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Diametrically Opposite Trends in Alkene Insertion in Late and Early Transition Metal Compounds: Relevance to Transition-Metal-Catalyzed Polymerization of Polar Vinyl Monomers

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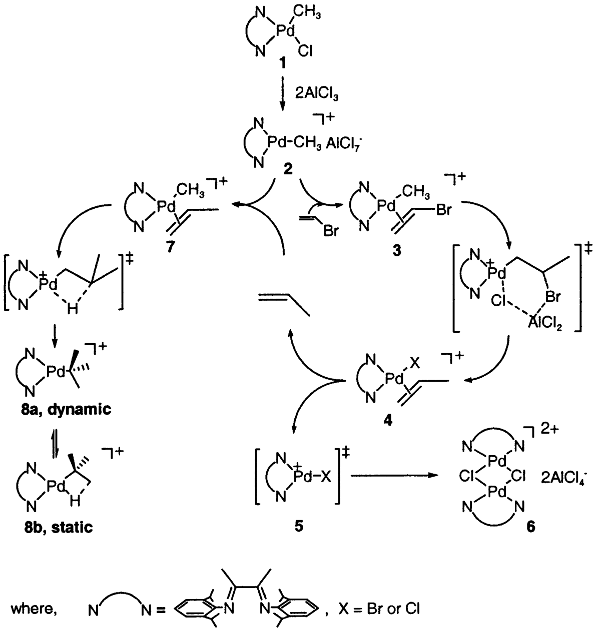
Metal-catalyzed insertion copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest in synthetic polymer chemistry, because the addition of functionalities to a polymer which is otherwise nonpolar can greatly enhance the range of attainable properties.[1] For vinyl monomers with pendant coordinating functionalities, such as acrylates, the principal problem has been catalyst poisoning through functional group coordination.[1−3] Interestingly, vinyl halides, which do not possess any strongly coordinating functionality, are also not polymerized by any known transition-metal-catalyzed systems. Recently, Jordan[4] and Wolczanski[5] have reported the reaction of vinyl halides with *rac*-(EBI)-ZrMe and $(^t\mathrm{Bu}_3\mathrm{SiO})_3\mathrm{TaH}_2$, respectively. It was demonstrated that, following 1,2-insertion of the alkene, β-halide elimination occurs to generate a metal−halide bond. Because the halophilicity of the transition metal ions tends to decrease on going from left to right in the periodic table, we undertook an examination of the reactivity of vinyl halides toward a late transition metal complex (palladium). While we have also observed β-halide elimination following insertion, one surprising result that has emerged is a linear *positive* Hammett correlation between the rate of insertion and the increasing electron-withdrawing effect of the substituent on the alkene. This stands in stark contrast with that observed for the above tantalum-based system where the second-order rate constants for vinyl halide insertions are significantly *smaller* than those for ethylene or vinyl ethers.[5] In addition, the generally slower rate of propene versus ethene insertion in metal complexes[6] is usually attributed to the steric bulk of the methyl group of the former. Our results suggest that even for the sterically encumbered Brookhart-type system, it is the donating ability of the methyl group, rather than its size, which results in slower rate for propene insertion. These results are clearly important in the context of alkene polymerizations proceeding by an insertion mechanism.

The starting point of our investigation was the Brookhart-type cationic Pd(II)−methyl species, **2**, generated in our case by the addition of 2 equiv of AlCl_3 to the corresponding neutral Pd(II)−methyl chloride, **1**[7] (Scheme 1). Several equivalents of vinyl bromide was added to a $\mathrm{CD}_2\mathrm{Cl}_2$ solution of **2** at −90 °C, and the reaction mixture was monitored by ^{1}H NMR spectroscopy as it was gradually warmed (Scheme 1). The coordination of vinyl bromide to the metal center in **2** was observed even at −86 °C, resulting in the formation of **3**. Warming the reaction mixture to −74 °C resulted in the formation of the propene coordinated species, **4**, suggesting 1,2-alkene insertion followed by β-bromo elimination. Propene is gradually lost from **4** and is trapped by unreacted **2** to form **7**. The cationic Pd(II)−halide species arising from **4** by propene loss converts to the chloro-bridged dimer, **6**. The structure of **6** as a dicationic complex with two aluminum tetrachloride counteranions was established by an X-ray crystal structure determination (Supporting Information). The identity of the halide ligand in **4** has not been established, but the formation of **6** opens up the possibility of an aluminum-assisted β-bromo abstraction pathway shown in Scheme 1.

