

Activation and Deactivation of Neutral Palladium(II) Phosphinesulfonato Polymerization Catalysts

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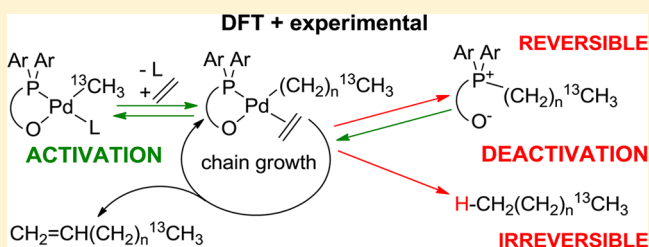
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S Supporting Information

ABSTRACT: ¹³C-Labeled ethylene polymerization (pre)-catalysts [κ^2 -(anisyl)₂P(O)Pd(¹³CH₃)(L) (**1**-¹³CH₃-L) (L = pyridine, dmsO) based on di(2-anisyl)phosphine benzenesulfonate were used to assess the degree of incorporation of ¹³CH₃ groups into the formed polyethylenes. Polymerizations of variable reaction time reveal that ca. 60–85% of the ¹³C-label is found in the polymer after already 1 min polymerization time, which provides evidence that the pre-equilibration between the catalyst precursor **1**-¹³CH₃-L and the active species **1**-¹³CH₃-(ethylene) is fast with respect to chain growth. The fraction of **1**-¹³CH₃-L that initiates chain growth is likely higher than the 60–85% determined from the ¹³C-labeled polymer chain ends since (a) chain walking results in in-chain incorporation of the ¹³C-label, (b) irreversible catalyst deactivation by formation of saturated (and partially volatile) alkanes diminishes the amount of ¹³CH₃ groups incorporated into the polymer, and (c) palladium-bound ¹³CH₃ groups, and more general palladium-bound alkyl(polymeryl) chains, partially transfer to phosphorus by reductive elimination. NMR and ESI-MS analyses of thermolysis reactions of **1**-¹³CH₃-L provide evidence that a mixture of phosphonium salts (¹³CH₃)_xP⁺(aryl)_{4-x} (**2**–**7**) is formed in the absence of ethylene. In addition, isolation and characterization of the mixed bis(chelate) palladium complex [κ^2 -(anisyl)₂P(O)Pd[κ^2 -(anisyl)(¹³CH₃)P(O)] (**11**) by NMR and X-ray diffraction analyses from these mixtures indicate that oxidative addition of phosphonium salts to palladium(0) species is also operative. The scrambling of palladium-bound carbyls and phosphorus-bound aryls is also relevant under NMR, as well as preparative reactor polymerization conditions exemplified by the X-ray diffraction analysis of [κ^2 -(anisyl)₂P(O)Pd[κ^2 -(anisyl)(CH₂CH₃)P(O)] (**12**) and [κ^2 -(anisyl)₂P(O)Pd[κ^2 -(anisyl)((CH₂)₃CH₃)P(O)] (**13**) isolated from pressure reactor polymerization experiments. In addition, ESI-MS analyses of reactor polymerization filtrates indicate the presence of (odd- and even-numbered alkyl)(anisyl)phosphine sulfonates (**14**) and their respective phosphine oxides (**15**). Furthermore, 2-(vinyl)anisole was detected in NMR tube and reactor polymerizations, which results from ethylene insertion into a palladium–anisyl bond and concomitant β -hydride elimination. In addition to these scrambling reactions, formation of alkanes or fully saturated polymer chains, bis(chelate)palladium complexes [κ^2 -P(O)]₂Pd, and palladium black was identified as an irreversible catalyst deactivation pathway. This deactivation proceeds by reaction of palladium alkyl complexes with palladium hydride complexes [κ^2 -P(O)Pd(H)(L)] or by reaction with the free ligand H[P(O)] generated by reductive elimination from [κ^2 -P(O)Pd(H)(L)]. The model hydride complex **1**-H-P^tBu₃ has been synthesized in order to establish whether **1**-H-P^tBu₃ or H[P(O)] is responsible for the irreversible catalyst deactivation. However, upon reaction with **1**-⁽¹³⁾CH₃-L or **1**-CH₂CH₃-PPh₃, both **1**-H-P^tBu₃ and H[P(O)] result in formation of methane or ethane, even though H[P(O)] reacts faster than **1**-H-P^tBu₃. DFT calculations show that reductive elimination to form H[P(O)] and (alkyl)[P(O)] from **1**-H/(alkyl)-P^tBu₃ is kinetically accessible, as is the oxidative readdition of the P–H bond of H[P(O)] and the P–anisyl bond of (alkyl)[P(O)] to [Pd(P^tBu₃)₂]. These calculations also indicate that for a reaction sequence comprising reductive elimination of H[P(O)] from **1**-H-P^tBu₃ and reaction of H[P(O)] with **1**-CH₃-P^tBu₃, **1**-CH₃-dmsO, or **1**-CH₂CH₃-PPh₃ to form methane or ethane, the rate-limiting step is reductive elimination of H[P(O)] with a barrier of 124 kJ mol^{–1}. However, a second reaction coordinate was found for the reaction of **1**-H-P^tBu₃ with **1**-CH₃-P^tBu₃ or **1**-CH₃-dmsO, which evolves into bimetallic transition-state geometries with a nearly linear H–(CH₃)–Pd alignment and which exhibits a barrier of 131 or 95 kJ mol^{–1} for the formation of methane.



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INTRODUCTION

Catalytic polymerizations of olefins are practiced on a large scale. However, an insertion polymerization of polar vinyl monomer is a long-standing challenge.^{1,2} Major advances were achieved recently by the finding that neutral κ^2 -P,O-phosphinesulfonato palladium(II) complexes (cf. 1-L) promote the formation of linear copolymers of ethylene with a broad scope of polar monomers including not only acrylates,³ but also acrylonitrile,⁴ vinylacetate,⁵ vinylfluoride,⁶ allylic monomers,⁷ acrylic acid,⁸ and acrylamides⁹ and also catalyze insertion homooligomerization of acrylates.^{10,11}

Many features of the catalytic chain growth in these (co)polymerizations have been revealed by detailed experimental and theoretical investigations,¹² and a fairly comprehensive mechanistic picture exists. Polar monomers ($\text{CH}_2=\text{CHX}$) reduce polymerization rates by chelating coordination of the growing polymeryl chain via functional groups (X) of a last or penultimate incorporated repeat unit. For many polar monomers κ -X coordination of free monomer can also block coordination sites required for π -coordination of monomer and chain growth. These and other features observed are all reversible, and they slow down but do not shut down chain growth.

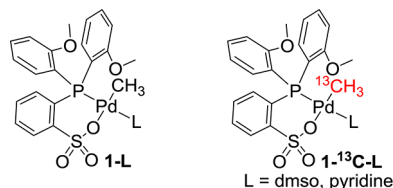
No irreversible steps have been reported to occur in polymerizations with these catalysts, although the importance of any such steps for polymer synthesis, catalyst development, and also mechanistic analyses is obvious. It appears that this unique class of catalysts is considered to be essentially stable during polymerization. Intimately related to issues of irreversible deactivation is the efficiency of activation of the catalyst precursor employed. A knowledge of the portion of metal sites that actually enter the catalytic cycle as an active species is essential in order to analyze decomposition pathways of the latter.

We now report on the identification and in-depth analyses of various reversible and irreversible deactivation reactions that occur extensively in polymerizations and have long-ranging implications, and provide a detailed analysis of catalyst precursor activation as a prerequisite for a comprehensive picture.

RESULTS AND DISCUSSION

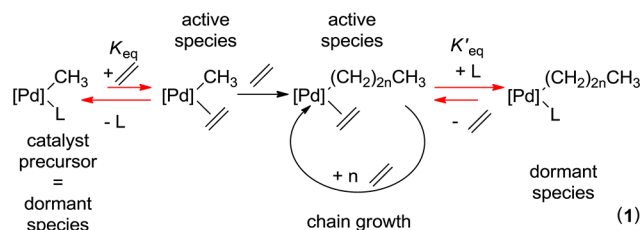
Methyl complexes $1\text{-CH}_3\text{-L}$ have been employed frequently as well-defined catalyst precursors (Chart 1).^{4–10,12} Activation

Chart 1. Natural Abundance and ^{13}C -Enriched Complexes $1\text{-}^{13}\text{CH}_3\text{-L}$



occurs by displacement of the monodentate ligand L by ethylene monomer and insertion in the resulting olefin complex $1\text{-CH}_3\text{-(ethylene)}$. Closely related to this activation pre-equilibrium (K_{eq}), the growing active species $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-(ethylene)}$ can be in equilibrium with a dormant state due to competitive binding of the olefin and the ligand L introduced with the catalyst precursor (K'_{eq} in eq 1).

Assuming these competitive binding equilibria to be fast, this overall scenario should result in a saturation kinetic behavior of the polymerization reaction. That is, with increasing ethylene



concentration, the overall rate of polymer formation should asymptotically approach a maximum value that corresponds to the equilibria being entirely in favor of the olefin complexes. Indeed, such saturation kinetic behavior was observed for $1\text{-CH}_3\text{-L}$ at $p(\text{ethylene}) > 5\text{--}10$ bar ($\text{L} = \text{dmsO}$) or >15 bar ($\text{L} = \text{pyridine}$) in 30 and 60 min polymerization runs.¹⁰ However, the assessment of a rapid equilibration of $1\text{-CH}_3\text{-L}$ and $1\text{-CH}_3\text{-(ethylene)}$ with respect to chain growth was never made. Moreover, the picture outlined in eq 1 suggests that precatalysts $1\text{-CH}_3\text{-L}$ quantitatively participate in the polymerization reaction and that no other competitive reaction pathways exist by which fractions of $1\text{-CH}_3\text{-L}$ or $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-L}$ may be excluded from forming polymer.

Activation of Precatalysts under Preparative Polymerization Conditions and Overall Incorporation of ^{13}C -Label in the Formed Polymer. In a first approach to elucidate these issues ^{13}C -labeled precatalysts $1\text{-}^{13}\text{CH}_3\text{-L}$ ($\text{L} = \text{dmsO}$, pyridine) were synthesized (for experimental details see Supporting Information). These complexes were employed for ethylene polymerizations with variable reaction times (1–10 min, 150–450 μM precatalyst, 5 bar ethylene, 333–363 K) to determine the fraction of ^{13}C -labeled methyl groups incorporated from the precatalyst $1\text{-}^{13}\text{CH}_3\text{-L}$ into the S1 end groups of the isolated polymer (Figure 1 shows an exemplified ^{13}C NMR spectrum including end group definitions).

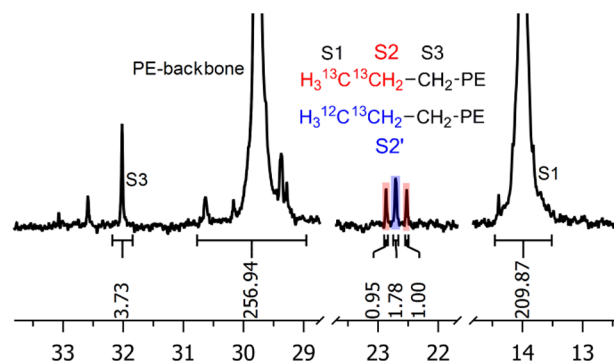


Figure 1. S1, S2, and S3 region of the ^{13}C NMR spectrum (inverse gated decoupled, 403 K, $\text{C}_2\text{D}_2\text{Cl}_4$) of polyethylene (Table 1, entry 7) obtained with $1\text{-}^{13}\text{CH}_3\text{-pyr}$ (54 TON ethylene, ca. 0.9 chain transfers per active $1\text{-}^{13}\text{CH}_3\text{-pyr}$) in a pressure reactor polymerization experiment.

A higher sensitivity in these experiments was achieved by increasing the concentration of the catalyst precursor, $[1\text{-}^{13}\text{CH}_3\text{-L}]$, and by decreasing the ethylene concentration as well as the polymerization time and temperature in comparison to standard polymerization conditions (which are typically 20–50 μM , 40 bar ethylene, 363 K, 30 min polymerization time),¹⁰ thus limiting the absolute turnover number per overall palladium.¹³ Aliquots of the polyethylenes thus obtained were subjected to quantitative ^{13}C NMR analysis,¹⁴ and the fraction of ^{13}C -labeled CH_3 end groups incorporated into the polymer was determined by comparing the overall backbone integral with the S1 and S2 end group integrals,

Table 1. Ethylene Polymerization Conducted with ^{13}C -Labeled Complexes $1\text{-}^{13}\text{CH}_3\text{-L}$

entry	catalyst precursor	T [K]	t [min]	yield [mg]	TON ^d	Me branches ^e	no. of chain transfers ^f	M_n^g [10^3 g mol^{-1}] (NMR)	$M_n/(M_w/M_n)^h$ [10^3 g mol^{-1}] (GPC)	inc. $^{13}\text{CH}_3$ ⁱ [%]	olefin to S2' ^j
1 ^a	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	333	1	138	328	1.0	4.2	2.8	9/(1.6)	69	1:10
2 ^a	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	333	3	165	393	0.9	5.0	3.3	n.d.	59	1:6
3 ^a	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	333	10	273	650	1	5.1	5.3	11/(2)	59	1:8
4 ^b	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	333	1	199	158	1.4	2.8	2.0	n.d.	71	1:10
5 ^a	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	343	1	231	550	2	10.5	3.4	10/(2)	41	1:8
6 ^a	$1\text{-}^{13}\text{CH}_3\text{-dmso}$	353	1	253	601	4.5	15.1	2.7	7/(2.1)	41	1:3
7 ^b	$1\text{-}^{13}\text{CH}_3\text{-pyr}$	333	1	68	54	0.7	0.9	1.7	1.6/(1.2)	86	1:8
8 ^c	$1\text{-}^{13}\text{CH}_3\text{-pyr}$	343	1	151	180	1.2	1.8	2.9	5.3/(1.3)	76	1:6
9 ^a	$1\text{-}^{13}\text{CH}_3\text{-pyr}$	353	1	144	343	2.8	4.1	2.9	7/(1.7)	72	1:6
10 ^a	$1\text{-}^{13}\text{CH}_3\text{-pyr}$	353	3	232	552	2.8	4.3	4.3	n.d.	73	1:6
11 ^a	$1\text{-}^{13}\text{CH}_3\text{-pyr}$	353	10	484	1153	2.7	4.7	8.1	10/(2)	72	1:4

^aPolymerization conducted with 15 μmol of $1\text{-}^{13}\text{CH}_3\text{-L}$ in 100 mL of toluene at 5 bar ethylene pressure. ^bPolymerization conducted with 45 μmol of $1\text{-}^{13}\text{CH}_3\text{-L}$ in 100 mL of toluene at 5 bar ethylene pressure. ^cPolymerization conducted with 30 μmol of $1\text{-}^{13}\text{CH}_3\text{-L}$ in 100 mL of toluene at 5 bar ethylene pressure. ^dMol ethylene converted per mol precatalyst. ^eMethyl branches per 1000 carbon atoms, determined in $\text{C}_2\text{D}_2\text{Cl}_4$ solution at 403 K in inverse gated decoupled experiments with a relaxation delay of >7 s. ^fDetermined by comparing the (^{13}C)S1(^{13}C)S2 and the (^{12}C)S1(^{13}C)S2 signal in inverse gated decoupled experiments with a relaxation delay of >7 s. ^gDetermined by the ratio of S1 end groups:remaining PE signals. ^hDetermined by high-temperature GPC in trichlorobenzene at 403 K vs linear PE standards. ⁱFraction of polymer-incorporated $^{13}\text{CH}_3$ groups from $1\text{-}^{13}\text{CH}_3\text{-L}$ determined by ^{13}C NMR spectroscopy; for details see SI. ^jDetermined by ^{13}C NMR spectroscopy by comparing the integrals of allylic and S2 signals in inverse gated decoupled experiments with a relaxation delay of 7 s.

assuming that the ^{13}C -label was exclusively incorporated in the S1 end groups. These data were corrected for additional occurring S1 and S2' end groups (containing natural abundance ^{13}C) resulting from chain transfer reactions during these polymerization experiments. A distinction of S2 end groups in the vicinity of ^{12}C - or ^{13}C -labeled S1 groups, respectively, can be made, since S2' end groups formed after chain transfer do not exhibit the characteristic $^1J_{\text{CC}} = 34.8 \text{ Hz}$ that is observed for S2 end groups adjacent to the ^{13}C -enriched S1 group (signals between 22 and 23 ppm in Figure 1; for a detailed description see Supporting Information).

This distinction in turn allows for an estimation of the number of chain transfers per $1\text{-}^{13}\text{CH}_3\text{-L}$. Chain transfer numbers per $1\text{-}^{13}\text{CH}_3\text{-L}$ determined in this fashion increase with increasing polymerization temperature and are in the range of ca. 1 to 5 using $1\text{-}^{13}\text{CH}_3\text{-pyr}$ and in the range of 3 to 15 using $1\text{-}^{13}\text{CH}_3\text{-dmso}$ (Table 1, column 8).

