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The Mechanism of Polymerization of Butadiene by “Ligand-Free” Nickel(II) Complexes

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The stereoselective polymerization of butadiene (BD) has been investigated using a variety of transition metal[1−4] and lanthanide catalysts.[5] Numerous Ni(II) π-allyl complexes have been used as initiators,[6−9] but the most reactive one identified to date is “ligand-free” Ni(II) wrap-around complex **A** (Scheme 1), which yields polybutadiene (PBD) exhibiting 93% *cis*-1,4 enchainment.[10,11]

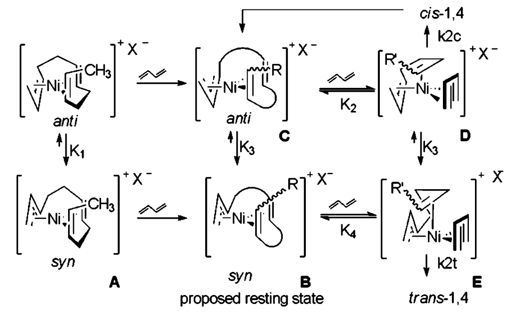
The chain growth mechanism proposed by Taube and Tobisch, based largely on DFT calculations,[12−15] is shown in Scheme 1. The most stable form of the propagating species (the catalyst resting state) is assumed to be *syn* complex **B** analogous in structure to initiator **A**. To achieve a *cis*-1,4 enchainment, isomerization to the *anti*-allyl species **C** must occur; C−C coupling is proposed to proceed from η^4-BD complex **D** formed from **C**. A key finding, based on DFT results, is that insertion is driven by a fifth ligand provided by the π-bond of the growing chain. Species **E** is proposed to account for *trans*-1,4 enchainment.

We report here low-temperature observation of highly reactive ligand-free π-allyl complexes $[(\text{allyl})\text{Ni}][\text{B}(\text{Ar}_\text{F})_4]$ (**1**) and $[(2\text{-methallyl})\text{Ni}][\text{B}(\text{Ar}_\text{F})_4]$ (**2**),[16] the first observation of η^4-BD and η^4-isoprene (IP) (allyl)Ni complexes $[(2\text{-methallyl})\text{Ni}(\eta^4\text{-BD})][\text{B}(\text{Ar}_\text{F})_4]$ (**3**) and $[(2\text{-methallyl})\text{Ni}(\eta^4\text{-IP})][\text{B}(\text{Ar}_\text{F})_4]$ (**4**), and their reactions with BD, which provide a modified, more complete mechanism of BD polymerization by ligand-free Ni(II) systems.

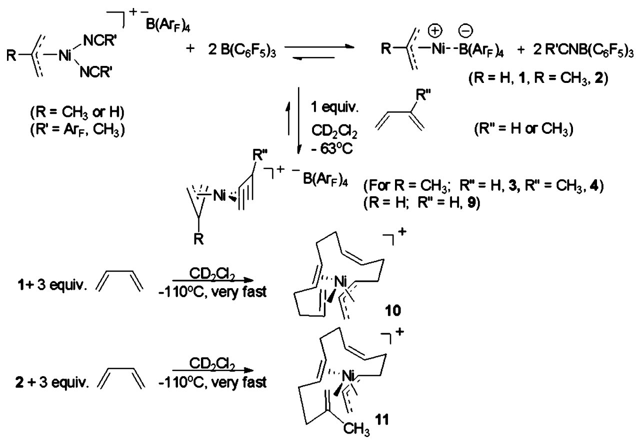
As shown in Scheme 2, reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with $[(\text{allyl})\text{Ni}(\text{NCR}')_2][\text{B}(\text{Ar}_\text{F})_4]$ (R′ = Me, **5**, or 3,5-$(\text{CF}_3)_2\text{C}_6\text{H}_3$, **6**) or the analogous 2-methallyl derivatives (**7**, **8**) at −60 °C generates the ligand-free complex **1** or **2** (in equilibrium with the starting catalyst), which were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy.[17] Ni is coordinated to a single aryl ring; separate ^{1}H and ^{19}F resonances are observed for the coordinated and three noncoordinated rings. ^{19}F VT NMR experiments (−60 to −18 °C) showed the barriers to intramolecular Ni migration among the rings as $\Delta G^\ddagger = 11.4$ kcal/mol for **1** and 11.8 kcal/mol for **2**. Exchange of coordinated $\text{B}(\text{Ar}_\text{F})_4^-$ with free $\text{B}(\text{Ar}_\text{F})_4^-$ occurs on the NMR time scale above 0 °C.

