

Intermediacy of Radicals in Rearrangement and Decomposition of Metal–Alkyl Species: Relevance to Metal-Mediated Polymerization of Polar Vinyl Monomers

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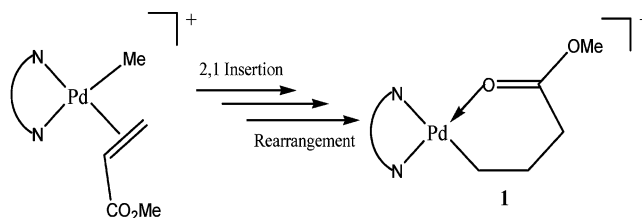
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Summary: The neutral compound $[2,3\text{-bis}(2,6\text{-diisopropylphenylimino)butane}]Pd(CH_2CH_2CH_2CO_2Me)(X)$ ($X = Cl, Br$) undergoes “reverse” chain walking to form $[2,3\text{-bis}(2,6\text{-diisopropylphenylimino)butane}]Pd(CH(CO_2Me)CH_2CH_3)(X)$ through a conventional β -hydrogen elimination/readdition pathway. However, reversible Pd–alkyl bond homolysis occurs for both alkyl complexes, and the resultant radicals can initiate the polymerization of acrylates.

In recent years, there has been considerable interest in the development of metal-mediated insertion (co)polymerization of polar vinyl monomers, especially acrylates.¹ The commonly cited problem that has stymied the development of suitable catalysts is the interaction of the oxygen functionality with the metal center, which hinders coordination of the next incoming monomer. This has led to the examination of newer systems that are less oxophilic: those involving late transition metals and those that are neutral.^{1,2} Unfortunately, with some notable exceptions, there have been few successes.³ However, there is a second, less appreciated reason for the failure of most metal-based systems to polymerize acrylates through a nonradical insertion mechanism. For electronic reasons, acrylates have a strong preference for 2,1-insertion into metal–carbon bonds.⁴ This results in the formation of 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.⁵ This paper focuses on this phenomenon and shows that metal–carbon bond homolysis can be facile for the relatively electron-rich neutral metal alkyls and can compete with β -hydrogen abstraction/readdition steps.⁶

Scheme 1. “Chain-Walking” Rearrangement To Form the Stable Six-Membered Chelate



One of the very few systems that copolymerize acrylates through an insertion mechanism is by Brookhart and involves cationic Pd(II)-based complexes of the general type $[(N\wedge N)\text{-Pd}(\text{Me})(\text{L})][\text{B}(\text{Ar}_f)_4]$ ($N\wedge N = 2,3\text{-bis}(2,6\text{-diisopropylphenylimino)butane}$, $\text{Ar}_f = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$, $\text{L} = \text{Et}_2\text{O}$).^{3a} This system is able to incorporate up to 15 mol % acrylate in copolymerizations with ethene and 1-alkenes. A novel feature of this system is the rearrangement that follows acrylate insertion, resulting in the removal of the ester functionality from the position α to the metal, eventually forming a six-membered chelate, **1** (Scheme 1). This unique feature of the system prompted us to examine the stability of the complex upon opening of the six-membered chelate by forming a neutral species.

One equivalent of tetraphenylphosphonium bromide was added to complex **1** in CD_2Cl_2 to open the chelate ring, and the reaction was monitored by ^1H NMR spectroscopy. A complete and rapid conversion from **1** to **2** was observed (Scheme 2). Compound **2** is not stable at room temperature and rearranges to **3** within minutes (66% overall yield). The driving force for this rearrangement is presumably the same as that for the 2,1-insertion of acrylates into Pd–C bonds; in the cationic Brookhart system the isomerization proceeds in the opposite direction because of the enhanced stability of the six-membered chelate over the smaller chelate rings. Finally, **3** was found to decompose on further standing at room temperature to yield methyl crotonate (68% overall yield), together with methyl butyrate (6% overall yield) and a trace amount of the diester, dimethyl suberate. While the transformations, **2** to **3** and **3** to methyl crotonate, can be explained by invoking the usual β -hydrogen abstraction/readdition mechanism, the formation of methyl butyrate suggested the possibility that the methyl butyrate and at least some of the methyl crotonate arose through Pd–carbon bond homolysis in **3** followed by the well-known disproportionation of the resultant radical. Likewise, the fragmentation of the palladium–alkyl bond in **2** followed by radical–radical combination would lead to the formation of

