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# Chain-Transfer Mechanisms of the Alternating Copolymerization of Carbon Monoxide and Ethene Catalyzed by Palladium(II) Complexes: Rearrangement to Highly Reactive Enolates

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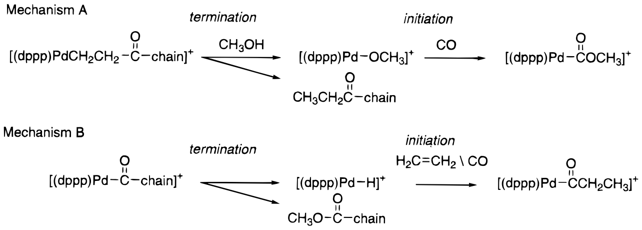
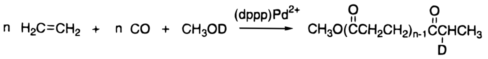
Since the discovery[1] of the efficient alternating copolymerization of olefins and carbon monoxide catalyzed by palladium(II) complexes there has been an increasing interest in these polymers,[2,3] as well as in the chemistry to prepare them.[2a,4] Mechanistic research has thus far concentrated on the insertion reactions.[5,6] There have been many speculations on the chain-transfer mechanism,[1,3,4,7] and the two chain-transfer mechanisms in Scheme 1 have been proposed.

Both chain-transfer mechanisms yield the same end groups, namely, ester and ethyl ketone groups in a 1:1 ratio. We report here on the preparation of the copolymer in monodeuterated methanol as the solvent. The positions of the deuterium incorporated show that the two mechanisms occur simultaneously in the dppp-based catalyst.

The results of the copolymerization of ethene and CO in CH$_3$OH and CH$_3$OD are listed in Table 1.[8] Surprisingly, the deuterium was found mainly in the ethyl ketone end groups as COCHDCH$_3$, while COCH$_2$CH$_2$D and COCH$_2$CH$_3$ end groups were obtained in smaller quantities. Only a negligible amount of deuterium was found to be incorporated in the backbone of the polymer (eq 1).

**Scheme 1**



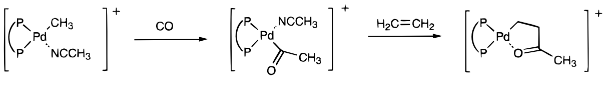


$$n\ H_2C{=}CH_2 + n\ CO + CH_3OD \xrightarrow{(dppp)Pd^{2+}} CH_3O(\overset{O}{\overset{\|}{C}}CH_2CH_2)_{n-1}\overset{O}{\overset{\|}{C}}\underset{D}{C}HCH_3 \quad (1)$$

To check whether H/D exchange could have occurred after the product was formed, copolymer prepared in CH$_3$OH was suspended in CH$_3$OD and heated under reflux for 8 h with *p*-toluenesulfonic acid present, but introduction of deuterium was observed neither in the end groups nor in the backbone.

GC−MS analysis of the filtrate containing soluble oligomers showed the formation of ketoesters, and some diketones and diesters, suggesting that two independent chain-transfer mechanisms are operating.[1b,2a] Mechanism B involves termination via methanolysis with CH$_3$OD, giving an ester end group and a palladium *deuteride* species. Subsequent initiation via insertion of ethene leads to [(dppp)PdCH$_2$CH$_2$D]$^+$, and consequently to a COCH$_2$CH$_2$D end group.[9] Mechanism A involves termination by *deuteration* of the palladium alkyl and initiation via insertion of CO into a palladium methoxy species. Thus, both mechanisms lead to COCH$_2$CH$_2$D end groups. The formation of the COCH$_2$CH$_3$ end groups in CH$_3$OD can only be explained by mechanism B. Mechanism A always leads to *deuterated* end groups, while mechanism B leads to all three species via fast and reversible insertion of ethene.[9,10] We do not expect that this would lead to as much as 46% COCHDCH$_3$ and only 26% COCH$_2$CH$_2$D. We propose that mechanism A must lead to the unexpected formation of excess COCHDCH$_3$ end groups, as is proven below.

