Chapter 2

Deactivation of Ni-Based Olefin Polymerization Catalysts in the Presence of Vinyl-Functionalized Olefins

2.1 Abstract

Neutral Ni salicylaldimine (Ni(sal)) complexes, such as **1.16**, are active catalysts for ethylene polymerization, but are deactivated during attempted copolymerization of ethylene with polar olefins, such as methyl acrylate (MA). In order to understand this deactivation, the products of reaction between **1.16** and MA were analyzed. Based on these studies, a major pathway for deactivation of Ni(sal) catalysts by Lewis basic monomers, involving hydrogen transfer from substrate to the active catalyst, is proposed. Significantly, this hydrogen transfer is not observed for substrates that do not feature Lewis basic functionality. This suggests that the deactivation of Ni(sal) catalysts in the presence of functionalized olefins is due to an interaction of the Lewis basic moieties with the metal center.

2.2 Introduction

As discussed in Chapter 1, neutral Ni(II) complexes of salicylaldimine ligands (Ni(sal)) have proven to be excellent catalysts for the homopolymerization of ethylene, as well as the copolymerization of ethylene with some functionalized comonomers.[1] However, attempts to copolymerize ethylene with *vinyl*-functionalized monomers, *e.g.*, acrylates and acrylonitriles, using Ni(sal) complexes has thus far resulted only in catalyst deactivation. Because the copolymerization of ethylene with these monomers is the stated goal of our research program, it is of vital importance to understand the origin of catalyst deactivation. Such an understanding may eventually lead to the development of catalysts that are capable of the desired copolymerization.

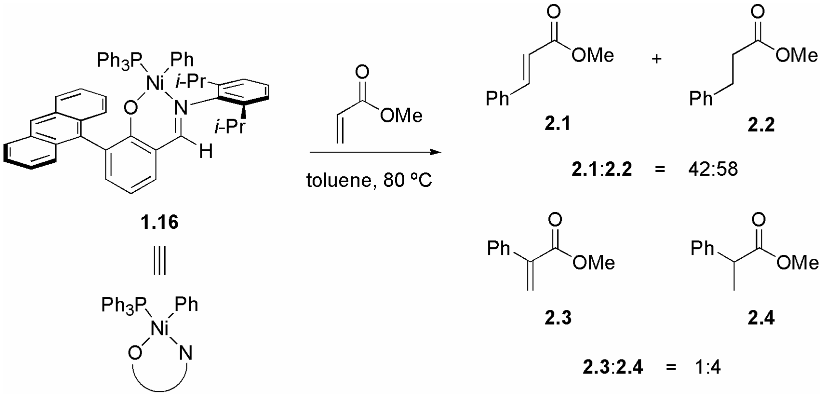
In the past decade, extensive mechanistic study of group 10 diimine catalysts has provided detailed information on polymerization of ethylene as well as the copolymerization of ethylene and polar olefins.[2] These processes are now very well understood. It was therefore hoped that an examination of the organic as well as the inorganic or organometallic products of the reaction between Ni(sal) complexes and functionalized olefins would provide insight into the mechanism of deactivation.

2.3 Experimental Protocol and Observations

Because Ni(sal) complex **1.16** was the preferred catalyst in our earlier work, it was chosen as the focus of this study. In a standard experiment, **1.16** was mixed with five equivalents of methyl acrylate (MA) in toluene at 80 °C (Scheme 2.1).[3] After 12 hours, the products were analyzed by GC-MS. The major components were methyl trans-cinnamate (**2.1**) and methyl 3-phenylpropionate (**2.2**) in a ratio of close to 1:1.

Methyl trans-cinnamate (**2.1**) might be expected from reaction between **1.16** and MA, in analogy to a Heck coupling. However, the formation of **2.2** was unexpected, and appears to arise from reduction of **2.1** by a hydrogen source, of which none are immediately apparent.

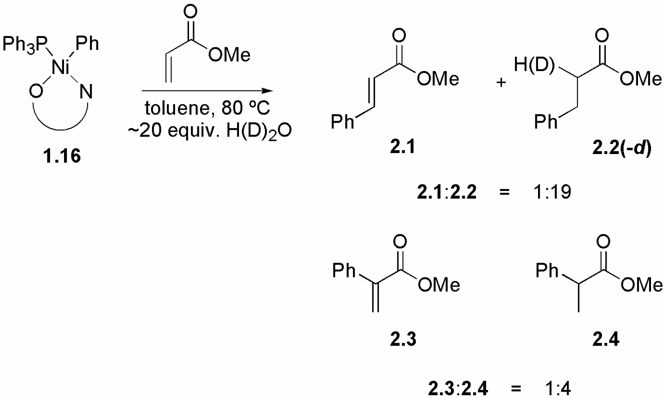
Scheme 2.1. Reaction between **1.16** and MA.



