Reaction of Palladium 1,5-Cyclooctadiene Alkyl Chloride with Norbornene Derivatives: Relevance to Metal-Catalyzed Addition Polymerization of Functionalized Norbornenes

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Summary: The insertions of norbornene, bicyclo[2.2.1]-hept-5-ene-endo-2-carboxylic acid ethyl ester, bicyclo-[2.2.1]hept-5-ene-exo-2-carboxylic acid ethyl ester, and bicyclo[2.2.1]hept-5-enyl-endo-2-methyl acetate into the palladium−methyl bond of (η^4-cycloocta-1,5-diene)chloromethylpalladium(II) were found to proceed at similar rates, with the product in every case being derived from insertion through the exo face.

Metal-catalyzed addition polymerization of functionalized alkenes is an area of great current interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise nonpolar can greatly enhance the range of attainable properties.[1] One particular area of interest has been the addition polymerization of functionalized bicyclo[2.2.1]hept-5-ene (norbornene) derivatives.[2] The resultant polymers exhibit superior etch resistance and thermal stability and are attractive candidates for deep UV photolithography.[3] A key problem in the development of metal-catalyzed routes to functionalized polyalkenes is the coordination of the functionality present both in the monomer and in the resulting polymer. Because they are synthesized by Diels−Alder reactions, functionalized norbornene derivatives sold commercially consist of exo and endo isomers with the latter predominating (approximate molar ratio: 1:3 to 1:4).[4] Earlier work in other laboratories,[5] as well as our own,[6] have shown that the endo-functionalized norbornenes are polymerized more slowly. The slow polymerization rate for commercial functionalized norbornene mixtures has previously been ascribed to the formation of a chelate by coordination of the functionality to the metal center and the C=C bond
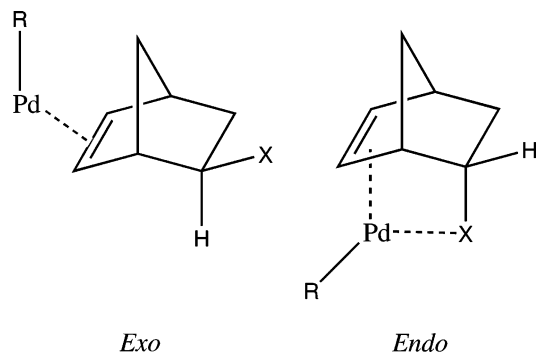

Figure 1. Modes of bonding for functionalized norbornene derivatives (X = coordinating functionality).

along the endo face (Figure 1).[5,6] This has two detrimental effects on polymerization. First, chelation strengthens the metal−alkene interaction, thereby raising the barrier for the insertion step. Second, it forces insertion through the endo face, in sharp contrast to the known propensity for norbornene to insert into metal−carbon bonds through the less hindered exo face.[7] Indeed, we had earlier isolated and characterized a platinum complex formed by the insertion of bicyclo-[2.2.1]hept-5-ene-*endo*-2-carboxylic acid ethyl ester into a Pt−H bond through the endo face.[6b]

The catalyst systems for which the relative exo versus endo reactivity have been reported are cationic. Theoretical calculations by Ziegler show that while the interaction of an oxygen functionality (e.g., an ester group) with the metal center is weaker in neutral complexes in comparison with the corresponding cationic species, the bonding of the vinyl functionality is not significantly affected, because the weaker alkene to metal charge transfer in the neutral complex is compensated by stronger metal to alkene back-bonding.[8] Here, we report the results of our studies encompassing the insertion of norbornene derivatives into palladium−carbon bonds in neutral (η^4-cycloocta-1,5-diene)chloromethylpalladium(II). In sharp contrast to the cationic norbornene polymerization systems, the coordination of alkene is favored over an ester functionality. Thus, no

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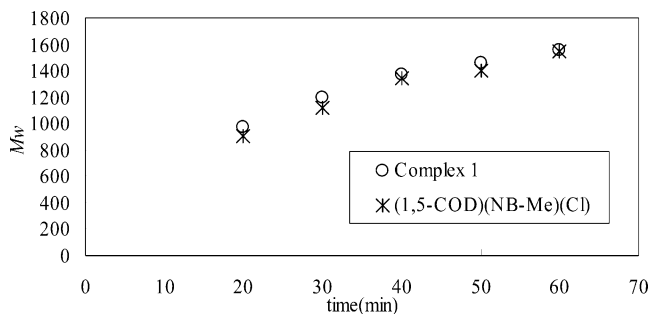(8) Michalak, A.; Ziegler, T. *Organometallics* **2001**, *20*, 1521−1532.