As a model for the growing chain on the catalyst the complex [(P−P)PdCH$_2$CH$_2$C(O) CH$_3$]$^+$CF$_3$SO$_3$$^-$ (**3a**, P−P = dppp, **3b**, P−P = dppf) was prepared by consecutive insertions of CO and ethene into the methyl complexes **1a**,**b** (eq 2). Complexes **3a**,**b** were identified by $^1$H, $^{31}$P, and $^{13}$C NMR spectroscopy and IR analysis, and they were found to contain a chelating alkyl ketone.[2a,5b,11] Compound **3b** was synthesized starting from [(dppf)PdCH$_3$(CH$_3$CN)]$^+$CF$_3$SO$_3$$^-$ (**1b**)[6c] and CO at −60 °C in CH$_2$Cl$_2$, and the resulting acetyl complex was made to react with



**1a,b** **2a,b** **3a,b** (2)

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[10] $^1$H NMR analysis of the MeOD solution and of the gas cap after the polymerization of entry 2 showed no detectable formation of MeOH and of deuterated ethene, respectively. On the basis of a degree of polymerization of ca. 150 ethene units/CO unit, ca. 50% chain transfer via mechanism B, and only 50% scrambling via H/D exchange during this chain-transfer, the overall scrambling would be less than 0.2%.

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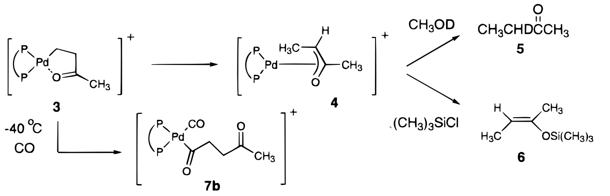
**Table 1.** Preparation of Ethene/CO Copolymers in Methanol and Methanol-$d_1$

| entry[a] | solvent | temp (°C) | rate ($kg \cdot g^{-1} \cdot h^{-1}$) | $M_n$[b] | $^{13}C$ NMR end group analysis (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | ester | ethyl | $CH_2CH_2D$ | $CHDCH_3$ | $CH_2CH_3$ |
| 1 | $CH_3OH$ | 95 | 10.8 | 5900 | 51 | 49 | | | 100 |
| 2 | $CH_3OD$ | 96 | 8.0 | 8500 | 50 | 50 | 26 | 46 | 28 |

[a] Experiments were carried out in 160 mL (90 mL of $CH_3OD$) or 250 mL (140 mL of $CH_3OH$) autoclaves at 55 bar; catalyst precursor $Pd(OAc)_2$:dppp:*p*-toluenesulfonic acid = 0.020:0.022:0.045 mmol; time 1 h; rate in (kg of polymer/g of Pd)/h. [b] Molecular weight determined via end group analysis ($^{13}C$ and $^2H$ NMR).

ethene at −20 °C. Crystals suitable for X-ray diffraction analysis were obtained from a solution of **3b** in $CH_2Cl_2/Et_2O$. The crystal structure proves the coordination of the carbonyl group to palladium.[12] The in situ reaction of **3b** with $^{13}CO$ in $CD_2Cl_2$ at −40 °C showed that $[(dppf)Pd^{13}C(O)CH_2CH_2C(O)CH_3(^{13}CO)]^+CF_3SO_3^-$ (**7b**) formed.

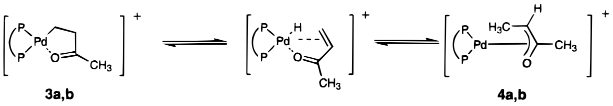
An NMR spectroscopy study of **3a**,**b** showed that these complexes are unstable at room temperature, and rearrang ($t_{1/2} \approx 1$ h, in $CD_2Cl_2$) to the palladium enolates (**4**) (eq 3). In the $^1H$ NMR spectrum the characteristic multiplets of the methylenes of **3a** at 1.47 and 3.22 ppm declined in favor of two new multiplets at 0.64 and 3.87 ppm with relative intensities of 3:1, respectively. In the $^{31}P$ NMR spectrum a new pair of doublets arose. Upon addition of $CD_3OD$, **4a** was deuterated immediately, forming 3-deuteriobutan-2-one (**5**). When trimethylchlorosilane (TMSCl) was added to **4a**, the silyl enol ether **6**[13] was obtained. Treatment of **3a** with $CD_3OD$ led to the formation of $CH_3CHDCOCH_3$ (**5**) at a rate similar to that of the rearrangement of **3a** into **4a**, the concentration of **4a** being very low now. Similarly, treatment of **3a** with TMSCl led to the slow formation ($t_{1/2} \approx 1$ h) of **6**, while no **4a** could be detected. When compound **3b** is stored in $CD_2Cl_2$ containing traces of water at −20 °C, it decomposes in a few weeks to give $[(dppf)PdOH]^+{}_2[CF_3SO_3^-]_2$ (**8b**),[14] a hydroxide palladium dimer, and 2-butanone in more than 95% selectivity according to $^1H$ NMR. No vinyl methyl ketone, the product of $\beta$-hydride elimination, was observed. To investigate the hydrolysis reaction in more detail, complex **3b** was dissolved in $CD_2Cl_2$ at −20 °C. When the temperature was raised to room temperature, a new complex formed which was characterized by the $^1H$ NMR spectrum. The new complex **4b** was in equilibrium with **3b** (1:1 at 25 °C), and no formation of vinyl methyl ketone was observed. Thus, **3** isomerizes slowly to the enolate **4**, which in the presence of electrophiles, such as TMSCl, water, or methanol, is trapped immediately (eq 3). Solutions of **1b** in wet solvents did not lead to hydrolysis products, not even at elevated temperatures, showing that cationic palladium alkyl complexes are not prone to hydrolysis. The relevance of transition metal enolates to organic synthetic chemistry is well-documented.[15,16] Saegusa *et al.*[15] have prepared palladium enolates from $Pd(OAc)_2$ and silyl enol ethers. Remarkably, we obtained selectively the *Z*-isomer of **6**, reflecting the chelating structure of its precursor (**3a**).