Scheme 1. Proposed Reaction Pathway[8]



Once formed, **7** undergoes 1,2-insertion of propene to form the known β-agostic Pd(II)-*tert*-butyl compound **8**.[9] The complexes **7** and **8** were also independently formed by the addition of propene to a $\mathrm{CD}_2\mathrm{Cl}_2$ solution of **2**. The initially formed **7** was found to convert to **8** when the solution was warmed to −36 °C. At ambient temperature, the three methyl groups of the *tert*-butyl complex exchange rapidly on the NMR time scale and appear as a singlet at −0.28 ppm. Upon lowering the temperature to −86 °C, a static ^{1}H NMR spectrum is observed, and the agostic proton appears as a singlet at −8 ppm.

The migratory insertion rates of bound vinyl bromide and propene in **3** and **7**, respectively, were directly measured by monitoring the disappearance of the corresponding Pd−CH_3 resonance. For propene, our value was in close agreement with that reported by Brookhart.[10] For vinyl bromide, an Arrhenius plot was constructed

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Table 1. Kinetic Data for Insertion of Alkenes into the Pd(II)−Me Bond[a]

	k ($\times 10^3$ s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/K·mol)
propene	0.54		
ethene[6]	1.9	14.2 ± 0.1	−11.2 ± 0.8
vinyl bromide	22.0	11.9 ± 0.1	−16.8 ± 0.1
methyl acrylate[10]	55.0	12.1 ± 1.4	−14.1 ± 7.0

[a] Measured or extrapolated to 236.5 K.

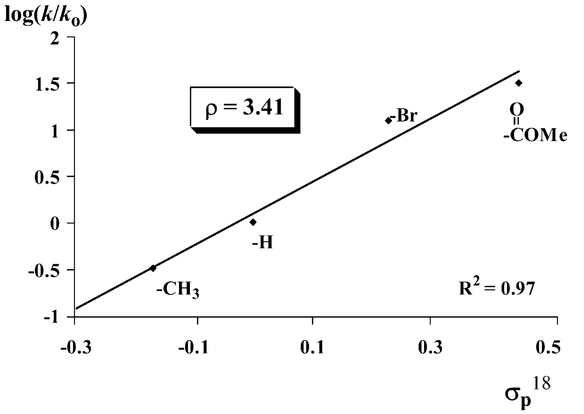

Figure 1. Hammett plot for migratory insertion of alkenes into the palladium(II)−methyl bond.

from rate measurements done between −74 and −37 °C. Our values together with those of Brookhart[6,10] are reported in Table 1.

A Hammett plot of the relative insertion rates of substituted alkenes versus σ_p[18] yielded a straight line with a *positive* ρ (+3.41) (Figure 1). Of note is that the line encompasses values obtained by both Brookhart[6,10] and us. Theoretical calculations have also led to a lower insertion barrier for acrylate as compared to ethene.[11] This can be contrasted with a *negative* value of ρ obtained by Bercaw for alkene insertion in Cp^*_2NbH(alkene).[12] Additionally, the second-order rate constants obtained by Wolczanski for alkene insertion into the Ta(V)−H bond follow the trend H ≈ OR ≫ halide (F, Cl, Br).[5] The decrease in the rate of insertion with increasing electron-withdrawing effect of the substituent on the alkene in the case of early transition metal compounds has been attributed to the development of positive charge on the carbon bearing the substituent either during alkene coordination or the subsequent insertion step.[5,12,13] In Wolczanski's case, it has not been possible to separate the effect of the substituent on binding versus insertion, and the trend for the actual insertion step remains an open question. We ascribe the increase in insertion rate for the palladium−methyl complex to a ground-state effect. An alkene with an electron-withdrawing substituent coordinates less strongly to the electrophilic metal (i.e., σ-donation is more important than π-back-donation).[14] Thus, a weaker metal−alkene bond has to be broken for the insertion to proceed (i.e., the destabilization of the alkene complex leads to a lower insertion barrier).[14] Another surprising observation is that the observed correlation extends to propene. The slower insertion and polymerization rates of propene, when compared to ethene, are usually attributed to the steric bulk of the methyl group of the former.[6,15−17] Our results suggest that, at least for the late transition metal compounds, it is the donating ability of the methyl group, rather than its size, which results in the slower rate for propene insertion and, hence, polymerization. This argument applies even for the sterically encumbered Brookhart-type system.

