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# Mechanistic Insights on Acrylate Insertion Polymerization

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***Abstract:*** Complexes [{(P∧O)PdMe}$_n$] (**1**$_\mathbf{n}$; P∧O = $\kappa^2$-*P*,*O*-$Ar_2PC_6H_4SO_2O$ with Ar = 2-$MeOC_6H_4$) are a single-component precursor of the (P∧O)PdMe fragment devoid of additional coordinating ligands, which also promotes the catalytic oligomerization of acrylates. Exposure of **1**$_\mathbf{n}$ to methyl acrylate afforded the two diastereomeric chelate complexes [(P∧O)Pd{$\kappa^2$-*C*,*O*-*C*H(C(O)OMe)$CH_2$CH(C(*O*)OMe)$CH_2CH_3$}] (**3-meso** and **3-rac**) resulting from two consecutive 2,1-insertions of methyl acrylate into the Pd−Me bond with the same or opposite stereochemistry, respectively, in a 3:2 ratio as demonstrated by comprehensive NMR spectroscopic studies and single crystal X-ray diffraction. These six-membered chelate complexes are direct key models for intermediates of acrylate insertion polymerization, and also ethylene-acrylate copolymerization to high acrylate content copolymers. Studies of the binding of various substrates (pyridine, dmso, ethylene and methyl acrylate) to **3-meso** and **3-rac** show that hindered displacement of the chelating carbonyl moiety by $\pi$-coordination of incoming monomer significantly retards, but does not prohibit, polymerization. For **3-meso,3-rac** + $C_2H_4$ $\rightleftarrows$ **3-meso-C$_2$H$_4$**, **3-rac-C$_2$H$_4$** an equilibrium constant K(353 K) ≈ $2 \times 10^{-3}$ L mol$^{-1}$ was estimated. Reaction of **3-meso**, **3-rac** with methyl acrylate afforded higher insertion products [(P∧O)Pd($C_4H_6O_2$)$_n$Me] ($n$ = 3, 4) as observed by electrospray ionization mass spectrometry (ESI-MS). Theoretical studies by DFT methods of consecutive acrylate insertion provide relative energies of intermediates and transition states, which are consistent with the aforementioned experimental observations, and give detailed insights to the pathways of multiple consecutive acrylate insertions. Acrylate insertion into **3-meso,3-rac** is associated with an overall energy barrier of ca. 100 kJ mol$^{-1}$.

## Introduction

Catalytic insertion polymerization of ethylene and propylene is one of the most well-studied chemical reactions. In terms of applications, it is employed for the production of more than 70 million tons of polyolefins annually.[1] By contrast, an insertion polymerization of electron deficient polar-substituted vinyl monomers like acrylates has remained elusive. In fact, until most recently not even consecutive incorporation of such monomers in polymerization reactions had been observed.

It was not until the mid 1990s that cationic Pd(II) diimine complexes were reported to catalyze the insertion copolymerization of ethylene and 1-olefins with acrylates.[2] These d$^8$-metal (late transition metal) complexes are less oxophilic by comparison to early transition metal polymerization catalysts, and therefore more tolerant toward polar moieties.[3] Due to "chain walking" of the catalyst, the highly branched copolymers, which consist of ethylene as the major component (≥75 mol %), contain acrylate units at the end of branches preferentially.[2,4] In-depth NMR spectroscopic studies, for which these systems are exceptionally well suited, provide an understanding of this unique microstructure, and the relevant underlying organometallic species. $\kappa^2$-*C*,*O*-coordinated Pd(II)-alkyl species [(diimine)Pd($\kappa^2$-*C*HR$CH_2CH_2$C(*O*)$OCH_3$)]$^+$ (*R* = growing polymer chain) with a carbonyl group coordinating in a chelating fashion are formed by insertion of methyl acrylate (MA), followed by a series of $\beta$-hydride elimination and reinsertion. Opening of these chelates by coordination of incoming monomer to form the corresponding olefin complexes is the turnover limiting step during copolymer chain-growth.[2,5]

While the copolymers obtained with cationic Pd(II) diimine catalysts are highly branched due to extensive chain walking, with analogous Ni(II) complexes, and with neutral Pd(II)

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(4) For a mechanistic study of the reactivity towards vinyl ether as the sole (electron-rich) substituted vinyl monomer, for which three consecutive insertions were observed, cf.: Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892–12893.

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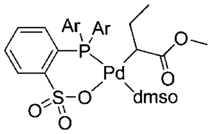
phosphinesulfonato complexes, linear ethylene-MA copolymers are formed.[6−8] Note that the latter are also compatible with a broad scope of functional vinyl monomers.[3h,9,10] By comparison with the cationic Pd(II) diimine system the formally neutral Pd(II) phosphinesulfonato complexes appear to be less reactive, which can be compensated, however, by higher polymerization temperatures by virtue of their remarkable temperature stability. These neutral Pd(II) catalysts have been studied as in situ mixtures of metal sources and ligands,[7,11] and employing complexes [(P∧O)PdMe(L)] ($L$ = pyridine, lutidine, $PPh_3$, 1/2 $Me_2NCH_2CH_2NMe_2$, dimethylsulfoxide) as well-defined single-component catalyst precursors[8,12−15] and as reagents for mechanistic studies.[16−18] Polyethylene chain growth,[16] and also the incorporation of single isolated acrylate monomer units in polyethylenes have also been studied theoretically.[19] By comparison to the aforementioned *N*- and *P*-based ligands L, dimethylsulfoxide (dmso) binds less strongly to the metal center and is more readily displaced by olefin substrate. This enabled insertion homooligomerizations of methyl acrylate to products with degrees of oligomerization of up to ca. $DP_n = 20$. Also, ethylene copolymers with up to 50 mol % acrylate incorporation containing consecutive acrylate-derived repeat units were prepared. By contrast to the well-studied catalytic dimerization of acrylates,[20] these homooligomerization reactions possess all mechanistic features of a polymerization reaction, namely multiple insertions occur prior to chain transfer. In view of this fundamental relevance, and also the accessibility of linear ethylene-acrylate copolymers with unprecedented compositions, an insight into the underlying reaction steps is desirable.

We now report on the observation and isolation of organometallic polymerization intermediates from multiple consecutive acrylate insertions, and a combined experimental and theoretical study of their reactivity.