In addition to products **2.1** and **2.2**, the unsaturated and saturated products of 1,2-insertion, i.e. methyl phenylacrylate (**2.3**) and methyl 2-phenylpropionate (**2.4**), were obtained in a roughly 1:4 ratio. The ratio of 2,1- to 1,2-insertion products was approximately 8:1. Due to the strong steric influence of the very bulky anthracenyl ligand of **1.16**, some 1,2-insertion is expected, but it has been established that 2,1-insertion is the normal mode in metal-mediated additions of alkyl groups to functionalized olefins.[4] Since the amount of 2,1-product obtained is much higher than the amount of 1,2-product, it will be the only one considered in the following mechanistic discussion. However, some of the same arguments to be made are valid for 1,2-insertion as well.

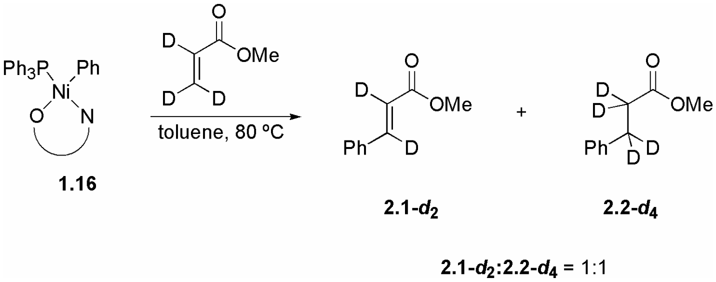
In studies of Ni-catalyzed cross-coupling of aryl halides with acrylates, it has been shown that the presence of water leads to the formation of saturated products such as those observed in the reaction described above (**2.2** and **2.4**).[5] With this in mind, the reaction was carried out with the addition of an excess (~20 equivalents) of water (Scheme 2.2). From this reaction reduced product **2.2** was obtained in a greatly increased amount (**2.2**:**2.1** = 19:1) (1,2-insertion products were obtained in the same ratio as before, **2.3**:**2.4** = 1:4).[6] This suggests that water can act as a hydrogen source. This fact was further confirmed when the use of D_2O provided mono-deuterated ***2.2-d***. Analysis of the ^{1}H NMR and mass spectra of ***2.2-d*** confirms that deuteration occurs at the α-position exclusively.[7] Though the role of the water-derived protons is clear, the fate of the water-derived oxygen is more obscure. It is likely that upon loss of a proton, the remaining hydroxide goes on to form insoluble Ni hydroxides (some precipitate was observed).

Scheme 2.2. Reaction between **1.16** and MA in the presence of excess $H(D)_2O$.



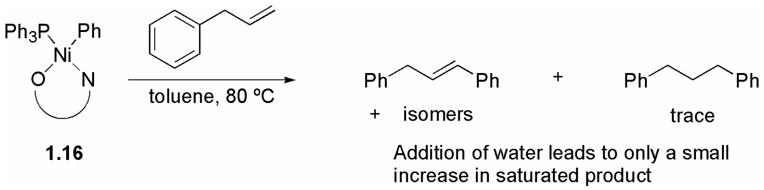
Although the formation of **2.2** can occur via reaction with water, it seemed unlikely that water was a major hydrogen source in the initial experiment since the solvent and other reagents were carefully dried (see experimental details). The only other obvious source of hydrogen atoms was the substrate itself. To determine if this was the case, methyl (2,3,3-trideutero)acrylate (MA-d_3) was allowed to react with catalyst **1.16** under the same conditions as the first reaction (Scheme 2.3). The same ratio of saturated and unsaturated products were obtained, but with complete deuteration. The exclusive appearance of deuterium in saturated product **2.2-*d*$_4$** strongly suggests that MA can act as a reductive source of hydrogen.

Scheme 2.3. Reaction between **1.16** and MA-d_3

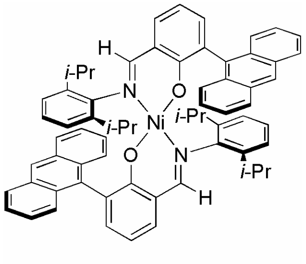


Next, it was deemed necessary to investigate the behavior of **1.16** in the presence of an olefin that more closely resembles ethylene. Pursuant to this, **1.16** was allowed to react with five equivalents of allylbenzene in toluene at 80 °C with and without added water (Scheme 2.4). In both cases, a similar mixture of unsaturated Heck-type products (1,3-diphenylpropylene and isomers) was obtained. The ratio of saturated product (1,3-diphenylpropane) to unsaturated product in the dry reaction was less than 1:50, and grew to only 13:87 when water was added. Similar results were obtained through the use of styrene and 1-hexene in place of allylbenzene.