All fractional incorporations of $^{13}\text{CH}_3$ -labeled groups into the isolated polymers even after only 1 min polymerization time are consistently >55% for $1\text{-}^{13}\text{CH}_3\text{-dmso}$ (Table 1, entries 1–4) at 333 K polymerization temperature and reach ca. 85% for $1\text{-}^{13}\text{CH}_3\text{-pyr}$ (Table 1, entry 7). They decrease with increasing polymerization temperature within the error limits (Table 1, entries 4–6 and 7–9) and do not increase with polymerization time (Table 1, entries 1–3 and 9–11). These data indicate that (a) the pre-equilibration of $1\text{-}^{13}\text{CH}_3\text{-L}$ and $1\text{-}^{13}\text{CH}_3\text{-(ethylene)}$ according to eq 1 is indeed rapid as compared to chain growth, and (b) side reactions triggered by increasing the polymerization temperature decrease the observed S1 incorporation of ^{13}C -label into the isolated polymer.

Turnover numbers do not increase linearly with time (entries 1–3 and 9–11, columns 4 and 6) and decrease with increasing [precatalyst], e.g., from 150 μM to 450 μM (entries 1 and 4). This indicates that deactivation of catalytically active species occurs to a relevant extent and may account for the observation that the ^{13}C -label is not incorporated completely into the isolated polymer, despite the rapid pre-equilibration of $1\text{-}^{13}\text{CH}_3\text{-L}$ and $1\text{-}^{13}\text{CH}_3\text{-(ethylene)}$.¹⁵ The finding that increasing chain transfer numbers also correlate with decreasing incorporation of ^{13}C -label into the polymer (Table 1, columns 8 and 11) points to

the chain transfer being directly linked to the deactivation of the catalytically active species.

We also note that the isolated polymers exhibit ratios of unsaturated groups to aliphatic end groups that, if corrected for methyl branches and internal olefins, significantly deviate from the expected 1:1 ratio (Table 1, last column). While an incomplete ^{13}C relaxation of olefinic ^{13}C resonances and possibly also polymer chains still attached to palladium may contribute to this observed deviation of olefinic:aliphatic end group ratios, we believe that part of the polymer consists of fully saturated chains, which will also contribute to deviating ratios of olefinic:aliphatic end group signals. Evidence that supports this assumption will be presented in the following sections.

Activation of Precatalysts under NMR-Tube Conditions and Position of Incorporated ^{13}C -Label in the Polymer Chains. Triggered by the observed catalyst deactivation and indication for the formation of fully saturated polymers, NMR monitoring of the reaction of ^{13}C -labeled complexes $1\text{-}^{13}\text{CH}_3\text{-pyr}$ and $1\text{-}^{13}\text{CH}_3\text{-dmso}$ with ethylene in pressure-stable J. Young NMR tubes was conducted: In $\text{thf-}d_8$ solution (dried over sodium–potassium alloy) $1\text{-}^{13}\text{CH}_3\text{-pyr}$ (6.6 mmol L^{-1}) reacts only very slowly with ethylene (initial concentration $[\text{ethylene}]_0 = \text{ca. } 46 \text{ mmol L}^{-1}$, 7 equiv) even at elevated temperature, and consumption of ca. 6.5 equiv of ethylene requires heating to 378 K for ca. 7 h. At this point the initially introduced $1\text{-}^{13}\text{CH}_3\text{-pyr}$ is totally consumed, as judged by ^1H NMR spectroscopy. Traces of palladium black were visible, and no further polymerization takes place upon repeated addition of ethylene and heating to 378 K. However, only an estimated ca. 65% of the initial $1\text{-}^{13}\text{CH}_3\text{-pyr}$ had initiated a polymer chain, as judged by additional resonances between $\delta = 13.5$ and 11.5 ppm in the ^{13}C NMR spectrum, accounting for ca. 35% of the introduced ^{13}C -label.¹⁶ These signals are split into a doublet of doublets with $J = \text{ca. } 35 \text{ Hz}$ (and $J = 3 \text{ Hz}$) at 150 and 100 MHz. While the observed $J = 35 \text{ Hz}$ are suggestive of $^1J_{\text{CC}}$ couplings,¹⁷ upon ^{31}P -decoupling all these signals collapsed into singlets (Figure 2). In addition they were identified as isotopomeric enriched $^{13}\text{CH}_3$ groups by phase-sensitive $^1\text{H}, ^{13}\text{C}$ gHSQC in combination with $^1\text{H}, ^{31}\text{P}$ gHMBC and $^1\text{H}, ^{31}\text{P}\{^{13}\text{C}\}$ gHMBC experiments with no further correlation in $^1\text{H}, ^{13}\text{C}$ gHMBC

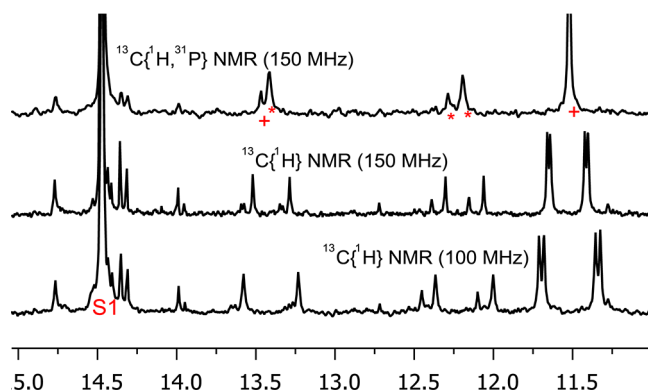


Figure 2. ^{13}C NMR methyl region of an oligomer sample obtained with $1\text{-}^{13}\text{CH}_3\text{-pyr}$ after 7 h at 378 K, with 7 equiv of C_2H_4 in a NMR-tube experiment. Signals marked (*) were assigned to $(^{13}\text{CH}_3)\text{-phosphine}$ palladium complexes. Signals marked (+) were assigned to $(^{13}\text{CH}_3)\text{-phosphine}$ palladium complexes containing one additional phosphine ligand (*vide infra*, Scheme 2 and Figure 4).

experiments (see SI). Thus, a substantial part of the ^{13}C -labeled CH_3 groups in these experiments is transferred to phosphorus-containing species.

The identity of these species will be discussed later, as the ^{13}C NMR spectrum of this ^{13}C -enriched sample also proves most informative with respect to the formed oligomers *vis à vis* the control experiment with natural abundance $1\text{-CH}_3\text{-pyr}$: First of all we have noticed a much better signal-to-noise ratio (S/N) for the ^{13}C -enriched sample not just for the ^{13}C -enriched S1 signal at $\delta = 14.47$ ppm, but for many other resonances attributable to products obtained by chain growth. However, an increased S/N was not observed for the identified signals of *cis*- and *trans*-but-2-ene, which are formed after β -hydride elimination and insertion of ethylene into palladium hydride species $[\kappa^2\text{-P,O}]\text{Pd}(\text{H})$ under NMR polymerization conditions (and therefore contain no ^{13}C -label introduced by $1\text{-}^{13}\text{CH}_3$, Figure 3).

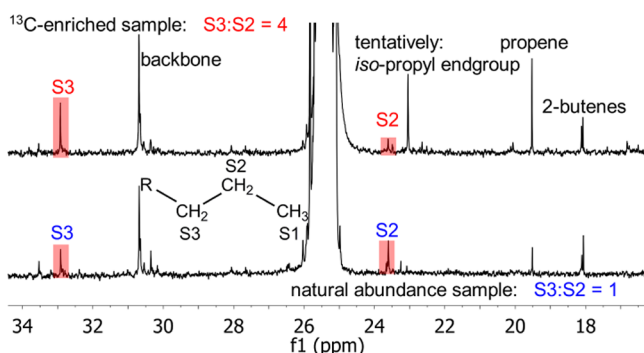


Figure 3. S3, S2, and methyl branch ^{13}C NMR region of ethylene oligomers obtained with $1\text{-}^{13}\text{CH}_3\text{-pyr}$ (top line) and $1\text{-CH}_3\text{-pyr}$ (bottom line).

Even more striking, substantial amounts of propylene were identified in both samples with virtually identical integral ratios of terminal methylenide (116.0 ppm)-to-methyl signals (19.52 ppm) of 0.8:1 in each case (see SI), while the internal methine carbon is hardly detectable. Since propylene can be formed only by ethylene insertion into $1\text{-}^{13}\text{CH}_3$ (1-CH_3 , respectively) and concomitant β -hydride elimination, the observed 0.8:1 ratio of methylenide:methyl resonances in the case of the ^{13}C -labeled precatalyst $1\text{-}^{13}\text{CH}_3\text{-pyr}$ is indicative of a rapid chain-walking reaction

(i.e., β -hydride elimination and reinsertion with opposite regiochemistry) along the growing chain, which exchanges ^{13}C -label between these two groups and is competitive to chain growth. This chain-walking process along the growing chain results in dissipation of the initially introduced ^{13}C -label at the chain terminus into every other position of a linear chain or, if methyl branching takes place, even into a methyl branch (Scheme 1).

A deeper analysis of the labeled oligomers obtained from $1\text{-}^{13}\text{CH}_3\text{-pyr}$ in the NMR-tube experiment supports that chain walking is operative in a polymerization-active palladium species. A ratio of S3:S2 end groups of ca. 4:1 was found, whereas a S3:S2 ratio of 1:1 was obtained starting from unlabeled $1\text{-CH}_3\text{-pyr}$. That is, some of the ^{13}C -label is indeed incorporated at the S3 position, resulting in increased S3 integrals. With respect to methyl branches we find an intensive ^{13}C signal at δ 23.04 ppm, which is correlated via $^1J_{\text{CH}}$ to an obscured signal at 0.88 ppm in the ^1H NMR spectrum and which is tentatively assigned to a ^{13}C -enriched isopropyl end group. With respect to the isopropyl end groups however, we note that they may also form after 1,2-insertion of 1-olefins into $1\text{-}^{13}\text{CH}_3$ and extensive chain walking through a tertiary carbon center (Scheme 1 and Figure 3).¹⁸

Overall, the increased signal-to-noise ratio for many resonances attributable to ethylene enchainment products obtained with $1\text{-}^{13}\text{CH}_3\text{-pyr}$ *vis à vis* unlabeled $1\text{-CH}_3\text{-pyr}$ clearly supports that these catalysts can undergo chain-walking on the same time scale as chain growth, particularly at low ethylene concentration and high temperature.

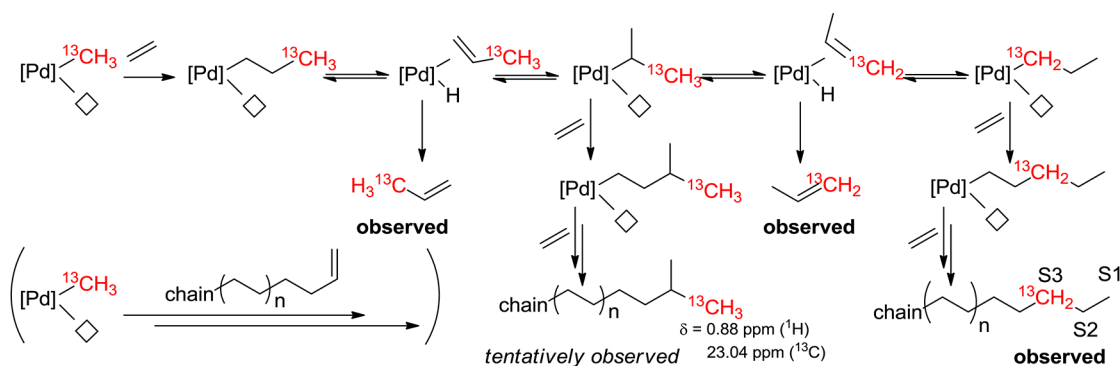
This chain-walking process, which was also observed on a preparative scale as judged by low but clearly quantifiable degrees of branching (Table 1, column 7: Me branches) and which is also supported by other studies,¹⁹ will apparently lower the calculated fraction of ^{13}C -label (Table 1, column 11) introduced into the polymer, as exclusively ^{13}C -labeled S1 positions have been considered. However, while chain-walking contributes to an apparently lowered ^{13}C incorporation into the polymer at low ethylene concentration and high temperature, the formation of ^{13}C -labeled phosphorus-containing side products results in a fraction of the ^{13}C -label not being incorporated at all into the polymer.²⁰

Furthermore, the formation of volatile saturated alkanes constitutes another reaction path by which ^{13}C -label is prevented from incorporation into the formed polymer in the above NMR experiments: We have unambiguously observed ^{13}C -enriched $^{13}\text{CH}_4$ identified by a doublet with $^1J_{\text{CH}} = 125.6$ Hz at δ 0.185 ppm in the ^1H NMR spectrum, which is correlated via $^1J_{\text{CH}}$ (phase-sensitive gHSQC) to a carbon signal with even-numbered hydrogen substitution at δ -4.675 ppm in the ^{13}C NMR spectrum.

In agreement with this assignment, the respective natural abundance methane formed by using $1\text{-CH}_3\text{-pyr}$ exhibits a singlet in the ^1H NMR spectrum at δ 0.184 ppm.²¹ In addition to (^{13}C -enriched) methane a triplet at δ 1.118 ppm, i.e., downfield from usually observed methyl end groups, or methyl branching at ca. 0.85 ppm was observed, which is coupled to a multiplet at 1.329 ppm partially obscured by the methylene backbone signal of the formed oligomers (for details, see SI). We have assigned these signals to propane after incremental addition of a genuine sample of propane to these samples. Incremental addition of ethane to these samples also revealed that natural carbon abundance ethane identified by a singlet at δ = 0.851 forms during these *in situ* NMR experiments.

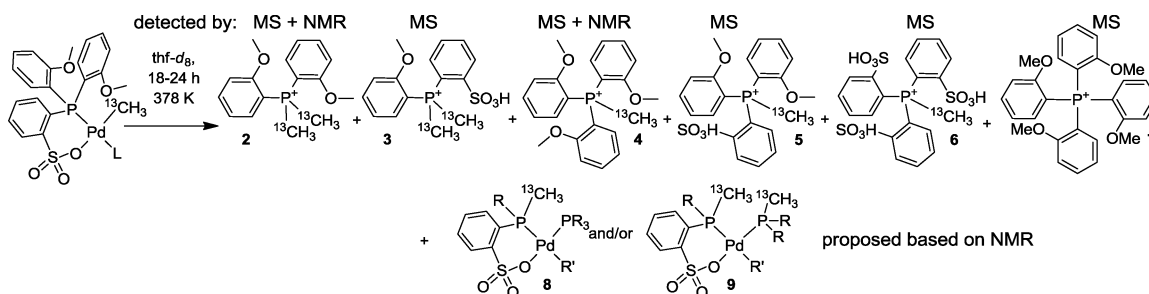
Scrambling of the Growing Alkyl Chain into the Phosphine Ligand. With respect to the phosphorus species

Scheme 1. Insertion and Chain Walking Reactions Explaining the Dissipation of ^{13}C -Label into Every Other Position of Linear Chains and into Branches Observed with $1\text{-}^{13}\text{CH}_3\text{-pyr}^a$



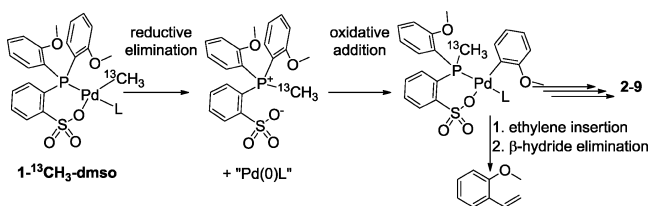
^aIn parentheses: alternative formation of ^{13}C -enriched isopropyl end groups after 1,2-insertion of 1-olefins into $1\text{-}^{13}\text{CH}_3$.