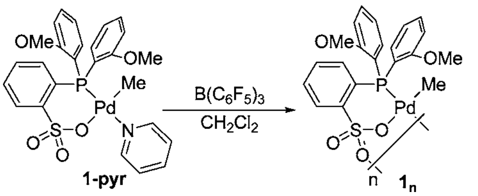
## Results and Discussion

**Reactive Precursors.** A prerequisite for such studies are precursors providing reactive (P∧O)PdR fragments (**1**), the reactivity of which is not overly diminished by the presence of any other strongly coordinating ligands or bases. As outlined, the aforementioned dmso complexes are relatively labile, and reaction with acrylate allows for observation of the single insertion product of MA into the Pd-Me bond, [(P∧O)Pd{CH(COOMe)$CH_2CH_3$}(dmso)] (**2-dmso**).[15]



**2-dmso**

However, the preparation and isolation of multiple acrylate insertion products was complicated by competing $\beta$-hydride elimination. An alternative concept for providing weakly coordinated precursors to the (P∧O)PdR fragment devoid of additional ligands and reagents is replacement of the ligand L in complexes [(P∧O)MR(L)] by the O-donor of another (P∧O)MR fragment. This has been demonstrated for dimeric Ni(II) complexes [{(P∧O)NiR}$_2$].[21] Recently, isolated Pd(II) complexes [{(P∧O)PdR}$_n$] (R = $-CH_2SiMe_3$, $-CH_2CMe_3$) with a chelating phosphinesulfonato ligand were obtained by abstraction of pyridine from [(P∧O)PdR(pyridine)] with $B(C_6F_5)_3$. In the solid state, a dimeric structure ($n$ = 2) was determined.[12] The reaction of [{(P∧O)Pd$CH_2CMe_3$}$_2$] with 6-chlorohex-1-ene afforded [(P∧O)PdCl] (trapped as the pyridine adduct) and oligomerization products of the 1-olefin. For [{(P∧O)PdMe}$_n$] the formation of a $\pi$-complex with vinyl ethers as well as slow 1,2 insertion was observed by NMR.[9b] Note, that reactive [(P∧O)PdMe] species have also been generated in situ without isolation.[9a,11,14,22,25f]



(1)

The weakly coordinated Pd(II)-Me complex $\mathbf{1_n}$ was obtained by pyridine abstraction from **1-pyr** in $CH_2Cl_2$ (eq 1). Layering with pentane afforded crystals of $\mathbf{1_n}$. While crystallization allows for the clean isolation of $\mathbf{1_n}$, unfortunately the crystals were not suited for single crystal structure analysis. $\mathbf{1_n}$ dissolves only in the presence of coordinating solvents (e.g., mixtures of dichloromethane with methanol or acetone) in concentrations sufficient for NMR analysis (cf. experimental section for complete

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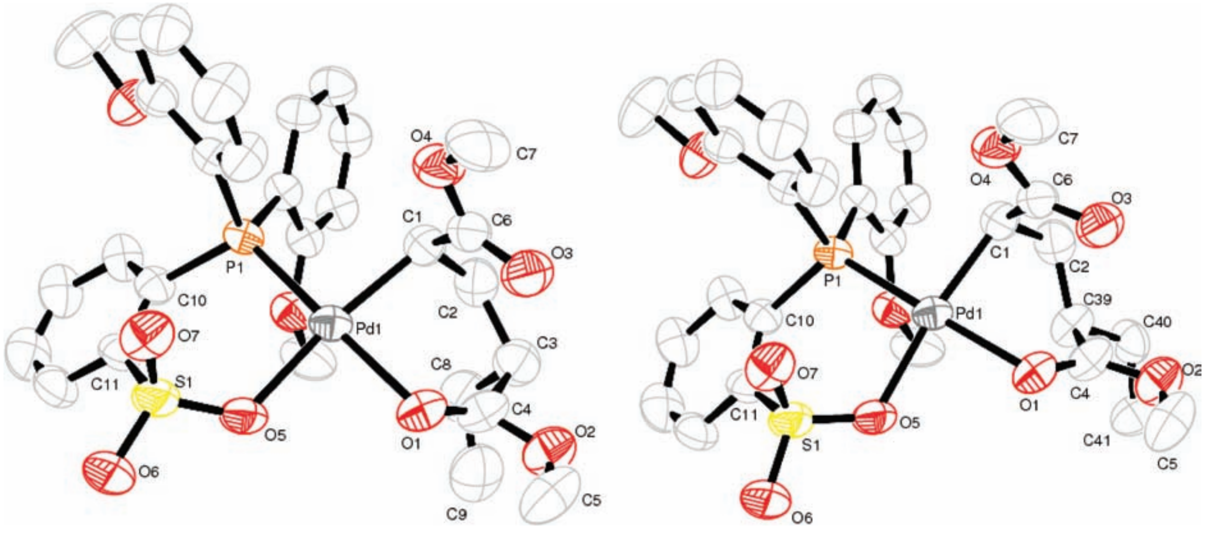
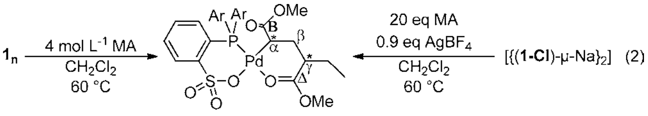


*Figure 1.* Molecular structures of **3-meso** (left) and **3-rac** at 50% probability ellipsoids. All hydrogen atoms and cocrystallized solvent molecules are omitted for clarity.

analytical data). This low solubility is a key advantage of $\mathbf{1_n}$, as it allows for the separation of unreacted starting material from the reaction products in insertion reactions (vide infra). Exposure of $\mathbf{1_n}$ to one equivalent of 2,6-lutidine or dmso resulted in the clean formation of soluble **1-lut**[9a] or **1-dmso**,[15] respectively. Noteworthy, the formation of **1-lut** occurred much faster than the formation of **1-dmso**, which required prolonged ultrasonication. This is inline with the stronger relative binding of lutidine vs dmso.[15] $\mathbf{1_n}$ is a single component precursor to very active catalysts for ethylene polymerization and ethylene-acrylate copolymerization at ethylene pressures of only 5 bar, and for the homopolymerization of acrylates (for comprehensive polymerization data cf. Supporting Information).

**Isolation of Multiple Insertion Products.** Ultrasonication of $\mathbf{1_n}$ in a 4 mol L$^{-1}$ MA solution in dichloromethane (with added 2,6-di-*t*-4-methylphenol (BHT) stabilizer) at 60 °C for 3 h results in partial consumption of $\mathbf{1_n}$ and generation of a ca. 3:2 mixture of two palladium complexes **3-meso** and **3-rac** (eq 2, identification vide infra). Preparative workup allows for the isolation of **3-meso** and **3-rac**, containing traces of BHT radical inhibitor and poly(methyl acrylate) from free-radical polymerization as observed by $^{1}$H NMR analysis. An alternative approach, affording pure **3-meso** and **3-rac** in high yield, was found to be halide abstraction from the recently reported dimeric cation-bridged anion [{(**1-Cl**)-$\mu$-Na}$_2$] which is easily available by the reaction of the sodium salt of the ligand (P∧ONa) with [(cod)Pd(Me)Cl].[23] Reaction of [{(**1-Cl**)-$\mu$-Na}$_2$] with AgBF$_4$ in the presence of MA (20 equivalents) in dichloromethane at 60 °C in a sealed tube for 90 min, followed by evaporation of volatiles and extraction with toluene afforded pure **3-meso,3-rac** (3:2) in good yields (>70%, eq 2).