Scheme 2.4. Reaction between **1.16** and allylbenzene.



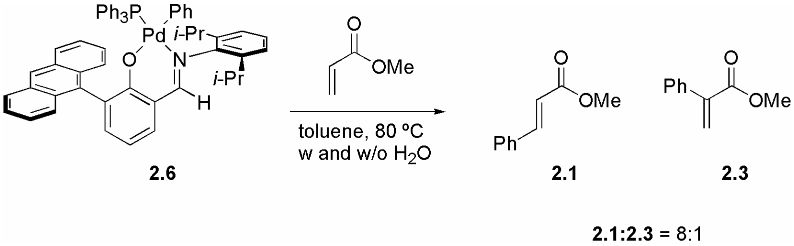
Having determined the organic products of reactions between **1.16** and MA and **1.16** and allylbenzene, it remained to determine the inorganic byproducts. The MALDI/TOF mass spectra of both reaction mixtures featured a peak at *m/z* 971.62, corresponding to bis-ligated complex **2.5**. Bis-ligated complexes of this type are commonly observed in Ni(sal) chemistry, and appear to represent a thermodynamically favored state.[8,9] Not surprisingly, in our own work, it has commonly been observed that the final inorganic products of Ni(sal)-catalyzed ethylene polymerizations are typically Ni(sal)$_2$ complexes.[10]



2.5

Finally, to determine the significance of the reactivity observed with Ni(sal) complex **1.16**, the corresponding Pd(sal) complex (**2.6**) was treated with MA under the same conditions (Scheme 2.5). In this case, only the unsaturated products **2.1** and **2.3** were obtained exclusively, with no trace of saturated **2.2** and **2.4**. The same result was obtained when water was added to the system.

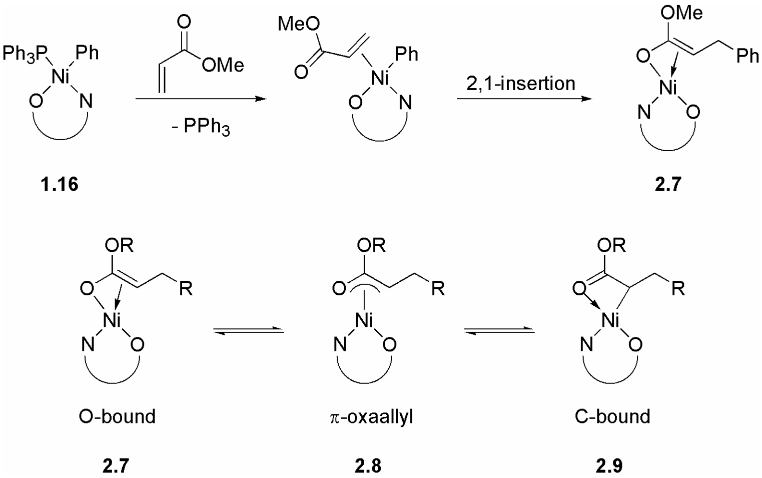
Scheme 2.5. Reaction between Pd complex **2.6** and MA.



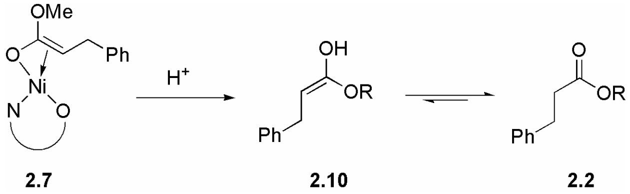
2.4 Mechanistic Considerations

Based upon the observations described above, we propose a mechanism for the deactivation of Ni(sal) catalyst **1.16** by reaction with MA. Following coordination of the olefin of MA to **1.16**, 2,1-insertion of the Ni-bound phenyl group into the acrylate olefin occurs to provide Ni enolate **2.7** (Scheme 2.6). There are three distinct binding modes possible for such a Ni enolate: an O-bound enolate (**2.7**), a π-oxaallyl complex (**2.8**) and a C-bound enolate (**2.9**). X-ray crystallographic structures of both O-bound[11] and C-bound[12] Ni-enolates have been obtained, but the oxaallyl structure has not been reported for Ni. In this case, the true character of the Ni-substrate bond is unknown. Given that the protonation observed in the presence of water (Scheme 2.2) may occur more readily at a Ni-O bond than a Ni-C bond, it is possible that **2.7** is best described as an O-bound enolate as depicted in Scheme 2.7. Protonolysis of **2.7** would provide **2.10** which would then tautomerize to **2.2** (Scheme 2.7).

