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Methacrylate Insertion into Cationic Diimine Palladium(II)−Alkyl Complexes and the Synthesis of Poly(alkene-*block*-alkene/carbon monoxide) Copolymers

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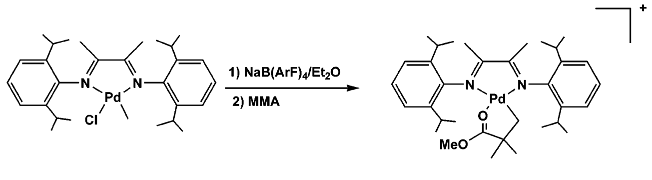
Summary: The reaction of cationic Pd(II) diimine complex $[(N^{\wedge}N)Pd(Me)(L)][B(Ar_f)_4]$ *(*$(N^{\wedge}N) = $ *2,3-bis(2,6-di-isopropylphenylimino)butane,* $Ar_f = 3,5\text{-}(CF_3)_2C_6H_3$, $L = Et_2O$*) with methyl methacrylate results in 1,2-insertion regiochemistry that is opposite of that observed with methyl acrylate. The enthalpy of activation for MMA insertion is 4 kcal/mol higher than that for the corresponding MA insertion. The MMA-inserted complex can be employed for ethene or 1-hexene homopolymerization and their alternating copolymerization with carbon monoxide. Further, the quasi-living nature of the polymerizations allows the synthesis of poly(hexene-b-hexene/CO) and poly(ethene-b-ethene/CO) copolymers.*

The catalytic copolymerization of polar vinyl monomers (e.g., acrylates and methacrylates) with unfunctionalized alkenes is an area of great current interest,[1] because of new desirable properties that may emerge from such copolymers. Due to their lower oxophilicity and relatively high functionality tolerance, late transition metal-based systems have been the focus of much of the recent work in the area. However, the interaction of the oxygen functionality of the polar vinyl monomer with the metal center and formation of cyclic chelates are the most commonly cited problems that have stymied the development of suitable catalysts. Additionally, for electronic reasons, acrylates have a strong preference for 2,1-insertion into metal−carbon bonds.[2] This insertion regioselectivity generates a metal−alkyl species that is particularly prone to homolysis because of the enhanced stability of the resultant alkyl radical, one that is essentially the same as the propagating species in radical-initiated acrylate polymerization.[3]

In principle, it should be possible to override the electronic preference for 2,1-insertion by increasing the steric crowding around the metal through the use of bulkier monomers and/or ligands. The ensuing alkyl will no longer have an ester functionality on the α-carbon, making it less prone to undergo metal−carbon bond homolysis due to lower stability of the resultant radical. Another potential bonus of tuning the catalysts to undergo 1,2-insertion of acrylate monomers is to be found in the case of methacrylates, a class of monomers that has not been shown to undergo metal-catalyzed addition polymerization. When a methacrylate inserts in a 2,1 fashion, the ensuing alkyl bears both an ester functionality and a methyl group on the α-carbon, resulting in extreme steric congestion. This greatly disfavors further monomer insertion but offers five *β*-hydrogens resulting in facile elimination with an methacrylate-derived end group.[3a,b,4] On the other hand, incorporation of a methacrylate with a 1,2 regioselectivity would potentially make it a good monomer since the ensuing alkyl would have no substituents on the α-carbon and would contain *no β*-hydrogens.

Scheme 1. Synthesis of MMA-Inserted Complex 2



(1,2-insertion)

2

The cationic Pd(II) diimine ligand based system $[(N^{\wedge}N)Pd(Me)(L)][B(Ar_f)_4]$, **1** ($(N^{\wedge}N) = $ 2,3-bis(2,6-di-isopropylphenylimino)butane, $Ar_f = 3,5\text{-}(CF_3)_2C_6H_3$, $L = Et_2O$), reported by Brookhart is among the very few systems that copolymerize acrylates via insertion mechanism.[5] The distinctive feature of this system is the 2,1-insertion of acrylate and subsequent rearrangement to form a six-membered cyclic chelate. The rearrangement pushes the ester functionality away from the α-carbon and prevents facile metal−carbon bond homolysis. This unique feature of the system prompted us to examine the corresponding insertion and polymerization of methacrylate. Our hope was that the bulkier methacrylate monomer may undergo 1,2-insertion, thereby opening the possibility of copolymerizing methacrylates by this system.

