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α-Iminoenamido Ligands: A Novel Structure for Transition-Metal Activation

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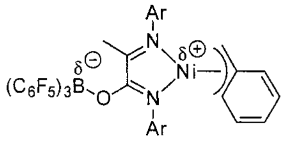
Summary: This communication shows that it is possible to activate nickel complexes containing the α-iminoenamide ligand using $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ to generate catalysts that polymerize ethylene. The polymerization of ethylene using these novel compounds is discussed. The novel activation method is confirmed by the X-ray crystallography studies of the methallyl analogs.

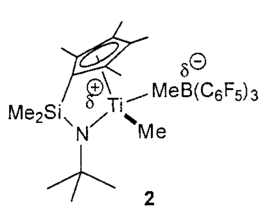
The mechanism of precatalyst activation is an essential consideration for the successful design and further improvement of homogeneous single-site catalysts for olefin polymerization.[1] During activation, a neutral transition-metal complex reacts with a cocatalyst to generate a more polarized and electrophilic species. The best-established methods[2] involve hydride or alkyl abstraction by a neutral Lewis acid, the protonation of an M−C (or M−H) bond and the use of aluminoxane-type reagents. A feature that characterizes the majority of catalytic species is the presence of a loosely coordinated base, which competes with the incoming monomer molecule for the vacant site of lowest energy.[3]

In work related to the synthesis of branched polyethylene by tandem catalysis,[4] we reported that it is possible to activate nickel complexes supported by α-iminocarboxamidato ligands by addition of tris(pentafluorophenyl)borane.[5] The key observation is that the carbonyl functionality of the carboxamide unit coordinates to the Lewis acidic boron and, in doing so, removes electron density from the nickel atom.[6] It is significant that the partially negative boron atom is situated on the side opposite from monomer insertion. We give the structure of $\{(H_3C)C[N(2,6\text{-}(CHMe_2)_2\text{-}C_6H_3)]C[OB(C_6F_5)_3][N(2,6\text{-}(CHMe_2)_2\text{-}C_6H_3)]\text{-}\kappa^2 N,N\}Ni(\eta^3\text{-}CH_2C_6H_5)$ (**1**), which produces polyethylene under mild conditions. For comparison, we show the structure of $\{[(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)]TiMe\}\{MeB(C_6F_5)_3\}$ (**2**), a widely used initiator for the copolymerization of ethylene with 1-alkenes.[7] Note how in **2** the $\{MeB(C_6F_5)_3\}$ anion is present within the wedge where olefin insertion takes place. The strength of the Ti−borate interaction is known to affect polymerization results.[8]



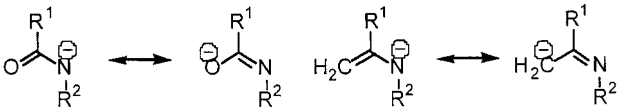
Ar = 2,6-$(CHMe_2)_2C_6H_3$

1



2

The well-developed chemistry of enamines is relevant to the discussion above. It is known that the C_α of enamines[9] and of metalloenamines is highly charged and is capable of reacting with electrophiles.[10] The relationship between the enamide and carboxamide functionalities is made clear by noting the similarity between the resonance structures



This similarity raises the possibility of activating complexes with α-iminoenamido ligands by creating structures similar to **1**.

Synthetic access into α-iminoenamides with suitable steric congestion[11] begins with the well-developed chemistry of α-diimines,[12] and in particular N-aryl-substituted α-diimine ligands.[13] Deprotonation

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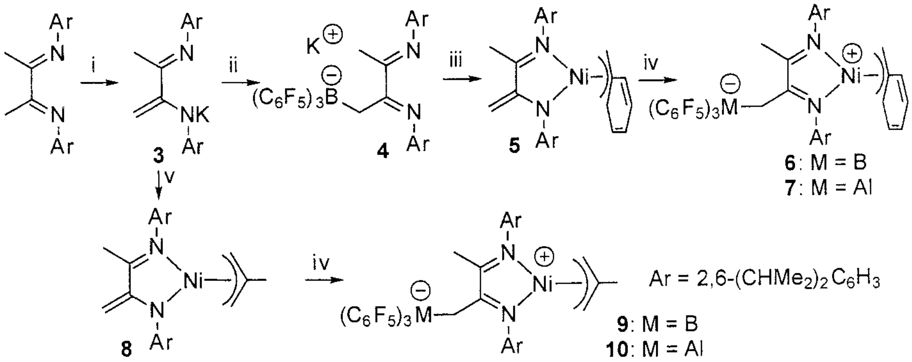
Scheme 1[a]