Complexes **1** and **2** react at −80 °C with 1−2 equiv of BD or IP to yield equilibrium quantities of π-allyl η^4-diene complexes $[(\text{allyl})\text{Ni}(\eta^4\text{-BD})]^+$ (**9**), $[(2\text{-methallyl})\text{Ni}(\eta^4\text{-BD})]^+$ (**3**), and $[(2\text{-methallyl})\text{Ni}(\eta^4\text{-IP})]^+$ (**4**).[17] Formation of the π-allyl diene complexes is favored for 2-methallyl as the allyl partner and IP as the diene partner, thus **4** can be formed nearly quantitatively from **2**.[17] Warming **4** to −30 °C results in no observable insertion; however, treatment of **4** (−50 °C) with BD results in rapid insertion and BD consumption supporting Taube and Tobisch’s contention that a fifth ligand drives insertion. Treatment of either **1** or **2** with 3 equiv of BD results in rapid insertion of 3 equiv of diene at temperatures as low as −110 °C to yield a single species $\text{Ni}(\text{C}_{15}\text{H}_{23})^+\text{B}(\text{Ar}_\text{F})_4^-$ (**10**) and $\text{Ni}(\text{C}_{16}\text{H}_{25})^+\text{B}(\text{Ar}_\text{F})_4^-$ (**11**),[17] respectively. No intermediates were detected in these reactions.

Scheme 1



Scheme 2



Two-dimensional HMQC and ^{1}H−^{1}H COSY NMR techniques established wrap-around structures as shown in Scheme 2 for complexes **10** and **11**.[17,18] The ^{1}H NMR spectrum of **10** is shown in Figure 1, and the molecular structure was verified by X-ray crystallography (Figure 2).[17] The π-allyl moiety is in an *anti* configuration, and all C−C double bonds are *cis* as expected from coupling of an *anti* π-allyl unit with BD. The coordinated π-bonds (C1−C2, C5−C6) exhibit C−Ni distances between 2.19 and 2.29 Å, while the noncoordinated π-bond shows C−Ni distances of 2.47 and 2.68 Å.

We expected that species analogous to **10** and **11** would be the catalyst resting states wherein the growing chain would be attached at C1. This proved *not* to be the case. Exposure of **10** to 45 equiv of BD at −30 °C results in uptake of BD and formation of a new complex, which contains an *anti*-π-allyl Ni unit and a coordinated vinyl group from 1,2 insertion (Figure S4). After ca. 15 turnovers, only 50% of **10** has been consumed (and after ca. 38 turnovers, 75% consumption), indicating the initial insertion of BD into **10** is slow relative to subsequent insertions. Reaction of **11** with BD is more straightforward and clarifies the situation (Scheme 3). Treatment with BD (42 equiv) at −30 °C results in rapid uptake of 15 equiv of BD and clean quantitative, formation of the vinyl-coordinated species (**12**). The hydrogens of the free vinylidene end group (δ 4.68 and 4.65) integrate for 1.0 H each relative to the

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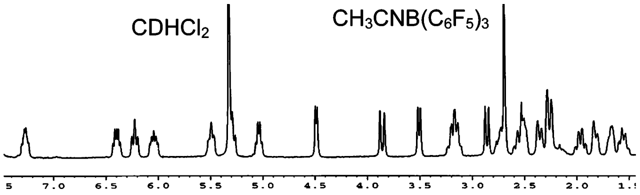


Figure 1. ^{1}H NMR of complex **10** (500 MHz) in CD$_2$Cl$_2$ at -30 °C.[17]

