Reactivity of Methacrylates in Insertion Polymerization

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Abstract: Polymerization of ethylene by complexes [{(P^O)PdMe(L)}] (P^O = κ^2-(P,O)-2-(2-MeOC$_6$H$_4$)$_2$-PC$_6$H$_4$SO$_3$)) affords homopolyethylene free of any methyl methacrylate (MMA)-derived units, even in the presence of substantial concentrations of MMA. In stoichiometric studies, reactive {(P^O)Pd(Me)L} fragments generated by halide abstraction from [({(P^O)Pd(Me)Cl}μ-Na)$_2$] insert MMA in a 1,2- as well as 2,1-mode. The 1,2-insertion product forms a stable five-membered chelate by coordination of the carbonyl group. Thermodynamic parameters for MMA insertion are $\Delta H^{\ddagger} = 69.0(3.1)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -103(10)$ J mol^{-1} K^{-1} (total average for 1,2- and 2,1-insertion), in comparison to $\Delta H^{\ddagger} = 48.5(3.0)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -138(7)$ J mol^{-1} K^{-1} for methyl acrylate (MA) insertion. These data agree with an observed at least 10^2-fold preference for MA incorporation vs MMA incorporation (not detected) under polymerization conditions. Copolymerization of ethylene with a bifunctional acrylate−methacrylate monomer yields linear polyethylenes with intact methacrylate substituents. Post-polymerization modification of the latter was exemplified by free-radical thiol addition and by cross-metathesis.

Introduction

Catalytic insertion polymerization of ethylene and propylene is one of the most well-studied chemical reactions. In terms of applications, it is employed for the production of more than 70 million tons of polyolefins annually.[1] An insertion (co)polymerization of electron-deficient polar-substituted vinyl monomers like acrylates remains a challenge, however.

It was not until the mid-1990s that cationic Pd(II) diimine complexes were reported to catalyze the insertion copolymerization of ethylene and 1-olefins with acrylates.[2] These d^8 metal (late transition metal) complexes are less oxophilic than early transition metal polymerization catalysts and, therefore, more tolerant toward polar moieties.[3] Due to "chain walking" of the catalyst, the highly branched copolymers, which consist of ethylene as the major component (≥ 75 mol %), contain acrylate units at the end of branches preferentially.[2,4] The mechanism of this branch formation is well understood from extensive variable-temperature NMR studies. Such studies have also provided an understanding of the problems associated with monomers not amenable for polymerization with these catalysts,

like vinyl acetate or vinyl chloride. β-X elimination (X = acetate, chloride) is one significant decomposition route.[5] While the copolymers obtained with cationic Pd(II) diimine catalysts are highly branched, with analogous Ni(II) complexes[6] and neutral Pd(II) phosphinesulfonato complexes, linear ethylene−methyl acrylate (MA) copolymers are formed.[7]
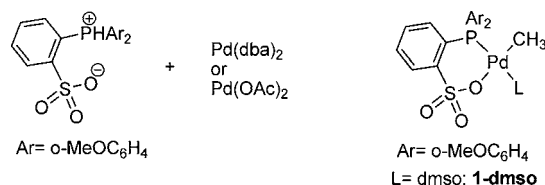
The latter catalysts, studied as *in situ* mixtures of ligands and metal sources (above, left)[7,8] as well as well-defined single-component catalyst precursors [(P^O)PdMe(L)] (L = pyridine, lutidine, PPh$_3$, ^{1}/$_2$Me$_2$NCH$_2$CH$_2$NMe$_2$, dimethylsulfoxide),[9−12] are compatible with a remarkably broad scope of vinyl monomers.[13] Ethylene copolymerization with vinyl amides,[14] vinyl ethers,[15] vinyl fluoride,[16] vinyl sulfones,[17] and even acrylonitrile[18] and vinyl acetate[19] has been reported. Multiple consecutive acrylate insertions can occur during copolymerization and

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in acrylate homooligomerization.[12] Copolymerization of ethylene with CO can occur in a non-alternating fashion,[20] and alternating copolymers of CO with methyl acrylate and vinyl acetate have been reported.[21]