[a] Legend: (i) KH; (ii) $B(C_6F_5)_3$; (iii) $Ni(\eta^3-CH_2C_6H_5)Cl(PMe_3)$; (iv) $B(C_6F_5)_3$ or $Al(C_6F_5)_3$; (v) $[Ni(\eta^3-CH_2CMeCH_2)Cl]_2$.

of $\{2,6-(CHMe_2)_2-C_6H_3\}N{=}C(CH_3)C(CH_3){=}N\{2,6-(CHMe_2)_2-C_6H_3\}$ with KH in THF results in potassium *N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-1-methylenepropylamide (**3**) in 92% yield. The vinyl protons ($H_2C{=}C$) were observed in the ^1H NMR spectrum as a pair of doublets at 4.22 and 3.59 ppm ($J_{HH} = 0.8$ Hz). When $Ni(\eta^3-CH_2C_6H_5)Cl(PMe_3)$ is added to a C_6D_6 solution of **3**, one observes the disappearance of these characteristic vinyl peaks. We suspect that the direct reaction of **3** and $Ni(\eta^3-CH_2C_6H_5)Cl(PMe_3)$ leads to the C-coordinated complex. To block C–Ni bond formation, compound **3** was first treated with $B(C_6F_5)_3$ to yield potassium [2,3-bis(2,6-diisopropylphenylimino)-butyl]tris(pentafluorophenyl)borate (**4** in Scheme 1). The reaction of **4** with $Ni(\eta^3-CH_2C_6H_5)Cl(PMe_3)$ results in the clean formation of [*N*-(2,6-diisopropylphenyl)-2-(2,6-diisopropylphenylimino)-1-methylenepropylamido-$\kappa^2 N,N$]-(η^3-benzyl)nickel(II) (**5**) and insoluble $Me_3P{\cdot}B(C_6F_5)_3$. The NMR data of compound **5** show two interconverting compounds, which are attributed to pseudorotamers of the η^3-benzyl ligand.

When 1.0 equiv of $B(C_6F_5)_3$ is added to a C_6D_6 solution of **5**, one observes by ^1H NMR spectroscopy the appearance of broad peaks at 3.26–3.36 and 3.16–3.26 ppm (3:1 ratio) corresponding to boron-bound methylene resonances. Signals from the benzyl ligand are consistent with η^3 coordination, and we assign the product as **6** in Scheme 1. Pseudorotamers exist which make isolation and complete spectral assignment difficult. Similar results were obtained using **5** and $Al(C_6F_5)_3$[14] to yield compound **7**.

To circumvent the problems associated with the isomeric preferences of the benzyl ligand, we targeted the synthesis of isoelectronic complexes supported with the η^3-methallyl fragment. Thus, compound **8** in Scheme 1 was obtained in 80% yield by addition of **3** to $[NiCl(\eta^3-CH_2CMeCH_2)]_2$.[15] Addition of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ to **8** gives compounds **9** and **10**, respectively. The diastereotopic $B{-}CH_2$ protons are observed as broad signals in C_6D_6 at 3.61–3.41 and 3.26–3.06 ppm in **9** and at 2.65–2.40 ppm for **10**.

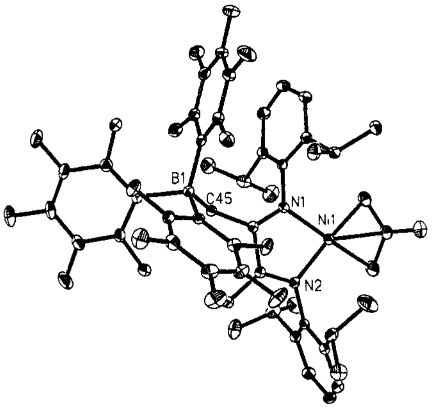


Figure 1. ORTEP drawing of **9** drawn at 30% probability. For clarity, hydrogen atoms are not shown.

Single crystals suitable for X-ray diffraction studies were obtained for **8**–**10**. In the case of **8**, the molecular connectivity shown in Scheme 1 is confirmed. However, two statistical orientations are encountered in the lattice because of a pseudo mirror plane which relates the two N-aryl groups. This orientational disorder does not allow for an accurate examination of metrical parameters. The results for **9** (Figure 1) and **10** (given in the Supporting Information) show that the two molecules have very similar overall connectivities. For both, the Ni–N(1) distance (1.935(2) Å for **9**, 1.923(2) Å for **10**) is slightly longer than that observed for Ni–N(2) (1.915(2) Å for **9**, 1.916(3) Å for **10**). Overall, these observations are consistent with a substantial positive charge on the nickel atom in **9** and **10**. Comparison of the two structures shows that the bulky N(1)-bound diisopropylphenyl group in **9** is closer to the methallyl ligand than in **10**. We attribute this difference to steric interference between the diisopropylphenyl group and the perfluoroaryl rings. In **10**, the longer Al–C(45) distance (2.053(4) Å) minimizes this interaction in comparison to the boron counterpart (d[B–C(45)] = 1.725(4) Å).