Scheme 2. Phosphonium Salts and Methylphosphine Complexes by Thermolysis of $1\text{-}^{13}\text{CH}_3\text{-L}$ in $\text{thf-}d_8$ at 378 K



containing the $^{13}\text{CH}_3$ -label (*vide supra*, Figure 2), several NMR spectroscopic and mass spectrometric observations led to the conclusion that these ^{13}C -labeled species correspond to palladium complexes of ^{13}C -labeled methylphosphines and not to palladium- $^{13}\text{CH}_3$ complexes, which implies that an exchange of aryl substituents on phosphorus and the palladium-bound $^{13}\text{CH}_3$ group takes place (Scheme 2 and Scheme 3).²² (a) the

Scheme 3. Exchange of Palladium-Bound Carbyls with Phosphorus-Bound Carbyls by Reductive Elimination and Oxidative Addition, and Formation of 2-Vinylanisole



observed $J_{\text{PC}} = 35$ Hz is neither in the range of a typical $^2J_{\text{PC, trans}}$ as observed in several diphosphine palladium methyl complexes (ca. 70–120 Hz)²³ nor in the range of typically observed $^2J_{\text{PC, cis}}$ in related phosphinesulfonato palladium methyl complexes (ca. 0–7 Hz).²⁴ (b) ^1H chemical shifts of the observed $^{13}\text{CH}_3$ groups (ca. 0.85–1.9 ppm) are not in the range of typical palladium methyl complexes (typically –2 to +0.85 ppm). (c) Traces of 2-vinylanisole were detected by ^1H - and $^1\text{H}, ^1\text{H}$ -gCOSY NMR experiments (see SI), which are likely formed by ethylene insertion into a palladium-(2-anisyl) complex followed by β -hydride elimination. (d) Mass spectrometric analysis of the obtained sample after heating $1\text{-}^{13}\text{CH}_3\text{-pyr}$ with 7 equiv of ethylene for 7 h at 378 K revealed the presence of quaternary

phosphonium cations $(^{13}\text{CH}_3)_x\text{P}^+(\text{anisyl})_{4-x}$ ($x = 1, 2$) **2** and **4** by ESI-MS and MALDI (Scheme 2, for details, see SI). (e) Despite the reported stability of $1\text{-CH}_3\text{-L}$,²⁵ thermolysis of $1\text{-}^{13}\text{CH}_3\text{-pyr}$ and $1\text{-}^{13}\text{CH}_3\text{-dmso}$ in $\text{thf-}d_8$ for 18–24 h at 378 K also in the absence of ethylene results in formation of quaternary phosphonium salts. However, in addition to **2** and **4**, tetra-(anisyl)phosphonium **7** is also detected by mass spectrometry. (f) The ^{13}C NMR spectrum of these samples obtained in the absence of ethylene contains several ^{31}P -coupled signals between $\delta = 15$ and 8.5 ppm with $^1J_{\text{PC}} \approx 54\text{--}62$ Hz typical for methyl phosphonium cations which are correlated to doublets of doublets with $^1J_{\text{CH}} \approx 135$ Hz and $^2J_{\text{PH}} \approx 15$ Hz in the ^1H NMR spectra. Comparison with independently prepared, but unlabeled **2** and **4** clearly indicates the formation of ^{13}C -labeled **2** and **4** in the aforementioned experiments starting from $1\text{-}^{13}\text{CH}_3\text{-L}$ at 378 K. (g) Thermolysis of $1\text{-}^{12}\text{CH}_3\text{-pyr}$ and $1\text{-}^{12}\text{CH}_3\text{-dmso}$ in dioxane for 18–24 h at 395 K yields the full range of phosphonium salts **2–7** as observed by ESI-MS.

In addition to phosphonium salts, the ^{13}C -labeled samples obtained by thermolysis of $1\text{-}^{13}\text{CH}_3\text{-dmso}$ in $\text{thf-}d_8$ for 18–24 h at 378 K also contain substantial amounts of the main ^{13}C -labeled side product observed under NMR-tube polymerization conditions. It is characterized by a doublet of doublets at $\delta = 11.51$ ppm with $J_{\text{PC}} = 35$ and 3 Hz (see Figure 2), which is assigned to a palladium diphosphine complex of the generic structure **8** or **9** (Scheme 2). This $(^{13}\text{CH}_3)$ phosphine species was unambiguously identified by X-ray diffraction analysis and NMR characterization of the collected X-ray quality crystals, which reveals that under polymerization conditions in the NMR tube $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(^{13}\text{CH}_3)\text{P,O}]$ (**10**) forms (Figure 4). The formation of **10** in NMR-tube polymerization and its isolation after thermolysis of $1\text{-}^{13}\text{CH}_3\text{-dmso}$ ultimately prove that (a) palladium-bound $^{13}\text{CH}_3$ groups can transfer to

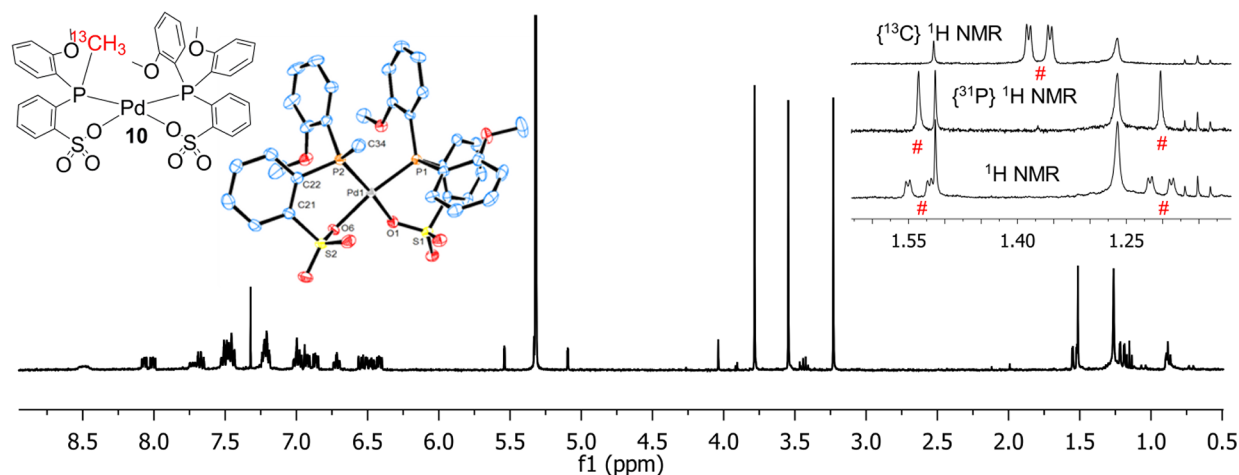


Figure 4. ^1H NMR spectrum (298 K, 400 MHz, methylene chloride- d_2) of isolated X-ray quality crystals identified as $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(^{13}\text{CH}_3)\text{P,O}]$ (**10**) with three characteristic methoxy singlets between 3.8 and 3.2 ppm and the $\text{P-}^{13}\text{CH}_3$ group at 1.37 ppm. The aliphatic inset shows ^1H (bottom line), $\{^{31}\text{P}\}^1\text{H}$ (middle line), and $\{^{13}\text{C}\}^1\text{H}$ NMR traces (top line), proving two ^{31}P and one ^{13}C coupling to the methyl protons marked (#).

phosphorus under these conditions and that (b) part of the palladium-bound ^{13}C -label therefore can be prevented from incorporation into the formed polymer. This is in accordance with the fractional incorporation of ^{13}C -label determined by the NMR polymer analyses (*vide supra*, Table 1) and reveals that eq 1 (*vide supra*) is simplistic in describing the polymerization reaction catalyzed by $1\text{-CH}_3\text{-L}$, as the palladium-bound $\kappa^2\text{-(P,O)}$ ligand may be altered during the polymerization reaction. In addition to the isolation of **10**, poorly methanol-soluble material from these samples was identified as $[\kappa^2\text{-(anisyl)}_2\text{P,O}]_2\text{Pd}$ (**11**) by its characteristic ^1H and ^{31}P resonances in $\text{dmsO-}d_6$ in comparison to independently prepared material.

These data fully corroborate the exchange of aryl substituents on phosphorus with methyl substituents on palladium (Scheme 3). Such exchange of substituents in transition metal complexes is not unprecedented and can be explained by consecutive reductive eliminations and oxidative additions of quaternary phosphonium salts followed, *inter alia*, by $[\text{P,O}]$ -ligand exchange reactions with palladium- CH_3 fragments.²⁶ It also provides a mechanistic scheme for the aforementioned formation of 2-vinylanisole after ethylene insertion into a palladium-(2-anisyl) bond (Scheme 3).

While proven in NMR-tube experiments, the relevance of these reactions under preparative polymerization conditions remained questionable at this point. We have therefore conducted additional experiments under polymerization conditions at which the catalyst is highly active [5 bar ethylene pressure, 20–30 min polymerization time, resulting in formation of ca. 6 g of PE (from 20 μmol of $1\text{-}^{12}\text{CH}_3\text{-dmsO}$) and ca. 16 g of PE (from 40 μmol of $1\text{-}^{12}\text{CH}_3\text{-dmsO}$), respectively]. The reaction mixture was precipitated by addition of methanol, the polymer was filtered off, and the methanol filtrate was concentrated. Part of this concentrated filtrate redissolves in methanol- d_4 , while the methanol-insoluble part was dissolved in $\text{dmsO-}d_6$ and identified as $[\kappa^2\text{-(anisyl)}_2\text{P,O}]_2\text{Pd}$ (**11**) by comparison to independently prepared material.

The methanol- d_4 -soluble fraction does not contain detectable amounts of **11** by ^1H or ^{31}P NMR spectroscopy. However, several CH_3 groups coupled to phosphorus were identified by analysis of the ^1H , ^{31}P , $^1\text{H}\{^{31}\text{P}\}$ -gHMBC, and $^1\text{H}\{^{13}\text{C}\}$ -gHSQC NMR spectra, one of which were assigned to phosphonium salt **5** (Scheme 2) on the basis of a doublet at $\delta = 3.05$ ppm with $^2J_{\text{PH}} = 15.5$ Hz in the ^1H NMR spectrum, which is correlated to one phosphorus at

27.7 ppm and agrees with the data of independently prepared **5** (for details, see SI). Furthermore, traces of 2-vinylanisole and one not fully identified styrene derivative were detected by ^1H NMR experiments. Most intriguing, one ethyl phosphine species was clearly identified by its characteristic splitting of the ethyl- CH_3 group into a doublet of triplets at $\delta = 1.05$ ppm with $^3J_{\text{PH}} = 20.5$ Hz, while the ethyl- CH_2 group exhibits diastereotopic protons resonating at $\delta = 1.89$ and 1.78 ppm with couplings to two phosphorus nuclei (Figure 5 and SI). This ethyl phosphine species was identified as $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(\text{ethyl})\text{P,O}]$ (**12**) by X-ray diffraction analysis. **12** cocrystallizes with $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(\text{butyl})\text{P,O}]$ (**13**) as a methanol- d_4 solvate with identical positions in the unit cell (Figure 5).

In addition, ESI-MS analyses (negative mode) of the methanolic polymerization filtrate exhibit peaks that fit the resonances expected for (2-anisyl)(alkyl)phosphine benzenesulfonates (**14**) and their respective phosphine oxides (**15**) (Figure 6). These data ultimately prove that the exchange of palladium-bound alkyl groups with phosphorus-bound carbyl substituents is also relevant under preparative reactor polymerization experiments, even if turnover numbers of ethylene per palladium present exceed 10,000. The ESI-MS assignments, particularly those of (odd-numbered alkyl)phosphines, imply that under preparative (high productivity) reactor polymerization conditions chain growth is significantly faster than exchange of phosphorus- and palladium-bound carbon substituents, but that chain transfer and exchange of phosphorus- and palladium-bound carbon substituents occur on a similar time scale. While not supported by thermolysis experiments of $1\text{-}(^{13}\text{CH}_3)\text{-dmsO}$ in the absence of ethylene (which takes up to 24 h at 378–395 K), this notion is clearly supported by the X-ray diffraction analysis of **12** and **13**.

While $[\kappa^2\text{-(anisyl)}_2\text{P,O}]_2\text{Pd}$ (**11**), $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(\text{ethyl})\text{P,O}]$ (**12**), and $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[\kappa^2\text{-(anisyl)}(\text{butyl})\text{P,O}]$ (**13**) separated (by crystallization) from the polymerization filtrates are not polymerization active in NMR-tube experiments, some of the species remaining in solution still enchain ethylene in $\text{thf-}d_8$ NMR experiments, whereby additional traces of 2-vinylanisole are formed apart from ethylene-oligomers/polymers. We therefore conclude that part of these complexes consist of palladium-anisyl complexes and that the transfer of palladium-bound alkyl groups to phosphorus does not

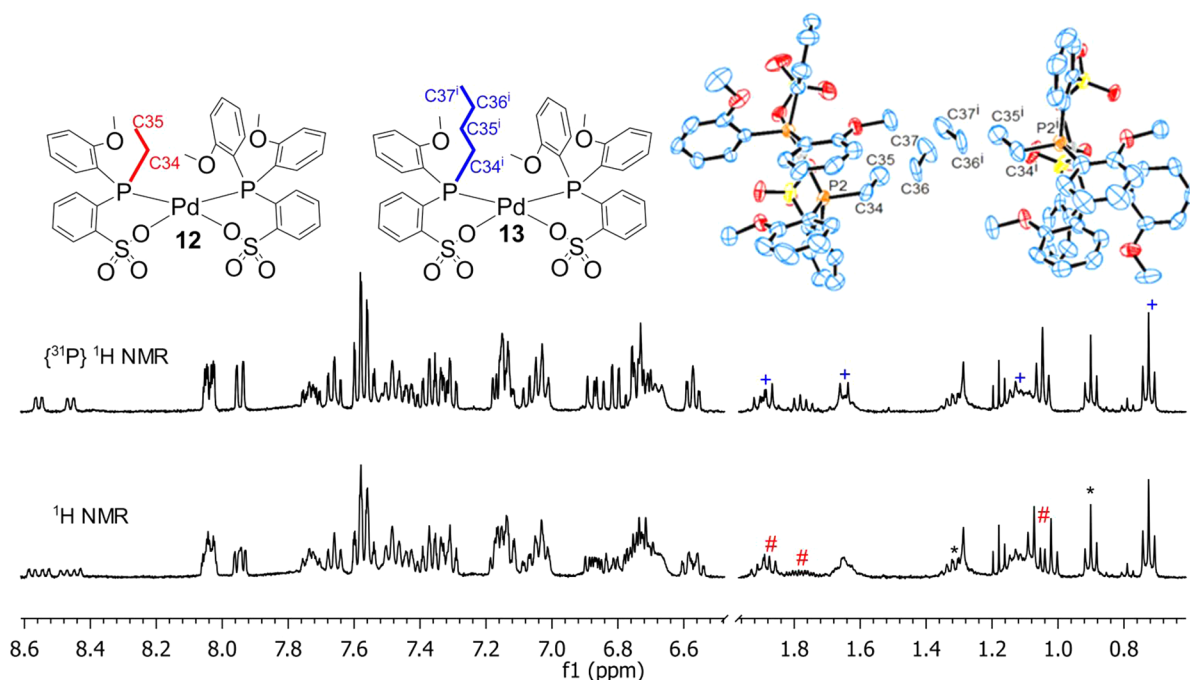


Figure 5. Aromatic and aliphatic region of the ^1H (bottom line) and $\{^{31}\text{P}\}^1\text{H}$ NMR spectra (298 K, 400 MHz, methanol- d_4) of isolated X-ray quality crystals identified as a mixture of $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[[\kappa^2\text{-(anisyl)(ethyl)P,O}]$ (**12**) and $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}[[\kappa^2\text{-(anisyl)(butyl)P,O}]$ (**13**). #: PCH_2CH_3 , +: $\text{P}(\text{CH}_2)_3\text{CH}_3$, *: pentane. **12** and **13** have been isolated from the filtrate of preparative reactor polymerizations [20(9) μmol of $1\text{-}^{12(13)}\text{CH}_3\text{-dmsO}$, 5 bar ethylene, 30 min polymerization time at 368 K, ca. 10^4 (10^4) turnovers ethylene per present palladium]. Also given: X-ray diffraction analysis of cocrystallized **12** and **13**. **12** and **13** occupy symmetry-equivalent positions in the unit cell. However, they likely form pairs, since the crystallographic void containing the $\text{P}(2)\text{-C34-C35}$ (ethyl-)/ $\text{P}(2')\text{-C34}'\text{-C35}'\text{-C36}'\text{-C37}'$ (butyl-) group (and a center of symmetry) allows for an alignment of six carbon atoms, e.g., $\text{C34}'$, $\text{C35}'$, $\text{C36}'$, $\text{C37}'$, C35 , and C34 , while C37 and $\text{C37}'$ are separated by only 1.247 Å. This is in accordance with an occupancy of C36 , C37 , which refined to 50% (for details, see SI).

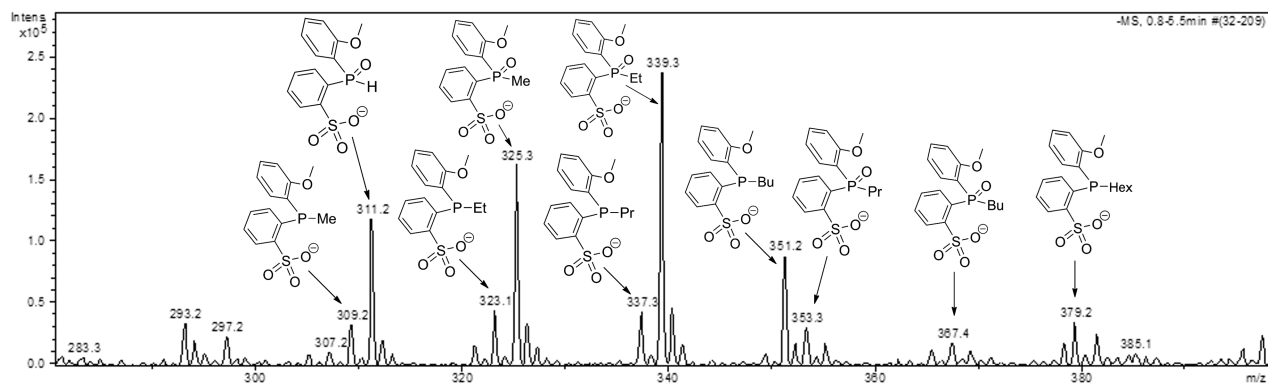


Figure 6. ESI-MS analysis (negative mode) of preparative reactor polymerization residue obtained from $1\text{-}^{12}\text{CH}_3\text{-dmsO}$ after separation of the formed polymer, indicating the presence of several alkylphosphines (**14**) and their respective alkylphosphine oxides (**15**).

necessarily result in deactivation of polymerization-active palladium complexes in preparative reactor polymerizations.