**3-meso,3-rac**

(2)

Complexes **3-meso** and **3-rac** were identified as diastereomeric six-membered chelates **3-meso** (major isomer) and **3-rac** resulting from two consecutive 2,1-insertions of MA into the palladium-methyl bond on the basis of a detailed analysis of $^{1}$H- $^{13}$C-, $^{1}$H,$^{1}$H-gCOSY, $^{1}$H{$^{13}$C}-gHSQC- and gHMBC-experiments (Supporting Information).[24] Key $^{1}$H NMR spectroscopic features comprise palladium-α-methine resonances at $\delta$ 2.07 and 1.94 ppm as well as palladium-$\gamma$-methine resonances at 3.16 (**3-meso**) and 2.98 (**3-rac**) with corresponding $^{13}$C NMR resonances at $\delta$ 28.08 and 27.19 (α-methine) and remarkably discriminated $\gamma$-methine resonances at $\delta$ 52.06 and 44.71 ppm. The existence of a six-membered chelate ring in **3-meso** and **3-rac** is evidenced by carbonyl resonances of a Pd(II)-coordinated C(O)OMe-group (Δ) at $\delta$ 185.67 (**3-meso**) and 185.40 (**3-rac**) as well as a noncoordinated carbonyl-group (B) at $\delta$ 179.62 (**3-meso**) and 177.95 (**3-rac**) ppm.[25] Thermolysis of **3-meso,3-rac** in methylene chloride-$d_2$ at 90 °C for 48 h in the absence of additional MA yields methyl 4-carbomethoxyhex-2-enoate by $\beta$-hydride elimination as the sole product.

The stereochemistry of **3-meso,3-rac** could be assigned by single-crystal X-ray diffraction analysis. Suitable crystals were obtained from a saturated solution of **3-meso,3-rac** in a benzene-pentane mixture at 4 °C. The solid state structure is disordered with both diastereomers **3-meso** and **3-rac** occupying identical positions. The refinement converged to an occupancy of 64:36 for both stereoisomers which is in agreement with the ratio determined by NMR spectroscopy (vide supra). In the major stereoisomer **3-meso**,[26] which results from two consecutive 2,1 acrylate insertions with the same stereochemistry the ethyl group (C8, C9) is positioned anti to the carbomethoxy group (O3−C6−O4−C7), while a syn-disposition is found in **3-rac**,[26] which results from two insertions with opposite stereochemistry (Figure 1).

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(23) Rünzi, T., *Master Thesis, University of Konstanz*, 2009.

(24) In this context note, that organometallic intermediates resulting from tail-to-tail dimerization of MA featuring either a $\eta^3$-allyl bonding of the dimer to the metal centre or $\sigma$-bonding of the dimer resulting in the formation of a bis-chelate have been isolated (ref. 20).

(25) For other examples of Pd(II) alkyl/carbonyl chelate complexes cf.: (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746–4764. (b) ref. 2. (c) ref. 5. (d) Fujita, T.; Nakano, K.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2006**, *128*, 1968–1975. (e) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770–7771. (f) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 8128–8129.

(26) This designation is based on consideration of the stereocenters as part of a growing chain that is in this respect of identical (**3-meso**) or opposite (**3-rac**) stereoconfiguration.

***Table 1.*** Selected Bond Distances (Å) and Angles (°) for **3-meso,3-rac**

| | | | |
|---|---|---|---|
| Pd1−P1 | 2.217(1) | C6−O3 | 1.207(6) |
| Pd1−C1 | 2.062(4) | C6−O4 | 1.337(7) |
| Pd1−O1 | 2.129(3) | C4−O1 | 1.217(6) |
| Pd1−O5 | 2.113(3) | C4−O2 | 1.295(6) |
| C1−C2 | 1.509(7) | P1−Pd1−O5 | 95.11(9) |
| C1−C6 | 1.502(6) | C1−Pd1−O1 | 86.43(17) |

***Table 2.*** Ethylene Polymerization with Complexes **3-meso,3-rac**[a]

| entry | $p$ [bar] | TOF [mol ($C_2H_4$) mol (Pd)$^{-1}$ h$^{-1}$] | polymer yield [g] | $M_n$ [b] [$10^3$ g mol$^{-1}$] | $M_w/M_n$[b] |
|---|---|---|---|---|---|
| 2−1 | 1 | $0.1 \times 10^5$ | 0.33 | 6.7 | 2.1 |
| 2−2 | 2 | $0.5 \times 10^5$ | 1.72 | 12.9 | 2.0 |
| 2−3 | 5 | $1.1 \times 10^5$ | 3.90 | 19.0 | 1.9 |
| 2−4 | 10 | $1.4 \times 10^5$ | 5.03 | 22.0 | 1.9 |
| 2−5 | 15 | $1.5 \times 10^5$ | 5.36 | 20.1 | 2.2 |
| 2−6 | 20 | $1.6 \times 10^5$ | 5.44 | 22.3 | 2.1 |

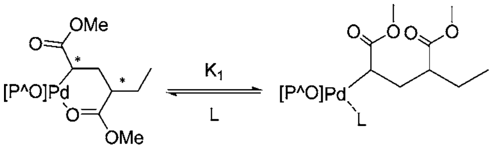
[a] Reaction conditions: 2.5 $\mu$mol Pd, 100 mL of toluene; 80 °C, 30 min polymerization time. [b] Determined by GPC at 160 °C vs linear PE.

The bond lengths around the Pd-atom (Table 1) are comparable to those of the 5-membered chelate complex [(P∧O)Pd((MeOOC)*C*HCH$_2$C(*O*)Me)][25f] and other related CO-methyl acrylate insertion products differing from the latter in the nature of the (P∧X) ligand.[5] The enlarged chelate size in **3-meso,3-rac** accounts for an increase of the binding angle O1−Pd−C1 (86.43(17) vs 82.61(21) in the aforementioned 5-membered chelate complex).

**Reactivity of Multiple Insertion Products. Polymerization Studies.** A first indication of the reactivity of **3-meso,3-rac** is given by studies of polymerization with the compounds as catalyst precursors. Exposure of **3-meso,3-rac** to ethylene results in polymerization with high rates also at low pressures. Activities in 30 min polymerization experiments are independent of monomer concentration at p($C_2H_4$) ≥ 5−10 bar for **3-meso,3-rac** (Table 2). Activation of **3-meso,3-rac** for ethylene polymerization requires an initial opening of the chelate by coordination of ethylene (vide infra), which apparently occurs efficiently under these conditions. **3-meso,3-rac** exhibits a slightly higher activity than **1-dmso** (**1-dmso**: $1.0 \times 10^5$ TO h$^{-1}$, **3-meso,3-rac**: $1.5 \times 10^5$ TO h$^{-1}$ under identical conditions). This is related to the irreversibility of the opening of the chelate. Once ethylene is inserted, the oxygen atom of the carbonyl group does not compete anymore with monomer coordination due to increasingly disfavored chelate sizes with their entropic contribution, while the entropic penalty of dmso coordinating to the metal center remains essentially unchanged over the whole polymerization reaction.