Scheme 2.6. 2,1-Insertion leads to a Ni-enolate (**2.7**). Three possible bonding modes of a Ni-enolate.



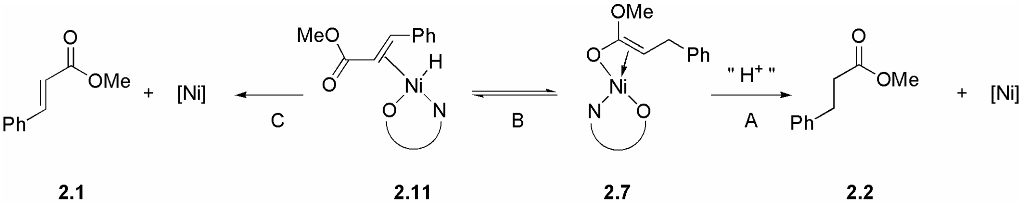
Scheme 2.7. Protonolysis of **2.7** leads to **2.10**, then **2.2** via tautomerization.



As was discussed in Chapter 1, the formation of a stable chelated complex derails the normal activity of Pd diimine polymerization catalysts in the presence of functionalized olefins such as MA (Scheme 1.8).[2a] Similarly, the stability of Ni-enolate **2.7** also seems to have an adverse effect on its reactivity. Because **2.7** features a relatively non-labile chelate between the Ni atom and the enolate, associative addition of another olefin may be slow and thus polymerization is significantly deterred or even stopped.

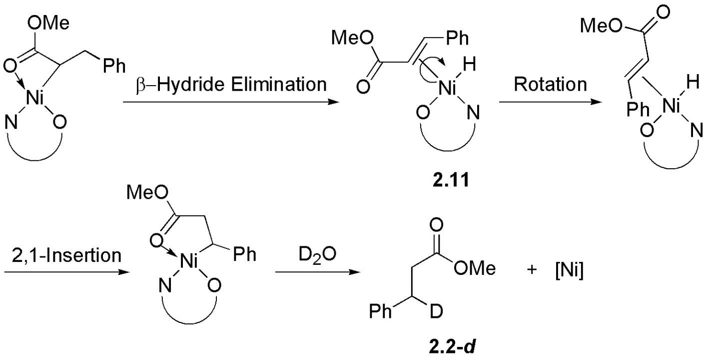
Because complex **2.7** is no longer in the catalytic cycle of olefin polymerization, it remains in solution as a non-reactive intermediate until it decomposes via one of at least two mechanisms (Scheme 2.8). One of these processes is β-hydride elimination to provide olefin/hydride complex **2.11**, as evidenced by the formation of unsaturated **2.1**. Another decomposition pathway is protonolysis, as evidenced by the formation of saturated **2.2**. The absolute rates of these two processes are unknown. However, the fact that, in the presence of water, **2.2** is produced almost exclusively suggests that reaction A occurs much faster than either reaction B, reaction C, or both.

Scheme 2.8. Fate of Ni-enolate **2.7**.



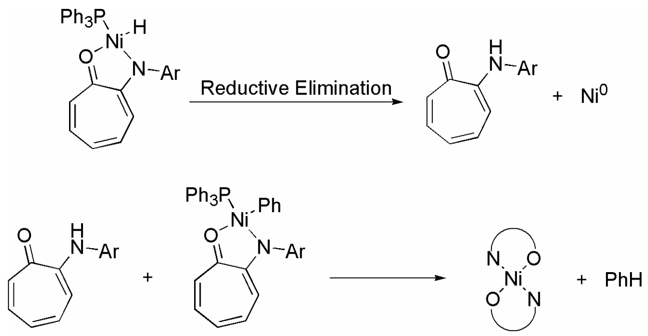
Brookhart has demonstrated in the Pd(diimine)-catalyzed copolymerization of MA and ethylene that the transient Pd-enolate complex undergoes multiple β-hydride elimination/reinsertion steps that isomerize the initial 4-membered chelate ring to more stable 5- and 6-member rings (Scheme 1.8). However, as mentioned above, reaction with D_2O provides only α-deuterated **2.2-*d***, suggesting that rotation and reinsertion of the olefin into the Ni–H bond of **2.11** to form a 5-membered chelate does not happen (at least in the presence of $H(D)_2O$ (Scheme 2.9). It is evident, then, that either this process cannot occur, or **2.7** reacts with $H(D)_2O$ before elimination/rotation/reinsertion can occur.[13]

Scheme 2.9. Hypothetical mechanism for the formation of β-deuterated **2.2-*d***, which is not observed.



