

## Low-Temperature Spectroscopic Observation of Chain Growth and Migratory Insertion Barriers in ( $\alpha$ -Diimine)Ni(II) Olefin Polymerization Catalysts

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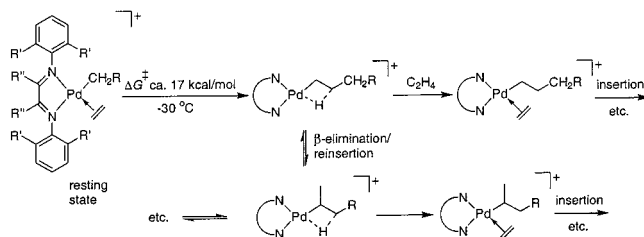
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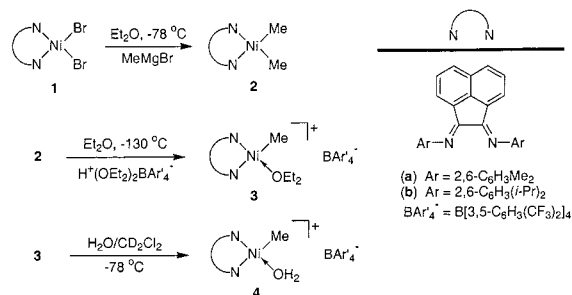
Access to well-defined transition metal olefin polymerization catalysts has allowed detailed mechanistic studies of this important class of catalysts. While much attention has centered on early transition metal  $d^0$  and lanthanide  $d^{0m}$  systems,<sup>1–7</sup> we have focused on developing single-site late metal catalysts. Our initial report<sup>8</sup> that Ni(II) and Pd(II) aryl-substituted  $\alpha$ -diimine complexes bearing bulky ortho substituents were capable of polymerizing ethylene and  $\alpha$ -olefins has stimulated extensive experimental<sup>9–20</sup> and theoretical<sup>21–27</sup> work on these catalysts. The Pd(II) systems yield highly branched polyethylene under typical polymerization conditions, while the microstructure of polyethylene produced by the Ni(II) systems is dependent on monomer concentration, reaction temperature, and ligand structure.

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### Scheme 1<sup>8</sup>



### Scheme 2



Extensive NMR spectroscopic studies of Pd(II) complexes<sup>8,28</sup> have established that (1) the catalyst resting state is an alkyl olefin complex and chain growth is dependent only on the rate of migratory insertion, (2) the barriers to migratory insertion are in the range 16.9–17.6 kcal/mol, and (3) the alkyl cation formed following insertion is a  $\beta$ -agostic complex and Pd can rapidly migrate along the chain via  $\beta$ -hydride elimination/reinsertion reactions. This process is responsible for the formation of branches in the polyethylene produced (see Scheme 1).

For use in polymerizations, analogous Ni-based cationic alkyl complexes are generated by the activation of nickel dihalide complexes with methylaluminoxane (MAO). The difficulty in preparation and the high reactivity of cationic nickel alkyl complexes has to date precluded mechanistic studies similar to those reported for the palladium systems. Here we describe the preparation of ( $\alpha$ -diimine)Ni(CH<sub>3</sub>)(solvent)<sup>+</sup>BAR'<sub>4</sub><sup>-</sup> (BAR'<sub>4</sub><sup>-</sup>  $\equiv$  B(3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub><sup>-</sup>) salts and the utilization of these complexes to study the mechanistic details of the chain growth process which allows a quantitative comparison of the Ni and Pd systems.

The ( $\alpha$ -diimine)NiMe<sub>2</sub> complexes **2a,b** are the precursors to the cationic nickel methyl complexes. These dimethyl complexes are air-sensitive and thermally unstable at 25 °C.<sup>29</sup> Isolation of the clean complexes can be accomplished by rapid filtration through Florisil at -78 °C.<sup>30</sup> Protonation of dimethyl complexes **2a,b** with [H<sup>+</sup>(OEt<sub>2</sub>)<sub>2</sub>][BAR'<sub>4</sub><sup>-</sup>] yields the cationic ether adducts **3** (Scheme 2). Rigorous exclusion of water is required to avoid the facile formation of aquo adducts **4**. Addition of stoichiometric amounts of water to CH<sub>2</sub>Cl<sub>2</sub> solutions of ether adducts **3** at -78 °C results in quantitative conversion to the aquo adducts **4**.

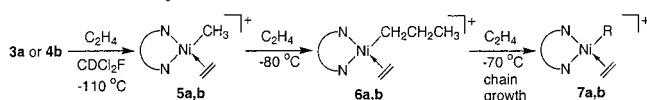
The kinetics of chain growth were monitored by generation of the nickel methyl ethylene complexes, **5a,b**, from the solvent adducts in CDCl<sub>2</sub>F, and the sequence of migratory insertion reactions was followed by low-temperature <sup>1</sup>H NMR spectroscopy as the alkyl chain grew (Scheme 3). Clean generation of the methyl ethylene complex **5a** from **3a** is not straightforward since migratory insertion of **5a** is competitive with associative displace-

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(29) Solutions of **2** in CD<sub>2</sub>Cl<sub>2</sub> eliminate ethane readily above 0 °C.