Curiously, in view of the aforementioned scope of vinyl monomers studied, little information exists on the behavior of methacrylates—one of the largest volume vinyl monomers—in such insertion polymerizations. Stoichiometric reaction of a cationic diimine complex with methyl methacrylate (MMA) yielded the isolable cationic chelate complex resulting from 1,2-insertion.[22] Polymerization of ethylene by neutral phosphineenolato Ni(II) catalysts in the presence of MMA resulted in chain termination upon MMA insertion, to yield enolate-terminated polyethylenes.[23] The nature of the products of ethylene polymerization with neutral Ni(II) salicylaldiminato complexes in the presence of MMA is a topic of current interest.[24] Otherwise, little has been reported on the reactivity or lack thereof of methacrylates in insertion polymerization. We now give a full

Table 1. Polymerization of Ethylene in the Presence of Methyl Methacrylate and Methyl Isobutyrate[a]

entry	concn of additive [mol/L]	yield [g]	TOF [mol (C₂H₄) mol (Pd)⁻¹ h⁻¹]	M_w/M_n[b]	M_n[b][g mol⁻¹]
1-1	–	3.14	9.0×10^4	2.1	1.8×10^4
1-2	0.10 MMA	2.74	7.8×10^4	2.4	1.5×10^4
1-3	0.25 MMA	1.60	4.6×10^4	2.2	1.6×10^4
1-4	0.50 MMA	0.83	2.4×10^4	1.9	1.8×10^4
1-5	1.00 MMA	0.32	0.9×10^4	n.m.	n.m.
1-6	0.10 MIB	3.17	9.1×10^4	2.1	1.8×10^4
1-7	0.50 MIB	2.17	6.2×10^4	2.1	1.8×10^4

[a] 100 mL total volume (toluene), 2.5 μmol of **1-dmso** (stock solution in CH₂Cl₂), 5 bar ethylene pressure, 80 °C reaction temperature, 0.5 h reaction time; 50 mg of radical inhibitor (galvinoxyl) was added. MMA, methyl methacrylate; MIB, methyl isobutyrate. [b] Determined by GPC in 1,2,4-trichlorobenzene at 160 °C vs PE standards, n.m., not measured.

account of the reactivity toward methacrylates in insertion polymerization catalyzed by neutral phosphinesulfonato Pd(II) complexes.

Results and Discussion

Polymerization in the Presence of Methyl Methacrylate. For polymerization studies, the dimethylsulfoxide-substituted **1-dmso**[12] was employed as a catalyst precursor. Due to the lability of the dmso ligand, this catalyst precursor enables polymerizations at low ethylene concentrations, and consequently relatively high [comonomer] vs [ethylene], which can favor comonomer incorporation. However, polymerizations in the presence of variable concentrations of MMA (Table 1) yielded ethylene homopolymer exclusively, as evidenced by high-temperature ¹H NMR and IR spectroscopic analysis of the polymer formed (Figures S1–S5, Supporting Information). Concerning the experimental accuracy of polymer analysis, in ethylene–MA copolymers with 0.1 mol % acrylate incorporation, the latter could be clearly observed by NMR and IR spectroscopy (Figures S6 and S7, Supporting Information). Taking into account the molecular weights of the polyethylenes formed (Table 1), the detection limit is less than one methacrylate unit per chain. That is, also MMA-derived end groups can be excluded. Indeed, only ethylene-derived vinyl and internal olefinic end groups are observed by ¹H NMR spectroscopy. By comparison to the ethylene homopolymerization essentially occurring in the presence of methacrylate, polymerization in the presence of acrylate (MA) under conditions similar to those of entry 1-4 (95 °C and 0.6 M methyl acrylate) resulted in the formation of a copolymer with a substantial acrylate incorporation of 9.4 mol %. This corresponds to a preference for acrylate vs methacrylate incorporation of at least 10^2.