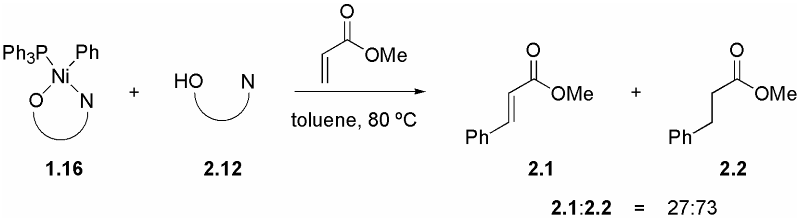
In the absence of water, it appears that the hydrogen atom of **2.11** resulting from β-hydride elimination reacts with **2.7** in some fashion to provide **2.2** as well as bis-ligated complex **2.5**. The exact nature of this transfer is unclear. In extensive studies of a related class of neutral Ni(II) catalysts featuring anilinotropone ligands, Brookhart and coworkers have demonstrated that reductive elimination from an olefin/hydride complex produces free ligand (Scheme 2.10).[14] The acidic proton of the ligand can then cleave the Ni–C bond of an active molecule of catalyst to form a free alkyl group and bis-ligated Ni complex.

Scheme 2.10. Deactivation of Ni-anilinotropone catalysts reported by Brookhart.

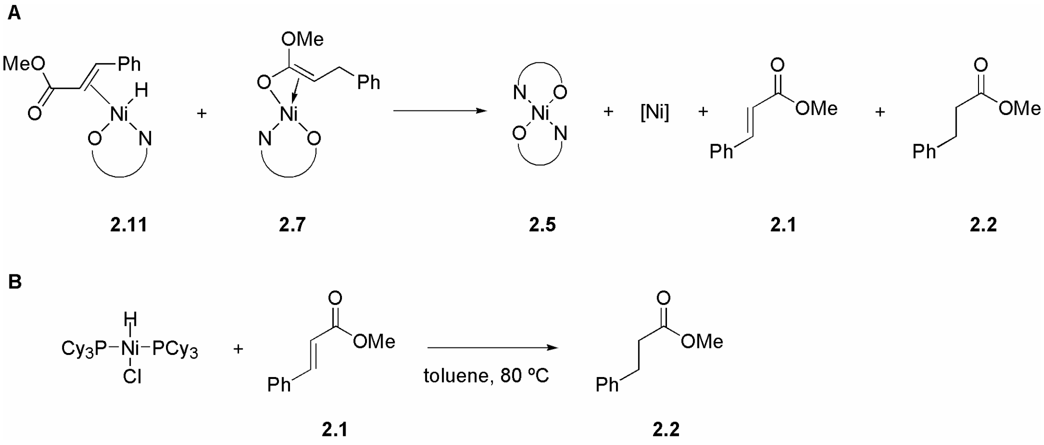


Protonation by free ligand generated by reductive elimination from a Ni-hydride may occur in the reaction of **1.16** with MA as well. Indeed, when **1.16** is treated with MA in the presence of one equivalent of free (protonated) ligand (**2.12**), a greater amount of **2.2** is obtained (73:27 ratio of **2.2** and **2.1**) than in the original experiment, suggesting that free ligand can act as a proton source (Scheme 2.11). Another possibility is direct hydride transfer from **2.11** to **2.7** (Scheme 2.12A), although the mechanism of such a transfer is not immediately obvious. Notably, treatment of methyl trans-cinnamate (**2.1**) with NiHCl(PCy_3)$_2$ yields **2.2**, suggesting that a Ni-hydride may be capable of reducing **2.1** to **2.2** (Scheme 2.12B); however, this reactivity could also be due to formation of HCl of in solution, which could then protonate Ni-enolates. Nonetheless, whether due to ligand-mediated protonolysis or direct hydride transfer, the ultimate result is the formation of bis-ligated complex **2.5**, which represents a dead end for catalysts such as **1.16**.

Scheme 2.11. Reaction between **1.16** and MA with added free phenolic ligand.