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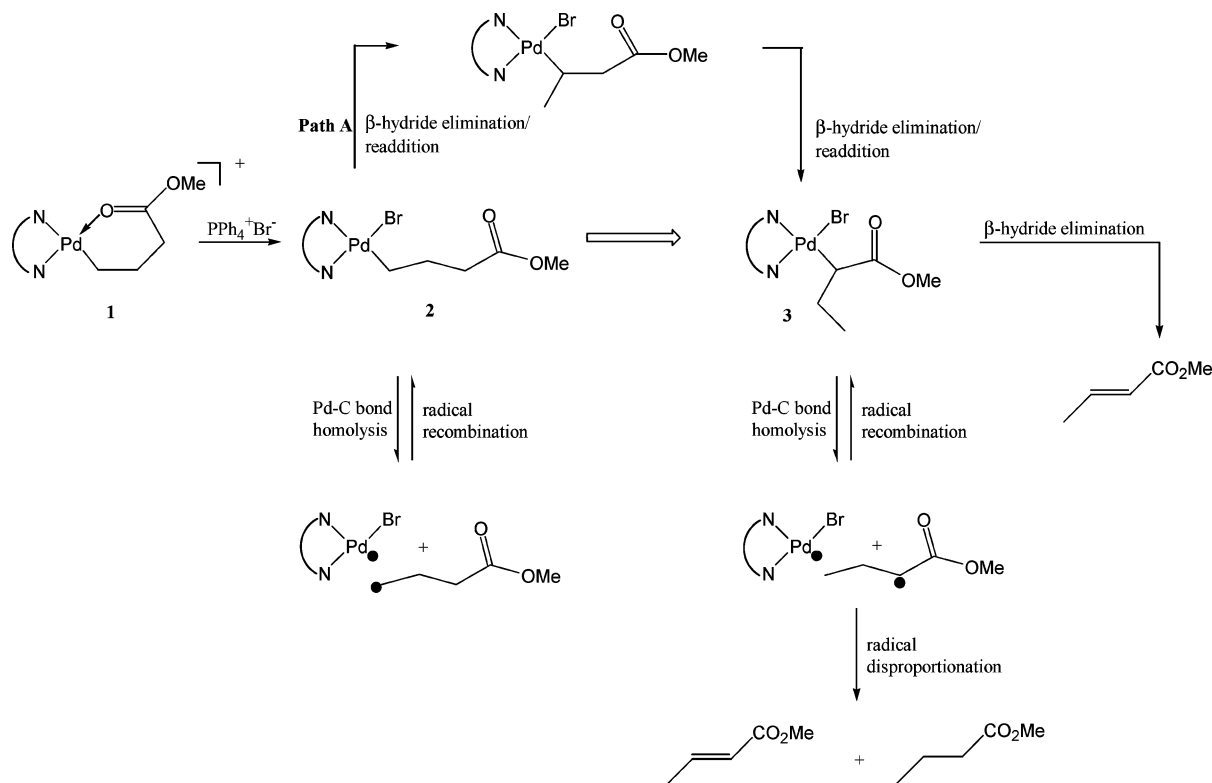
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Scheme 2. Proposed Reaction Pathways following Disruption of the Six-Membered Chelate

Table 1. Quantification of Decomposition Products^a

Entry	Halide Salt	CBr ₄ (mmol)	Br-CH ₂ -CH ₂ -CH ₂ -CO ₂ Me	CH ₃ -CH(Br)-CH ₂ -CO ₂ Me	CH ₂ =CH-CO ₂ Me	CH ₃ -CH ₂ -CH ₂ -CO ₂ Me
1	Ph ₄ P ⁺ Br ⁻	0	---	---	68%	5.3%
2	Ph ₄ P ⁺ Br ⁻	0.075	38%	20%	22%	5.6%
3	Et ₄ N ⁺ Cl ⁻	0.075	33%	14%	22%	8.5%

^a Reaction conditions: 0.0136 mmol of **1**, 0.032 mmol of halide salt, 1 mL of CH₂Cl₂, stirred at ambient temperature for 18 h.

dimethyl suberate. Further support for the intermediate formation of radicals came from the observation that when the bromide salt was added to compound **1** in the presence of excess of methyl acrylate (MA) (350× excess, relative to Pd) at room temperature, the homopolymerization of MA ensued (22% conversion, $M_w = 60\,760$, and PDI = 1.71). No polymer formation was observed in the absence of the palladium species.