In acrylate insertion oligomerization, productivities of **3-meso,3-rac** are similar to the activity of **1-dmso** (DP$_n$ ∼ 7, TON ∼ 100). After every consecutive insertion, 6-membered chelated complexes similar to **3-meso,3-rac** are invariably formed. NMR characterization of these higher insertion products is hampered by the extreme complexity of the spectra resulting from the growing number of stereocenters in the metal-bound growing chain, and simultaneous $\beta$-hydride elimination reactions. However, mass spectrometry enabled the direct observation of the organometallic products of further insertion of acrylates into **3-meso,3-rac** (Scheme 1, Figure 2). A solution of **3-meso,3-rac** and 30 equivalents methyl acrylate in benzene was kept for 4 h at 60 °C. Evaporation of solvent and extraction with Et$_2$O yielded a white precipitate upon addition of pentane to the ether extract. Electrospray ionization (ESI) as a particularly mild technique allowed for the recording of mass spectra from MeOH solutions. Triethylammonium salts were found to be suited as a cationizing agent.[27] HNEt$_3^+$ adducts of the [(P∧O)PdR] complexes (M + 102.13) represent the major species observed by ESI-MS (Figure 2). The observed very specific isotope pattern is in agreement with the expected peak structure (Figure 2, insets).[28] Apart from the starting material ($m/z$ = 796), the products of two further consecutive methyl acrylate insertion into **3-meso,3-rac** are clearly detected ($m/z$ = 882; 968). Further minor signals ($m/z$ = 782; 868) result from the consecutive insertion of methyl acrylate into the Pd−H bond of the hydride [(P∧O)PdH], which is formed by $\beta$-hydride elimination. In a similar manner products from multiple insertion of butyl acrylate into **3-meso,3-rac** and [(P∧O)PdH] were generated and characterized (cf. Supporting Information). The direct observation of these higher insertion products further confirms that this polymerization of acrylate follows an insertion pathway.[29]

**Coordination Equilibria.** The reactivity of **3-meso,3-rac** towards the olefinic substrates is of interest, as $\pi$-coordination of substrate (ethylene, MA) is a prerequisite for further chain growth. Exposure of CD$_2$Cl$_2$-solutions of **3-meso,3-rac** (0.04 mol L$^{-1}$) to excess ethylene (30 equivalents) or methyl acrylate (27 equivalents) at temperatures down to −80 °C resulted in no reaction as observed by $^1$H and $^{13}$C NMR spectroscopy, that is the chelating carbonyl group is not displaced by the substrates under these conditions. This corresponds to equilibrium constants of $K_{eq} < 10^{-2}$ (eq 3).[30] By comparison, the more strongly coordinating ligand pyridine appears to react virtually completely with **3-meso,3-rac** to **3-meso-pyr**, **3-rac-pyr** (Figure 3).



**3-meso, 3-rac** **3-meso-L, 3-rac-L** (3)

With dmso as a ligand, a directly observable equilibrium exists at room temperature. The equilibrium constants $K_1$(T) = [**3-meso-dmso**,**3-rac-dmso**]/([**3-meso,3-rac**] × [dmso]) were determined by $^{13}$C NMR spectroscopy in the temperature range between 278 to 308 K, based on the chemical shift of the Δ-carbonyl resonances.[31] The values of the reaction enthalpy Δ$H$° = −3.0(6) kJ mol$^{-1}$ and entropy Δ$S$° = −3(2) J mol$^{-1}$ K$^{-1}$ were obtained by a Van't Hoff plot (Figure S19,

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(27) The addition of a cationizing agent is necessary to obtain reasonable signal intensities.

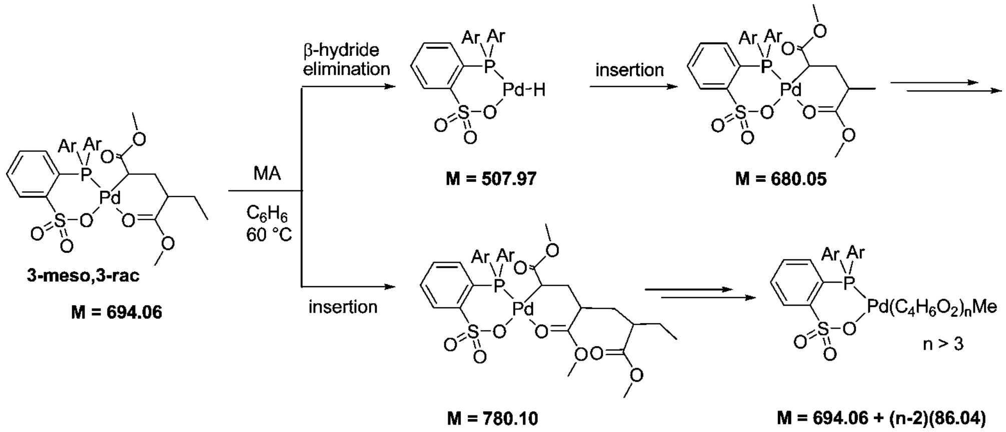
(28) The isotope patterns of the masses for MA insertion into **3-meso,3-rac** ($m/z$ = 796, 882, 968) show a tailing. This can be explained by appearance of minor peaks from the Na adducts (M+23) of these complexes, which becomes evident from the isolated peak for the starting material [**3-meso,3-rac**+Na]$^+$ ($m/z$ = 717).

(29) In this context note that for other types of organometallic Pd(II) complexes free-radical polymerization of acrylates to high-molecular-weight polymer triggered by acrylate insertion has been found: (a) Albeníz, A. C.; Espinet, P.; López-Fernández, R. *Organometallics* **2003**, *22*, 4206–4212. (b) López-Fernández, R.; Carrera, N.; Albeníz, A. C.; Espinet, P. *Organometallics* **2009**, *28*, 4996–5001.

(30) Conservatively assuming a detection limit of 5% for the chelate opening.

(31) The temperature range was limited by the cryo-coil probehead employed to obtain sufficient spectral quality. A fast site exchange between free and chelated carbonyl resulted in the observation of one averaged resonance (Figure 3 and supporting information).

***Scheme 1.*** Insertion of Methyl Acrylate into Complexes **3-meso,3-rac**[a]



[a] M represents major mass of the isotope pattern, detected by ESI-MS as the $HNEt_3$-adducts (M+102.13).

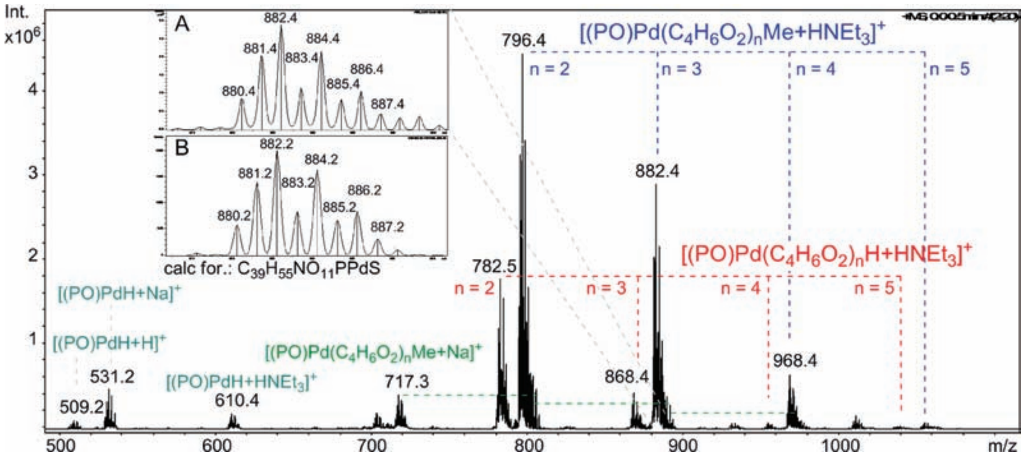


***Figure 2.*** Positive-ion ESI-mass spectrum of multiple insertion products (methanol solution with added $[HNEt_3][B(C_6F_5)_4]$). Inset A: found isotope pattern; inset B: calculated isotope pattern for $C_{39}H_{55}NO_{11}PPdS$.