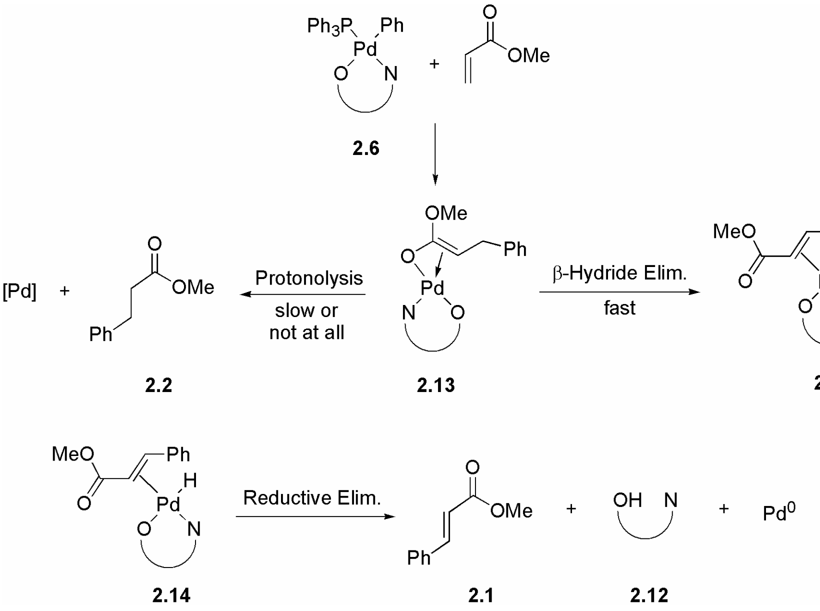


Scheme 2.12. A: Direct hydride transfer between **2.11** and **2.7** may lead to deactivation. **B:** Reaction of **2.1** with a Ni-hydride provides **2.2**



In light of the mechanistic insight gained for Ni complex **1.16**, we can reconsider the reaction of Pd(sal) complex **2.6** with MA. A proposed mechanism for this reaction is presented in Scheme 2.13. Because only unsaturated products (**2.1** and **2.3**) are observed in the reaction between **2.6** and MA, it is clear that Pd-enolate **2.13**, which presumably forms upon insertion of MA into the Pd–Ph bond of **2.6**, only undergoes β-hydride elimination (rather than protonolysis), to give a Pd olefin/hydride complex (**2.14**) from which **2.1** is derived. This is either because Pd-enolate **2.13** is not reactive to protonolysis, or β-hydride elimination from **2.13** is faster than protonolysis, even in the presence of water. Such rapid β-hydride elimination is also observed with Pd diimine complexes, as discussed in Chapter 1. It was also mentioned that Pd(sal) complexes are not active catalysts for ethylene polymerization because they tend to reductively eliminate the sal ligand (**2.12**) from Pd-hydrides, which likely occurs in this case as well (Scheme 2.13).

Scheme 2.13. Proposed mechanism of reaction between Pd complex **2.6** and MA.

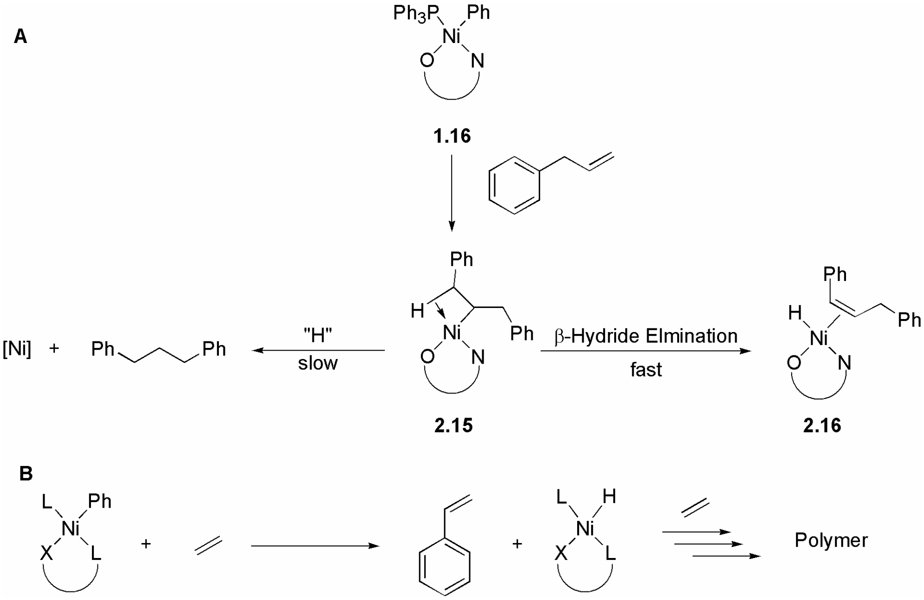


2.5 Discussion

On the basis of the evidence described above, we suggest a rationale for the observed difference between reaction of **1.16** with functionalized and non-functionalized olefins, and by extension, why the catalyst succeeds at ethylene homopolymerization and fails at ethylene/functionalized-olefin copolymerization.