While no incorporation was observed, increasing amounts of MMA in the reaction mixture resulted in decreased polymerization productivities (entries 1-1 to 1-5).[25] By comparison to ethylene polymerization in the absence of MMA, no enhanced loss of polymerization activity with polymerization reaction time is evident (Table S1, Supporting Information). This suggests that MMA is not primarily involved in an irreversible deactivation process. In polymerizations in the presence of the saturated analogue of MMA, methyl isobutyrate (MIB), a similar lowering of productivity with increasing MIB concentrations is observed (entries 1-6 and 1-7), albeit the effect is less pronounced than with MMA itself. Likely, coordination of the ester moiety to

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(24) The presence of methyl acrylate was reported to suppress any polymer formation: (a) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci. Part A* **2002**, *40*, 2842–2854. Other studies report formation of (co)polymer in the presence of acrylates or methacrylates, respectively: (b) Johnson, L. K.; Bennett, A. M. A.; Dobbs, K. D.; Ionkin, A. S.; Ittel, S. D.; Wang, Y.; Radzewich, C. E.; Wang, L. Patent WO 01/92347, 2001. (c) Wang, L.; Hauptman, E.; Johnson, L. K.; McCord, E. F.; Wang, Y.; Ittel, S. D. Patent WO 01/92342, 2001. (d) Shen, H.; Goodall, B. L. U.S. Patent 2006/0270811, 2006. (e) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902–5919. However, the distinct ¹³C NMR resonances of the methylene carbons adjacent to a carbonyl group resulting from random acrylate or methacrylate incorporation—C^{b}H₂C^{a}H₂CR(COOMe)C^{a}H₂C^{b}H₂—were not observed; e.g., for methyl acrylate (R = H), δ 32.4 (α), 27.4 (β), ref 7. For ¹³C NMR data of an ethylene/methyl methacrylate copolymer from acyclic diene metathesis, cf.: (f) Schwendeman, J. E.; Wagener, K. B. *Macromolecules* **2004**, *37*, 4031–4037.

(25) It is assumed that the solubility of ethylene does not differ significantly for variable concentrations of toluene solutions of methyl methacrylate and methyl isobutyrate.

Scheme 1. Synthesis of Complex **2**
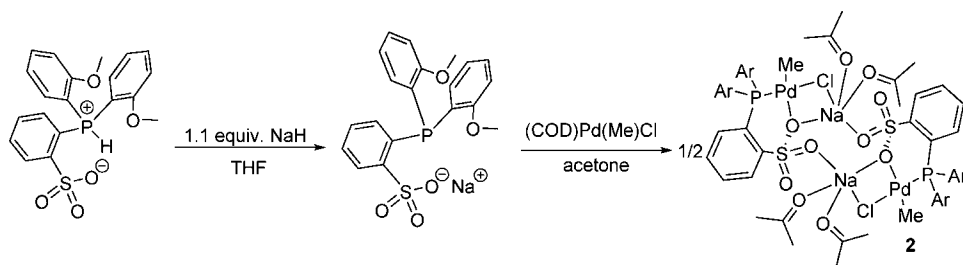
the active sites during polymerization reversibly blocks coordination sites and contributes to retardation of polymerization by methacrylate.

Synthesis of Reactive Precursors. The aforementioned observations raise the question whether MMA can insert at all for the catalyst studied. Prerequisite for insertion studies are reactive precursors free of any other strongly coordinating ligands or bases. While dmso complexes are relatively labile,[12] dmso can still compete with monomers for coordination to the metal center and hamper preparative and stoichiometric insertion reactions. Recently, base-free oligomeric complexes $[\{(P^{\wedge}O)Pd(Me)\}_n]$ (**1$_n$**) were obtained by abstraction of pyridine from [(P^O)Pd(Me)-pyridine] with $B(C_6F_5)_3$.[11] The low solubility of these base-free complexes is a key advantage in synthesis, as it allows simple separation of unreacted starting material; however, for mechanistic studies, a complete and immediate solubility of the reactive [(P^O)Pd(Me)] fragment is desirable. An appropriate precursor that fulfills these conditions was found in the new dimeric compound $[(\{(P^{\wedge}O)Pd(Me)Cl\}\mu\text{-Na})_2]$ (**2**), which is available in quantitative yield by the reaction of the sodium phosphinesulfonate, (P^O)Na, with [(COD)Pd(Me)Cl] in acetone (Scheme 1). Crystals suitable for X-ray analysis were grown directly from the reaction mixture. The solid-state structure confirms a distorted square planar coordination geometry at the Pd center, with the methyl and the phosphine mutually cis to each other (Figure 1, Table 2). In addition, two Pd fragments are bridged by a sodium atom coordinated by a sulfonato oxygen atom of each fragment, a chloride atom, and two acetone molecules.