Figure 2. Plot of the molecular weight of oligo(nor-bornene) versus time. Reaction conditions: catalyst (2 × 10^{-4} mol), norbornene (5 × 10^{-2} mol), chlorobenzene (10 mL), 60 °C.

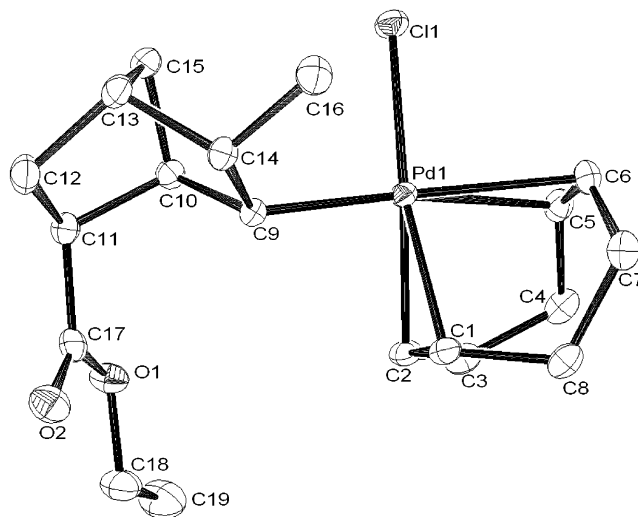**Figure 3.** ORTEP view of the *endo*-5-ethyl ester 2-nor-bornene inserted complex (1,5-cyclooctadiene)Pd(Cl)(3-CH$_3$-5-C(=O)OC$_2$H$_5$C$_7$H$_8$), showing 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C9, 2.0717(19); Pd1−Cl1, 2.3486(7); Pd1−C1, 2.184(2); Pd1−C2, 2.161(2); Pd1−C5, 2.442(2); Pd1−C6, 2.367(2); C9−Pd1−Cl1, 98.05-(6); C14−C9−Pd1, 115.90(12); C16−C14−C13, 113.28(17).

coordination of the pendant functionality is observed and the insertion invariably occurs through the exo face. This system is the first which exhibits similar insertion rates for norbornene and its *exo-* and *endo*-5-ester derivatives bicyclo[2.2.1]hept-5-ene-*exo*-2-carboxylic acid ethyl ester and bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid ethyl ester, thereby supporting Ziegler's calculations and the notion that catalytic polymerization of functionalized monomers may be more facile by moving from a cationic to a less electrophilic, neutral metal center.

The neutral palladium(II) compound (η^4-cycloocta-1,5-diene)chloromethylpalladium(II)[9] (**1**) was found to be effective for the oligomerization of norbornene. An increase in molecular weight was observed with time, with M_w reaching 1600 (versus polystyrene standard) in approximately 60 min at ambient temperature (Figure 2).[10] The behavior suggests that the oligomerization was at least quasi-"living". The relatively slow reaction rate gave us the opportunity to examine the mechanism of norbornene insertion into the palladium−carbon bond in some detail. The products of the reaction of **1** with norbornene (NB), bicyclo[2.2.1]hept-5-ene-*endo*-2-carboxylic acid ethyl ester and bicyclo[2.2.1]hept-5-ene-*exo*-2-carboxylic acid ethyl ester (*endo* and *exo*-Etester-NB, NB-COOCH$_2$CH$_3$), and bicyclo[2.2.1]hept-5-enyl-*endo*-2-methyl acetate (*endo*-MeOAc-NB, NB-CH$_2$OC(O)CH$_3$) were isolated,[11] and their structures were determined

