Materials and Methods. All reactions were set up in a nitrogen glovebox. Methyl acrylate, and allylbenzene were purchased from the Sigma-Aldrich Chemical Company, Milwaukee, WI. They were dried over CaH_2 and distilled under reduced pressure. Methyl acrylate 2,3,3-d_3 and toluene-d_8 were purchased from Cambridge Isotope Laboratories, Inc., Andover, MA. Methyl acrylate 2,3,3-d_3 was used as received. Toluene-d_8 was dried over Na^0/benzophenone and distilled under reduced pressure. The synthesis of compound **1** is described elsewhere.[1] ^1H 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**) and methyl 3-phenylpropionate (**3**) were confirmed by comparison with authentic samples, obtained from Sigma-Aldrich and Lancaster Synthesis, Pelham, NH, respectively. The identities of methyl phenylacrylate[2] and methyl 2-phenylpropionate[3] were confirmed by independent synthesis. The identities of the products of reaction between **1** 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.[4] 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 with methyl acrylate (representative procedure). Compound **1** (15.1 mg, 18 μmol, 1 equiv.) was weighed out in the 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 hours. After 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. It was then injected on the GC-MS spectrometer and subjected to the oven program described above. Relative percent yields were determined by GC integration.

Reaction of 1 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.

Further discussion: In reaction of **1** with allylbenzene there is much lower yield of saturated products, even in the presence of excess water, than in reaction of **1** with MA. This observation seems to be the crux of the problem of deactivation of **1** and related catalysts by acrylates. Two plausible explanations arise:

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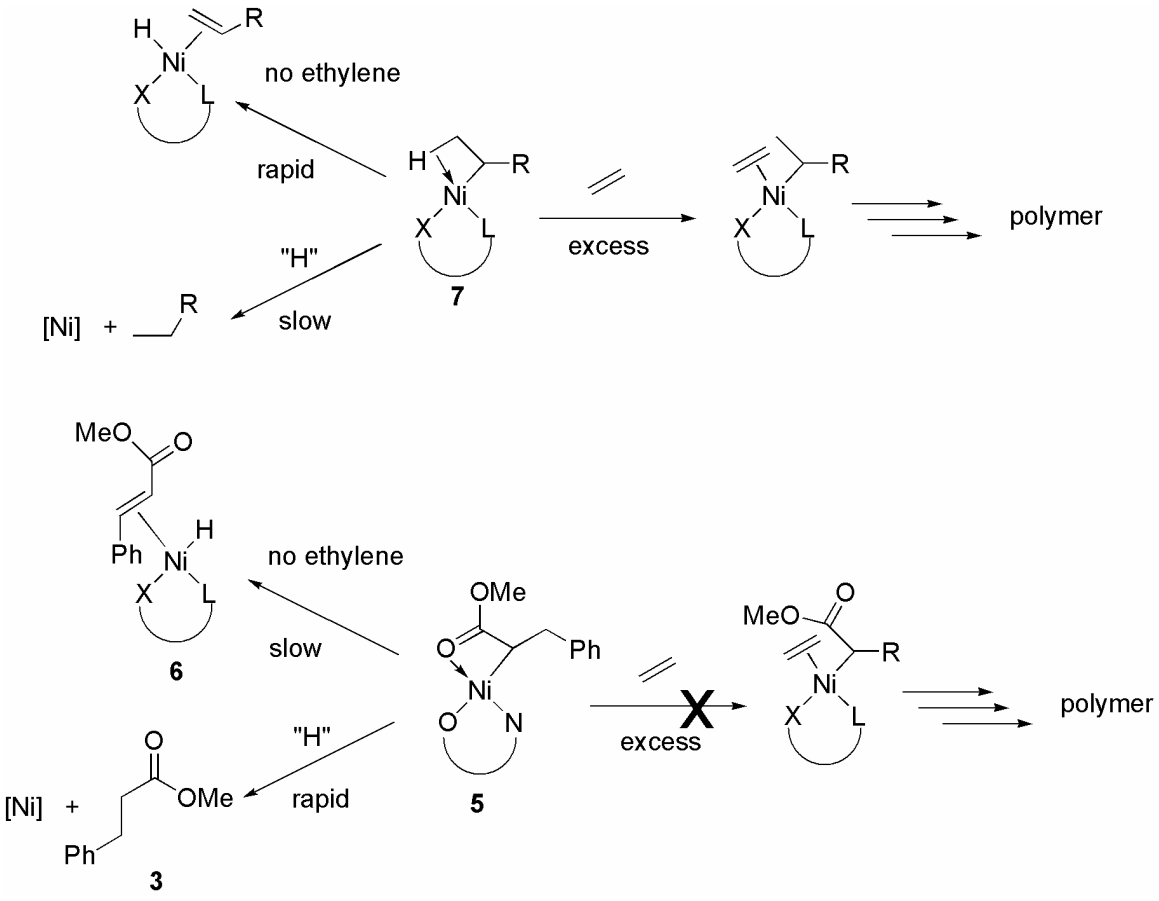
[1] Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272–2273.
[2] Hin, B.; Majer, P.; Tsukamoto, T. *J. Org. Chem.* **2002**, *67*, 7365–7368.
[3] Maruoka, K.; Nakai, S.; Sakurai, M.; Yamamoto, H. *Synthesis* **1986**, *2*, 130–132.
[4] For an extensive study on the mass spectrometry of 1,3-diphenylpropylene and its isomers, see: Johnstone, R. A. W.; Millard, B. J. *J. Chem. Soc. C* **1966**, 1955–1959.

1) While reaction with MA can provide chelate complex **5**, the product of reaction of **1** and allylbenzene is not stabilized by a similar chelate. This allows the β-agostic interaction (**7**) which precedes β-hydride elimination. This would account for the formation of unsaturated products which are observed in reaction of **1** with allylbenzene. Because saturated products are not observed to a large extent, β-hydride elimination must be rapid as compared to deprotonation. Such rapid β-hydride elimination is not as important a factor in a typical ethylene homopolymerization because there is a large excess of ethylene present to bind the catalyst and preclude deactivation through β-hydride elimination. However, when a Lewis basic olefin such as MA is present, formation of a chelate complex such as **5** appears to be rapid and largely irreversible, preventing further coordination of ethylene. Because the catalyst can no longer bind ethylene, it stops making polymer. In addition, because it does not readily participate in a β-agostic interaction, it does not rapidly β-hydride eliminate. Before β-hydride elimination occurs, the inert complex is deactivated by reaction with a hydrogen source. This is illustrated in the figure below:



2) Because **5** is a nickel enolate, it may be more prone to reaction with protic sources than a typical nickel-alkyl complex. This would be especially plausible if **5** can be described as an O-bound enolate. In that case, reaction of a labile Ni-O bond with a proton source could be facile. Tautomerization to **3** would then follow. Although nickel

enolates are traditionally thought of as C-bound,[5] there is recent precedent for reactive O-bound enolates.[6]

Unfortunately, there is not currently enough evidence to prove or disprove either proposition. The ^{1}H NMR spectra of reaction of **1** with olefins appears to be complicated by formation of **4,** which is paramagnetic.

[5] Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30–44.
[6] (a) Amarasinghe, K. K. D.; Chowdhury, S. K.; Heeg, M. J.; Montgomery, J. *Organometallics*, **2001**, *20*, 370–372. (b) Cámpora, J; Maya, C. M.; Palma, P.; Carmona, E.; Gutiérrez-Puebla, E.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1482–1483.