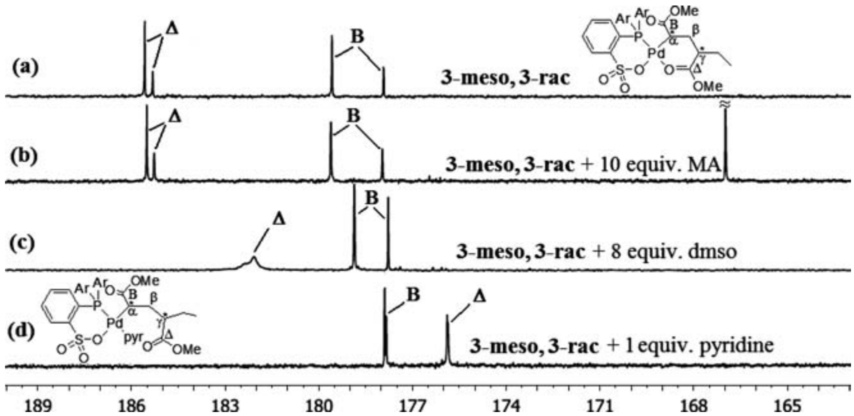


***Figure 3.*** $^{13}C$ NMR spectra (carbonyl region, $CD_2Cl_2$, 298 K, [Pd] ~ 0.04 $moL^{-1}$) of pure **3-meso,3-rac** (a) and in the presence of 10 equiv MA (b); 8 equiv of dmso (c); 1 equiv of pyridine (d).

Supporting Information).[32] The observed entropy loss is surprisingly low for a chelate opening process A + B ⇄ C. Indeed, for cationic (N∧N)Pd(II) complexes much more negative entropies have been observed.[2b,33] However, it has also been noted that the nature of the incoming ligand (L; eq 3) in chelate opening can have an unexpectedly strong impact on the reaction entropy.[33]

The equilibrium constant for the opening of the double acrylate insertion product **3-meso,3-rac** with ethylene substrate ($K_2$) is of relevance in the context of copolymerizations affording linear ethylene-acrylate copolymers with high MA contents (> ca. 20%), in which consecutive MA insertions occur to a considerable extent.[15] As outlined, an opening of the chelate by olefinic substrate could not be observed even at low temperatures; thus, a direct determination especially at the elevated temperatures typically employed for polymerization reactions (80 °C) was not possible. $K_2$(353 K) could be estimated by combining the equilibrium constant for chelate opening with

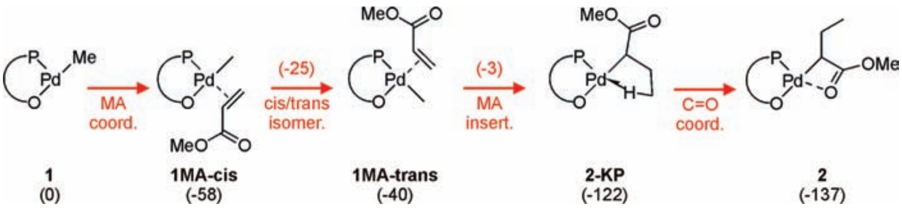


***Figure 4.*** Methyl acrylate coordination and insertion in **1**. Relative energies of the various species are given in parentheses (in kJ mol$^{-1}$; black: intermediates; red: transition states).

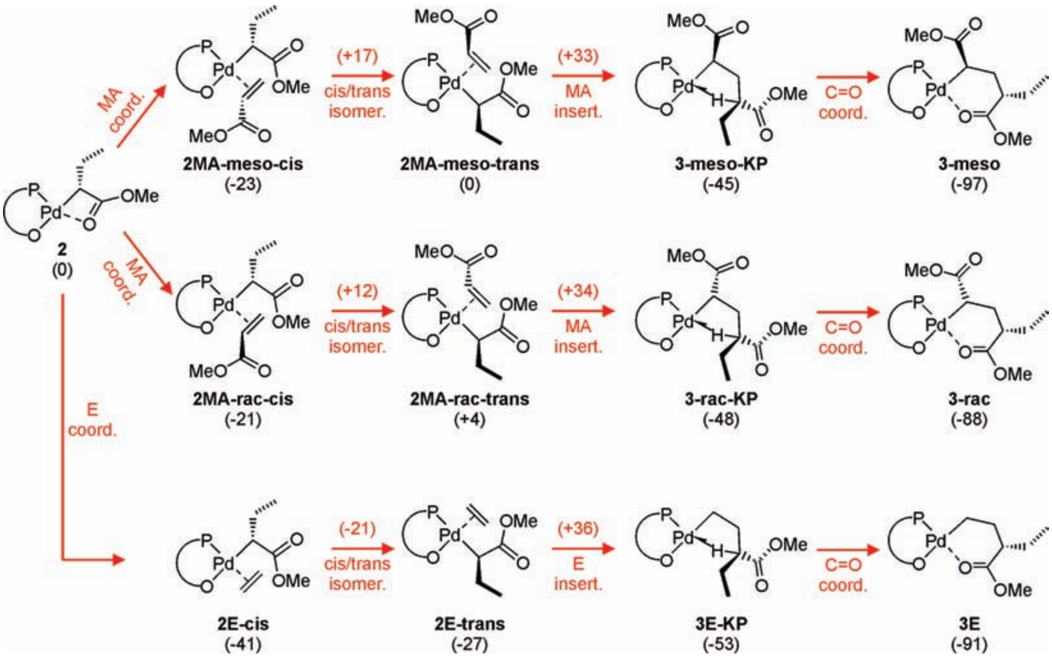


***Figure 5.*** Methyl acrylate and ethylene insertion from **2**. Relative energies of the various species are given in parentheses (in kJ mol$^{-1}$; black: intermediates; red: transition states).

dmso ($K_1$) with the relative binding strength ($K_3$) of dmso vs ethylene ($[(P\wedge O)PdR(dmso)] + C_2H_4 \rightleftarrows [(P\wedge O)PdR(C_2H_4)] + dmso$). The relative binding strength was determined from the observed inhibition of polymerization rates by variable amounts of added dmso in ethylene polymerization experiments at 80 °C and 10 bar ethylene pressure (Table S5, Supporting Information). A plot of TOF$_{max}$/TOF against the ratio of concentrations [dmso]/[ethylene] gives $K_3(353\ K) = 1.1(2) \times 10^{-3}$ (Figure S22, Supporting Information). Recently, Claverie et al. estimated the relative binding strength of ethylene vs pyridine for **1-pyr** to $K_4 \sim 10^{-7}$.[17] The higher value for $K_3$ compared to $K_4$ is consistent with dmso being the more labile ligand. Combining K$_3$ with $K_1(353\ K) \approx 1.9$ L mol$^{-1}$ extrapolated from the thermodynamic data (Figure S19, Supporting Information), $K_2 = K_1 \times K_3$, yielded an estimated value of $K_2(353\ K) \approx 2 \times 10^{-3}$ L mol$^{-1}$ for the chelate opening with ethylene at 80 °C. This illustrates the stability of the six-membered chelate, which hinders but does not suppress polymerization.[34]