by single-crystal X-ray analysis. In every case, the insertion of the monomer into the palladium−carbon bond had occurred through the exo face with no evidence for interaction of the ester functionality with the metal (e.g., Figure 3). Interestingly, in the crystals formed from the last three monomers, of the two possible regioisomers with the metal and the ester group in 1,3- and 1,4-relationships, only the former isomer was observed. The oligomerization of norbornene by the insertion product derived from **1** and NB was also examined. An increase in molecular weight with a slope similar to that seen starting with **1** was observed (Figure 2), strongly suggesting that the initial insertion product was an intermediate in norbornene oligomerization by **1**.

The kinetics of the reaction of **1** with NB and *exo-* and *endo*-EtEster-NB was investigated by ^{1}H NMR spectroscopy for up to 50% monomer conversion.[12] In each case, the reaction was first order in the monomer (Figure 4) with rate constants of 2 × 10^{-5}, 1 × 10^{-5}, and 5 × 10^{-6} s^{-1}, respectively. The simplest mechanism that accounts for this observation involves alkene coordination to the fifth coordination site of the metal, followed by insertion into the cis metal−carbon bond. The effect of potential coordinating moieties, C=C, chloride, and ester group, on the rate of norbornene polymerization (=rate of insertion) was probed by the addition of 1,5-cyclooctadiene, NR$_4$$^+Cl^-$, and ethyl acetate. As shown in Table 1, the extent of inhibition clearly

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(10) General procedure for the oligomerization reaction: in a 100 mL Schlenk flask, **1** was dissolved in chlorobenzene and norbornene or its derivative was introduced into the flask (see Figure 2 for amounts). The reaction mixture was stirred at the desired temperature, and aliquots were removed at fixed time intervals and quenched with methanol. The precipitated polymer was filtered, washed with methanol, and dried under vacuum overnight.

(11) Typical reaction: to **1** (100 mg, 0.38 mmol) in methylene dichloride (5 mL) was added 5-*endo*-ethyl ester norbornene (63 mg, 0.38 mmol) dropwise at room temperature. The solution was stirred for 2 h at room temperature. After filtration to remove any metallic palladium, evaporation of solvent in vacuo yielded a yellow oil, which solidified from an ether/pentane (1:1, v/v) mixture in the freezer (−20 °C). Upon filtering and washing with pentane, the compound **3** was obtained as a yellow solid. Recrystallization from methylene dichloride by slow evaporation gave a yellow crystalline solid which was suitable for X-ray crystal structure analysis. Yield: 0.12 g, 74%. ^{1}H NMR (CD$_2$Cl$_2$, ppm): 5.87 (m, 2H, −C*H*=C*H*−), 5.01 (m, 2H, −C*H'*=C*H'*−), 4.12 (m, 2H, −OC*H$_2$*CH$_3$), 2.72−2.43 (m, 11H, two =CHC*H$_2$*C*H$_2$*CH=, two bridgehead C*H*, and −C*H*C(=O)O−), 1.86 (d, 1H, PdC*H*−), 1.75 (m, 1H, CH$_3$C*H*−), 1.73 (m, 1H, *exo*-C*H*H−), 1.45 (m, 1H, *endo*-C*H*H−), 1.44 (d, 3H, C*H$_3$*−), 1.31 (t, 3H, −OCH$_2$C*H$_3$*), 1.20 (m, 2H, *syn* and *anti* apical −CH*H'*− and −CH*H'*−). ^{13}C NMR (CD$_2$Cl$_2$) (ppm): 125.8 (=C*H*CH$_2$CH$_2$CH=), 60.4 (−O*C*H$_2$CH$_3$), 49.1 (*C*H$_3$C*H*−), 47.4 (*C*H), 45.9 (Pd−*C*H−), 37.3 (apical *C*H$_2$), 32.0 (*C*H$_2$), 31.5, 31.4 (−*C*H=*C*H−), 27.8, 27.7 (−*C'*H=*C'*H−) 22.7 (*C*H$_3$−), 14.7 (−OCH$_2$*C*H$_3$).