DFT calculations of the reductive elimination and oxidative addition of methylphosphonium salts indicate that reductive elimination is kinetically accessible and thermodynamically favorable, while oxidative addition of the P-CH_3 moiety is thermodynamically prohibitive (*vide infra*). Thus, the multiple methylation of phosphorus to form, for example, **2** starting from $1\text{-}^{13}\text{CH}_3\text{-L}$ and the formation of palladium anisyl complexes (and 2-vinylanisole in the presence of ethylene) likely reflect the thermodynamic stability of the palladium–aryl vs the palladium–methyl bond, which is supported by DFT calculations (*vide infra*).

Details of the Formation of Saturated Polymer Chains.

In contrast to NMR-tube oligomerizations with $1\text{-}^{13}\text{CH}_3\text{-pyr}$ and

$1\text{-}^{(13)}\text{CH}_3\text{-dmsO}$ and to preparative reactor polymerizations with $1\text{-CH}_3\text{-dmsO}$, these side reactions resulting in the formation of phosphonium salts, 2-vinylanisole, and methylphosphine (or more general: alkylphosphine) palladium complexes can be completely avoided by using the weaker coordinated and thus more reactive $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ (5 mmol L^{-1} , ca. 39 mmol L^{-1} ethylene, 8 equiv) in anhydrous $\text{thf-}d_8$ at 298 K in NMR-tube experiments: Albeit slow, $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ already inserts ethylene at room temperature and ca. 95% of $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ is consumed within 165 min at 298 K, while ca. 5.5 equiv of ethylene has been enchainment.²⁷ In these room-temperature studies, chain transfer by β -hydride elimination and chain-walking/isomerization is negligible, as concluded from the appearance of only traces of α -olefins (<2% with respect to all palladium complexes present)

and the absence of internal olefins. In addition, palladium propyl, pentyl, heptyl, and higher alkyl complexes were identified in the ^1H NMR spectra to contain ^{13}C -labeled CH_3 end groups exclusively on the basis of characteristic $^1J_{\text{CH}} = 124\text{--}125$ Hz and the absence of the respective $^{12}\text{CH}_3$ signals. These palladium alkyl complexes $1\text{-(CH}_2)_{2n}^{13}\text{CH}_3\text{-L}$ constitute the only products formed from $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ and indicate that true activation efficiencies of ca. 95% are already reached after ca. 5.5 turnovers of ethylene. They also indicate that at 298 K the polymerization of ethylene by $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ has a living character in that the formed $1\text{-(CH}_2)_{2n}^{13}\text{CH}_3\text{-L}$ complexes do not undergo decomposition or chain transfer even at very low ethylene concentration over prolonged periods of time: After an additional 12 h at 298 K ca. 7.3 of the initially 8 equiv of ethylene have been consumed. Simultaneously, trace amounts (ca. 5% vs palladium complexes) of 1-olefins have formed by β -hydride elimination, while the formed palladium hydride complex reinserts ethylene, as concluded from the observation of palladium ethyl and butyl complexes 1-Et-L and 1-But-L . The stability of these complexes $1\text{-(CH}_2)_{2n}^{13}\text{CH}_3\text{-L}$ has allowed for a full characterization by 2D NMR techniques, which reveals that the most characteristic palladium-bound methylene group of a growing polymer chain resonates at $\delta(^1\text{H}) = 0.73$ ppm and $\delta(^{13}\text{C}) = 32.75$ ppm with $^2J_{\text{PC}} = 5.8$ Hz (for details, see SI).

Heating this sample for 16 h to 313 K results in depletion of all signals corresponding to identified odd-numbered palladium alkyl complexes $1\text{-(CH}_2)_{2n}^{13}\text{CH}_3\text{-L}$, while ca. 2% of $1\text{-}^{13}\text{CH}_3\text{-dmsO}$, 5% of 1-Et , and traces of 1-But are still detectable. With respect to organic products we have unambiguously detected 1-alkenes, 2-alkenes, internal (α -)alkenes with $x > 2$ (4:4:1 ratio), and traces of $^{13}\text{CH}_3\text{-CH=CH}_2$ and $\text{CH}_3\text{-CH=}^{13}\text{CH}_2$ (in a ca. 3:1 ratio), 2-methyl-1-alkenes, $^{13}\text{CH}_3\text{CH}_2\text{CH}_3$, and $^{13}\text{CH}_4$ in the ^1H NMR spectra (for further details, see SI).

The presence of $^{13}\text{CH}_4$ and $^{13}\text{CH}_3\text{CH}_2\text{CH}_3$ in all these NMR experiments with both $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ and $1\text{-}^{13}\text{CH}_3\text{-pyr}$ suggests that also higher alkanes may form during ethylene polymerization. While the ratio of 1-olefins:2-olefins:internal olefins ($n > 2$) allows for an estimate of the expected $^{13}\text{CH}_3\text{:}^{12}\text{CH}_3$ end group ratio in these samples (internal olefins contain one $^{12}\text{CH}_3\text{-S1}$ end group even if initiated by $1\text{-}^{13}\text{CH}_3\text{-L}$), we find $^{13}\text{CH}_3\text{:}^{12}\text{CH}_3$ ratios that indicate the presence of additional saturated chains. However, since chain transfer as a source of $^{12}\text{CH}_3$ end groups is not quantified here, an accurate proof for the formation of fully saturated ethylene oligomers is hardly possible with these experiments. Therefore further experiments have been devised that circumvent the complicating issue of chain transfer and allow for the quantification of olefinic and aliphatic chains formed by $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ and ethylene (*vide infra*).

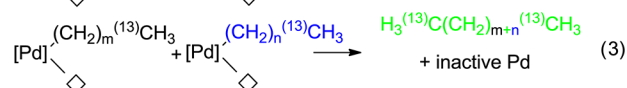
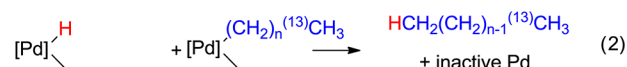
On the basis of these data we conclude here that the formation of the catalytically active species $1\text{-}^{13}\text{CH}_3\text{-(ethylene)}$ ($1\text{-CH}_3\text{-(ethylene)}$), $1\text{-(CH}_2)_{2n}^{13}\text{CH}_3\text{-(ethylene)}$, and $1\text{-(CH}_2)_{2n}\text{CH}_3\text{-(ethylene)}$, respectively) from $1\text{-}^{13}\text{CH}_3\text{-L}$ ($1\text{-CH}_3\text{-L}$, respectively) is indeed a rapid equilibrium reaction with respect to the following ethylene insertion, which justifies (a) the simplified reaction scheme given in eq 1 and (b) the assumption of a high activation efficiency. However, the reaction scheme of the overall polymerization according to eq 1 is simplistic in that it does not account for the observed exchange of palladium- and phosphorus-bound alkyl and aryl substituents and the polymerization activity of the species formed thereby. We also note that there is a strong indication that part of the formed ethylene oligomers in preparative (reactor) and analytical (NMR) experiments are fully saturated.

Deactivation of Catalytically Active Species by Endo- and Exogenic Pathways. An exogenic (and thus avoidable) catalyst deactivation pathway at low ethylene concentration has been reported in the presence of chlorinated solvents, e.g., $\text{C}_2\text{D}_2\text{Cl}_4$ or CDCl_3 , and resulted in isolation of $[\kappa^2\text{-P,O}]\text{Pd}(\text{Cl})(\text{L})$ complexes.^{12a} While the presence of water has been reported not to affect the stability of $1\text{-CH}_3\text{-L}$ at temperatures of 343 to 373 K,²⁵ we have now found that thermolysis of $1\text{-(}^{13}\text{CH}_3\text{-L)}$ at 378–395 K apart from several phosphonium salts (*vide supra*) also yields $^{(13)}\text{CH}_4$ or $^{(13)}\text{CH}_3\text{D}$ if the solvent is not rigorously dry. Complete consumption of $1\text{-CH}_3\text{-dmsO}$ in the presence of 30 equiv of D_2O in tetrachloroethane- d_2 solution takes ca. 3 h at 368 K, while a ca. 8:1 mixture of CH_3D and CH_4 forms (see SI). We therefore consider hydrolysis of palladium–methyl/alkyl species a further exogenic decomposition pathway.³⁰

In contrast, reductive elimination of methyl/alkyl phosphonium salts, e.g., **2–7** (*vide supra*), as observed in the NMR-tube experiments and in preparative polymerizations, constitutes an endogenic (and unavoidable) deactivation pathway if the formed palladium(0) does not completely reenter the catalytic cycle by oxidative addition of phosphonium salts, with, for example, formation of palladium-anisyl complexes (*vide supra*).

Additionally, we will present evidence that there is a second endogenic and totally irreversible catalyst deactivation pathway that is directly linked to the reactivity of palladium hydrides $[\kappa^2\text{-P,O}]\text{Pd}(\text{H})(\text{L})$ formed by β -hydride elimination from a growing palladium polymeryl species and that these palladium hydrides are (directly or indirectly) responsible for the formation of fully saturated oligomers.

Considering the increased catalyst decomposition with increasing concentration of $1\text{-}^{13}\text{CH}_3\text{-L}$ in preparative ethylene polymerizations (*vide supra*, Table 1, entries 1–3 and 9–11), the most straightforward hypothesis to rationalize the formation of saturated polymer chains and the decreasing activity over time is a bimolecular reaction of catalytically active palladium complexes, which is greater than first-order in active palladium and results in inactive palladium species according to eq 2 or eq 3.



With respect to a coupling reaction of two palladium carbyl complexes according to eq 3 the experimental data do not support such a possibility:²⁹ (a) $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ ($1\text{-}^{13}\text{CH}_3\text{-pyr}$, respectively) does not decompose to ^{13}C -enriched/natural abundance ethane in anhydrous $\text{thf-}d_8$ solution up to 378 K, 8 h, and (b) INADEQUATE, 2D ADEQUATE, or ^{13}C , ^{13}C - J -resolved experiments conducted with the oligomer sample obtained with $[1\text{-}^{13}\text{CH}_3\text{-pyr}]$ (6.6 mmol L^{-1}) and $[\text{ethylene}]_0$ (50–55 mmol L^{-1} , ca. 8 equiv) in $\text{thf-}d_8$ under chain-walking conditions (*vide supra*) revealed no measurable ^{13}C – ^{13}C connectivity between, for example, $^{13}\text{CH}_3$ - and $^{13}\text{CH}_2\text{-S3}$ -(or backbone $^{13}\text{CH}_2$ groups), i.e., to form, for example, 1,2- $^{(13)}\text{C}$ -butane from $1\text{-}^{13}\text{CH}_3$ and $1\text{-}^{13}\text{CH}_2\text{CH}_2\text{CH}_3$ [or higher even-numbered $\alpha,(\alpha+1)\text{-(}^{13}\text{C)}$ -alkanes].

In contrast, the formation of ^{13}C -labeled methane and propane as well as natural abundance ethane can likely be traced to a formal reaction of palladium hydride and palladium methyl, propyl, or ethyl complexes according to eq 2. In order to provide

hard evidence that also higher saturated alkanes can form, we have repeated the formation of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ under conditions where β -hydride elimination/chain-walking is negligible (298 K), then removed excess ethylene, and finally heated the sample in order to induce β -hydride elimination and formation of palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd}(\text{H})(\text{L})$. Under these reaction conditions the overall number of oligomer chains will not increase after β -hydride elimination since initiation of a new chain requires ethylene to be present. Consequently, easily identified $^{12}\text{CH}_3\text{-CH}_2$ end groups are expected only for internal (n -)olefins ($n > 2$) and for fully saturated polymer chains formed according to eq 2. Furthermore, a quantification of fully saturated chains is possible since the amount of internal olefins is accessible (for details see SI). After heating the ethylene-free sample of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ for 3 min at 363 K, more than >90% of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ is already decomposed, while a mixture of 1-olefins, 2-olefins, internal olefins, propane $^{13}\text{CH}_4$, and alkanes forms. The sample was heated for a further 22 min at 363 K, after which time $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ is no longer detected, while palladium black deposited in the NMR tube and four new signals in the ^{31}P NMR spectrum at $\delta = 30.03$, 22.81, 3.83, and -24.06 ppm in a 3:25:1:1 ratio were detected. The signals at 30.03 and 22.81 ppm (accounting for more than 90% of all ^{31}P detected) were identical to those obtained when dissolving the bis(chelate) palladium complex $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}$ (**11**) in $\text{thf-}d_8$ after prolonged heating. The other two phosphorus-containing species at 3.83 and -24.06 ppm have not been identified.

Figure 7 shows the olefinic and aliphatic regions of the ^1H NMR spectrum obtained after heating the ethylene-free mixture

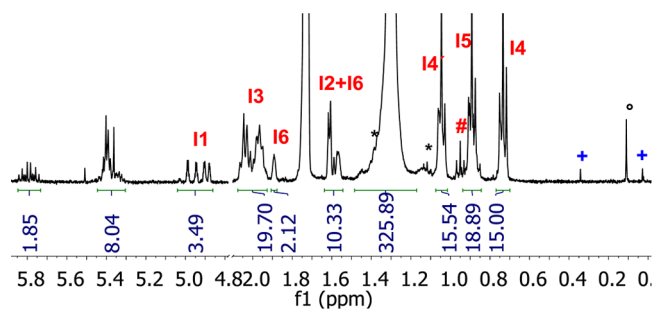
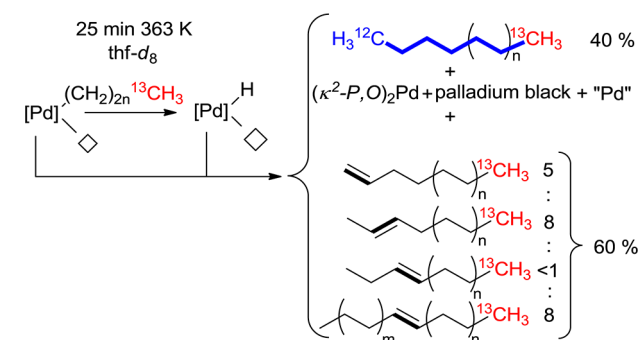


Figure 7. Olefinic and aliphatic region of the ^1H NMR spectrum of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ after 25 min at 363 K in the absence of additional ethylene. **I1**: integral of $=\text{CH}_2$ of 1-olefins, **I2**: integral of the allylic CH_3 of *cis*- and *trans*-2-olefins, **I3**: integral of all allylic CH_2 in 1-, 2-, and internal olefins, **I4**: integral of all $\text{CH}_2^{13}\text{CH}_3$ introduced by $1-^{13}\text{CH}_3\text{-dmsO}$, **I5**: integral of $\text{CH}_2^{12}\text{CH}_3$ of *n*-olefins and fully saturated chains, **I6**: integral of the ^{13}C -satellite of $\text{thf-}d_8$ -x [**I2** is obtained by $(\text{I2} + \text{I6}) - \text{I6}$]; *: propane, #: $\text{CH}_2^{12}\text{CH}_3$ group of 3-olefins, +: $^{13}\text{CH}_4$, °: grease.

of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ for 25 min at 363 K. Analysis of the integrals **I1** (1-olefins), **I2** (2-olefins), and **I3** (allylic CH_2 groups of all olefins) reveals a 25:38:37 ratio of 1-olefins:2-olefins:internal olefins. In combination with the integrals **I4** ($^{13}\text{CH}_3\text{CH}_2$ end groups) and **I5** ($^{12}\text{CH}_3\text{CH}_2$ end groups) a ratio of olefins:alkanes of 60:40 was determined (Scheme 4; for details, see SI).

Since formation of alkanes requires equimolar amounts of palladium hydride $[\kappa^2\text{-P,O}]\text{Pd}(\text{H})(\text{L})$ (formed by β -hydride elimination and release of equimolar amounts of olefins) and palladium carbyl complexes $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ according to eq 2, a quantitative reaction according to eq 2 will result in a 50:50 mixture of olefins and alkanes. Thus, the observed 60:40

Scheme 4. Formation of ^{13}C -Labeled Olefins from $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ and ^{13}C -Labeled Alkanes by β -Hydride Elimination and Reaction of the Formed Palladium Hydride with $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$



mixture corresponds to an 80% yield with respect to $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ accessible for the formation of saturated chains (Scheme 4).