**Computational Studies.** In order to gain a deeper understanding of the catalytic methyl acrylate insertion polymerization, reaction pathways of chain growth were studied theoretically employing DFT methods. Regarding consecutive insertions of acrylate into a metal-alkyl species, the first three insertions are expected to exhibit distinctly different energy profiles, as the starting species are different in energy due to different modes of chelating coordination of already incorporated acrylate repeat units via the carbonyl group, and also the substitution of the migrating alkyl group differs particularly between the first and the second insertion. Consecutive insertions were studied starting from the palladium methyl species **1**. Exclusively the 2,1-insertion modus of methyl acrylate was considered, since it is the predominant insertion mode observed experimentally. Note that the first insertion is similar to previous studies by Ziegler et al. of methyl acrylate insertion into a Pd-*n*-propyl bond in the context of acrylate/ethylene copolymerization with this catalyst system.[19]

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(32) Observations of the **3-meso,3-rac** + dmso $\rightleftarrows$ **3-meso-dmso,3-rac-dmso** equilibrium at 193 K are in qualitative agreement with the low temperature dependence of the equilibrium derived from the NMR data acquired at 278 to 308 K. At low temperature, exchange is slow on the NMR time scale, which actually facilitates the experiment, but additional non-identified species observed (possibly as a result of slow exchange between conformers) hamper a full analysis (cf. supporting information).

(33) For the (5-membered) chelate [(N∧N)Pd(R*C*(H)OC(*O*)CH$_3$)], it was found that opening with acetonitrile resulted in a much lower entropy ($\Delta S = -38$ J mol$^{-1}$ K$^{-1}$) in comparison to the opening with ethylene ($\Delta S = -96$ J mol$^{-1}$ K$^{-1}$). This was tentatively related to acetonitrile losing fewer degrees of freedom by its linear coordination by comparison to $\eta^2$-coordination of ethylene, also a possible stronger organization of the solvent by free acetonitrile vs. ethylene; and motion of the OC(*O*)CH$_3$-moiety being more extensively restricted by ethylene coordination: Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132–5146.

As expected, methyl acrylate coordination to **1** is strongly favorable and the most stable coordination intermediate **1MA-cis,** with the Pd−C σ-bond cis to the P atom, is nearly 60 kJ mol$^{-1}$ lower in energy than **1** (Figure 4). This π-complex is slightly more stable, by about 15 kJ mol$^{-1}$, than the alternative isomer in which the acrylate molecule is κ-O bound to the metal by the carbonyl oxygen atom. In agreement with previous calculations,[16,19] the preferred pathway for methyl acrylate insertion into the Pd−C bond proceeds through isomerization of **1MA-cis**, with a barrier of 33 kJ mol$^{-1}$, to the less stable species **1MA-trans** which is roughly 20 kJ mol$^{-1}$ higher in energy than **1MA-cis**. 2,1- insertion into the Pd−C bond of **1MA-trans**, associated with an energy barrier of ca. 40 kJ mol$^{-1}$, affords the kinetic product **2-KP**, stabilized by a γ-agostic interaction, and finally the monoinsertion product **2**. **2** is stabilized by coordination of the C=O group of the inserted methyl acrylate unit, forming a four-membered chelate.

The second methyl acrylate insertion requires dissociation of the O-coordinated carbonyl moiety from the Pd center in **2**, with simultaneous methyl acrylate coordination (Figure 5). Due to the stabilizing effect of the carbonyl coordination, this step is less favorable by ca. 35 kJ mol$^{-1}$ by comparison to methyl acrylate coordination to the alkyl species **1**. By comparison to methyl acrylate, π-coordination of ethylene to **2** is remarkably favored with an energy gain of 41 kJ mol$^{-1}$, in line with previous calculations on both cationic and neutral Pd catalysts.[19,35,36] Again, migratory insertion requires first cis/trans isomerization to the less stable geometry with the monomer coordinated cis to the P donor (**2MA-trans** both meso and rac, and **2E-trans** in Figure 5).[37] This isomerization proceeds through a concerted mechanism without dissociation of the coordinated monomer, as already indicated by Ziegler et al.,[19] and Morokuma and Nozaki et al.[16] for polyethylene chain growth or an isolated insertion of acrylate, respectively. It requires ca. 30 to 40 kJ mol$^{-1}$ for the methyl acrylate complex, while the barrier is roughly 20 kJ mol$^{-1}$ lower for the ethylene complex. This slightly lower barrier for isomerization of the ethylene complex is consistent with the reduced destabilization of **2E-trans** relative to **2E-cis** (ca. 15 kJ mol$^{-1}$) by comparison to a destabilization of ca. 25 kJ mol$^{-1}$ for both **2MA-trans** species relative to the corresponding **2MA-cis** species. Both methyl acrylate- and the ethylene-insertion transition states collapse into γ-agostic complexes as the first kinetic product, which convert to the six-membered carbonyl-coordinated chelates (**3-meso**, **3-rac** and **3E**) as the final stable products. Overall, the insertion liberates ca. 90 to 100 kJ mol$^{-1}$ (energy difference **2** vs **3-meso**, **3-rac** or **3E**). At this point, the main difference between coordination−insertion of methyl acrylate and ethylene in **2** is the more favorably π-coordination of ethylene.

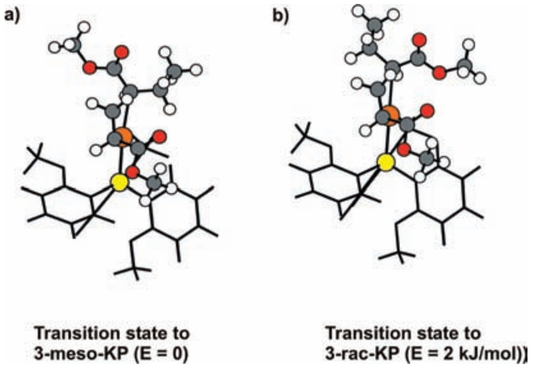

***Figure 6.*** Transition states for methyl acrylate insertion affording **3-meso-KP** and **3-rac-KP**, respectively.

Considering that experimental studies[2b,25a] (the results of which have also been employed previously for theoretical considerations)[19] indicate an unfavorable entropic contribution of about 40 kJ mol$^{-1}$ for coordination of either monomer, formation of the olefin complexes **2MA-cis** from **2** should be endoergonic by ca. 20 kJ mol$^{-1}$, whereas formation of **2E-cis** is probably exoergonic. Further, still on a free energy profile, and considering a minor entropic change between the coordination intermediates and the corresponding transition states, for insertion of both methyl acrylate and ethylene the transition states are roughly 70 kJ mol$^{-1}$ higher than **2** + free monomer.

Concerning the stereochemistry of acrylate insertion from **2**, all species along the reaction pathway leading to **3-meso** are slightly lower in energy than the corresponding species leading to **3-rac**. The preference for the transition state leading to **3-meso** is rather small, 2 kJ mol$^{-1}$ only, which agrees well qualitatively with the experimentally observed formation of a ca. 3:2 meso:rac mixture of the two diastereomers.[26] The preferred transition state (Figure 6) is likely favored due to the relative anti disposition of the two −COOMe groups, which minimizes steric and electrostatic repulsion.