The reaction of complex **1** with 2 equiv of methyl methacrylate (MMA) displaces ether and results in formation of 1,2-inserted product $[(N^{\wedge}N)Pd(CH_2{-}C(Me)_2{-}C(O)OMe][B(Ar_f)_4]$, **2** (Scheme 1). The ^{1}H NMR spectrum (Figure 1) confirmed the formation of complex **2**. The methyl protons on the C-2 carbon of inserted MMA appear as a singlet at 1.1 ppm, whereas the $Pd{-}CH_2$ protons appear at 1.32 ppm. The $-C(O)OCH_3$ protons

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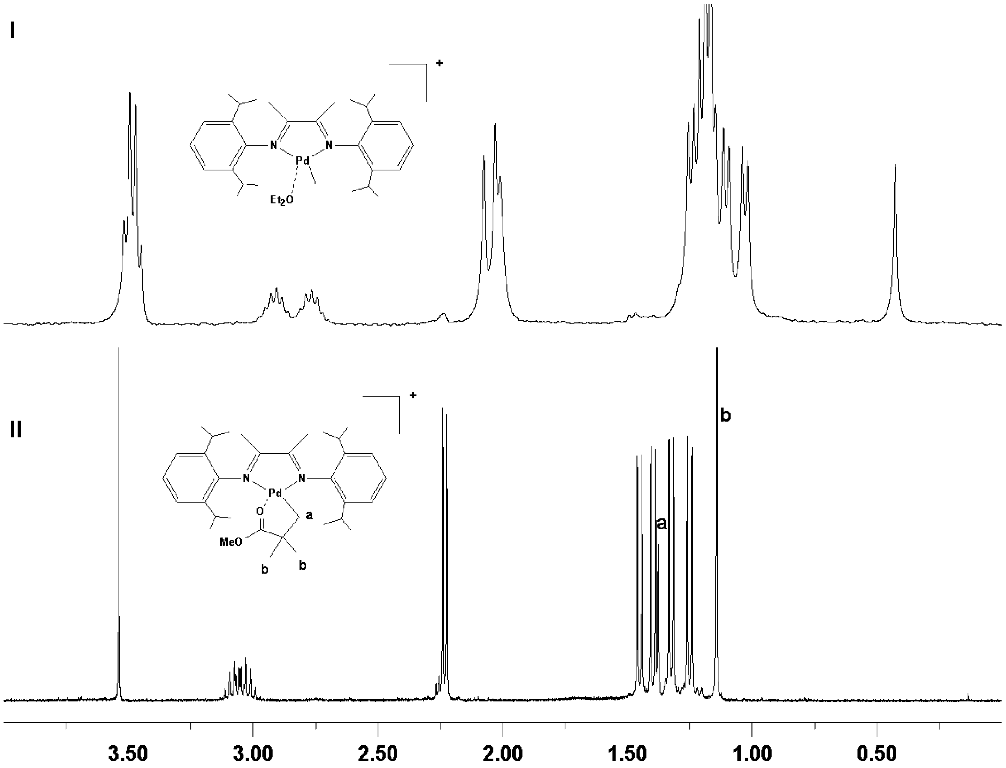


Figure 1. ^{1}H NMR (CD_2Cl_2) spectra of **1** (I) and MMA-inserted complex **2** (II).

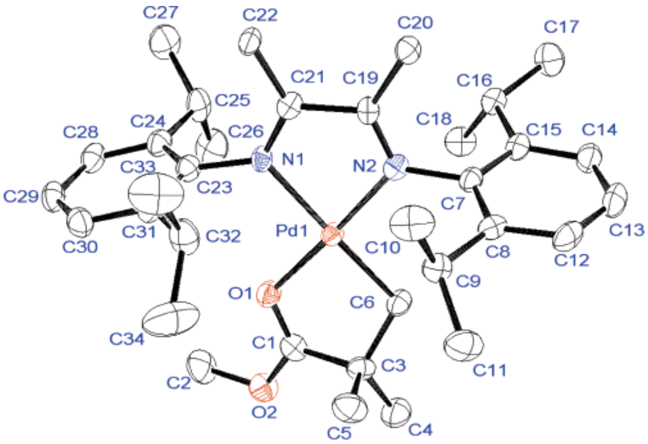


Figure 2. ORTEP diagram of the MMA-inserted complex **2**. The hydrogen and $BArF_4$ anion are omitted for clarity.