Palladium black, $[\kappa^2\text{-(anisyl)}_2\text{P,O}]\text{Pd}$ (**11**), and the two remaining phosphorus-containing species in this sample do not initiate new oligomer chains upon repeated addition of ethylene; that is, all polymerization-active species have been decomposed at this point.³⁰ However, trace amounts of ethane are clearly detected already after 5 min at 298 K upon addition of ethylene. While we have not detected hydrogen directly after the thermolysis in the ^1H NMR spectrum (Figure 8 and SI), we

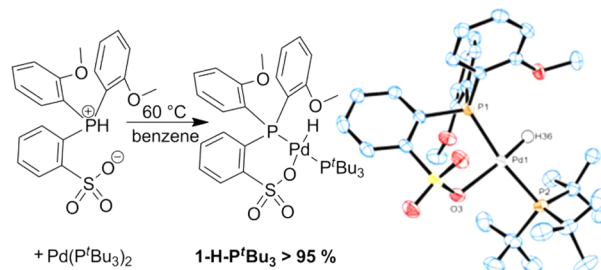
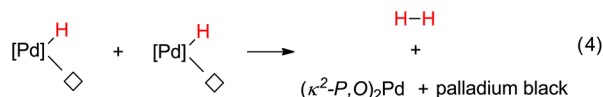


Figure 8. Synthesis of 1-H-P'Bu_3 by oxidative addition of P-protonated phosphonium salt $\text{H}[\text{P,O}]$ to $\text{Pd}(\text{P'Bu}_3)_2$ and ORTEP plot of 1-H-P'Bu_3 at the 50% probability level. Hydrogen atoms (except for Pd-H36) and one cocrystallized benzene molecule are omitted for clarity. The hydride bound to palladium was located in the electron density map and refined isotropically.

believe that the observed presence of ethane after ethylene addition results from palladium black catalyzed hydrogenation of ethylene; that is, hydrogen is also formed during the thermolysis of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ but not observable under these conditions. This assumption is supported by incremental addition of hydrogen (1.2 bar) to the ethylene-containing reaction mixture, which results in rapid growth of the ethane singlet at $\delta = 0.851$ ppm in the ^1H NMR spectrum, while no hydrogen at $\delta = 4.545$ ppm is detectable until all ethylene has been hydrogenated. Notably, hydrogenation of the propene present is much slower (12 h, 363 K), as evidenced by its disappearance and the observed growth of the propane triplet at $\delta = 1.118$ ppm in the ^1H NMR spectrum. In contrast to propene, 1-olefins with $\text{C} > 3$ are mainly isomerized to internal olefins, which even after 20 h at 363 K are not hydrogenated.

The assumed presence of hydrogen after thermolysis of $1-(\text{CH}_2)_{2n}^{13}\text{CH}_3\text{-dmsO}$ (which is responsible for ethane

formation upon ethylene addition) indicates that formation of hydrogen is another reaction path by which palladium hydride complexes may be deactivated according to eq 4.



Thus, $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$ at elevated temperature in part β -hydride eliminates olefins, while the formed palladium hydride $[\kappa^2\text{-P,O}]\text{Pd(H)}$ decomposes by bimolecular reaction with $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$ to form alkanes and with further palladium hydride $[\kappa^2\text{-P,O}]\text{Pd(H)}$ to form hydrogen, which is finally responsible for the detection of ethane upon ethylene addition. The hydrogen formed likely also participates in further irreversible decomposition reactions with $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$, as $1\text{-}^{13}\text{CH}_3\text{-dmsO}$ in the presence of hydrogen was found to decompose to $^{13}\text{CH}_4$, palladium black, and mainly $[\kappa^2\text{-(anisyl)}_2\text{P,O)]}_2\text{Pd}$ (**11**) in thf-d_8 solution. However, the reaction takes >8 h at 363 K, which indicates that under polymerization conditions, i.e., in the presence of ethylene, (a) hydrogen present will hydrogenate ethylene to ethane once palladium black forms instead of cleaving growing polymer chains in $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$, and (b) therefore palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd(H)}$ are mostly responsible for deactivating polymerization-active species by cleaving polymer chains from $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$.

Synthesis of the Model Hydride Complex $[\kappa^2\text{-P,O}]\text{Pd(H)}$ ($\text{H-P}^t\text{Bu}_3$). As we did not directly observe palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd(H)}$ in any of the above-mentioned experiments, we sought to synthesize a suitable palladium hydride complex **1-H-L** that could model the decomposition reactions, e.g., of $1\text{-CH}_3\text{-dmsO}$ and $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$ to form methane, alkanes, and hydrogen. Since the seminal work of Drent, Pugh, and co-workers, it is known that a combination of $[\text{Pd(0)(dba)}_2]$ and zwitterionic, P-protonated phosphine benzenesulfonic acid ($o\text{-MeOC}_6\text{H}_4\text{)}_2\text{PH}^+(\text{C}_6\text{H}_4\text{SO}_3^-)$ (H[P,O]) generates active species for the copolymerization of ethylene and acrylates ($\text{dba} = 1,5\text{-diphenylpenta-1,4-dien-3-one}$).³ While the nature of the active species has not been investigated in detail, it is likely a palladium hydride $[\kappa^2\text{-P,O}]\text{Pd(H)}$ that forms upon formal oxidative addition of the protonated phosphine to palladium(0).

In need for a suitable $[\kappa^2\text{-P,O}]\text{Pd(H)}$ model complex we therefore explored the reaction of zwitterionic phosphine benzenesulfonic acid with palladium(0) sources. While $[\text{Pd(0)(dba)}_2]$ and $(o\text{-MeOC}_6\text{H}_4\text{)}_2\text{PH}^+(\text{C}_6\text{H}_4\text{SO}_3^-)$ (H[P,O]) indeed forms a palladium hydride (even though in less than 5% yield as evidenced by *in situ* ^1H NMR), this hydride is not stable and at room temperature eludes isolation. However, oxidative addition of H[P,O] to $\text{Pd(P}^t\text{Bu}_3)_2$ generates $[(\kappa^2\text{-P,O})\text{-(}o\text{-MeOC}_6\text{H}_4\text{)}_2\text{P-(C}_6\text{H}_4\text{SO}_3\text{)]Pd(H)(P}^t\text{Bu}_3)$ (**1-H-P}^t\text{Bu}_3**) in virtually quantitative yield, which was isolated and fully characterized by NMR techniques and X-ray diffraction analysis (Figure 8 and Table 2). Notably, the palladium-bound hydride was located in the electron

density map with a distance to palladium of $1.48(4)$ Å.³³ The coordination geometry of palladium in the solid state and in solution is corroborated by the ^1H and ^{31}P NMR solution data, which confirm the *trans*-disposition of both phosphorus atoms, as concluded from a $^2J_{\text{PP,trans}} = 357.4$ Hz and two $^2J_{\text{PH,cis}} = 13.6$ and 1.9 Hz, which split the hydridic resonance into a doublet of doublets at $\delta(^1\text{H}) = -18.02$ ppm.

Reactivity of the Model Palladium Hydride Complex.

In order to understand the cross-reactivity of **1-H-P}^t\text{Bu}_3** with **1-CH}_3\text{-L}** (*vide infra*), the reactivity of **1-H-P}^t\text{Bu}_3** alone was also evaluated: **1-H-P}^t\text{Bu}_3** slowly decomposes in tetrachloroethane- d_2 solution within ca. 11 h at 373 K with concomitant evolution of hydrogen ($\delta = 4.70$ ppm). In addition, the bis(chelate) palladium complex $[\kappa^2\text{-(anisyl)}_2\text{P,O)]}_2\text{Pd}$ (**11**) crystallizes from these samples, as proven by single-crystal X-ray diffraction analysis (Figure 9).³²

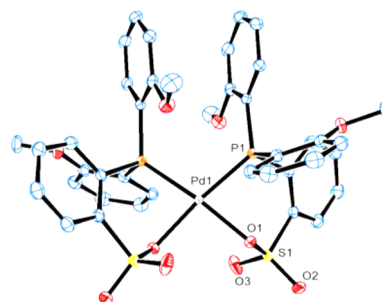


Figure 9. ORTEP plot of $[\kappa^2\text{-(anisyl)}_2\text{P,O)]}_2\text{Pd}$ (**11**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms and two cocrystallized $\text{C}_2\text{D}_2\text{Cl}_4$ molecules are omitted for clarity.

With these observations in hand we monitored the reactivity of **1-CH}_3\text{-dmsO}** with **1-H-P}^t\text{Bu}_3** by ^1H NMR spectroscopy: **1-CH}_3\text{-dmsO}** (30 mM) disappears in the presence of **1-H-P}^t\text{Bu}_3** (1.2 equiv) within 1.5 h at 373 K in tetrachloroethane- d_2 solution, while methane (characteristic singlet at $\delta = 0.23$ ppm) and traces of hydrogen ($\delta = 4.71$ ppm) were detected as decomposition products.³³ The formation of methane may originate from adventitious traces of water in the solvent (*vide supra*). However, we note that upon reaction of partially deuterated **1-D-P}^t\text{Bu}_3** (ca. 71% deuteride content) with **1-CH}_3\text{-dmsO}** under otherwise identical reaction conditions (i.e., same solvent batch, temperature, concentration), methane- d_1 and methane are formed in a 66:34 ratio, as identified by the additional 1:1:1 triplet at $\delta = 0.21$ ppm with a $^2J_{\text{HD}} = 1.8$ Hz in the ^1H NMR spectrum. That is, the solvent does not contain a significant amount of H_2O , as the amount of deuterium-label found in the methane is not significantly altered with respect to **1-D-P}^t\text{Bu}_3**. While these data clearly indicate that methane (mainly) originates from a reaction of **1-H-P}^t\text{Bu}_3** with **1-CH}_3\text{-dmsO}**, we note that in tetrachloroethane- d_2 solution only ca. 0.7 equiv of **1-H-P}^t\text{Bu}_3** is necessary to decompose 1 equiv of **1-CH}_3\text{-dmsO}**; that is, there is likely a second (and unidentified) decomposition reaction operative. In contrast, such an alternative decomposition pathway is not operative in thf-d_8 solution (ca. 24 h at 363 K), as **1-CH}_3\text{-dmsO}** and **1-H-P}^t\text{Bu}_3** (2 equiv) were consumed in a 1:1 ratio, while the remaining equivalent of **1-H-P}^t\text{Bu}_3** only very slowly decomposes to hydrogen (additional 120 h, 383 K).

While much slower than in the thermolysis of $1\text{-(CH}_2\text{)}_{2n}\text{CH}_3\text{-dmsO}$, the formation of methane and particularly of methane- d_1 (from **1-D-P}^t\text{Bu}_3**) and hydrogen clearly supports our assumption that palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd(H)}$ are responsible

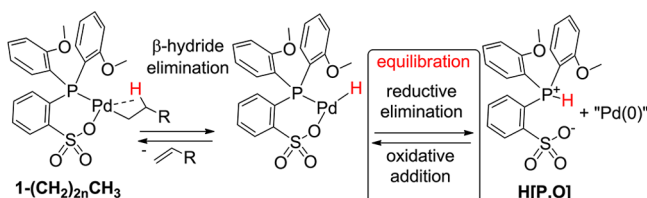
Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **1-H-P}^t\text{Bu}_3**

Pd1–H36	1.48(4)	P1–Pd1–P2	166.28(2)
Pd1–O3	2.191(2)	P2–Pd1–H36	85.8(14)
Pd1–P1	2.3072(7)	O3–Pd1–H36	174.5(13)
Pd1–P2	2.3473(8)	O3–Pd1–P1	92.66(5)

for the deactivation of polymerization-active palladium complexes and the formation of saturated hydrocarbons. Further evidence for this assumption also comes from the reaction of the isolated palladium ethyl complex **1-Et-PPh₃**, which models the mixture of palladium alkyl complexes **1-(CH₂)_{2n}-¹³CH₃-dmsO** obtained by *in situ* NMR experiments. Upon heating **1-Et-PPh₃** in tetrachloroethane-*d*₂ solution, a mixture of ethylene, ethane, and hydrogen forms along with detectable amounts of **1-H-PPh₃** characterized by two ³¹P nuclei resonating at $\delta = 24.42$ and 7.92 ppm with a ²J_{PPtrans} = 395 Hz and one hydridic resonance at $\delta(^1\text{H}) = -17.36$ ppm with observable ³J_{PHcis} = 16.5 Hz (for details, see SI).

Enhanced Decomposition in the Presence of Zwitterionic (*o*-MeOC₆H₄)₂PH⁺(C₆H₄SO₃[−]), H[P,O]. All experimental data presented so far point to an inherent reactivity of palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd(H)}$, which results in a deactivation of polymerization-active species by formation of saturated hydrocarbons and hydrogen as well as palladium black and $[\kappa^2\text{-(anisyl)}_2\text{P,O)]}_2\text{Pd}$ (**11**) (*vide supra*). However, as reductive elimination and oxidative addition of methylphosphonium salts were proven under NMR-tube conditions as well as in high-activity, high-pressure polymerization experiments (*vide supra*), and oxidative addition of (*o*-MeOC₆H₄)₂PH⁺(C₆H₄SO₃[−]) to palladium(0) is obviously a viable strategy to generate polymerization-active palladium hydride species (*vide supra* and ref 3), we hypothesized that the microscopic reverse, i.e., reductive elimination of phosphonium salt (*o*-MeOC₆H₄)₂PH⁺(C₆H₄SO₃[−]) (H[P,O]) from palladium hydride complexes, may in principle be possible and that therefore H[P,O] may be responsible for the deactivation of polymerization-active palladium complexes and the formation of saturated polymer chains (Scheme 5).³⁴ While thermodynamically the formation

Scheme 5. Reductive Elimination As a Source of H[P,O]



of **1-H-P^tBu₃** from stoichiometric amounts of H[P,O] and Pd(P^tBu₃)₂ is preferred (Figure 8), heating of **1-H-P^tBu₃** in dmsO-*d*₆ solution in the presence of excess P(^tBu)₃ results in the formation of $[\text{HP}^t\text{Bu}_3]^+[\text{P,O}]^-$, which thermodynamically likely reflects the higher basicity of P^tBu₃ vs [P,O] (cf. SI) and reduces the amount of H[P,O] accessible for oxidative addition to Pd(0). These experiments establish that oxidative addition and reductive elimination of P-protonated phosphonium sulfonate H[P,O] to palladium(0) are kinetically accessible and equilibrated.

Therefore, the reactivity of H[P,O] toward **1-CH₃-dmsO**, **1-CH₃-P^tBu₃**, **1-CH₂CH₃-PPh₃**, **1-H-P^tBu₃**, and **1-(CH₂)_{2n}-¹³CH₃-dmsO** was studied. Intriguingly, the reaction of **1-CH₃-dmsO** or **1-CH₃-P^tBu₃** with 1.1 equiv of H[P,O] (instead of **1-H-P^tBu₃**) also yields methane, but the reaction is already complete within 5 min at 298 K in tetrachloroethane-*d*₂ solution, which contrasts with ca. 1.5 h at 373 K for the complete decomposition of **1-CH₃-dmsO** by **1-H(D)-P^tBu₃** to form methane(-*d*₁).

Decomposition of **1-H-P^tBu₃** by H[P,O] to form hydrogen is much slower than decomposition of **1-CH₃-dmsO** or **1-CH₃-P^tBu₃** by H[P,O] (4 h, 373 K vs <5 min, 298 K) but faster than

decomposition of **1-H-P^tBu₃** alone in the absence of H[P,O] (11 h, 373 K, *vide supra*). Finally, **1-Et-PPh₃** decomposes to ethane, ethylene, butenes, and higher oligomers in the presence of H[P,O] at a similar rate as in the absence of H[P,O]. While the relatively slow formation of ethane from **1-CH₂CH₃-PPh₃** and H[P,O] *vis à vis* the much faster formation of methane from **1-CH₃-dmsO** or **1-CH₃-P^tBu₃** and H[P,O] is intriguing, we believe that it is caused by a much slower dissociation of PPh₃ from **1-Et-PPh₃** than the dissociation of bulky P^tBu₃ or dmsO from **1-CH₃-dmsO** or **1-CH₃-P^tBu₃** and that the reaction of **1-alkyl-PR₃** complexes with H[P,O] only qualitatively models a catalyst decomposition during polymerization experiments with **1-CH₃-dmsO** or **1-CH₃-pyr**. To verify this hypothesis, further ethylene oligomerizations were conducted in NMR-tube experiments. Thus, **1-¹³CH-dmsO** was reacted with ca. 7.5 equiv of ethylene for 90 min at 298 K in thf-*d*₈, while 5.5 equiv of ethylene was enchainment to form a mixture of **1-(CH₂)_{2n}-¹³CH₃-dmsO** complexes in 74% NMR yield and 26% **1-¹³CH-dmsO** remained unreacted. At this point no signals indicating the presence of terminal or internal olefins were detectable by ¹H NMR spectroscopy. After addition of 1.5 equiv of H[P,O] (which is virtually insoluble in pure thf-*d*₈) the complete disappearance of **1-¹³CH-dmsO** and formation of ¹³CH₄ were evident within less than 5 min at 298 K, while complete depletion of the aliphatic signals of **1-(CH₂)_{2n}-¹³CH₃** complexes was observed within 25 min at 298 K. Simultaneously, characteristic signals of linear alkanes (internal methylene groups at $\delta = 1.293$ ppm and of CH₃ groups at $\delta = 0.891$ ppm) and traces of propane were detected. The ratio of ¹³CH₃ and ¹²CH₃ as well as (¹³C)S1-S2:(¹²C)S1-S2 in these linear alkanes is virtually 1:1, while only trace amounts of olefins (<5%, mainly 1-olefins) were detected by means of ¹H and ¹³C NMR spectroscopy. This experiment confirms that in the real catalytic system H[P,O] (if formed by reductive elimination from a palladium hydride according to Scheme 5) rapidly cleaves the palladium–polymeryl bond to form saturated hydrocarbons and that palladium-coordinated PPh₃ may significantly reduce the rate of this decomposition reaction in the **1-CH₂CH₃-PPh₃** model complex. ³¹P NMR analysis of this sample indicates a virtually quantitative formation of $[\kappa^2\text{-(anisyl)}_2\text{P,O)]}_2\text{Pd}$ (**11**), as concluded from two signals at $\delta = 30.03$ and 22.81 ppm in a 1:8 ratio, also observed with independently prepared material in thf-*d*₈:dmsO-*d*₆ 4:1 (*vide supra*).