Concerning the third insertion of methyl acrylate, in view of the rather similar energetics revealed for the pathways corresponding to insertion of the two enantiofaces of methyl acrylate in the second insertion, only coordination−insertion from the slightly more stable complex **3-meso** leading to another meso diad, thus overall affording an isotactic triad, is considered (Figure 7).

The third methyl acrylate insertion, which is representative for acrylate insertion polymerization chain growth, requires dissociation of the carbonyl moiety from the Pd center in **3-meso**, with simultaneous methyl acrylate coordination, associated with an energy gain of about 15 kJ mol$^{-1}$. By comparison, ethylene coordination to **3-meso** releases ca. 35 kJ mol$^{-1}$. The equilibrium constant for the chelate opening with ethylene $K_2$(353 K) ≈ 2 × 10$^{-3}$ L mol$^{-1}$ estimated from the experimental data corresponds to a $\Delta H$ of −32 kJ mol$^{-1}$ at 353

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(34) As a commentary concerning the significance and utility of this equilibrium data, note that while it is subject to experimental error and includes the assumption of similar relative binding strength of ligands in different Pd-alkyls, otherwise from the viewpoint of thermodynamics the argument is fully valid and only includes the assumption that $\Delta H_1°$ and $\Delta S_1°$ of the chelate opening with dmso are temperature-independent. A $K_2(353\ \text{K}) = 2 \times 10^{-3}$ L mol$^{-1}$ corresponds to $\Delta G_2°(353\ \text{K})$ ca. 18 kJ mol$^{-1}$. Working-hypothesis-level considerations at other temperatures utilizing this data require an assumption on the contributions of $\Delta H_2°$ and $\Delta S_2°$ of chelate opening by monomer to this free enthalpy value. It is common practice to assume that for equilibria $\text{ML}_1 + \text{L}_2 \rightleftarrows \text{ML}_2 + \text{L}_1$ the entropy contribution is negligible. For the particular case discussed ($\text{L}_{1,2}$ = dmso, monomer), this would translate to the assumption that the entropy of chelate opening by monomer ($\Delta S_2°$) is the same as for dmso ($\Delta S_1°$), the latter being amenable to experimental observation. However, the aforementioned (ref 33) experimental findings of very different $\Delta S°$ for a cationic diimine systems for ($\text{L}_{1,2}$ = acetonitrile, ethylene) question the validity of this argument. An, arguable, alternative is an educated guess of $\Delta S_2°$ assuming that it is similar to the entropies of comparable carbonyl-chelate opening process in cationic Pd(II) diimine complexes, which have been determined experimentally (for example $\Delta S = -96^{33}$ and $-151^{25a}$ J mol$^{-1}$ K$^{-1}$ (five-membered chelates), $-100^{25a}$ and −121 to $-142^{2b}$ J mol$^{-1}$ K$^{-1}$ (six-membered chelates)).

(35) Michalak, A.; Ziegler, T. *Organometallics* **2001**, *20*, 1521–1532.

(36) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 12266–12278.

(37) Calculations indicated that for both monomers the insertion transition state from **2-monomer-cis** is at least 25 kJ mol$^{-1}$ higher in energy than from **2-monomer-trans**.

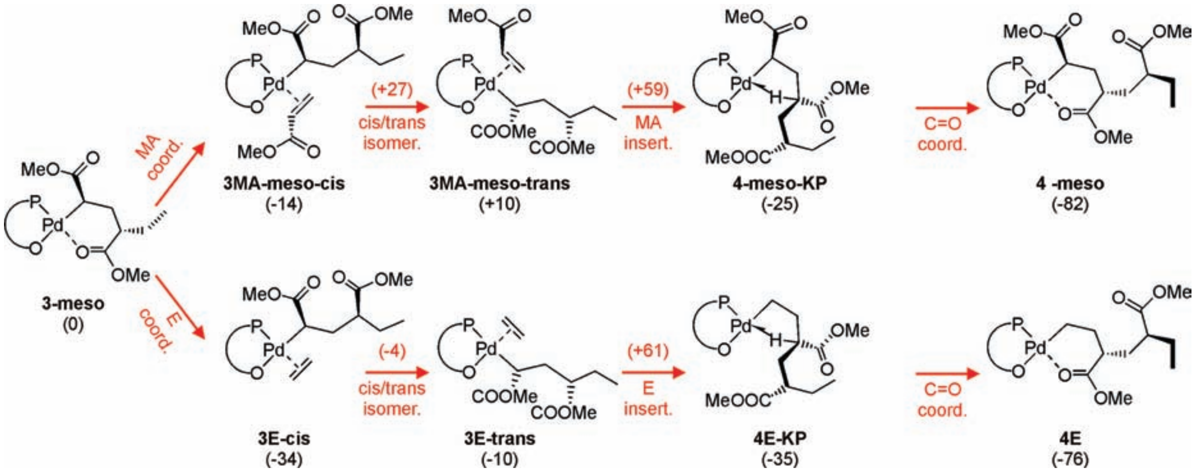

***Figure 7.*** Methyl acrylate and ethylene insertion from **3-meso**. Relative energies of the various species are given in parentheses (in kJ mol$^{-1}$; black: intermediates; red: transition states).

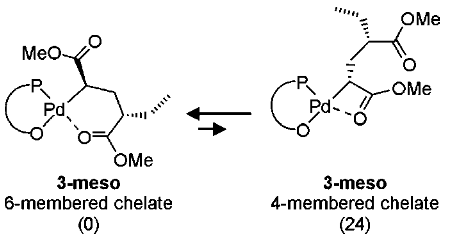

***Figure 8.*** Six- and four-membered chelate structures of **3-meso**, energies in kJ mol$^{-1}$ in parentheses.

K. This is in good agreement with the calculated energy gain.[38] The coordination energies are about 10 kJ mol$^{-1}$ lower by comparison to monomer coordination to **2**, due the higher stability of the six-membered chelate ring of **3-meso** relative to the four-membered chelate **2**. Indeed, calculations show that also the four-membered chelate geometry of **3-meso** is less stable than the six-membered geometry by about 25 kJ mol$^{-1}$ (Figure 8).

Considering the strong prevalence found for the second insertion for this pathway, it can be assumed that also the third migratory insertion requires isomerization of the more stable geometries **3MA-meso-cis** and **3E-cis** to the less stable **3MA-meso-trans** and **3E-trans**, respectively. Also in this case isomerization barriers were calculated to amount to roughly 30−40 kJ mol$^{-1}$. The insertion transition states are thus reached from the **3MA-meso-trans** and **3E-trans** intermediates, with barriers of 73 and 95 kJ mol$^{-1}$ relative to **3MA-meso-cis** and **3E-cis**, respectively. Both methyl acrylate and ethylene insertion transition states collapse first into the kinetic $\gamma$-agostic product, which rearranges to the six-membered O-coordinated chelates as the stable final products. Overall, the third insertion liberates ca. 80 kJ mol$^{-1}$ (energy difference **3-meso** vs **4-meso** or **4E**).