show a sharp singlet at 3.5 ppm and are slightly shifted upfield from the corresponding monomer. The structural assignment was further confirmed from ^{13}C NMR and DEPT-135 NMR spectra. The FT-IR analysis showed the carbonyl absorbance at 1599 cm^{-1} for complex **2**. Finally, the 1,2-insertion of MMA in the $Pd-CH_3$ bond was established by single-crystal X-ray analysis. The X-ray quality single crystals were grown from methylene chloride/pentane. The crystal structure of complex **2** is shown in Figure 2. The structure clearly shows 1,2-insertion of MMA and the formation of a five-membered cyclic chelate with Pd to O1 and C6 distances of 2.04(4) and 2.014(5) Å, respectively. The methyl group from the starting complex migrates to the C2 carbon of MMA, and the observed bond angles for Pd1−C6−C3 and C4−C3−C5 carbons are 107.3(4)° and 109.5(5)°, respectively.

The kinetics of MMA insertion was studied under pseudo-first-order conditions and suggested that the insertion of MMA is first order. Figure 3 shows the Eyring plot for MMA insertion, and the obtained data gave $\Delta H^{\#} = 16.4$ kcal/mol and $\Delta S^{\#} = -12.7$ eu; the corresponding values for methyl acrylate (MA) insertion are 12.1 kcal/mol and −14.1 eu as reported by Brookhart and co-workers.[5b]

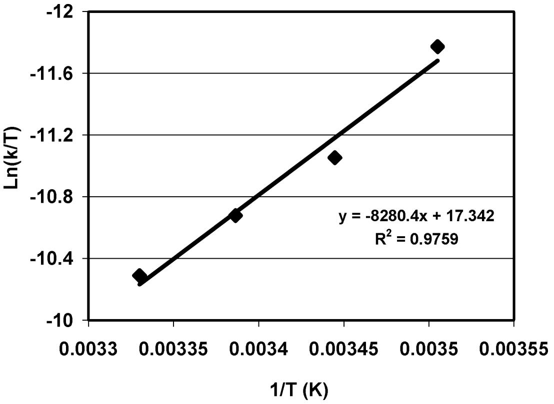
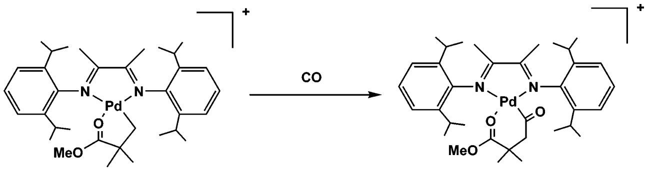


Figure 3. Eyring plot for MMA insertion into the $Pd-CH_3$ bond of **1**.

Unlike the copolymerization of MA with ethene reported by Brookhart, attempts at the copolymerization of MMA with ethene resulted in the formation of essentially branched polyethene (PE). We ascribe the failure to incorporate MMA into the polymer chain to the significantly higher enthalpy of activation for MMA insertion compared to MA insertion. Clearly, the same steric effect that forces the 1,2-insertion of the bulkier MMA also severely attenuates its insertion rate.

The ability of the MMA-inserted complex, **2**, to initiate alkene homopolymerization and alkene/carbon monoxide copolymerization was examined. Carbon monoxide (CO) was found to insert into the $Pd-CH_2$ bond of **2** as indicated by the shift in CH_2 protons from 1.32 to 2.42 ppm in the ^{1}H NMR spectrum (Scheme 2). However, the insertion step is reversible, as shown by the re-formation of the starting complex **2** upon removal of CO from the solution. As the CO concentration in the solution is decreased, the ^{1}H NMR spectrum shows the formation of

Scheme 2. Schematic Presentation of CO Insertion in Complex 2



2 **3**

starting MMA-inserted complex. The addition of both CO and an alkene to **2** results in the formation of the alternating copolymer.