(12) General procedure for NMR experiments: in a drybox under a nitrogen atmosphere, **1** (10 mg) was weighed into an NMR tube. CD$_2$Cl$_2$ (0.1 mL) was added to the NMR tube. The tube was then capped with a septum, removed from the drybox, and cooled to ca. −90 °C using a liquid nitrogen/acetone slurry. A portion of 10 wt % norbornene or functionalized norbornene in CD$_2$Cl$_2$ solution (1 mL) was then added to the NMR tube via a gastight syringe at that temperature, and the septum was wrapped with Parafilm. The tube was shaken very briefly and transferred to the NMR probe. For conversion kinetics, NMR spectra were acquired every 15 min at the desired temperature. TMS was employed as an external standard.
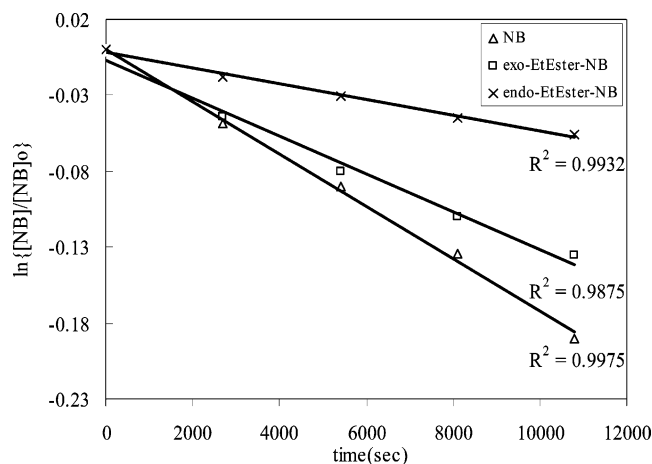
Figure 4. Plot of $\ln\{[NB]/[NB]_0\}$ versus time. Reaction conditions: **1** (3.7×10^{-5} mol), norbornenes (7.5×10^{-4} mol), CD_2Cl_2 (1 mL), 23 °C.

Table 1. Effect of Additives on the Polymerization of Norbornene Using (1,5-COD)PdMeCl (1)[a]

additive (amt (equiv))	amt of norbornene (equiv)	yield[b] (%)
none	200	85
1,5-COD[c] (20)	200	n.r.
1,5-COD[c] (200)	200	n.r.
Bu$_4$NCl (20)	200	14
MeCO$_2$Et (20)	200	67
MeCO$_2$Et (200)	200	58

[a] In all cases the amount of (1,5-COD)PdMeCl (**1**) was 1.13×10^{-4} mol. [b] Isolated solid polymer. Reaction conditions: 60 °C, 2 h, PhCl (7 g). [c] 1,5-cyclooctadiene.

decreases in the order $C=C > Cl^- > RC(=O)OR$, with the ester group having minimal effect on the polymerization. This observation is in stark contrast to the cationic norbornene polymerization systems, whose activities are sharply attenuated by the presence of a

coordinating solvent such as ethyl acetate.[6] One interesting aspect of the above chemistry is that the insertion of a C=C bond of 1,5-cyclooctadiene is never observed. Presumably, the norbornene C=C bond is more reactive due to greater ring strain.

Taken together, the twin observations that (a) ethyl acetate does not inhibit norbornene polymerization and (b) norbornene derivatives with pendant endo ester functionalities insert into the metal–alkyl bond through the exo face with rates similar to that seen with norbornene clearly demonstrate that there is no coordination of the ester group, and in this respect, the less electrophilic, neutral metal species have an advantage over the corresponding cationic species. However, the neutral compounds described above exhibit reaction rates that are too slow for a practical polymerization system.

Supporting Information Available: Text giving experimental procedures, NMR data, and details of crystal structure determinations, tables of positional parameters for atoms, bond distances and angles, and anisotropic thermal parameters, and CIF files for the crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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