What is the implication of our work with respect to the metal-catalyzed polymerization of polar vinyl monomers? First, for the late metal compounds, the polar vinyl monomers can clearly outcompete ethene and simple 1-alkenes with respect to insertion. However, the ground-state destabilization of the alkene complex that favors the migratory insertion of the polar vinyl monomers is a two-edged sword because it biases the alkene coordination toward ethene and 1-alkenes. Indeed, we have observed the near quantitative displacement of vinyl bromide by propene to form **7** from **3**. Thus, the extent of incorporation of the polar vinyl monomer in the polymer will depend on the opposing trends in alkene coordination and migratory insertion. The above discussion does not take into account the problem of functional group coordination for acrylates or β-halide abstraction for vinyl halides. With respect to the latter, we are currently exploring approaches to suppress this "termination" step, for example, decreasing the electrophilicity of the metal center.

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Supporting Information Available: Experimental, NMR spectra (PDF), and crystal structure data for compound **6** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Selected ^{1}H NMR data (CD_2Cl_2, 300 MHz, *d* in ppm): (a) ^{1}H NMR of **2** (25 °C) 7.42−7.34 (m, 6H, Ar-H), 3.04 (septets, 4H, Ar−CHMeMe′), 2.22 and 2.17 (s, 3H each, $N{=}C(CH_3){-}C(CH_3'){=}N$), 0.76 (s, 3H, Pd−$CH_3$); (b) ^{1}H NMR of **3** (−70 °C) 5.58 (m, 1H, coordinated $CH_2{=}CHBr$), 5.0 (m, 2H, coordinated $CH_2{=}CHBr$), 2.44 and 2.33 (s, 3H each, $N{=}C(CH_3){-}C(CH_3'){=}N$), 0.65 (s, 3H, Pd−$CH_3$); (c) ^{1}H NMR of **4** (−50 °C) 5.47 (m, 1H, coordinated $CH_2{=}CHCH_3$), 4.21 (m, 2H, coordinated $CH_2{=}CHCH_3$), 2.00 (m, coordinated $CH_2{=}CHCH_3$); (d) ^{1}H NMR of **7** (−40 °C) 4.31 (m, 2H, coordinated $CH_2{=}CHCH_3$), $CH_2{=}CHCH_3$ obscured $CH_2{=}CHCH_3$ obscured 0.32 (s, 3H, Pd−CH_3); (e) ^{1}H NMR of **8a**, dynamic (−20 °C) −0.28 (br s, 9H, $Pd(C(CH_3)_3)$), ^{1}H NMR of **8b**, static (−70 °C) 0.00 (br s, 6H, $Pd(C(CH_2\text{-}\mu\text{-}H){-}(CH_3)_2)$), −8.00 (br s, 1H, $Pd(C(CH_2\text{-}\mu\text{-}H){-}(CH_3)_2)$); (f) ^{1}H NMR of **6** (25 °C) 2.33 (s, 12H, $N{=}C(CH_3){-}C(CH_3'){=}N$), 1.35 and 1.23 (d, 24H each, J = 6.59 and 6.86 Hz).
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