Upon addition of $AgBF_4$ to a CD_2Cl_2 solution of **2**, instantaneous halide abstraction occurs, as evidenced by AgCl visibly precipitating within seconds. In the presence of MMA, a clear

Table 2. Selected Bond Distances (Å) and Angles (°) for Complex **2**

Pd1−C1	2.025(3)	C1−Pd1−P1	87.11(9)
Pd1−P1	2.2191(7)	C1−Pd1−O1	176.51(10)
P1−O1	2.190(2)	P1−Pd1−Cl1	174.21(3)
Pd1−Cl1	2.3804(7)	O1−Pd1−Cl1	86.20(6)
Pd1−Na1	3.6940(11)	O1−Pd1−Na1	74.56(6)
Cl1−Na1	2.7400(14)	Pd1−Cl1−Na1	92.07(3)
Na1−O1	2.402(2)	Pd1−O1−Na1	106.99(9)

solution results; no insoluble oligomeric $[\{(P^{\wedge}O)Pd(Me)\}_n]$ species form. Presumably, under these conditions, the nascent [(P^O)Pd(Me)] species are trapped to [(P^O)Pd(Me)(MMA)]. Mixtures of complex **2** and MMA in CD_2Cl_2 remain totally homogeneous after addition of $AgBF_4$ and removal of AgCl and $NaBF_4$ by filtration, and this allows for a more concise investigation of the MMA insertion into the [(P^O)Pd(Me)] fragment under conditions where no reagents or ligands other than MMA (and 2 equiv of acetone) are present.

Stoichiometric Methacrylate Insertion. Heating of a CD_2Cl_2 solution obtained by halide abstraction from **2** in the presence of 60 equiv of MMA to 80 °C for 2 h resulted in the formation of three new complexes, **4**−**6**, as well as methyl tiglate (**7**), as evidenced by ^1H and ^{31}P NMR spectroscopy (Scheme 2). The major product (ca. 62%) is the 1,2-insertion product (**4**) of MMA into the Pd−Me bond of [(P^O)Pd(Me)]. In addition, the products of 1,2-insertion of MMA into a [(P^O)Pd(H)] fragment, complex **5** (ca. 30%), and of 2,1-insertion of MMA into a fragment [(P^O)Pd(H)], complex **6** (ca. 8%) were observed. (For detailed characterization, see Figures S9−S13, Supporting Information, and Experimental Section.) The intermediate formation of [(P^O)Pd(H)] is further evidenced by the formation
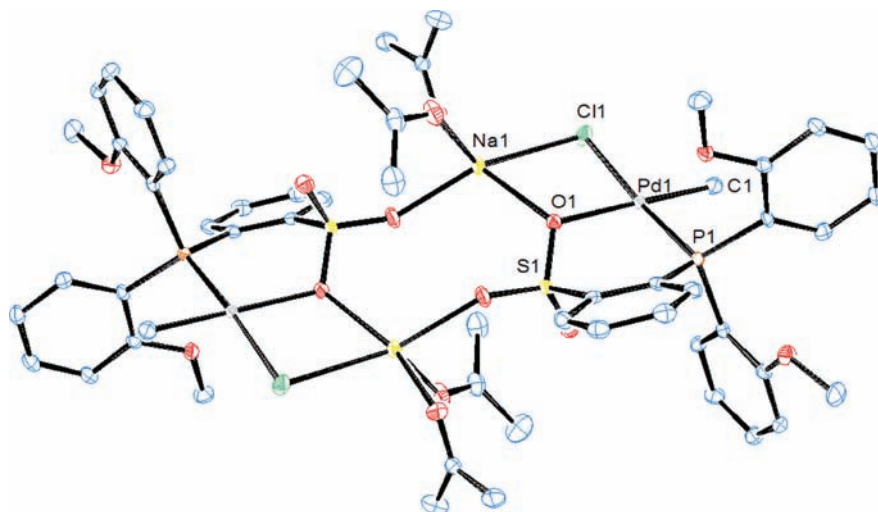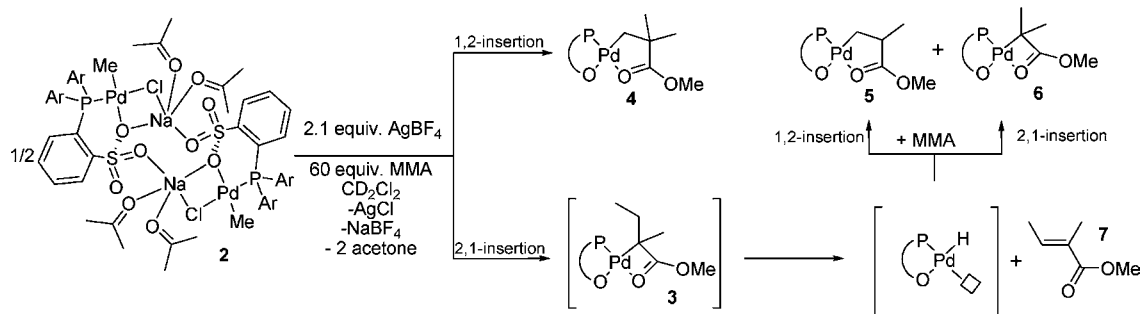