At this point it remains unresolved whether palladium hydride complexes $[\kappa^2\text{-P,O}]\text{Pd(H)}$ or H[P,O] are directly responsible for the deactivation of polymerization-active palladium complexes and the formation of saturated hydrocarbons. However, DFT calculations have been conducted in order to clarify this issue (*vide infra*).

Implications for Copolymerizations of Ethylene with Polar Vinyl Monomers. The tendency of **1-alkyl-L** for β -hydride elimination under preparative reactor polymerization conditions ultimately opens a catalyst decomposition pathway by the inherent reactivity of formed $[\kappa^2\text{-P,O}]\text{Pd(H)}$ or the reductive elimination product H[P,O] formed thereof. In general, in copolymerizations of ethylene with polar vinyl monomers catalyzed by **1-CH₃-L** polymer molecular weights tend to be lower vs ethylene homopolymerizations, due to an enhanced propensity for β -hydride elimination after enchainment of polar monomer. That is, the issue of irreversible catalyst deactivation initiated by palladium hydride complexes becomes increasingly important. As the decomposition reaction of **1-(CH₂)_{2n}-¹³CH₃** with $[\kappa^2\text{-P,O}]\text{Pd(H)}$ or H[P,O] will be greater than first-order in palladium {due to $d[\text{H[P,O]}]/dt = -k \times [[\kappa^2\text{-P,O}]\text{Pd(H)}]}$, the

most promising strategy to suppress this decomposition without changing the nature of the catalyst will be (a) to reduce the catalyst concentration in (co)polymerization experiments and (b) to lower the reaction temperature, thereby reducing the tendency for β -hydride elimination. While lowering the reaction temperature, e.g., to 298 K, already was proven to reduce the tendency for β -hydride elimination due to the living character of ethylene enchainment (*vide supra*), the viability of this strategy is limited for preparative polymerizations due to decreased polymerization rates. We have therefore focused on the effect of catalyst concentration in ethylene–methyl acrylate (MA) copolymerization experiments.

Copolymerizations of ethylene and MA were performed with varying concentrations of **1-CH₃-dmsO** (from 0.2 to 1.0 mM under otherwise identical conditions). In these experiments, clearly a decreasing *productivity* was found with increasing catalyst loading (i.e., with increasing [Pd]). Furthermore, although methyl acrylate incorporation did not change significantly, molecular weights of the obtained copolymers decreased with increasing [Pd], which indicates that growing copolymer chains may be terminated not only by β -hydride elimination but on a similar time scale also by reaction with $[\kappa^2\text{-P,O}]\text{Pd(H)}$ or $[\text{P,O}]\text{H}$, with formation of saturated copolymer chains (Table 3).

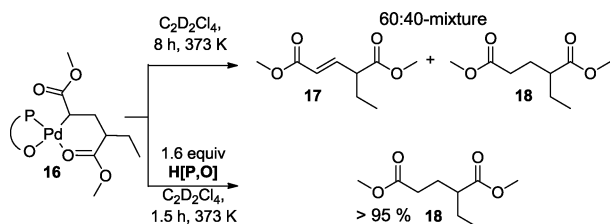
Table 3. Ethylene–Methyl Acrylate Copolymerizations at Variable Concentrations of the Catalyst Precursor^a

entry	conc Pd(II) [mM]	yield [g]	TON C ₂ H ₄ ^b	TON MA ^b	χ_{MA}^c	M_n^d [10 ³ g mol ⁻¹]	M_w/M_n^d
1	0.2	0.47	603	77	11.3	8000	1.4
2	0.5	0.97	486	67	12.2	7100	1.4
3	1.0	1.61	414	53	11.3	5800	1.5

^aReaction conditions: 100 mL 0.6 M MA in toluene, 5 bar [C₂H₄]; 95 °C; 30 min polymerization time, catalyst (**1-CH₃-dmsO**) added as methylene chloride solution. ^bTurnover number per palladium. ^cFrom ¹H NMR in C₂D₂Cl₄ at 100 °C. ^dFrom GPC at 40 °C vs polystyrene standards.

The reactivity of the methyl acrylate diinsertion product **16**, which is isolable upon reaction of **1-CH₃-L** with methyl acrylate,^{12b} was studied. Complex **16** is a suitable model for catalyst deactivation in ethylene–methyl acrylate copolymerizations, as β -hydride elimination after acrylate insertion can be modeled. Thus, heating **16** in tetrachloroethane-*d*₂ solution to 373 K for 8 h results in formation of a ca. 60:40 mixture of unsaturated 4-ethylpent-2-enedioic acid dimethyl ester (**17**) and saturated 2-ethylpentanedioic acid dimethyl ester (**18**) (Scheme 6; for details, see SI). This experiment proves that in ethylene–acrylate copolymerizations palladium hydride $[\kappa^2\text{-P,O}]\text{Pd(H)}$ or P-protonated phosphonium salt H[P,O] is capable of cleaving palladium polymeryl species formed after an acrylate insertion.

Scheme 6. Formation of Unsaturated **17** and Saturated **18** by Thermolysis of Complex **16** in the Absence or Presence of H[P,O]



Furthermore, upon addition of 1.6 equiv of H[P,O] to complex **16** the saturated product **18** is formed in nearly quantitative NMR yield within 1.5 h under otherwise identical reaction conditions.

Theoretical Investigations on Reversible and Irreversible Catalyst Deactivation Reactions. DFT calculations were performed with Gaussian09³⁵ using the BP86^{36–38} functional and the LANL2DZ ECP C5³⁹ with the associated valence basis set on the Pd atom and the 6-31G (d) basis set on all the other atoms. All geometries were localized in the gas phase at the BP86 level. Minima were localized by full optimization of the starting structures, while transition states were approached through a linear transit procedure and then located by a full transition-state search. All structures were confirmed as minimum or transition state through frequency calculations. The natural bond orbital analyses were performed by using NBO version 3.^{40–47} The reported energies were obtained through single-point energy calculations on the BP86 geometries using the M06 functional, the SDD ECP with the associated valence basis set on the Pd atom, and the TZVP basis set on all other atoms. Dichloroethane solvent effects were included with the continuum solvation model PCM.⁴⁸

Since products obtained after reductive elimination of phosphonium salts $(\text{aryl})_{3-x}\text{P}^+\text{R}_{x+1}$ ($x = 0, 1$) from $[(\kappa^2\text{-P,O})\text{-}(o\text{-MeOC}_6\text{H}_4)_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3)]\text{Pd(R)(L)}$ (**1-R-L**) were formed during preparative reactor polymerizations, NMR *in situ* polymerizations, and thermolysis of complexes **1-R-L** (*vide supra*), mechanistic pathways for these reductive elimination reactions were investigated. Due to the potential participation of P-protonated phosphonium salt $(o\text{-MeOC}_6\text{H}_4)_2(\text{C}_6\text{H}_4\text{SO}_3)\text{-P}^+(\text{H})$ (H[P,O]) in an irreversible catalyst deactivation (*vide supra*), we first investigated the formation of H[P,O] starting from the synthesized model complex **1-H-P'Bu₃** and P'Bu_3 (note that **1-H-P'Bu₃** was synthesized by oxidative addition of H[P,O] to $[\text{Pd}(\text{P'Bu}_3)_2]$).

These calculations indicate that the reductive elimination of H[P,O] occurs through a transition state (TS) lying 124 kJ mol⁻¹ higher in energy than **1-H-P'Bu₃**, with the P'Bu_3 ligand still coordinated to the Pd (see Scheme 7). The transition-state geometry **1-H-TS1** (Scheme 7 and Figure 10) exhibits a still short palladium–hydride and palladium–oxygen bonds (Pd–H: 1.58 vs 1.48 Å and 2.28 vs 2.19 Å in **1-H-P'Bu₃**, see Figure 8 and Table 2), while the cleaving palladium–phosphine bond is

Scheme 7. Energetics (kJ mol⁻¹) of the Reductive Elimination of H[P,O] from **1-H-P'Bu₃**.

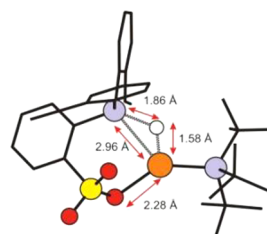
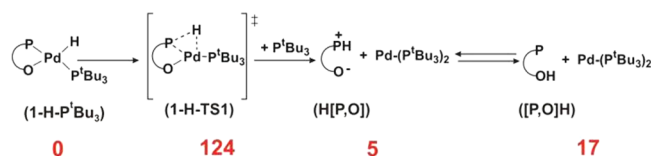
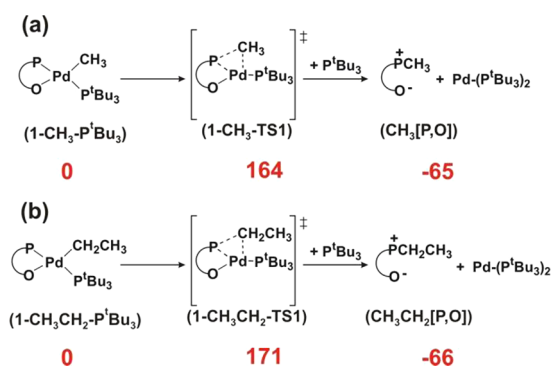


Figure 10. Transition-state geometry for the reductive elimination reaction of H[P,O] from **1-H-P'Bu₃**.

already 2.96 Å long, as compared to 2.31 Å in **1-H-P^tBu₃**. Finally the evolving phosphine–hydrogen bond is still 1.86 Å long, as compared to ca. 1.33–1.40 Å in reported P-protonated phosphonium salts.⁵¹ After reductive elimination of H[P,O] the departing Pd–P^tBu₃ fragment is stabilized by incoming P^tBu₃ to form [Pd(P^tBu₃)₂]. The overall reaction is essentially thermo-neutral, with **1-H-P^tBu₃** + P^tBu₃ favored by 5 kJ mol^{–1} over H[P,O] + [Pd(P^tBu₃)₂], which is in qualitative agreement with the synthesis of **1-H-P^tBu₃** from H[P,O] + [Pd(P^tBu₃)₂]. Considering the principle of microscopic reversibility and the calculated energies of educts, products, and the transition state **1-H-TS1**, these results indicate a fully reversible formation of **1-H-P^tBu₃** + P^tBu₃ from H[P,O] + [Pd(P^tBu₃)₂].

A similar reaction profile was also found for the reductive elimination of P-methylated and P-ethylated phosphonium salts Me[P,O], and Et[P,O] from **1-CH₃-P^tBu₃** and **1-CH₂CH₃-P^tBu₃** + P^tBu₃. However, the formed products Me[P,O] (Et[P,O], respectively) + [Pd(P^tBu₃)₂] are much more stable than the educts by 65 (66, respectively) kJ mol^{–1}, while the transition states **1-CH₃-TS1** (**1-CH₂CH₃-TS1**, respectively) lie 164 (171) kJ mol^{–1} higher than the educts (Scheme 8).

Scheme 8. Energetics (kJ mol^{–1}) of the Reductive Elimination of Me[P,O] from **1-CH₃-P^tBu₃ (a) and of the Elimination of Et[P,O] from **1-CH₂CH₃-P^tBu₃** (b)**



Thus, although thermodynamically much more favorable than reductive elimination of H[P,O], the reductive elimination of Me[P,O] (Et[P,O], respectively) requires a 40 (47, respectively) kJ mol^{–1} higher activation energy than reductive elimination of H[P,O]. These significantly increased activation energies also manifest in the transition-state geometries **1-CH₃-TS1** (**1-CH₂CH₃-TS1**, respectively, Figure 11) with already short P–CH₃ (P–CH₂CH₃, respectively) distances of 1.92 (1.95, respectively) Å for the evolving P–C bond as compared, for example, with 1.80 Å in P-methylated complex **10** or 1.84 Å in

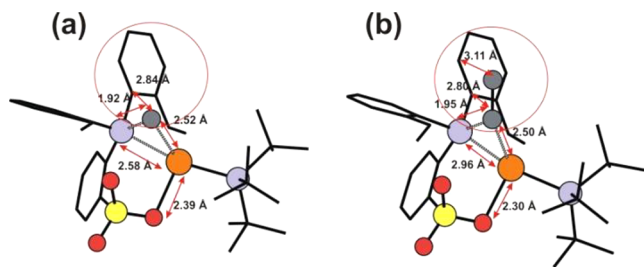


Figure 11. Transition states **1-CH₃-TS1 and **1-CH₂CH₃-TS1** for the reductive elimination of H[P,O] from **1-CH₃-P^tBu₃** (a) and from **1-CH₂CH₃-P^tBu₃** (b).**

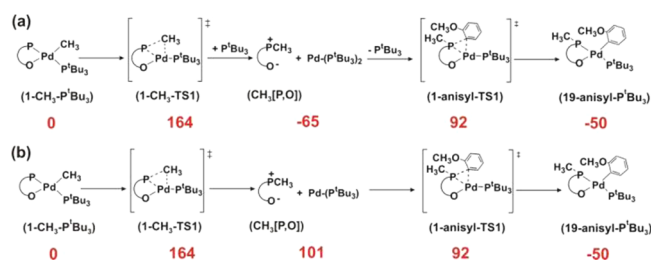
P-ethylated complex **12** or with a calculated ground-state distance of 1.84 (1.86) Å in Me[P,O] (Et[P,O]).

To rationalize the remarkable thermodynamic difference between reductive eliminations from the Pd–H complex on one hand and the Pd–Me and Pd–Et complexes on the other hand, we compare the homolytic bond dissociation energy (BDE) of the Pd–R bond in the Pd–H, Pd–Me, and Pd–Et complexes. The calculated BDEs indicate that the Pd–H bond is roughly 100 kJ mol^{–1} stronger than the Pd–C bonds. On the other hand, the BDE of the P–H, P–Me, and P–Et bonds in the corresponding R[P,O] zwitterions indicates that the P–H bond is only ca. 30 kJ mol^{–1} stronger than the P–C bonds. Thus, the main difference in the thermodynamics of the reductive elimination is caused by the difference in the strength of the Pd–H and Pd–C bonds and can be reasonably approximated by the calculated differences of the BDE of the Pd–R and P–R bonds.

Furthermore, the transition-state energy differences seem to have a steric term. As indicated in Figure 11, steric interactions between the migrating Me or Et group and one of the anisyl rings of the ligand with close contacts of ca. 2.8 Å to the *ipso*-anisyl carbon atom may be responsible for the higher energy of **1-CH₃-TS1-P^tBu₃** and **1-CH₂CH₃-TS1-P^tBu₃** compared with the TS calculated for the less encumbered **1-H-TS1** (Figure 10).

