C, 300 psig, 30 min	207	1188	5.7[f]	32	90
8/5	500 MMAO, 50 °C, 450 psig, 10 min	813	625	2.2	45	85
9/5	500 MMAO, 75 °C, 300 psig, 30 min	157	183	2.6	53	73

[a] Entry/μmol **2**. [b] Entries 1–6 were carried out in a 300 mL autoclave reactor in 100 mL toluene, entries 7–9 were carried out in a 2000 mL autoclave reactor in 1000 mL toluene. [c] M_n [g mol^{-1}] determined by gel permeation chromatography (GPC) versus polystyrene standards. [d] Number of branches per 1000 carbon atoms determined by ^{13}C NMR spectroscopy. [e] Determined by DSC. [f] The broad PDI may be due to the rapid formation of high molecular weight PE and long reaction time.

obtain ethylene polymerization with activities on the order of 1800 kg PE (mol Ni)$^{-1}$ h^{-1} at 32 °C and 300 psig ethylene pressure ($P_{C_2H_4}$). MAO can also serve as an activator (Table 1, entries 2–6). Table 1, entry 2 shows a PE with low polydispersity (PDI = 1.1) when the reaction is carried out at 10 °C. Comparison of Table 1, entries 2 and 4 shows an increase in polymerization activity from 269 to 3500 kg PE (mol Ni)$^{-1}$ h^{-1} upon increasing the temperature from 10 to 32 °C. There is no substantial increase in activity when $P_{C_2H_4}$ is increased from 300 to 800 psig, consistent with rate-limiting migratory insertion (Table 1, entries 4–6).[14] The results of ^{13}C NMR spectroscopy (see the Supporting Information) indicate that the branching length and frequency increase at lower pressures and at elevated temperatures, as in the case of α-diimine-based nickel initiators.[7] Differential scanning calorimetry (DSC) analysis shows that the polymer products display a range of melting temperatures; those with more linear backbones display higher melting transitions.

Table 1 also contains the results obtained using MMAO.[11] This activator was found to yield higher activities, thus larger reactors were used for the polymerizations in Table 1, entries 7–9. A larger excess of MMAO was also used (500 equivalents) to serve as a scrubbing agent. At 32 °C with $P_{C_2H_4}$ = 300 psig, an activity of 5800 kg PE (mol Ni)$^{-1}$ h^{-1} is observed (Table 1, entry 7). The fact that ethylene consumption does not decrease over the course of the reaction, as measured by an ethylene flow rate meter, demonstrates that the catalytic species is long-lived under these conditions. Increasing the reaction temperature to 50 °C and $P_{C_2H_4}$ to 450 psig leads to an activity of 22 800 kg PE (mol Ni)$^{-1}$ h^{-1}, that is, an apparent turnover frequency (TOF) of 8.1×10^5 h^{-1} (Table 1, entry 8). Activities of this magnitude are comparable to the α-diimines,[7] salicylaldimines,[1c] and "classical" metallocenes.[15] Table 1, entry 9 illustrates that the catalytic species is stable over the course of 30 min at 75 °C; however, the high viscosity of the reaction medium under these conditions may lead to an underestimation of the polymerization rate.

It is informative at this point to compare the ethylene polymerization activities obtained with **2** and **3**. Complex **3** in the presence of MMAO leads to an activity of approximately 14.5 kg PE (mol Ni)$^{-1}$ h^{-1} (30 °C and 280 psig), an apparent TOF of 514 h^{-1}.[10] Under the conditions in Table 1, entry 7 but using complex **3** (i.e. **3**/MMAO, 32 °C, 300 psig, 30 min), we obtained an activity of approximately 8 kg PE (mol Ni)$^{-1}$ h^{-1}. The higher activity attained with **2**/MMAO (5800 kg PE (mol Ni)$^{-1}$ h^{-1}, corresponding to an apparent TOF of 2.07×10^5 h^{-1}), illustrates that complex **2** is a precursor to a significantly more active catalyst.

Propene and 1-hexene can also be polymerized using **2** to yield high-molecular-weight polymers (Table 2). Using **2**/MAO at a propene pressure of 150 psig and 35 °C leads to an activity of 98 kg polymer (mol Ni)$^{-1}$ h^{-1}, that is, an apparent TOF of 2330 h^{-1} (Table 2, entry 3). Table 2, entries 1–3 show an increase in activity with increasing reaction temperature similar to the trend observed with ethylene. Table 2, entry 5 illustrates that 1-hexene can be polymerized at 25 °C to high-molecular-weight product with an activity of 31 kg polymer (mol Ni)$^{-1}$ h^{-1}. The polymerization of propene (Table 2, entry 1) and 1-hexene (Table 2, entry 4) at 0 °C leads to polymers with narrow molecular weight distributions (PDI = 1.1 and 1.2 respectively). Microstructural analysis (see the Supporting Information) by ^{13}C NMR spectroscopy revealed that the polypropylene and poly-1-hexene products are atactic; signatures arising from 2,1-insertions were not detected.[16]

Table 2: Propene and 1-hexene polymerization reactions.

Entry[a]	Conditions[b]	TOF [h^{-1}]	$M_n \times 10^{-3}$ [c]	PDI	T_g[d] [°C]
1/30	250 MAO, 0 °C, 5 mL propene, 60 min	14	138	1.1	−23
2/30	250 MAO, 25 °C, 150 psig propene, 30 min	1780	316	1.5	−25
3/5	250 MAO, 35 °C, 150 psig propene, 30 min	2330	191	2.1	−32
4/10	250 MAO, 0 °C, 10 mL 1-hexene, 60 min	89	157	1.2	−55
5/10	250 MAO, 25 °C, 10 mL 1-hexene, 60 min	356	120	2.0	−56

[a] Entry/μmol **2**. [b] Entries 1–3 carried out in a 300 mL autoclave reactor in 100 mL toluene; entries 4 and 5 carried out in a Schlenk flask in 10 mL toluene. [c] M_n [g mol^{-1}] determined by GPC versus polystyrene standards. [d] Determined by DSC.

In short, we report on a new type of highly active late transition metal catalyst precursor that can be used to polymerize olefins to high molecular weight polymers in the presence of various activators. Comparison with the reactivity observed with the β-diimine complex **3** illustrates that the presence of the carbonyl functionality in **2** leads to an increase in activity by approximately two orders of magnitude for ethylene polymerization under analogous reaction conditions. Furthermore, α-olefins can be polymerized to high molecular weights by **2**.

On the basis of the considerations above, we propose that the increase in reactivity with **2** versus **3** is a result of the attachment of a Lewis acid to the exocyclic oxygen site on the propagating cationic species. The general concept is illustrated in Scheme 2, which shows one of several possible resonance structure interpretations and is not meant to serve as a complete description of the electronic structure. MAO and related activators are known to be Lewis acidic.[17] It is straightforward to anticipate reduction of the electron density at the nickel center by inductive effects and formation of a partial positive charge on the nitrogen donors, which leads to the delocalized structure illustrated in Scheme 2. A detailed picture requires additional mechanistic and theoretical examination; however, it is helpful to recall the widely used activation of organic substrates with carbonyl functionalities in the presence of aluminum species.[18] Further optimization of reaction conditions, types of activators, and variations in α-keto-β-diimine frameworks will enable improvements in polymerization control. Our current efforts are aimed at delineating the nature of the propagating species.

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