(3)

Treatment of the ester analogue of **3a**, $[(dppp)PdCH_2CH_2C(O)OCH_3]^+CF_3SO_3^-$ (**9**), with $CH_3OD$ yielded $CH_3CHDCOOCH_3$.[17] Thus, also in this instance isomerization to the enolate occurred prior to the deuteration.[18] A palladium enolate that cannot undergo $\beta$-hydride elimination was synthesized via an alternative route. Chloroacetone was oxidatively added to Pd(0) at room temperature in benzene. The product was contaminated with about 4% of the dichloride complex. Subsequent addition of dppf and silver triflate in $CH_2Cl_2$ yielded the enolate, $[(dppf)Pd(\eta^3\text{-}CH(H')C(CH_3)O)]^+CF_3SO_3^-$, **10**.

The alkyl to enolate isomerization can be explained by a sequence of a slow $\beta$-elimination and a fast reinsertion into the palladium hydride (eq 4).[19] The same mechanism has also been proposed as a step in the hydrocarbonylation of ethene to diethyl ketone.[9]



(4)

We thus conclude that there are two competing chain-transfer mechanisms in the alternating copolymerization of CO and ethene. One involves termination via an unexpected isomerization into the enolate followed by protonation with methanol and subsequent initiation by insertion of CO in the palladium methoxy species. Interestingly, the rate of this reaction should be independent of the concentration of the protic species. The second one comprises termination via methanolysis of the acylpalladium species and subsequent initiation by insertion of ethene into the palladium hydride bond.

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**Supporting Information Available:** Spectral data of **3**, **4**, **5**, **6**, **7b**, **8b**, **9**, and **10** (17 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[12] Zuideveld, M. A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. To be published.

[13] For the $^1H$ and $^{13}C$ NMR data of **6** see the Supporting Information. The structure of **6** was confirmed by comparison of these data with those of an authentic sample prepared according to House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

[14] Longato, B.; Pilloni, G.; Valle, G.; Corain, B. *Inorg. Chem.* **1988**, *27*, 956.

[15] Saegusa *et al.* described the preparation of palladium(II) enolates from $Pd(OAc)_2$ and silyl enol ethers. In acetonitrile the enolates were prone to $\beta$-elimination. They do not describe any reaction of their enolates with proton sources: (a) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011. (b) Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494. (c) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873.

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[17] **9** was prepared *in situ* by adding methyl acrylate to $[(dppp)(PPh_3)PdH]^+/CF_3SO_3^-$ in the presence of an excess of sulfur (to oxidize $PPh_3$). Due to decomposition and isomerization we were not to able to isolate **9**.

[18] This result is in contrast with results reported by Ashby and Halpern who performed the $Ru(BINAP)(O_2CR)_2$-catalyzed hydrogenation of tiglic acid ($MeCH{=}C(Me)COOH$) using $H_2$ and $CD_3OD$ and obtained $MeCHDCH(Me)COOH$ without the apparent intermediacy of metal enolates: Ashby, M. T.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 589.

[19] As no vinyl ketone end groups are formed[1b] we conclude that the reinsertion must be fast.