Given the strong thermodynamic preference for the reductive elimination to form P-alkylated phosphonium salts, the microscopic reverse, i.e., oxidative addition of Me[P,O] to [Pd(P^tBu₃)₂] with an activation energy of 229 kJ mol^{–1} (237 kJ mol^{–1} for Et[P,O], respectively), seems highly unlikely based on these calculations. However, since mass spectrometric and NMR data prove the formation of double-methylated phosphonium salts, e.g., **2**, and in addition 2-(vinyl)anisole was detected by NMR experiments (*vide supra* and SI), the oxidative addition of a P-anisyl bond of Me[P,O] to [Pd(P^tBu₃)₂] was investigated. Remarkably, a transition-state geometry **1-anisyl-TS1** was found, which lies 157 kJ mol^{–1} higher than Me[P,O] + [Pd(P^tBu₃)₂]. This barrier is similar to that of reductive elimination of Me[P,O] from **1-CH₃-P^tBu₃** (164 kJ mol^{–1}) and is therefore kinetically accessible considering that formation of Me[P,O] takes place under experimental conditions. The transition state **1-anisyl-TS1** evolves into the palladium anisyl complex **19-(anisyl)-P^tBu₃**, which, though thermodynamically 15 kJ mol^{–1} less stable than Me[P,O] + [Pd(P^tBu₃)₂], is 50 kJ mol^{–1} more stable than **1-CH₃-P^tBu₃** (Scheme 9a). These results are in accordance with the

Scheme 9. Energetics (kJ mol^{–1}) of the Reductive Elimination of Me[P,O] from **1-CH₃-P^tBu₃ and of the P-Anisyl Oxidative Addition of Me[P,O] to [Pd(P^tBu₃)₂] (a) and to [Pd(P^tBu₃)] (b)**



more general trend observed in metal–carbon bond energies experimentally determined by Wolczanski et al. for titanium carbonyl complexes^{50a} and by Jones et al. for rhodium carbonyl complexes.^{50b} They indicate that the respective metal–methyl bonds tend to be ca. 30 kJ mol^{–1} (Ti) or ca. 65 kJ mol^{–1} (Rh) less stable than the respective metal–phenyl bonds. They are also in accordance

with DFT calculations of the Wolczanski and Jones series at the B3PW91 and BP86 levels of theory, which clearly support the higher stability of metal–phenyl vs metal–methyl bonds.^{50c}

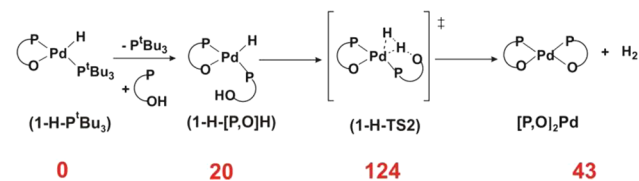
In the absence of free P^tBu_3 the $Pd(P^tBu_3)$ fragment evolving from **1-CH₃-TS1- P^tBu_3** will not be stabilized by formation of $[Pd(P^tBu_3)_2]$, and reaction of $Me[P,O] + Pd(P^tBu_3) \rightarrow$ **19-anisyl- P^tBu_3** becomes energetically barrierless (Scheme 9b). Simultaneously, the absence of free P^tBu_3 makes **19-anisyl- P^tBu_3** a global and not just a local thermodynamical minimum when compared to the reaction shown in Scheme 9a.⁵¹

These results indicate that reductive elimination of methyl/alkylphosphonium salts $Me[P,O]/(alkyl)[P,O]$ in the real catalytic system constitutes a reversible deactivation pathway of polymerization-active palladium complexes to form palladium(0) species. Reactivation of palladium(0) species, however, proceeds by oxidative addition of a P-anisyl bond as supported by experimental results and DFT calculations.

In contrast, the formation of fully saturated alkanes under polymerization conditions and the additional formation of dihydrogen in model reactions result in an irreversible catalyst deactivation. The experimental data, however, do not allow for a precise mechanistic scheme, since palladium hydride complexes $[(\kappa^2-P,O)Pd(H)(L)]$ or reductively eliminated P-protonated phosphonium salts $H[P,O]$ may be responsible for the formation of inactive palladium and saturated alkanes. Therefore several mechanistic schemes were investigated by DFT methods: (a) the reactions of P-protonated phosphonium salt $H[P,O]$ with synthetically accessible **1-H- P^tBu_3** , **1-CH₃- P^tBu_3** , and **1-CH₃CH₃-PPh₃**, (b) the reaction of **1-CH₃- P^tBu_3** with **1-H- P^tBu_3** , and finally (c) the reaction **1-CH₃-dmsO** with **1-H- P^tBu_3** .

With respect to the reactions of P-protonated phosphonium salt $H[P,O]$, we note that low-lying transition states were formed only after tautomerization into the O-protonated sulfonic acid form $[P,O]H$, which is 12 kJ mol^{−1} less stable than the P-protonated $H[P,O]$ form (Scheme 7).⁵² The reaction of **1-H- P^tBu_3** with $[P,O]H$ is then initiated by substitution of the P^tBu_3 ligand for the phosphine $[P,O]H$ to form **1-H- $[P,O]H$** , which is 20 kJ mol^{−1} higher in energy than **1-H- P^tBu_3** + O-protonated $[P,O]H$. **1-H- $[P,O]H$** directly evolves to the transition state **1-H-TS2** lying 124 kJ mol^{−1} higher than **1-H- P^tBu_3** + O-protonated sulfonic acid (Scheme 10). Considering the tautomerization of

Scheme 10. Energetics (kJ mol^{−1}) of the Reaction of $[P,O]H$ with **1-H- P^tBu_3**



P-protonated $H[P,O]$ into O-protonated $[P,O]H$, which costs 12 kJ mol^{−1}, the overall barrier amounts to 136 kJ mol^{−1} to reach **1-H-TS2**. **1-H-TS2** then decomposes to form dihydrogen and $[\kappa^2-(anisyl)_2P,O]_2Pd$ (**11**), which lie 43 kJ mol^{−1} higher in energy than **1-H- P^tBu_3** + O-protonated $[P,O]H$. The endoergicity of the overall reaction is in accordance with a late transition state in which the hydrogen–hydrogen distance is only 0.80 Å (Figure 12), i.e., very close to the distance in free H_2 (0.74 Å) and certainly at the lower limit even of dihydrogen complexes (0.8–1.0 Å).⁵⁵

Comparison of the energy profile of the three reactions involved in the deactivation process (i.e., reductive elimination of

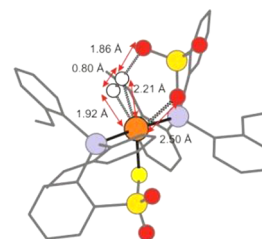
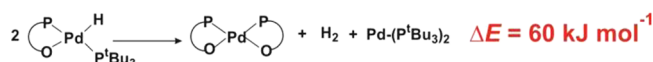


Figure 12. Transition-state geometry of **1-H-TS2** for the reaction leading to $[P,O]_2Pd$ (**11**) + H_2 .

$H[P,O]$, tautomerization of $H[P,O]$ into $[P,O]H$, and reaction of $[P,O]H$ with **1-H- P^tBu_3** shows that the reactions **1-H- P^tBu_3** + $P^tBu_3 \rightarrow [Pd(P^tBu_3)_2] + H[P,O]$ and **1-H- P^tBu_3** + $H[P,O] \rightarrow$ **1-H- P^tBu_3** + $[P,O]H \rightarrow [\kappa^2-(anisyl)_2P,O]_2Pd$ (**11**) + H_2 have very similar energy barriers, i.e., 124 and 12 + 124 = 136 kJ mol^{−1} (Scheme 10). The energy balance of the overall decomposition reaction, shown in Scheme 11, is endoergic by ca. 60 kJ mol^{−1},

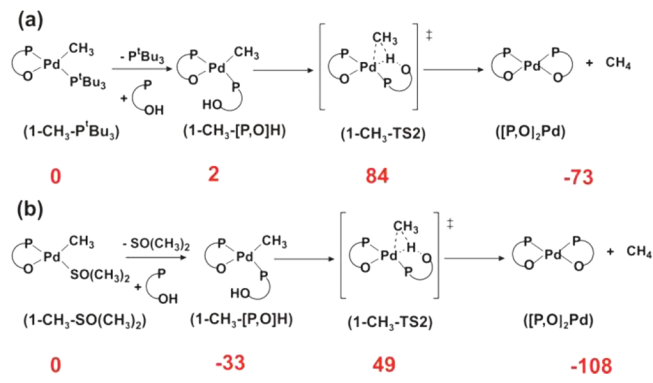
Scheme 11. Energetics (kJ mol^{−1}) of the Overall Decomposition Reaction of **1-H- P^tBu_3**



which is mostly caused by the formation of **11** and H_2 from **1-H-TS2**. However, despite the endoergicity, release and irreversible removal of H_2 from the reaction mixture is a plausible driving force for this reaction to proceed.

The reaction of O-protonated $[P,O]H$ with **1-CH₃- P^tBu_3** to form complex **11** and methane proceeds along a similar reaction coordinate to the reaction of $[P,O]H$ with **1-H- P^tBu_3** . However, substitution of P^tBu_3 by $[P,O]H$ leads to intermediate **1-CH₃- $[P,O]H$** + P^tBu_3 , which lie 2 kJ mol^{−1} higher than the educts and evolve to transition state **1-CH₃-TS2** for the formation of methane and **11**, which lies 84 kJ mol^{−1} higher than the educts (as compared to 124 kJ mol^{−1} for the formation of H_2 and **11**) (Scheme 12, line (a)). The overall formation of methane and **11**

Scheme 12. Energetics (kJ mol^{−1}) of the Reaction of $[P,O]H$ with **1-CH₃- P^tBu_3** (line (a)) and with **1-CH₃-dmsO** (line (b))

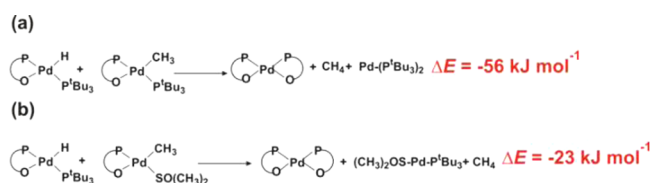


is exoergic (and therefore thermodynamically favorable) by 73 kJ mol^{−1} starting from O-protonated $[P,O]H$ and **1-CH₃- P^tBu_3** . When $[P,O]H$ is reacted with **1-CH₃-dmsO**, substitution of dmsO for $[P,O]H$ to form the new ground state **1-CH₃- $[P,O]H$** + dmsO is exoergic by 33 kJ mol^{−1} and evolves into the transition state **1-CH₃-TS2**, which now lies 49 kJ mol^{−1} above $[P,O]H$ + **1-CH₃-dmsO**.⁵⁶ The rate-limiting step to reach **1-CH₃-TS2**,

however, is 82 kJ mol⁻¹ in energy for the transformation of 1-CH₃-[P,O]H + dmsO into 1-CH₃-TS2 + dmsO (Scheme 12, line (b)) and therefore very similar to the overall barrier of 84 kJ mol⁻¹ calculated for the reaction of [P,O]H with 1-CH₃-P^tBu₃ (compare lines (a) and (b) in Scheme 12).

The overall formation of methane and 11 is also exoergic by 56 kJ mol⁻¹ starting from 1-H-P^tBu₃ and 1-CH₃-P^tBu₃ and 23 kJ mol⁻¹ starting from 1-H-P^tBu₃ and 1-CH₃-dmsO by following a reaction sequence composed of reductive elimination of H[P,O] from 1-H-P^tBu₃, tautomerization of H[P,O] into [P,O]H, and reaction of [P,O]H with 1-CH₃-P^tBu₃ or 1-CH₃-dmsO (Scheme 13).

Scheme 13. Energetics (kJ mol⁻¹) for the Overall Formation of Methane and 11 from the Reaction of 1-CH₃-P^tBu₃ with 1-H-P^tBu₃ (line (a)) and from the Reaction of 1-CH₃-dmsO with 1-H-P^tBu₃ (line (b))



However, the rate-limiting step for the formation of methane and 11 starting from 1-H-P^tBu₃ and 1-CH₃-P^tBu₃ or 1-CH₃-dmsO is now reductive elimination of H[P,O] with a barrier of 124 kJ mol⁻¹, as compared to the 84 kJ mol⁻¹ barrier calculated for the reaction of O-protonated [P,O]H with 1-CH₃-P^tBu₃ and compared to the 82 kJ mol⁻¹ calculated barrier for the reaction of [P,O]H with 1-CH₃-dmsO (compare Schemes 7 and 12).

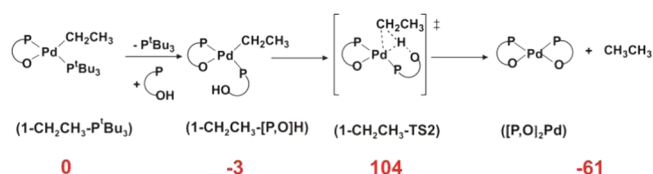
A rate-limiting reductive elimination of H[P,O] is in accordance with the experimental finding that upon addition of H[P,O] to 1-CH₃-P^tBu₃ or 1-CH₃-dmsO, formation of methane and 11 takes place within <5 min at 298 K, while complete formation of methane and 11 takes 1.5 h at 373 K starting from 1-CH₃-dmsO + 1-H(D)-P^tBu₃ in tetrachloroethane-d₂ (*vide supra*).

While formation of H₂ and 11 from 1-H-P^tBu₃ is thermodynamically disfavored by 60 kJ mol⁻¹, but due to removal of H₂ still observable in the experimental system, formation of methane and 11 from 1-H-P^tBu₃ and 1-CH₃-P^tBu₃ is favored by 56 kJ mol⁻¹. This huge calculated energy difference of 116 kJ mol⁻¹ for the formation of H₂ and methane seems odd at first glance. However, it is in accordance with calculated homolytic bond dissociation energies of the Pd-CH₃ bond and the Pd-H bond in 1-CH₃-P^tBu₃ and 1-H-P^tBu₃, which indicates that the Pd-CH₃ bond is ca. 100 kJ mol⁻¹ weaker than the Pd-H bond (see SI),⁵⁷ while the respective H₃C-H and H-H bonds are reported to be ca. 440 (H₃C-H) and 436 kJ mol⁻¹ (H₂).⁵⁶ Thus the calculated difference of 116 kJ mol⁻¹ for the formation of a H-H bond as compared to a H₃C-H bond starting from 1-CH₃-P^tBu₃ and 1-H-P^tBu₃ originates mainly from the differences in bond dissociation energies of the respective Pd-H and Pd-CH₃ bonds.

We move now to the decomposition of 1-CH₂CH₃-P^tBu₃ promoted by reaction with the protonated ligand [P,O]H; see Scheme 14. Overall, the energy profile is rather similar to that of the corresponding methyl complex 1-CH₃-P^tBu₃ (Scheme 12); the main difference is in the energy barrier for ethane elimination, which is roughly 25 kJ mol⁻¹ higher than the barrier for methane elimination.

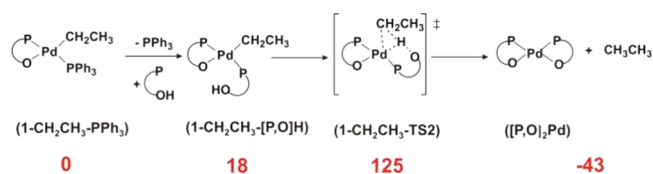
A rather similar energy profile is also calculated when the experimentally employed ethyl complex with a PPh₃ ligand in

Scheme 14. Energetics (kJ mol⁻¹) of the Decomposition Reaction of 1-CH₂CH₃-P^tBu₃ with 1-H-P^tBu₃



place of P^tBu₃ is considered. The main difference is in the energy of PPh₃ substitution by [P,O]H, which is disfavored by 18 kJ mol⁻¹; see Scheme 15. This is related to the lower steric

Scheme 15. Energetics (kJ mol⁻¹) of the Reaction of [P,O]H with 1-CH₂CH₃-PPh₃



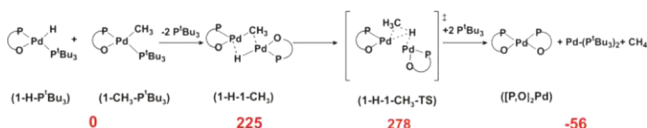
bulkiness of PPh₃ compared to P^tBu₃. The stronger binding of PPh₃ compared to P^tBu₃ translates into a decomposition pathway shifted about 20 kJ mol⁻¹ higher in energy; compare Schemes 14 and 15.⁵⁷ The reasonable energy barrier we found for the decomposition of 1-CH₂CH₃-PPh₃ promoted by the protonated ligand [P,O]H is in agreement with the experimental evidence: (a) 1-CH₂CH₃-PPh₃ decomposes with formation of ethane and trace amounts of hydrogen at 343 K, (b) the reaction of H[P,O] with 1-CH₂CH₃-PPh₃ is slower than the reaction with 1-CH₃-P^tBu₃, and (c) the reaction of H[P,O] with 1-(CH₂)_{2n}¹³CH₃-dmsO at 298 K is slower than with 1-¹³CH₃-dmsO (*vide supra*).

In conclusion, the experimentally observed reactivity differences are largely not due to the different binding strengths of the monodentate phosphine or dmsO. While the substitution of monodentate phosphines for [P,O]H in 1-alkyl-PR₃ is essentially thermoneutral or slightly endoergic, replacement of dmsO in 1-CH₃-dmsO by [P,O]H is exoergic (Schemes 12, 14, and 15). However, all these substitution reactions lead to 1-CH₃/CH₂CH₃-[P,O]H, which eliminates methane with a barrier of 82 kJ mol⁻¹ or ethane with a barrier of 107 kJ mol⁻¹. Thus, the experimentally observed finding, that 1-¹³CH₃-dmsO reacts faster with [P,O]H to form methane than with 1-(CH₂)_{2n}¹³CH₃-dmsO to form alkanes (*vide supra*) is mainly due to the difference in the respective barriers for methane vs ethane elimination. However, as shown for the model compound 1-H-P^tBu₃, reductive elimination of H[P,O] with a barrier of 124 kJ mol⁻¹ seems rate limiting for the formation of alkanes whenever H[P,O] is not deliberately added to catalytically active species.