On a free energy profile, assuming an entropic contribution of roughly 40 kJ mol$^{-1}$ for coordination of either monomer (vide infra), formation of **3MA-meso-cis** and **3E-cis** from **3** are endoergonic by ca. 30 and 10 kJ mol$^{-1}$ respectively. Further, the transition states for insertion of both methyl acrylate and ethylene are roughly 100−110 kJ mol$^{-1}$ above **3-meso** + free monomer. This indicates that the high stability of the six-membered resting state formed by chelating coordination of the penultimate inserted acrylate unit is a key limitation in acrylate homopolymerization.

At this point, a comparison with the behavior of cationic Pd(II) catalyst systems is instructive. From calculations by Ziegler et al.,[19,36] the main difference between cationic and neutral Pd-systems is the oxophilicity of the metal center, which is higher in the cationic Pd-systems. Consequently, the rupture of the six-membered chelate resting state in the cationic Pd(II)-system by monomer $\pi$-coordination is much more disfavored relative to the same process in the neutral Pd-systems. This can rationalize the better ability of neutral Pd(II) catalysts to enchain consecutive methyl acrylate units. The different oxophilicity of cationic and neutral Pd systems is also exemplified by the unability of the neutral Pd-system to assume square pyramidal geometries in the olefin complexes (Figure 9). Both for methyl acrylate and ethylene coordination to **3-meso**, the isomer with a four-membered chelation of the carbonyl group of the last inserted methyl acrylate unit in the axial position of the square pyramid is not stable, and all geometry optimizations resulted in the breaking of chelation. Differently, the isomer with a six-membered chelation of the carbonyl group of the penultimate inserted methyl acrylate unit in the axial position of the square pyramid is stable, but quite high in energy, roughly 20 to 40 kJ mol$^{-1}$ relative to the simple square planar complex **3-meso**. This differs strikingly from ethylene insertion after a methyl acrylate unit promoted by cationic Pd(II) complexes.[36] In this case the square pyramidal isomer with a six-membered chelating carbonyl moiety in the axial position was found to be the most stable isomer in the case of ethylene coordination, the square pyramidal four-membered chelate isomer was found to be stable and ca. 5 kJ mol$^{-1}$ higher in energy, and the least stable isomer is the simple four-coordinate square planar isomer at least 10 kJ mol$^{-1}$ higher in energy relative to six-membered chelate square pyramidal geometry.[36]

## Summary and Conclusions

The exposure of reactive species [{(P∧O)PdMe}$_n$] (**1**) to methyl acrylate (MA) yields the isolable product of two consecutive acrylate insertions into the Pd-Me bond (**3-meso** and **3-rac**). Single crystal X-ray diffraction analysis as well as comprehensive NMR studies reveal **3-meso,3-rac** to be two

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[38] The calculation of $\Delta H$ includes an unfavorable entropic contribution of 50 kJ mol$^{-1}$ at 353 K, estimated from the experimentally observed typical entropy for olefin complexation to related cationic Pd complexes, which varies between −113 and −151 J mol$^{-1}$ K$^{-1}$ (refs 2a and 25a).

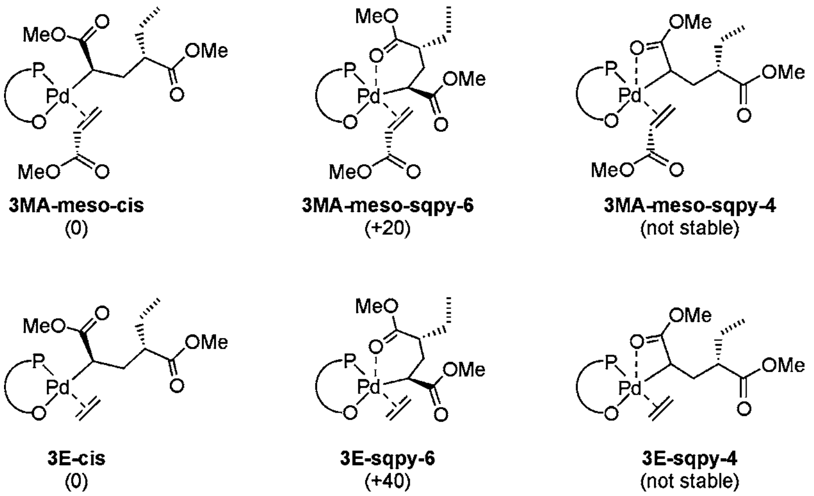

***Figure 9.*** Relative energies (in kJ $mol^{-1}$) of different isomers formed by coordination of methyl acrylate or ethylene to **3-meso**.

diastereomers formed by 2,1-insertions of MA, in which the carbonyl moiety of the first inserted monomer unit coordinates to the metal center in a chelating fashion. This finding is consistent with theoretical studies, which demonstrate that significant stabilization of the primary multiple acrylate insertion product results from such chelating coordination. The experimentally observed low preference for the major diastereomer (3:2) is in agreement with theoretical studies of the insertion steps, and it is in line with the nonstereoregular nature of the methyl acrylate oligomers and low-molecular-weight polymers generated with catalysts based on the same phosphinesulfonato ligand.[15]

**3-meso,3-rac** are a direct analogue of the key intermediates in catalytic acrylate insertion polymerization as well as ethylene-acrylate copolymerization to high acrylate content copolymers. Displacement of the chelating carbonyl group by incoming olefinic substrate is a prerequisite for further chain growth. The relative stability of the chelate **3** is reflected by the fact that an opening with neither ethylene nor methyl acrylate could be observed by NMR spectroscopy even at low temperature. A fast equilibrium is observed at room temperature with dmso and the thermodynamic parameters $\Delta H_1° = -3.0(6)$ kJ $mol^{-1}$ and $\Delta S_1° = -3(2)$ J $mol^{-1}$ $K^{-1}$ could be obtained via a $^{13}C$ NMR study from a Van't Hoff plot. Combined with polymerization inhibition studies affording the relative binding strength of ethylene vs dmso, an approximation for the chelate opening with ethylene (**3-meso,3-rac** + $C_2H_4 \rightleftarrows$ **3-meso,3-rac**-$C_2H_4$) under typical polymerization conditions (80 °C) yielded $K_2(353\ K) \approx 2 \times 10^{-3}$ L $mol^{-1}$. Energy values from DFT, which does not consider entropy contributions, are in good qualitative agreement with this conclusion that chelating coordination of a second-last inserted acrylate unit retards chain growth significantly, but not prohibitively. This is in line with polymerization experiments showing that **3-meso,3-rac** are precursors for very active ethylene polymerization catalysts at 5 bar and 80 °C.

Theoretical studies give insight also to key steps which were not amenable to direct experimental observation. $\pi$-coordination of acrylate to the products of multiple acrylate insertion is associated with a relatively low energy gain and, on a free energy level, likely endergonic, as a consequence of the aforementioned relatively favorable chelating coordination. The overall insertion barrier amounts to ca. 100 kJ $mol^{-1}$, which does not differ much from the overall insertion barrier for ethylene, in-line with an insertion mechanism of acrylate polymerization with these catalysts. Indeed, products of multiple insertion of acrylate into a Pd-alkyl bond $[(P{\wedge}O)Pd(C_4H_6O_2)_nMe]$ up to $n = 4$ formed by the reaction of **3-meso,3-rac** with acrylates could be directly observed by mass spectrometry.

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**Supporting Information Available:** Full list of authors for ref 6c, experimental procedures, and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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