The homopolymerization of both ethene and 1-hexene initiated by **2** was found to have some "living" characteristics. Fractions withdrawn at different time intervals for hexene homopolymerization (reaction conditions: **2**, 10 mg; 1-hexene, 0.5 g; CH_2Cl_2, 5 mL, RT) showed an increase in M_n with time (2 h, $M_n = 23\,900$; 8.5 h, $M_n = 32\,100$; 22 h, $M_n = 47\,400$). That the M_n value does not continue to increase linearly with time suggests that a fraction of the growing polymer chains terminates at longer reaction times. Taking advantage of the quasi-living nature of the polymerization, we successfully synthesized polymers with poly(alkene) and poly(*alt*-alkene/CO) blocks by sequential addition of monomers. For example, a poly(1-hexene) block was synthesized by the reaction of **2** with 1-hexene (reaction conditions: **2**, 5 mg; 1-hexene, 0.35 g; CH_2Cl_2, 5 mL) at ambient temperature for 2 h (at this point, a significant amount of 1-hexene remains). A small fraction of the reaction mixture was syringed out, the reactor was charged with 20 psi of CO, and the polymerization was continued for a further 6 h. The polyhexene fraction withdrawn after the first step had $M_n = 65\,600$ and $M_w/M_n = 2.48$. The final diblock copolymer had $M_n = 90\,100$ and $M_w/M_n = 1.99$. The length of the second block was kept short to avoid the solubility issues. The formation of block copolymer was further confirmed by ^1H NMR spectroscopy (CD_2Cl_2); the first block had resonances at 0.9 and 1.0−1.6 ppm due to poly(1-hexene). The ^1H NMR spectrum of the final copolymer shows formation of additional resonance at 2.4 ppm due to hexene/CO block. Because of the relatively high molecular weight, it is difficult to observe the CH and CH_2 groups connecting the two blocks by NMR spectroscopy (however, see below). To further test the formation of a diblock copolymer versus a mixture of two single block polymers, the material was washed in hexane (which dissolves polyhexene). The ^1H NMR spectrum (CD_2Cl_2) of the hexane-insoluble residue showed slightly higher hexene/CO content (27 mol % versus 15 mol % before hexane wash), suggesting the presence of some polyhexene in the original material. As discussed above, this is consistent with the observation of some termination of the initially synthesized polyhexene chains with time. Similarly synthesized were diblock copolymers with branched polyethene (PE) and poly(*alt*-ethene/CO) (PK) blocks. In one example, a PE block was first synthesized by performing the polymerization for short time (reaction conditions: **2**, 5 mg; ethene, 300 psi; CH_2Cl_2, 10 mL, RT, 1 h), and then the PK block was synthesized by charging the same reactor with a mixture of ethene and CO (ethene, 300 psi, CO, 50 psi, 0.5 h). The obtained polymer was dissolved in a hexafluoroisopropyl alcohol and trace chloroform-*d* mixture and analyzed by ^1H NMR spectroscopy. The NMR spectrum shows resonances at 1.3 and 2.8 ppm due to PE and PK blocks, respectively (82 mol % PE, 18 mol % PK; M_n, 4000; M_w/M_n, 1.57). Similar to the poly(hexene-*b*-hexene/CO) copolymer, the ^1H NMR spectrum recorded after washing the PE-*b*-PK copolymer with hexane (which dissolves the branched PE) shows higher PK content (72 mol % PE and 28 mol % PK). The difference can be attributed to some chain termination in the initially synthesized PE. However, the presence of ^1H NMR resonances for both PE and PK chains in the hexane-insoluble fraction confirms that this material is a real copolymer and not a mixture of two homopolymers (PE and PK). In an experiment performed in a