Finally we have investigated two reaction schemes in which 1-H-P^tBu₃ directly reacts with 1-CH₃-P^tBu₃ or with 1-CH₃-dmsO (i.e., without prior reductive elimination of H[P,O]). The first reaction coordinate we investigated comprises the reaction of 1-H and 1-CH₃ formed after P^tBu₃ dissociation from 1-H-P^tBu₃ and 1-CH₃-P^tBu₃. The formed intermediate 1-H-1-CH₃ exhibits a bridging hydride and methyl group with short Pd(1)-H (1.877 Å), Pd(2)-H (1.646 Å), Pd(1)-CH₃ (2.044 Å), and Pd(2)-CH₃ (2.538 Å) distances, which evolves into transition state 1-H-1-CH₃-TS1, in which the two palladium atoms, the hydrogen atom, and the carbon atom adopt a

distorted four-membered ring. However, $1\text{-H-1-CH}_3 + 2 \text{P}^t\text{Bu}_3$ and $1\text{-H-1-CH}_3\text{-TS1} + 2 \text{P}^t\text{Bu}_3$ are 225 and 278 kJ mol^{-1} higher in energy than $1\text{-H-P}^t\text{Bu}_3 + 1\text{-CH}_3\text{-P}^t\text{Bu}_3$ and thus prohibitively high for the reaction to proceed (Scheme 16). The reason for

Scheme 16. Energetics (kJ mol^{-1}) of the Decomposition Reaction of $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ with $1\text{-H-P}^t\text{Bu}_3$ Initiated by P^tBu_3 Dissociation from $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ and $1\text{-H-P}^t\text{Bu}_3$

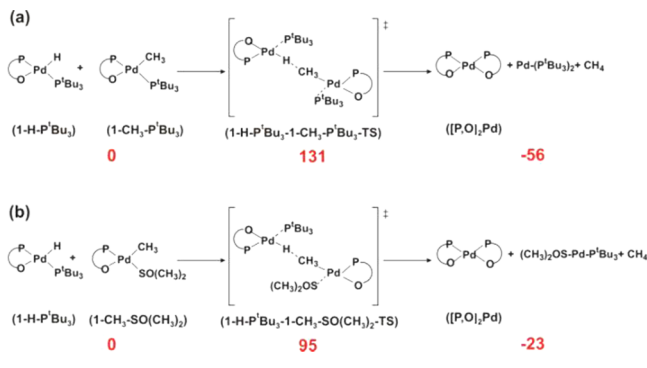


these high energies of $1\text{-H-1-CH}_3 + 2 \text{P}^t\text{Bu}_3$ and $1\text{-H-1-CH}_3\text{-TS} + 2 \text{P}^t\text{Bu}_3$ is likely a huge energetic penalty for the dissociation of P^tBu_3 in both educt complexes, which cannot be compensated for by the bridging interaction of hydride and the methyl group in 1-H-1-CH_3 .

In order to avoid such high energetic penalties due to ligand dissociations, we have investigated a second reaction coordinate, which comprises the reactions of two four-coordinate palladium complexes, namely, $1\text{-H-P}^t\text{Bu}_3 + 1\text{-CH}_3\text{-P}^t\text{Bu}_3$ and $1\text{-H-P}^t\text{Bu}_3 + 1\text{-CH}_3\text{-dmsO}$, i.e., without dissociation of P^tBu_3 or dmsO.

Intriguingly, transition state $1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-P}^t\text{Bu}_3\text{-TS}$ was located lying only 131 kJ mol^{-1} higher than $1\text{-H-P}^t\text{Bu}_3 + 1\text{-CH}_3\text{-P}^t\text{Bu}_3$ (Scheme 17, line (a)). An even lower transition state,

Scheme 17. Energetics (kJ mol^{-1}) of the reaction of $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ Leading to $1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-P}^t\text{Bu}_3\text{-TS}$ (line (a)) and of $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-dmsO}$ Leading to $1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-dmsO-TS}$ (line (b))



$1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-dmsO-TS}$, was located for the reaction of $1\text{-H-P}^t\text{Bu}_3 + 1\text{-CH}_3\text{-dmsO}$ with a barrier of 95 kJ mol^{-1} (Scheme 17, line (b)). Characteristic geometric features of these two transition state evolving into the elimination of methane comprise a nearly linear alignment of the reacting $\text{H-CH}_3\text{-Pd2}$ moieties of ca. 165° and a substantial planarization of the central CH_3 group (Figure 13), which are highly reminiscent of bimolecular substitution reactions. While it has been suggested in theoretical studies that evolution of hydrogen from homoleptic manganese hydride complexes may proceed through a similar, fully linear Mn-H-H-Mn transition-state geometry,⁶⁰ to our knowledge a linear hydride-alkyl-metal transition state for the reductive elimination of alkane has not been proposed or investigated for transition metal complexes. However, the reduction of haloalkanes by complex hydrides, e.g., LiBEt_3H or LiAlH_4 , was found to exhibit typical characteristics of an $\text{S}_\text{N}2$ reaction.⁶¹ We note, however, that the barriers

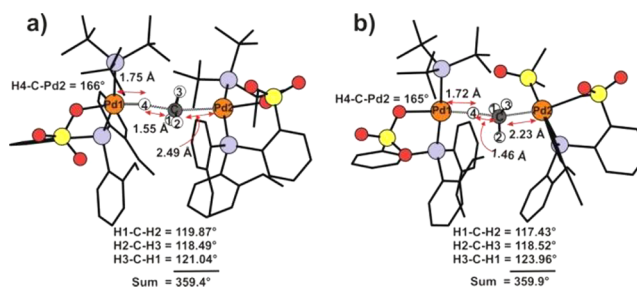


Figure 13. Geometry of $1\text{-H-(P}^t\text{Bu}_3\text{)-1-CH}_3\text{-P}^t\text{Bu}_3\text{-TS}$ (left) and $1\text{-H-(P}^t\text{Bu}_3\text{)-1-CH}_3\text{-dmsO-TS}$ (right) for the methane elimination starting from $1\text{-H-P}^t\text{Bu}_3$ and $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ or $1\text{-CH}_3\text{-dmsO}$.

associated with $1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-P}^t\text{Bu}_3\text{-TS}$ and $1\text{-H-P}^t\text{Bu}_3\text{-1-CH}_3\text{-dmsO-TS}$ (Scheme 17 and Figure 13) are prone to systematic errors caused by the self-interaction error of DFT,⁶⁰ which results in a potentially overestimated stability of these transition states due to artificially stabilized delocalized states. Consequently, the real barriers might be higher than determined here.

The calculated reaction coordinate for the overall reaction of $1\text{-H-P}^t\text{Bu}_3$ and $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ with a barrier of 131 kJ mol^{-1} according to Scheme 17a indicates that it may contribute to the formation of methane since it is very similar to the rate-limiting barrier (124 kJ mol^{-1}) of reductive elimination of H[P,O] in the reaction sequence composed of reductive elimination of H[P,O] from $1\text{-H-P}^t\text{Bu}_3$, tautomerization of H[P,O] into $[\text{P,O}]\text{H}$, and reaction of $[\text{P,O}]\text{H}$ with $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ according to Schemes 7 and 12a. For the formation of methane from $1\text{-H-P}^t\text{Bu}_3$ and $1\text{-CH}_3\text{-dmsO}$ a $\text{S}_\text{N}2$ -like reaction with an activation barrier of 95 kJ mol^{-1} according to Scheme 17b is favored over reductive elimination of H[P,O] from $1\text{-H-P}^t\text{Bu}_3$, tautomerization of H[P,O] into $[\text{P,O}]\text{H}$, and reaction of $[\text{P,O}]\text{H}$ with $1\text{-CH}_3\text{-dmsO}$ with a rate-limiting barrier of 124 kJ mol^{-1} (Scheme 7 and 12b).

In summary, two viable reaction coordinates for the irreversible deactivation of polymerization-active 1-(alkyl)-L/1-H-L and formation of saturated hydrocarbons have been disclosed: (a) A reaction sequence comprising reductive elimination of the P-protonated H[P,O] from $1\text{-H-P}^t\text{Bu}_3$, followed by tautomerization of H[P,O] into O-protonated $[\text{P,O}]\text{H}$ (Scheme 7), substitution of P^tBu_3 in $1\text{-(alkyl)-P}^t\text{Bu}_3$ by $[\text{P,O}]\text{H}$, and finally formation of alkane and $[\text{P,O}]_2\text{Pd}$ (11) (Schemes 12, 14, and 15). The rate-limiting step in this sequence is reductive elimination of H[P,O] with a barrier of 124 kJ mol^{-1} . (b) A bimolecular reaction of fully intact $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-L}$ according to Scheme 17 in which the transition-state geometries resemble a bimolecular substitution at a sp^3 -carbon atom. The energy barrier found for the reaction of $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-P}^t\text{Bu}_3$ along this reaction coordinate is 131 kJ mol^{-1} , whereas it is 95 kJ mol^{-1} for the reaction of $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-dmsO}$.

On the basis of these results, both reaction channels starting with reductive elimination of H[P,O] and starting with direct evolution into a bimetallic $\text{S}_\text{N}2$ -like substitution can contribute to the overall deactivation of $1\text{-H-P}^t\text{Bu}_3$ and $1\text{-(alkyl)-P}^t\text{Bu}_3$. However, when modeling the reaction of $1\text{-H-P}^t\text{Bu}_3$ with $1\text{-CH}_3\text{-dmsO}$, which is closer to the real catalytic system 1-H-L and 1-(alkyl)-L (L = olefin, dmsO), the bimetallic substitution pathway appears favorable.

CONCLUSIONS

These studies involving (a) direct monitoring of the polymerization reaction by NMR spectroscopy with isotope-labeled catalyst precursors, (b) analysis of end groups and distribution of

catalyst precursor-derived labeled carbon atoms in polymers obtained under preparative polymerization conditions, (c) direct isolation and full identification of catalyst decomposition products from typical polymerization mixtures, (d) clean preparation, isolation, and full characterization of relevant intermediates of the polymerization reaction, namely, different palladium alkyls as well as a palladium hydride, and (e) theoretical and experimental elucidation of the reactivity of these intermediates reveal the following reaction and decomposition pathways:

(1) Under typical polymerization conditions, extensive formation of mixed tetraaryl/alkyl phosphonium salts occurs by their reductive elimination from the polymerization-active Pd(II) alkyl species. That is, the growing polymeryl chain is transferred to the P atom of the phosphinesulfonato ligand. The reaction is in principle reversible as long as palladium black does not precipitate. It can afford Pd(II) aryl complexes with a P-alkyl phosphinesulfonato ligand by net scrambling of the growing polymeryl chain and the aryl moieties introduced with the catalyst precursor between the metal center and the phosphorus atom of the ligand. Such a species inserts ethylene, suggesting that it is polymerization-active. In fact, di(alkyl)phosphinesulfonato and (aryl)(alkyl)phosphinesulfonato Pd(II) complexes are precursors to active catalysts.⁶¹ This implies that in polymerizations with this class of catalysts for a given catalyst precursor actually a range of active species with different chelating P,O ligands including P-polymeryl- and P-dipolymeryl-substituted ligands may be involved. The overall productivity and selectivity will be the sum of all their contributions. Thus, the catalytic properties observed for a given phosphinesulfonato catalyst precursor may actually reflect its propensity for the aforementioned net scrambling reactions.

(2) Also the Pd(II) hydride, which is an ubiquitous intermediate in polymerization resulting from β -hydride elimination as the key chain transfer step, undergoes reductive elimination to form the free neutral (zwitterionic, P-protonated) phosphoniumsulfonate $\text{H}[\text{P},\text{O}]$ and palladium(0). This reaction again is reversible. However, once formed, the prevailing reaction of $\text{H}[\text{P},\text{O}]$ is a rapid irreversible reaction with the active growing polymeryl species to yield an alkane and the bis-chelated $[\kappa^2-(\text{P},\text{O})]_2\text{Pd}$. This stable compound is the final product of decomposition. Also, hydrogen can be formed from two equivalents of hydride, $2[\kappa^2-(\text{P},\text{O})]\text{Pd}(\text{H}) \rightarrow \text{H}_2 + [\kappa^2-(\text{P},\text{O})]_2\text{Pd} + \text{Pd}(0)$. This reaction again occurs most likely via reaction of the Pd hydride with free ligand, $\text{H}[\text{P},\text{O}]$, formed by reductive elimination from another equivalent of Pd hydride. A second irreversible catalyst deactivation pathway yielding alkanes, $[\kappa^2-(\text{P},\text{O})]_2\text{Pd}$, and palladium(0) was identified comprising the direct reaction of Pd(II) hydride with growing polymeryl species without reductive elimination of $\text{H}[\text{P},\text{O}]$.

These irreversible decomposition pathways originating from Pd hydrides will be particularly pronounced in (co)-polymerization reactions of polar vinyl monomers. The metal carbyl insertion products of vinyl monomers, such as methyl acrylate, are more prone to chain transfer by β -hydride elimination than unsubstituted metal alkyls from ethylene incorporation. This is reflected in an overproportional number of unsaturated end groups based on the polar monomer in ethylene copolymers.

These reactions not only limit catalyst lifetime but also result in the formation of relevant amounts of fully saturated polymer chains. This can falsify molecular weight analysis substantially in NMR determination of M_n under the common assumption that each chain will carry an unsaturated end group (from β -H elimination) whenever chain transfer numbers are small.

(3) Concerning the efficiency of activation of the catalyst precursor for polymerization, a weakly coordinated ($\text{L} = \text{dmsO}$) complex $[(\text{P},\text{O})\text{PdMe}(\text{L})]$ is activated rapidly and completely even at room temperature and low ethylene concentrations. Under these mild conditions, polymerization is living, which allows for clean observation of the activation reaction. For less labile coordinated catalyst precursors, activation typically will also be complete, but at the elevated temperatures required not only will the aforementioned irreversible deactivation reactions complicate studies of activation and chain growth but also scrambling of the isotope label from the $\text{Pd}^{13}\text{CH}_3$ initiator into the polymer backbone by propene elimination and reinsertion can simulate a seemingly incomplete inactivation.

These findings suggest strategies for improving catalyst stability. As key reactions are bimolecular, low catalyst concentrations reduce deactivation rates, as illustrated in this study. Site isolation, by appropriate bulky and repulsive ligand environments, multidentate ligands, or ultimately binding to soluble or solid supports, is the further elucidation of this concept. While the aforementioned reductive eliminations to phosphonium sulfonates and Pd(0) are reversible, an agglomeration to palladium black will render this step irreversible. Colloidal stabilization toward further aggregation of $[\text{Pd}(0)]_n$ at the stage of nanoparticles or addition of further tetraalkyl/aryl phosphonium sulfonates $\text{R}[\text{P},\text{O}]$ to the reaction mixture may be advantageous.

■ ASSOCIATED CONTENT

Supporting Information

Preparative procedures for the synthesis of complexes $1\text{-}^{13}\text{CH}_3\text{-L}$, $1\text{-H(D)-P}^t\text{Bu}_3$, and 1-Et-PPh_3 , experimental procedures for preparative and NMR-tube polymerizations of ethylene, algorithms for the quantification of ^{13}C -label incorporation and for the quantification of unsaturated and saturated oligomers, X-ray diffraction data of complexes **10**, **11**, **12** cocrystallized with **13**, and $1\text{-H-P}^t\text{Bu}_3$ (CCDD nos. 897155–897158), NMR spectra of key experiments, ESI-MS data, and DFT data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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- (14) On exemplified polyethylene samples we have determined T_1 -relaxation times in the range of 1–1.5 s for all aliphatic carbon atoms. Based on these T_1 -values, quantitative ^{13}C NMR analyses were conducted with a relaxation delay of 7 s using inverse gated decoupling techniques.
- (15) We note that at lower [precatalyst], e.g., $[1\text{-}^{13}\text{CH}_3\text{-L}] = 20\text{--}50\text{ }\mu\text{mol L}^{-1}$, under saturation kinetic behavior (>10 bar ethylene for $1\text{-CH}_3\text{-dmsO}$ and >15 bar for $1\text{-CH}_3\text{-pyr}$), negligible catalyst deactivation is observed over 30 and 60 min polymerization experiments by mass flow monitoring, resulting in nearly polymerization time-independent turnover numbers; cf. ref 10.
- (16) Note that the respective ^{13}C NMR experiments do not allow for an accurate quantification, since the relaxation delay was set to 1 s, and magnetization transfer from ^1H was not suppressed during the relaxation delay.
- (17) ^{13}C , ^{13}C -J-resolved NMR experiments and INADEQUATE experiments did not support the existence of measurable quantities of $^{13}\text{C}\text{--}^{13}\text{C}$ connections for these signals under discussion, while a $^{13}\text{C}\text{--}^{13}\text{C}$ connection was established for the S1–S2 end group couple of formed oligomers.
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- (52) The reaction between $1-H-P^tBu_3$ and the zwitterionic $H[P,O]$ ligand leads to an intermediate substitution product with the oxygen atom of $H[P,O]$ coordinated to Pd that is about 40 kJ mol^{-1} higher in energy than $1-H-[P,O]H$. The related TS is about 60 kJ mol^{-1} less favored than TS $1-H-TS2$.
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