Insights into the Deactivation of Neutral Nickel Ethylene Polymerization Catalysts in the Presence of Functionalized Olefins

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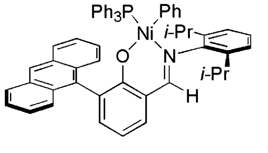
Summary: A study on the products of reaction between a neutral nickel(II) olefin polymerization catalyst and methyl acrylate is presented. A deactivation mechanism involving hydrogen transfer from substrate to catalyst is suggested.

Olefin addition polymerization is one of the most important processes in industrial chemistry. Although this field typically has been the domain of early-metal catalysts, in the past decade there has been growing interest in late-transition-metal catalysts.[1] Among these are neutral nickel(II) complexes developed by Brookhart, DuPont, and this group.[2] The primary driving force for the development of late-metal catalysis is the potential for the copolymerization of ethylene with vinyl-functionalized polar comonomers such as methyl acrylate (MA). Late-metal catalysts are potentially more tolerant of functionality than their oxophilic early-metal counterparts. Unfortunately, although there have been promising breakthroughs,[3] there remain few industrially feasible systems for the incorporation of functionalized olefins into a linear polyethylene backbone.[4] In an effort to address this problem, we herein report studies toward understanding the reactivity of neutral nickel salicylaldimine (sal)-based catalysts with functionalized olefins.

Ni^{II}(sal) compounds, of which **1** is representative, polymerize ethylene in the presence of Lewis basic additives: e.g., esters, alcohols, and water.[2g] In addition, these catalysts copolymerize ethylene and olefins that possess functionality distant from the C−C double bond. However, attempts to copolymerize vinyl-functionalized monomers and ethylene using Ni(sal) catalysts have led only to catalyst deactivation. Therefore, an understanding of the behavior of catalysts such as **1** toward functionalized monomers is crucial for the development of catalysts capable of copolymerization.



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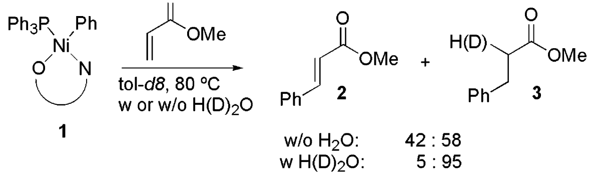
Compound **1** was mixed with 5 equiv of MA in toluene-d_8 at 80 °C (Scheme 1).[5] After 12 h, the products were analyzed by GC-MS. The major components were methyl *trans*-cinnamate (**2**) and methyl 3-phenylpropionate (**3**) in a ratio of close to 1:1.[6] Product **2** is the expected product of reaction between **1** and MA, in

Scheme 1. Reaction between 1 and Methyl Acrylate



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(3) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267−268. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899.

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(5) **Representative procedure**: compound **1** (15.1 mg, 18 μmol, 1 equiv) was weighed out in a glovebox. It was dissolved in toluene-d_8 (0.7 mL). To this was added methyl acrylate (8 μL, 88 μmol, 5 equiv). The resulting orange solution was transferred to an NMR tube and placed in an oil bath at 80 °C for 12 h. During this time, the reaction mixture turned dark red. The solution was diluted with acetone (~10-fold excess) and passed through a plug of alumina to remove any undissolved solids.

(6) In addition, the unsaturated and saturated products of 1,2-insertion, i.e. methyl phenylacrylate and methyl 2-phenylpropionate, were obtained. The ratio of 2,1- to 1,2-insertion products was roughly 8:1.

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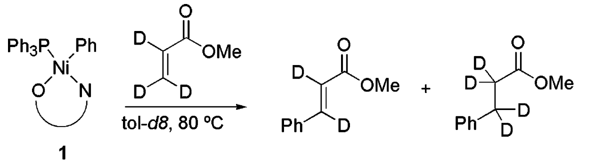
analogy to a Heck coupling. However, the formation of **3** was unexpected and appears to be the product of reduction of **2** by a hydrogen source, of which none are immediately apparent.

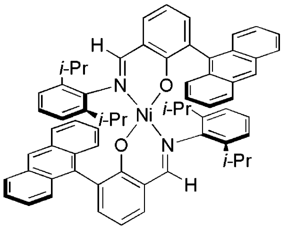
In studies of nickel-catalyzed cross-coupling of aryl halides with acrylates, it has been shown that the presence of water leads to saturated products.[7] With this in mind, the reaction was carried out with the addition of an excess (∼20 equiv) of water. From this reaction **3** was obtained in greatly increased yield (∼95% as compared to **2**), which suggests that water can act as a hydrogen source.[8] This was further confirmed when the use of D_2O provided monodeuterated **3**.[9]

Although the observation of **3** could be explained by the presence of water, it seemed unlikely that water was a major hydrogen source in the initial experiment, since the solvent was assumed to be dry. The only other obvious source of hydrogen was the substrate itself. To determine if this was indeed the case, methyl acrylate-2,3,3-d_3 was allowed to react with catalyst **1**. The same ratio of **2** and **3** was obtained, but with complete deuteration (Scheme 2), implying that complex **1** facilitates hydrogen transfer from one molecule of substrate to another.