(30) The nickel dimethyl complexes were prepared using a procedure similar to that earlier reported: Svoboda, M.; tom Dieck, H. J. *Organomet. Chem.* **1980**, *191*, 321–328. See Supporting Information for experimental details.

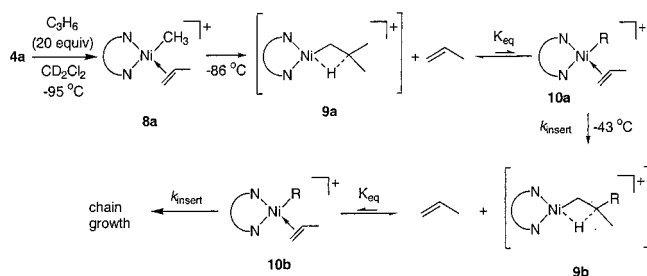
## Scheme 3. Ethylene Chain Growth Kinetics

Table 1. Olefin Migratory Insertion Barriers<sup>a</sup>

complex	first insertion		subsequent insertions	
	$k$ (temp)	$\Delta G^\ddagger$ , kcal/mol	$k$ (temp)	$\Delta G^\ddagger$ , kcal/mol
<b>5a</b>	$1.22 \times 10^{-3} \text{ s}^{-1}$ (-80.9 °C)	13.6	$2.80 \times 10^{-3} \text{ s}^{-1}$ (-71.4 °C)	14.0
<b>5b</b>	$3.08 \times 10^{-4} \text{ s}^{-1}$ (-92.9 °C)	13.3	$1.03 \times 10^{-3} \text{ s}^{-1}$ (-83.0 °C)	13.5
<b>8a</b>	$3.45 \times 10^{-4} \text{ s}^{-1}$ (-85.9 °C)	13.7	$1.5 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ (-43.4 °C)	see text

<sup>a</sup> Errors in  $\Delta G^\ddagger$  are estimated as  $\pm 0.1$  kcal/mol.

## Scheme 4. Propylene Chain Growth Kinetics



ment of ether by ethylene to form **5a**. Quantitative generation could be accomplished by treatment of **5a** with excess  $\text{C}_2\text{H}_4$  (20 equiv) at very low temperatures ( $-110$  °C). Displacement requires  $\sim 3$  h. The first insertion of ethylene was monitored at  $-80$  °C by measuring the first-order disappearance of the Ni- $\text{CH}_3$  singlet for **5a** ( $\delta -0.53$ ), and the first-order rate constant and activation barrier were determined (Table 1). Subsequent ethylene insertions were followed by measuring the zero-order rate of ethylene consumption at  $-70$  °C;<sup>31</sup> kinetic data are summarized in Table 1. The catalyst resting state during chain growth is the alkyl olefin complex **7a**. Following complete consumption of ethylene, a complex containing an agostic hydrogen ( $\delta -13.0$ , d,  $^2J_{\text{HH}} = 16$  Hz) is observed at  $-120$  °C, but the exact structure of this species has not yet been determined.

Kinetic measurements of chain growth using the sterically bulkier ether adduct **3b** proved difficult, as ether displacement to form **5b** was competitive with migratory insertion. Even though water displaces ether from **3b**, water was rapidly displaced from **4b** by ethylene at  $-130$  °C, to yield the desired methyl ethylene complex **5b**. Kinetic measurements of ethylene insertion in this bulkier complex were carried out as previously described; results are shown in Table 1.

Kinetic measurements of the migratory insertion of propylene were carried out using water adduct **4a** under the conditions shown in Scheme 4.<sup>32</sup> The first-order disappearance of methyl propylene complex **8a** was followed at  $-86$  °C. In contrast to the ethylene kinetic studies, no alkyl olefin resting state complex was observed following the first insertion. Instead, an agostic resting state species was observed at  $-120$  °C in  $\text{CDCl}_2\text{F}$ .<sup>33,34</sup> The reaction

(31) In monitoring chain growth of **5a** by  $^1\text{H}$  NMR spectroscopy, specific resonance assignments can be made for (diimine)Ni( $\text{C}_2\text{H}_4$ )( $\text{CH}_2$ ) $_n$  $\text{CH}_3^+$ :  $n = 2$  (first insertion product),  $n = 4$  (second insertion), and  $n = 6$  (third insertion). See Supporting Information for illustrated spectra.