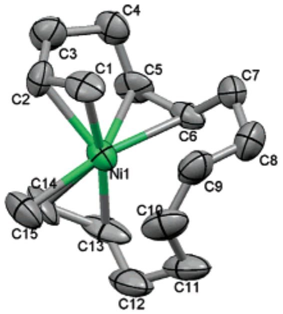
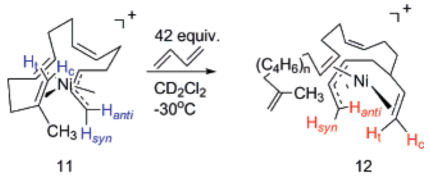
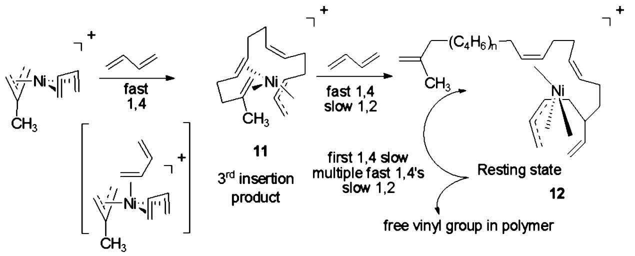


Figure 2. Molecular structure of complex **10**. Atomic displacement ellipsoids are drawn at 50% probability. Selected bond lengths (Å): Ni(1)−C(1) 2.189(8), Ni(1)−C(2) 2.218(8), Ni(1)−C(5) 2.248(7), Ni(1)−C(6) 2.285(7), Ni(1)−C(9) 2.678, Ni(1)−C(10) 2.465(10), Ni(1)−C(13) 2.087(8), Ni(1)−C(14) 2.051(8), Ni(1)−C(15) 2.116(9). H atoms and B(Ar$_F$)$_4^-$ are omitted.

Scheme 3



Scheme 4



coordinated vinyl end group protons (δ 3.95 (d, $J = 16.5$ Hz), 3.65 (d, $J = 9.0$ Hz)) and the *syn* (δ 4.46 (d, $J = 7.5$ Hz)) and *anti* (δ 2.94 (d, $J = 13.5$ Hz)) π-allyl signals (Figure S3).

Scheme 4 summarizes a proposed mechanism for PBD chain growth using catalyst **11**. Complex **11** initiates rapidly, and multiple, fast 1,4 BD insertions occur until a 1,2 insertion takes place to form a stable vinyl-coordinated species, **12**. Subsequent insertions occur via a slow 1,4 insertion of BD into **12** followed by a sequence of rapid 1,4 insertions until another 1,2 insertion takes place and the stable vinyl-coordinated species **12** is regenerated. In the case of **10**, the terminal unsubstituted double bond (C1−C2) is more strongly coordinated then the 2-Me-substituted double bond in **11**; thus, the first 1,4 insertion of BD is slow relative to subsequent 1,4 insertions, and a considerable amount of **10** remains after multiple BD insertions along with formation of a vinyl-coordinated species analogous to **12**. NMR studies establish the vinyl-coordinated species to have the same structures with exception of the end group[17] (Figures S3 and S4).

These experiments show that the true catalyst resting state is a stable vinyl-coordinated species, **12**, formed following a (rare) 1,2 insertion.[19] The *cis*-1,4 insertions may well proceed through a Taube/Tobisch-type precursor **D** (Scheme 1), but if so, it seems likely that species analogous to complexes **10** or **11**, rather than **C**, would result.

Polymerization of BD, catalyzed by in situ generated complex **2**, was carried out in CH$_2$Cl$_2$ at -30 °C under argon yielding PBD, which has the following microstructure: 94% *cis*-1,4, 5% *trans*-1,4, and 1% 1,2 enchainment. The M_n values are approximately 8000 with a PDI of 1.5.[17]

In summary, the identities of key intermediates and catalyst resting states in the polymerization of BD by ligand-free (allyl) Ni(II) species have been observed for the first time. Cationic (2-methallyl)Ni(II) complexes of η^4-BD and η^4-IP were prepared and characterized by low-temperature NMR. These highly reactive species insert 3 equiv of BD or IP at very low temperatures to yield stable wrap-around complexes of types **10** and **11**. Although these species insert BD, they do not represent the catalyst resting state(s). The resting states are formed following a 1,2 BD insertion and exhibit coordination of the resulting vinyl group as shown in structure **12**.

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Supporting Information Available: Experimental procedures and characterization of complexes **1**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) See Supporting Information.
(18) Reaction of complex **10** with 2 equiv of NC(C$_6$H$_3$(CF$_3$)$_2$) results in decoordination of the olefins as evidenced by the downfield shifts in the ^{1}H NMR spectrum. See Supporting Information.
(19) From the presence of ca. 1% vinyl groups in the PBD formed, on average, 100 1,4 insertions must occur prior to a 1,2 insertion. These ratios are consistent with our NMR observations.

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