Figure 1. ORTEP plot of complex **2**. Ellipsoids are shown with 50% probability. Hydrogen atoms are omitted for clarity.

Scheme 2. Products of MMA Insertion into the Palladium Methyl Bond of the [(P^O)PdMe] Fragment

of **7** (ca. 40%), identified by ^1H and $^1H,^1H$ COSY experiments. **7** is the product of β-H-elimination from the product of 2,1-insertion into the [(P^O)Pd(Me)] fragment, **3** (not directly observed). Since a β-H elimination is not possible from complex **4**, we conclude that the aforementioned [(P^O)Pd(H)] fragments are formed along with **7** by β-H elimination from **3**. The conceivable 1,2-insertion of **7** into a Pd–H species, i.e., the "rearrangement" product of **3**, is not observed likely due to hindered insertion of the bulky trisubstituted olefin. The overall product distribution observed in this NMR experiment corresponds to a ca. 3:2 ratio of 1,2- vs 2,1-insertion of MMA into the palladium methyl bond. Upon workup of the reaction mixture, complexes **5** and **6** decomposed, presumably via β-H-elimination. This allowed for the isolation of complex **4** as the only organometallic species in ca. 60% yield.

A detailed analysis by ^1H, ^{13}C, $^1H,^1H$ gCOSY, $^1H,\{^{13}C\}$ gHSQC, and gHMBC NMR experiments, FAB mass spectrometry, and elemental analysis confirmed the identity of complex **4**. Key ^1H NMR spectroscopic features comprise a palladium–α-methylene doublet resonance at δ 1.09 ppm with a $^3J_{PH} = 2.6$ Hz and a β-methyl singlet resonance at δ 1.15 ppm. A chelating coordination of the carbonyl group in **4** is evidenced by the low-field-shifted resonance of the C(O)OMe group at δ 192.74 ppm (for ^1H and ^{31}P NMR spectra, see Figure S9, Supporting Information). The identification of complexes **5** and **6** is based on a detailed NMR analysis of the reaction mixture in the presence of MMA. While the indicative key resonance of complex **6** is the low-field-shifted carbonyl resonance at 208 ppm, indicating a four-membered carbonyl chelate, complex **5** was identified by the characteristic β-methyl doublet coupling to the methine multiplet with $^3J_{HH} = 7.6$ Hz (for additional information, see Supporting Information).