When ethylene gas was added to an NMR tube containing a solution of **6** in C_6D_6, one observes fast consumption of ethylene with a concomitant precipitation of polymer. However, no polymer is obtained when the polymerization was conducted in a glass reactor under high-dilution conditions (10 μmol, 30 mL of

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Table 1. Ethylene Reactivity[a]

entry	compd	temp (°C)	activity[b]	M_w[c]	M_w/ M_n[c]	branches[d]	T_m (°C)
1	**6**	22	130	1 330 000	4.7	48	68
2	**6**	45	490	1 050 000	2.4	65	41
3	**6**	60	500	708 000	2.4	87	n.d.[f]
4	**6**	80	800	495 000	2.5	104	n.d.
5	**6**	100	510	387 000	2.5	100	n.d.
6	**7**	22	200	1 530 000	3.1	57	87
7	**7**	45	400	1 120 000	3.0	61	66
8	**7**	60	530	945 000	2.8	74	42
9	**7**	80	550	729 000	2.9	82	37
10	**7**[e]	80	430	574 000	2.5		40
11	**7**	100	560	491 000	2.6	94	n.d.
12	**5**	60	0				
13	**9**	60	0				
14	**10**	60	0				

[a] Polymerization conditions: 30 mL of toluene, 0.33 mM [Ni], 100 psig of ethylene, 10 min, 2.5 equiv of $B(C_6F_5)_3$ for **6** and **9** or of $Al(C_6F_5)_3$ for **7** and **10**. [b] Activity in kg of product/((mol of Ni) h). [c] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C against polystyrene standards. [d] Determined by ^{1}H NMR and corresponds to the number of branches/1000 carbons. [e] 1.0 equiv of $Al(C_6F_5)_3$. [f] Not detected.

toluene). Instead, a color change was observed from red to blue, presumably due to the decomposition of the catalyst. When an additional 2.5 equiv of $B(C_6F_5)_3$ was added in the reactor, we observed fast consumption of monomer at a monomer pressure of 100 psig. The results of a series of ethylene polymerization studies are summarized in Table 1. The activity increases from 22 to 80 °C and then decreases at 100 °C, probably as a result of catalyst decomposition.[16] These activities are similar to those observed with **1**/C_2H_4 under similar reaction conditions; however, the molecular weight of the product is considerably higher.[5] A range of molecular weight distributions is observed (MWD, 2.4−4.7). This range is presumably due to the failure to keep homogeneous conditions because of polymer precipitation and the formation of highly viscous solutions. No ethylene consumption was observed when the unactivated form of the complex was used (entry 12). Entries 6−11 show that the aluminum activator $Al(C_6F_5)_3$ serves equally well as $B(C_6F_5)_3$ for generating a productive catalyst. Finally, no product is observed when using the methallyl-containing compounds **9** and **10** (entries 13 and 14). It seems that the methallyl ligand is too tightly bound to nickel and does not open a coordination site for ethylene to initiate the reaction.

To clarify the role of the additional $B(C_6F_5)_3$ or $Al(C_6F_5)_3$, additional studies were carried out. No changes were observed in ^{1}H NMR spectra of **6** or **7** in C_6D_6 by the addition of 2.5 equiv of $B(C_6F_5)_3$ or $Al(C_6F_5)_3$. Adding a drop of THF-d_8 to a C_6D_6 solution of **6** or **7** produces **5**. These observations, coupled with the comparison of entries 9 and 10 in Table 1, suggest that the additional $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ required to obtain high polymerization activity acts to remove polar impurities from the reaction mixture.

In summary, attachment of a Lewis acid at the C_α site of α-iminoenamido ligands can be used to activate ethylene polymerization catalysts. This is a novel approach to transition-metal activation. The use of the labile η^3-benzyl ligand is important for allowing efficient conversion to the propagating species.

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Supporting Information Available: Text giving complete details for the synthesis of all compounds and polymerization procedures and tables giving data from the crystallographic studies of **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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