The reaction between Ni catalyst **1.16** and allylbenzene will be used as a surrogate for the homopolymerization of ethylene by **1.16** (Scheme 2.14A). The initial step in this reaction is likely allylbenzene insertion into the Ni–Ph bond of **1.16** to form a β-agostic complex (**2.15**). This is followed by rapid β-hydride elimination to provide hydride/olefin complex **2.16**. Because saturated products are not observed to a large extent in the reaction between **1.16** and allylbenzene, protonolysis of β-agostic compound **2.15** either does not occur, or occurs much more slowly than β-hydride elimination and olefin dissociation to form 1,3-diphenylpropylene and a Ni-hydride. It has been suggested that in the polymerization of ethylene by Ni–Ph complexes, the first step is ethylene insertion into the Ni–Ph bond, followed by β-hydride elimination to give styrene and a Ni-hydride, which is the true catalytically active species (Scheme 2.14B).[15] Therefore, in the reaction between **1.16** and allylbenzene, the appearance of 1,3-diphenylpropylene and its isomers is not surprising – indeed it is indicative of the fact that allylbenzene serves as a competent ethylene mimic, and were there ethylene present, polymerization would likely occur.

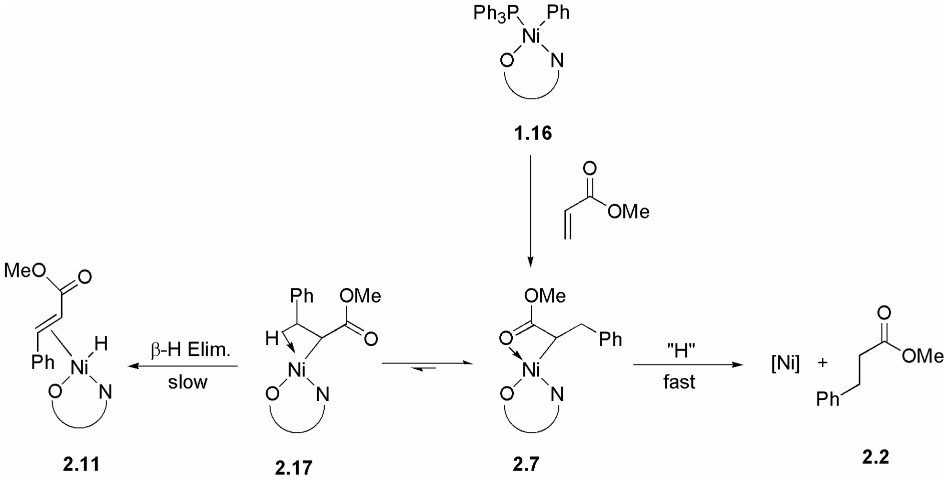
Scheme 2.14. A: Proposed mechanism of the reaction between **1.16** and allylbenzene. **B:** Initiation of Ni–Ph precatalysts via formation of styrene and a Ni-hydride.



The reaction between MA and **1.16** likely leads to the formation of a chelate complex (**2.7**) that is incapable of coordination of ethylene (Scheme 2.15). Because of the tight enolate chelate of **2.7**, formation of β-agostic structure **2.17**, the necessary precursor to β-hydride elimination, is disfavored. Therefore, though β-hydride elimination does occur, as evidenced by the formation of unsaturated products **2.1** and **2.3**, it is a relatively slow process. In addition, the formation of Ni-hydrides, which are the true catalytically active species, is also slow.

Meanwhile, complex **2.7** can be readily deactivated by protonolysis, which as mentioned above, must be significantly more rapid than β-hydride elimination. In a reaction free of external proton sources, *e.g.*, water, β-hydride elimination from **2.7**, while slow, is the only reactive pathway available early on. As β-hydride elimination from **2.7** produces significant quantities of Ni-hydride (**2.11**) or free phenolic ligand by reductive elimination from **2.11**, the protolytic pathway becomes available. This would account for the nearly 1:1 ratio of **2.1** and **2.2** observed in the initial reaction between **1.16** and MA (Scheme 2.1). Because Ni-hydrides are the putative catalytically active species, their brief lifetime limits catalyst activity.

Scheme 2.15. Proposed mechanism of reaction between **1.16** and MA.