Scheme 2. Reaction between 1 and Deuterated Methyl Acrylate



Further insight into the reaction between **1** and MA was obtained through analysis of the inorganic byproducts. A MALDI/TOF mass spectrum of the reaction mixture featured a peak at *m*/*z* 971.62, corresponding to the bis-ligated complex **4**. Bis-ligated complexes of this type are commonly observed in Ni(sal) chemistry and appear to represent a thermodynamically favored state.[2d,10]



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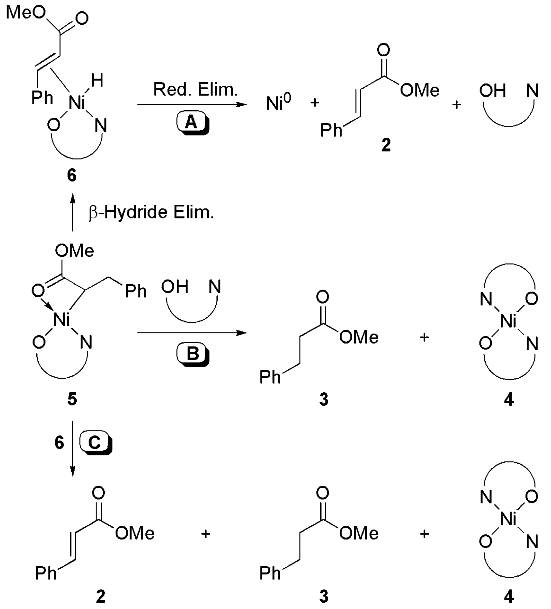
Consideration of the organic and inorganic products of this reaction suggests a mechanism by which **1** is deactivated in the presence of functionalized olefins (Scheme 3). Upon coordination of MA to **1**, 2,1-insertion provides the nickel enolate **5**.[11] The formation of such chelated complexes is well precedented in late-transition-metal-catalyzed olefin polymerization chemistry.[3] Because **5** features a relatively nonlabile chelate, associative addition of another olefin may be slow, and thus the rate of polymerization significantly decreased. Complex **5** can, however, undergo *β*-hydride elimination to provide the olefin/hydride complex **6**, as evidenced by the formation of **2**. However, the rate of *β*-hydride elimination is slow compared to protonolysis, because reaction with excess water provides almost exclusively **3**.[12]

Scheme 3. Proposed Mechanisms of Decomposition



At this point, the hydrogen atom of **6** resulting from *β*-hydride elimination reacts with a molecule of **5** to provide **3** as well as bis-ligated complex **4**. The exact nature of this transfer is unclear. In extensive studies of a related class of neutral nickel(II) catalysts featuring

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[7] (a) Boldrini, G. P.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Organomet. Chem.* **1986**, *301*, C62−C64. (b) Lebedev, S. A.; Lopatina, V. S.; Petrov, E. S.; Beletskaya, I. P. *J. Organomet. Chem.* **1988**, *344*, 253−259. (c) Sustmann, R.; Hopp, P.; Holl, P. *Tetrahedron Lett.* **1989**, *30*, 689−692. For related chemistry in a Rh-based system, see: (d) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829−2844 and references therein. (e) Boiteau, J.-G.; Minaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2003**, *68*, 9481−9484.

[8] Although it is clear that water acts as a proton donor, the eventual fate of its oxygen is more obscure. One possibility is that it serves to oxidize the free phosphine. However, triphenylphosphine oxide is not observed. It seems likely that, upon loss of a proton, the remaining hydroxide goes on to form insoluble nickel hydroxides.

[9] Analysis of the ^{1}H NMR and mass spectrum of **3** confirms that deuteration occurs at the 2-position with extremely high selectivity. See also: Francalanci, F.; Gardano, A.; Abis, L.; Firoani, T.; Foa, M. *J. Organomet. Chem.* **1983**, *243*, 87−94.

[10] (a) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350−4361. (b) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272−2273. In addition to sal systems, this behavior has also been observed in the [P,O]-chelating SHOP system; see: (c) Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1989−2003. (d) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134.