The homogeneous nature of the reaction solution obtained from **2** and silver tetrafluoroborate in CD_2Cl_2 also allowed for

a detailed kinetic analysis of the disappearance of the Pd–Me species formed after chloride abstraction under pseudo-first-order conditions (20 equiv of monomer). Isothermal studies at different temperatures in the range of 30–69 °C provided an Eyring analysis (Figure 2), from which the average activation enthalpy for the disappearance of complex **2** by 1,2- or 2,1-insertion of MMA was determined to be $\Delta H^\ddagger = 69.0(3.1)$ kJ mol^{-1}, while the respective activation entropy was determined to be $\Delta S^\ddagger = -103(10)$ J mol^{-1} K^{-1}. At 25 °C, the average free activation enthalpy $\Delta G^\ddagger(25 °C)$ is 99.8(4.2) kJ mol^{-1}. The corresponding experiment for the disappearance of the chloride-free Pd–Me species in the presence of 20 equiv of MA (by exclusive 2,1-insertion) was performed between -20 and 26 °C. This temperature range resulted from the much higher rates of this reaction. Eyring analysis gave $\Delta H^\ddagger = 48.5(3.0)$ kJ mol^{-1} and $\Delta S^\ddagger = -138(7)$ J mol^{-1} K^{-1}. This corresponds to a free activation enthalpy of $\Delta G^\ddagger(25 °C) = 89.5(3.6)$ kJ mol^{-1}.[26] Comparison with the $\Delta G^\ddagger(25 °C)$ for MMA insertion yields a preferential insertion of MA vs MMA by ~10^2. A comparison of MA vs MMA insertion at polymerization conditions, 80 °C, requires extrapolation of the thermodynamic data to this temperature. This introduces a larger error, due to the error in the determined $\Delta S^\ddagger$ values, and includes the assumption that the ratio of 1,2- vs 2,1-insertion of MMA is temperature independent. Keeping this in mind, the thermodynamic data correspond to a preference by $10–10^2$ of acrylate vs methacrylate.

Reactivity of the Isolated Insertion Product. A prerequisite for chain growth is a free coordination site for incoming monomers. In the case of **4**, this corresponds to an opening of the (C,O)-chelate. As a model reaction, the strong donor PPh₃ was found to displace the carbonyl group and open the chelate of **4** in an equilibrium, as indicated by the appearance of a set of doublets with a coupling constant of trans-$^2J_{PP} = 525$ Hz, followed by a cis–trans isomerization to a species bearing the
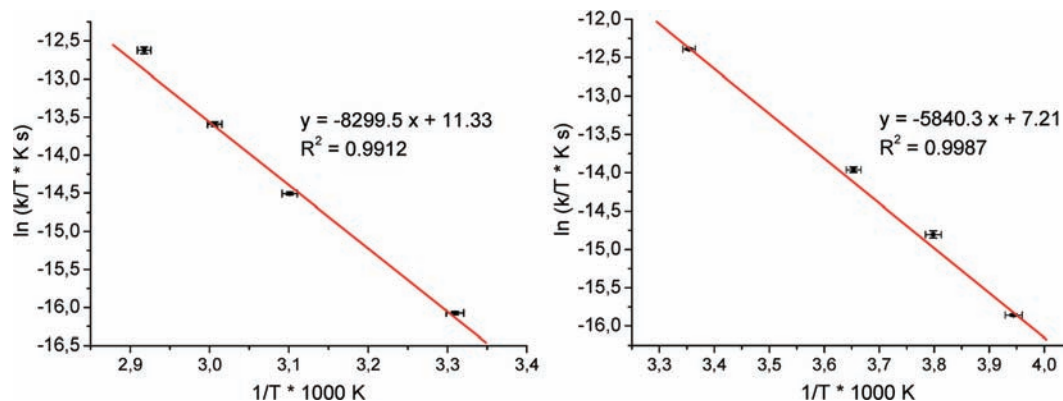

Figure 2. Eyring plot of MMA insertion (left) and MA insertion (right) into the Pd–Me bond of [(P^O)Pd(Me)].