To provide more convincing evidence for the presence of radicals, 1 equiv of CBr₄ was added to **1** and PPh₄⁺Br⁻ (see Table 1). After several hours, the reaction mixture contained methyl 2-bromobutyrate (20% overall yield), the trapped product from homolytic cleavage of the palladium–alkyl bond in **3**. A second species, methyl 4-bromobutyrate, was also observed in a much greater concentration (38% overall yield).

There is a possibility that the observed alkyl bromides arise, not from radical trapping with CBr₄ but through reductive elimination from the corresponding Pd(alkyl)(Br) species, **2** and **3**. To further clarify the origin of the alkyl bromides, NEt₄⁺Cl⁻ was used to disrupt the chelate and CBr₄ was used as the radical trapping agent. In this case, alkyl radicals trapped by CBr₄ would generate bromides while reductive elimination would lead to the formation of chlorides. Only alkyl bromides were observed by GC and NMR spectroscopy, the yields being similar to those observed previously (Table 1). As a final control experiment,

we verified that CBr₄ by itself did not react with **1**. Our observations clearly suggest that the palladium–alkyl species present in the system readily undergo bond homolysis to generate alkyl radicals.

To examine whether radicals were also involved in the conversion of **2** to **3**, the kinetics of the rearrangement in methylene chloride was monitored by ¹H NMR spectroscopy. The rearrangement was found to follow a linear first-order kinetic plot. An Eyring analysis of this reaction over the temperature range of 5–29 °C gives $\Delta H^\ddagger = 12.1 \pm 1.1$ kcal/mol and $\Delta S^\ddagger = -14.1 \pm 7.0$ e.u. If this rearrangement was occurring by a migratory “chain-walking” mechanism, a slightly negative entropy of activation would be expected, due to the ordered transition state needed for β -hydrogen elimination.^{6b} On the other hand, a large positive activation entropy should accompany a mechanism involving bond homolysis. The dissociation of the diimine ligand does not appear to play a role in the conversion of **2** to **3**, since the addition of an excess of the N∧N ligand had no effect on the rate. Likewise, the dissociation of the bromide leading to ion pair formation does not appear to occur, since the rate of the rearrangement did not decrease on moving from methylene chloride to less polar chlorobenzene (CH₂Cl₂, $k = 0.039$ s⁻¹; PhCl, $k = 0.093$ s⁻¹).

Our results are most consistent with the pathways shown in Scheme 2. The rearrangement of **2** to **3** appears to proceed via the traditional β -hydrogen elimination/readdition pathway (path A). On the other hand, both **2** and **3** appear to readily undergo (reversible) Pd–C bond homolysis and the resultant radicals get trapped as bromides in the presence of CBr_4 . Methyl crotonate can form via either radical disproportionation or β -hydrogen elimination, whereas methyl butyrate can only arise by radical disproportionation. Consequently, the low observed ratio of methyl butyrate to methyl crotonate suggests that Pd–C bond homolysis is reversible and that the predominant route to methyl crotonate is by traditional β -hydrogen abstraction from **3** rather than Pd–C bond homolysis. Nevertheless, sufficient alkyl radicals can and do escape the solvent cage and are capable of initiating traditional radical polymerization of polar vinyl monomers. This possibility needs to be taken into account before mechanistic claims can be made with respect to metal-mediated polymerization of these monomers. For example, the formation of copolymers whose compositions vary significantly from those predicted from the radical reactivity ratios must be demonstrated before a nonradical mechanism can be invoked.

In conclusion, our findings illustrate the propensity of neutral Pd–alkyl species to undergo Pd–C bond homolysis. In the present instance, the blocking of one of the coordination sites on palladium by the halide ligand, a possible strategy to prevent

coordination of the acrylate ester group, favors this pathway. Thus, simply preventing the coordination of the functionality present on the polar vinyl monomer may not necessarily result in a viable system for insertion polymerization. Indeed, it appears that the success of the Brookhart system in copolymerizing acrylates is due to stable chelate formation following acrylate insertion (complex **1**); as discussed, when **1** is forced open by forming a neutral halide-coordinated complex, homolysis of the Pd–C bond is observed. The price paid for chelate formation in the Brookhart system is slow polymerization and the placement of the functionality predominantly at the branch ends. One possible solution to the issues discussed above is to use a sufficiently sterically encumbered system that forces 1,2-insertion of acrylate into Pd–C bond, as predicted by Ziegler.⁷

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Supporting Information Available: Text and figures giving experimental procedures and NMR data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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