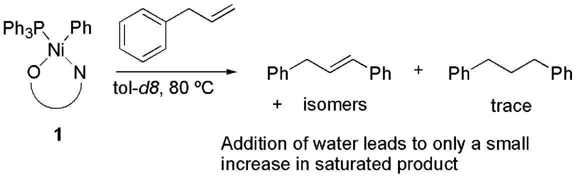
[11] Although the C-bound enolate is depicted here, the true binding mode is unknown. Both O- and C-bound enolates are known for nickel. See: (a) Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30−44. (b) Amarasinghe, K. K. D.; Chowdhury, S. K.; Heeg, M. J.; Montgomery, J. *Organometallics* **2001**, *20*, 370−372. (c) Cámpora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Gutiérrez-Puebla, E.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1482−1483.

[12] In addition, because reaction with D_2O provides no *β*-deuterated **3**, rotation and reinsertion of the olefin into the Ni−H bond of **6** to form a five-membered chelate does not appear to occur or is at least slower than protonolysis in the presence of $H(D)_2O$. Brookhart has observed that this reorganization occurs readily for cationic group 10 polymerization catalysts.[3]

anilinotropone ligands, Brookhart and co-workers have demonstrated that reductive elimination from an olefin/hydride complex produces free ligand (Scheme 3, path A).[2d] The acidic proton of the ligand can then cleave the nickel−carbon bond of an active molecule of catalyst to form a free alkyl group and bis-ligated nickel complex.[13] Protonation by free ligand may occur in the reaction of **1** with MA as well (path B). Indeed, when **1** is treated with MA in the presence of 1 equiv of free (protonated) ligand, a greater yield of **3** is obtained (73% relative to **2**) than in the original experiment, suggesting that free ligand may act as a proton source. Another possibility is direct hydride transfer from **6** to **5** (path C), although the mechanism of such a transfer is not immediately obvious.[14] Because the reaction of **1** with MA presented above involves cleavage of the nickel−alkyl bond, it appears to represent the pathway to deactivation of **1** in the presence of functionalized olefins. Bis-ligated **4**, without an alkyl group bound to nickel, is unable to reinitiate polymerization.

To determine whether this deactivating reaction is specific to MA, **1** was allowed to react with 5 equiv of allylbenzene in toluene-d_8 at 80 °C with and without added water (Scheme 4). In both cases, a similar mixture of unsaturated Heck-type products (1,3-diphenylpropylene and isomers) was obtained. The yield of saturated product (1,3-diphenylpropane) in the dry reaction was less than 2% and grew to only 13% when water was added.[15] In addition, bis-ligated **4** was observed in the MALDI/TOF spectrum at the end of the reaction.[16]

Scheme 4. Reaction of 1 with Allylbenzene



Since **1** is capable of ethylene homopolymerization, the deactivation pathways described above are not as significant a problem in an ethylene homopolymerization as they are in an attempted copolymerization with functionalized olefins. Although deactivation to form **4** also occurs in the reaction of **1** with allylbenzene, the much lower yield of saturated products suggests that hydrogen transfer to a nickel alkyl species is not the major deactivation pathway. The key difference, then, between reaction of **1** with MA and with nonoxygenated monomers appears to be the greater rate at which intermediate **5** in the former reaction is attacked by a hydrogen source. This derails the desired reactivity of the catalysts and effectively stops polymerization.

Although the origin of the reactivity difference described above is currently unclear, some plausible mechanisms may be suggested. The difference may be due to the increased reactivity of a nickel enolate (**5**) toward protonolysis, as compared to a nonchelating alkyl group. Another possibility is that the intermediates in the reaction between **1** and nonchelating olefin β-hydride eliminate before Ni−alkyl cleavage can occur.[17]

The results of this study have important implications for the development of catalysts for the copolymerization of functionalized olefins and ethylene. To make viable catalysts, chelation with functionalized monomers must be less favorable. Current work is ongoing to incorporate the results of this study into the development of new nickel and palladium catalysts capable of facing the formidable challenge of functionalized copolymerization.

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Supporting Information Available: Text giving reaction protocols and GC-MS and MALDI/TOF conditions along with further mechanistic discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] Considering the potentially enolic character of the substrate in complex **5**, it is possible that protonolysis occurs at the Ni−O bond, providing a vinyl alcohol which would rapidly tautomerize to **3**.

[14] Indeed, treatment of methyl *trans*-cinnamate (**2**) with NiHCl-$(PCy_3)_2$ yields **3** as well, although this could also be due to formation of HCl in solution.

[15] Similar results were obtained with the use of styrene and 1-hexene.

[16] It appears that bis-ligated complexes are the eventual deactivation product in any polymerization involving [L,X]-chelated neutral nickel complexes, as noted before.[2d,10] The overall pathway to the formation of bis-ligated complexes probably varies on the basis of the nature of the catalyst and the reaction conditions but will always occur, even when extremely bulky ligands are used.

[17] For further speculative discussion on the nature of the deactivating reactivity between **1** and MA, see the Supporting Information.