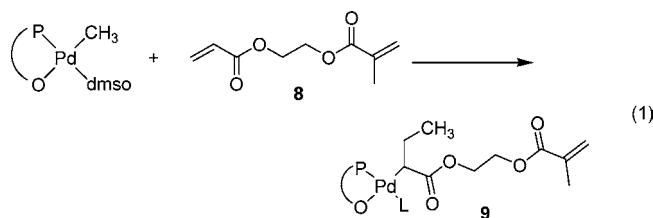***Table 3.*** Polymerization of Ethylene with **4** and **1-dmso**[a]

entry	catalyst precursor	p(ethylene) [bar]	yield PE [g]	TOF [mol (C_2H_4) mol (Pd)$^{-1}$ h^{-1}]	M_w/M_n[b]	M_n[b] [g mol^{-1}]
3-1	**4**	30	5.82	8.0×10^4	2.0	2.3×10^4
3-2	**4**	20	5.36	7.7×10^4	1.9	2.5×10^4
3-3	**4**	10	2.20	3.1×10^4	2.0	1.3×10^4
3-4	**1-dmso**	10	5.04	1.0×10^5	1.9	1.3×10^4
3-5	**1-dmso**	5	4.92	1.0×10^5	2.2	1.3×10^4

[a] Reaction conditions: 100 mL of toluene, 80 °C, entry 3-1 to 3-3 with 2.5 μmol of Pd(II), entries 3-4 and 3-5 with 3.5 μmol of Pd(II).[12] [b] Determined by GPC at 160 °C vs linear PE.

phosphine ligands cis to each other (cis-$^2J_{PP}$ = 11 Hz) (Figures S18 and S19, Supporting Information). At low temperature (−80 °C), which favors chelate opening by reducing the entropic contribution to the equilibrium position, opening was also observed with 3 equiv of pyridine (Figure S20, Supporting Information). With ethylene (∼20:1 ratio ethylene:Pd) as a weaker ligand in NMR experiments in the temperature range of −80 to 25 °C, no opening was observed. Exposure of **4** to ethylene under polymerization conditions resulted in polyethylene formation, however (Table 3). Activation requires an initial opening of the chelate by coordination of ethylene, but once insertion has occurred for a given catalyst precursor molecule, coordination of the carbonyl groups no longer appears relevant due to the increasingly large, unfavorable chelate ring sizes. Polymerization activities with **4** are independent of ethylene concentration at $p \geq 20$ bar (entries 3-1 to 3-3). By comparison, with **1-dmso** as a catalyst, precursor activities are independent of ethylene pressure at $p \geq 5$ bar (entries 3-4 and 3-5 and ref 12). This again suggests a quite strong coordination of the methacrylate-derived ester group to the Pd center in the five-membered chelate **4**.

Methacrylate-Functionalized Polyethylene. The large differences in reactivity observed in the above polymerizations and mechanistic studies for acrylate and methacrylate correspond to an orthogonal reactivity in insertion polymerizations with the catalyst studied. An acrylate and a methacrylate moiety are combined in the bifunctional ethylene glycol ester **8**.[27] As anticipated, **8** reacts exclusively with the acrylate moiety (eq 1). In an NMR tube, 13 equiv of **8** were added to a CD_2Cl_2 solution of **1-dmso**. The tube was kept at room temperature, and ^{1}H NMR spectra were acquired periodically (Figure S16, Supporting Information). Complete conversion of the starting compound occurred within 150 min. The first-order rate constant for the consumption of **1-dmso**, monitored by the disappearance of the Pd−Me ^{1}H NMR resonance, is $k_{obs} = 2.80 \times 10^{-4}$ s^{-1} at 25 °C (Figure S17, Supporting Information). Simultaneously, a triplet at 0.25 ppm, resulting from 2,1-insertion of the acrylate moiety, increases. No signals corresponding to an insertion of methacrylate were observed. The insertion product (**9**) was isolated after removing the excess of **8** by washing the complex with ether. One equivalent of dmso, resonating at δ = 2.76 ppm in the ^{1}H NMR spectrum, is evidence for **9** occurring in the nonchelated form, as depicted in eq 1 (δ = 2.54 ppm for free dmso in CD_2Cl_2). The inertness of methacrylates in olefin insertion polymerization (*vide supra*) and the remarkably different reactivity versus acrylates in this respect offer the