2.6 Conclusion

As described in Chapter 1, Ni(sal) complexes have been found to be excellent catalysts for the copolymerization of ethylene and olefins that feature functionality removed from the C–C double bond, *e.g.*, methyl 10-undecenoate (Scheme 1.9). Thus, it is clear that the Ni(sal) catalysts are not poisoned simply by the presence of ester functionality in the reaction mixture. An olefin that features functionality distant from the C–C double bond is closer in reactivity to allylbenzene than to MA, and thus should be expected to take part in normal polymerization, as is observed. The deactivation of Ni(sal) catalysts observed in the reaction with MA is peculiar to olefins that feature vinyl functionalization. From the results of this study, two reasons for this deactivation are apparent: (1) the formation of a chelate such as **2.7** prevents coordination of ethylene and prevents further polymerization; (2) Ni-enolates such as **2.7** are much more reactive to protonolysis than a typical Ni–C bond, and protonolysis equates to catalyst death.

The results of this study have important implications for the development of catalysts for the copolymerization of functionalized olefins and ethylene. In order to make viable catalysts, chelation with functionalized monomers must be made less favorable. One could envision a number of approaches to solving this problem. One approach that has shown moderate success is the use of a Lewis acid to coordinate the oxygen functionality of the comonomer, preventing its coordination to the metal atom of the catalyst. This Lewis acidic component can either be attached the catalyst,[16] or can be a cocatalyst added to the reaction mixture.[17] Another approach is the use of a very electron-donating ligand set. This would make the metal center less oxophilic and could disfavor the formation of a strong enolate chelate, which would presumably circumvent the difficulties observed in the study described above. Our work toward the implementation of the latter approach is the subject of Chapter 3.

2.7 Acknowledgments

This work was supported by the Rohm and Haas Corporation. Todd Younkin performed the initial reaction between **1.16** and MA and provided helpful advice. Mona Shahgholi performed the MALDI-TOF measurements.

2.8 Experimental Details

Materials and Methods. All reactions were set up in a nitrogen glovebox. Methyl acrylate and allylbenzene were purchased from the Sigma-Aldrich Chemical Company, and were dried over CaH_2 and distilled under reduced pressure. Methyl (2,3,3-d_3)-acrylate and toluene-d_8 were purchased from Cambridge Isotope Laboratories. Methyl (2,3,3-d_3)-acrylate was used as received. Toluene-d_8 was dried over Na^0/benzophenone and distilled under reduced pressure. Compound **1.16** was synthesized according to literature procedure.[1a] ^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz). GC-MS data were obtained on an HP 5890 GC with an Agilent DB-5MS+DG column, and an HP 5970 EI mass selective detector. The GC was operated with the following oven program: begin at 70 °C, heat to 270 °C at a rate of 15 °C/min., maintain for 5 min., return to 70 °C at a rate of 50 °C/min. The GC traces of methyl cinnamate (**2.1**) and methyl 3-phenylpropionate (**2.2**) were confirmed by comparison with authentic samples, obtained from Sigma-Aldrich and Lancaster Synthesis, respectively. The identities of methyl phenylacrylate[18] (**2.3**) and methyl 2-phenylpropionate[19] (**2.4**) were confirmed through independent synthesis. The identities of the products of reaction between **1.16** and allylbenzene (six isomers of 1,3-diphenylpropylene and two isomers of 1,3-diphenylpropane) were confirmed by their mass spectra in the GC-MS spectrum.[20] MALDI/TOF spectra were obtained with an Applied Biosystems Voyager DE PRO with a 20 Hz N_2 laser. The matrix was dithranol (5 mg/mL) in acetonitrile and was used in twofold excess relative to analyte.

Reaction of 1.16 with methyl acrylate (representative procedure). Ni(sal) complex **1.16** (15 mg, 18 μmol, 1.0 equiv) was weighed in the glovebox and was dissolved in toluene-d_8 (0.70 mL). To this was added methyl acrylate (8.0 μL, 0.88 μmol, 5.0 equiv). The resulting orange solution was transferred to an NMR tube, which was then placed in an oil bath at 80 °C for 12 hrs. After this time, the reaction mixture became dark red. The solution was diluted with acetone (~10-fold excess), and passed through a plug of alumina to remove any undissolved solids. It was then injected on the GC-MS spectrometer and subjected to the oven program described above. Product ratios were determined by GC integration.

Reaction of 1.16 with methyl acrylate and added $H(D)_2O$ (representative procedure). The same protocol as described above was followed with the exception of the addition of water or deuterium oxide (10 μL, ~20 equiv relative to catalyst) before heating.

2.9 References

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[6] It is notable that the same ratio of 1,2-insertion products (**2.4**:**2.3** = 4:1) was obtained in both the reaction with and without added water. The significance of this fact is unclear. However, it seems that to indicate something about the reactivity of the initial product of 2,1-insertion (a Ni-enolate), since it is affected so much more by the presence of water than the initial product of 1,2-insertion.

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