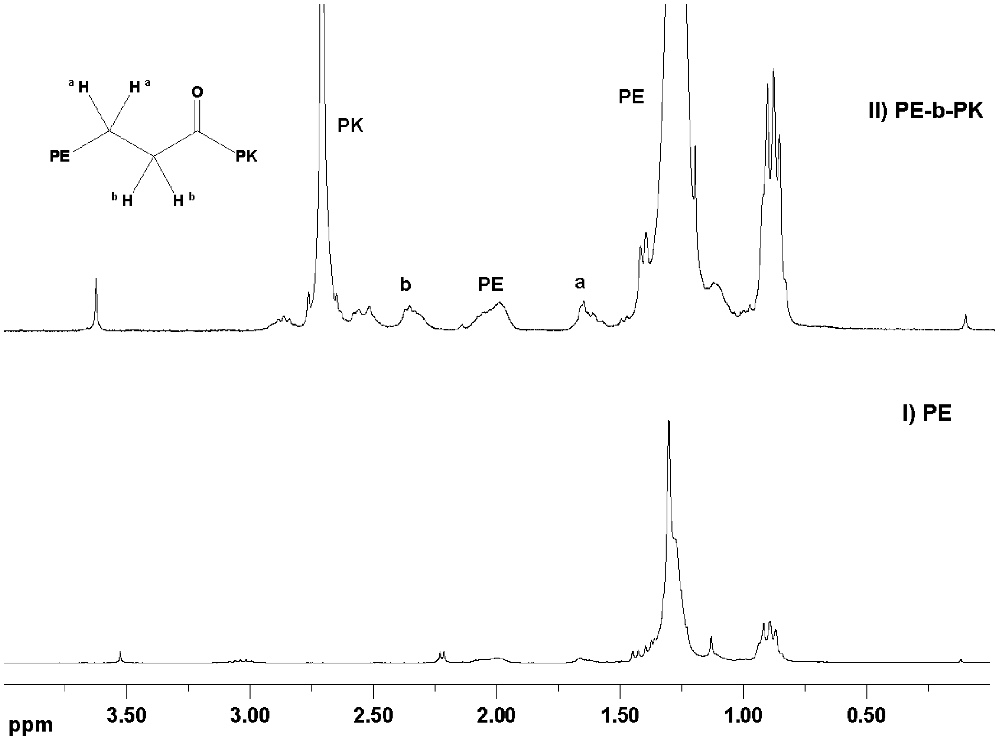


Figure 4. ^1H NMR (CD_2Cl_2) spectra of (I) polyethene (PE) and (II) polyethene-*b*-polyketone (PE-*b*-PK) copolymer.

high-pressure NMR tube, a PE block was first formed (reaction conditions: **2**, 5 mg; ethene, 50 psi; CD_2Cl_2, 0.5 mL, RT, 1 h). After the addition of CO (50 psi) to the preformed PE block a new resonance attributable to the formation of a PK block was observed at 2.6 ppm, and the intensity of this resonance increased over time. In addition, the resonances at 1.6 and 2.3 ppm observed are the CH_2 protons at the interface between PE and PK blocks, respectively (Figure 4). The correlation between the two sets of protons on the connecting carbons at the interface was established by HCOSY analysis. The assignment of the connecting CH_2 groups was also confirmed by comparing with the ^1H NMR shifts of 3-hexanone. The protons labeled *a* and *b* in $Et{-}C(O){-}C^bH_2{-}C^aH_2{-}Me$ resonate at 1.6 and 2.4 ppm, respectively. The methoxy protons from the end group derived from the initially inserted MMA were observed at 3.7 ppm. Continuing the reaction for longer times results in polymer precipitation.

The DSC of the PE-*b*-PK copolymer synthesized shows two melt transitions at 105 and 220 °C, and these remain unaltered after hexane wash. The first corresponds to that reported by Brookhart for the branched PE formed by the diimine−Pd system.[5b] The second is ascribable to the PK block and is approximately 40 °C lower than that for pure PK.[6] Pure PK is very highly crystalline, and the lowered T_m in PE-*b*-PK is presumably due to the disruption of the crystallinity because of the presence of the branched PE block.

In conclusion, the reaction of a cationic Pd(II) diimine complex with methyl methacrylate results in 1,2-insertion regiochemistry that is *opposite* of that observed with methyl acrylate. NMR, FT-IR, and single-crystal X-ray analysis confirms the 1,2-insertion of MMA and formation of a five-membered cyclic chelate. The enthalpy of activation for MMA insertion is 4 kcal/mol higher than that for the corresponding MA insertion. The MMA-inserted complex, **2**, can be employed for ethene or 1-hexene homopolymerization and their alternating copolymerization with carbon monoxide. Further, the quasi-living nature of the polymerizations allows the synthesis of poly(hexene-*b*-hexene/CO) and poly(ethene-*b*-ethene/CO) copolymers. The polymerization activity of **2** is comparable to that of the starting Brookhart complex, **1**. However, the stability of **2** is higher than **1** under ambient conditions and is, therefore, a more attractive starting point.

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Supporting Information Available: Experimental procedures and crystal structure data are available free of charge via the Internet at http://pubs.acs.org.

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