(32) Water adduct **4a** was used instead of ether adduct **3a** because ether displacement by propylene is competitive with migratory insertion, whereas formation of methyl propylene complex **8a** from **4a** is rapid at  $-80$  °C.

was warmed to  $-43$  °C to measure the rate of subsequent propylene insertions. Pseudo-first-order kinetics are observed in the initial phases of consumption of the remaining 19 equiv of propylene from which a second-order rate constant can be calculated as  $0.15 \text{ M}^{-1} \text{ s}^{-1}$  ( $-43$  °C). Assuming that species **10** and the resting state **9** are in equilibrium and that the  $\Delta G^\ddagger$  for migratory insertion of **10a** is  $\sim 14$  kcal/mol ( $k_{\text{insertion}}$  estimated as  $0.24 \text{ s}^{-1}$ ,  $-43$  °C), the ratio of species **9** to **10** is  $\sim 2000$  under these conditions ( $K_{\text{eq}}$  estimated as 0.0017).

The results reported here allow a detailed comparison of the Pd and Ni analogues and direct comparison of insertion barriers to theoretical calculations. The (diimine)Pd( $\text{C}_2\text{H}_4$ )R<sup>+</sup> systems previously reported<sup>8</sup> exhibit barriers in the range 16.9–17.6 kcal/mol; thus, the barriers for the Ni analogues are  $\sim 4$ –5 kcal/mol less. These barrier differences translate to differences in turnover frequencies of  $\sim 10^3$ – $10^4 \text{ h}^{-1}$  at 25 °C, consistent with observations.<sup>8</sup> Assuming a negligible  $\Delta S^\ddagger$  for migratory insertions, the predicted TOF of **5b** is  $\sim 1700 \text{ s}^{-1}$  at 35 °C and compares favorably<sup>35</sup> to an observed TOF of  $800 \text{ s}^{-1}$  for the catalyst generated by MAO activation in toluene.<sup>36</sup> As an additional comparison, it is interesting to contrast the  $\Delta\Delta G^\ddagger$  of 5 kcal/mol for ethylene insertion for these Group 10 Ni and Pd complexes to the  $\Delta\Delta G^\ddagger$  of 8 kcal/mol measured for the Group 9 Co and Rh complexes [Cp<sup>\*</sup>M(P(OMe)<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>)(Et)<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] (M = Co, Rh).<sup>37</sup> Theoretical calculations by Ziegler<sup>23</sup> estimate the insertion barrier in a complex similar to **5b** to be 13.2 kcal/mol ( $\Delta H^\ddagger$ ), which is in good agreement with the range of values observed here (Table 1). In addition, barriers to ethylene insertion are 0.3–0.5 kcal/mol lower for the complex bearing the bulkier 2,6-(diisopropyl)aryl-substituted diimine ligand. Theoretical calculations<sup>21,23</sup> suggest that increased steric bulk of the diimine ligand aryl substituents leads to an increase in the ground state energy of the resting state species relative to the migratory insertion transition state, and consequently, lower migratory insertion barriers are expected with bulkier diimine substituents. Consistent with the observations for Pd systems, the barriers to insertion in the methyl ethylene complexes are quite similar to barriers for subsequent insertions. Also comparable to the Pd systems, the barrier to propylene insertion in the methyl propylene complex **8a** is similar to the insertion barrier in the methyl ethylene complex **5a**. The much lower TOFs observed for  $\alpha$ -olefin polymerizations (as compared to ethylene) in the Ni systems studied here are a consequence of the fact that after methyl migration the catalyst resting state is now the agostic species and chain growth becomes first-order in  $\alpha$ -olefin.

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**Supporting Information Available:** Synthetic procedures and NMR spectroscopic data for complexes **2**–**8**, sample NMR spectra, and kinetic data for ethylene and propylene insertions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(33) A  $\beta$ -agostic resting state in polymerization of cyclopentene using Ni and Pd diimine complexes has been reported: McLain, S. J.; Feldman, J.; McCord, E. F.; Gardner, K. H.; Teasley, M. F.; Coughlin, E. B.; Sweetman, K. J.; Johnson, L. K.; Brookhart, M. *Macromolecules* **1998**, *31*, 6705–6707.

(34) Species **9a** is highly dynamic and exhibits broad agostic signals even at  $-120$  °C at  $-12.3$ ,  $-12.5$ , and  $-13.2$  ppm in a  $\sim 2:6:2$  ratio. From bulk polymer analyses, both 1,2 and 2,1 modes of insertion are observed; thus **9a** may exist as a dynamic, interconverting mixture of as many as five agostic nickel-butyl complexes. Structural assignments are not possible at this stage. Only one isomer is shown in Scheme 4 for simplicity.

(35) The two complexes being compared were measured in different solvents ( $\text{CDCl}_2\text{F}$  vs toluene) and had different counterions.

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