(1)

possibility of introducing intact methacrylate units in polyethylenes. Copolymerization of ethylene with **8** results in polymers bearing unsaturated methacrylate groups in the side chain; e.g., for a 0.33 M toluene solution of **8** and 5 bar ethylene pressure, poly(ethylene-*co*-**8**) was obtained with 3.9 mol % of **8** incorporated.[28] ^{13}C NMR (Figure 3) confirms that the acrylate units are incorporated in the linear polyethylene chain, while the methacrylate units remain unreacted in the side chain.

The intact methacrylate moieties in the linear polyethylene lend themselves to post-polymerization reactions, which can provide otherwise inaccessible polymers. Free-radical-initiated addition of thiols, namely 3-mercaptopropionic acid, occurred virtually quantitatively (>95%), as confirmed by elemental analysis. Consumption of the methacrylic moieties was confirmed by ^{1}H NMR (Scheme 3 and Figure S22, Supporting Information). The polymer remains soluble upon modification. This demonstrates that no radical cross-linking has occurred under these conditions. By this reaction of thiocarboxylic acid, both thiol and carboxylic acid groups were introduced. Such functional groups are known to be problematic for most polymerization catalysts, hindering introduction by direct polymerization.

As another example of post-polymerization modification of the methacrylate-substituted polyethylene, cross-metathesis was studied preliminarily. Methacrylates are convertible via cross-metathesis with other 1-olefins by Grubbs second-generation catalyst.[29] Exposure of the terpolymer poly(ethylene-*co*-**8**-*co*-APEG) (APEG = oligoglycol monoacrylate) to Grubbs second-generation alkylidene and an excess of 4-phenylbutene in $C_2H_2Cl_4$ at 70 °C resulted in cross-metathesis degrees of up to 15% (Scheme 3 and Figure S23, Supporting Information). Comparison of gel permeation chromatography (GPC) traces before and after modification revealed that metathesis proceeds exclusively between methacrylates and the added olefins (Figure S24, Supporting Information). No substantial increase in molecular weight, as would be expected for interchain homometathesis of methacrylates (or metathesis with the olefinic end groups of the polymer), was observed.

Summary and Conclusions

Even in the presence of substantial concentrations of MMA, polymerization of ethylene by the catalyst studied provides linear ethylene homopolymer without any detectable incorporation of methacrylate. The detection limit amounts to less than one methacrylate unit per chain. By comparison to MA, which is incorporated to a substantial degree under identical polymeri-

(26) Similar activation energies were reported for the cationic diimine Pd complex (refs 2 and 22). In our experiments with MA, further insertion into the monoinserted complex was observed. For details cf. ref 12b.

(27) Schmider, M.; Müh, E.; Klee, J. E.; Mülhaupt, R. *Macromolecules* **2005**, *38*, 9548–9555.

(28) Copolymerization conditions and results: 0.33 M toluene solution of **8** (50 mL total volume), 5 bar ethylene pressure, 20 μmol of **1-dmso,** 90 °C polymerization temperature, 1 h polymerization time, 200 mg of BHT (free radical inhibitor); TOF C_2H_4 [mol(C_2H_4) mol Pd^{-1} h^{-1}], 2400; TOF **8** [mol(**8**) mol Pd^{-1} h^{-1}]: 100; 3.9 mol % of **8** (determined from the glycol resonances in ratio to the aliphatic protons by ^{1}H NMR); M_n = 6500, M_w/M_n = 1.88 (determined by GPC at 160 °C vs linear PE).

(29) Chatterjee, K.; Choi, T.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.
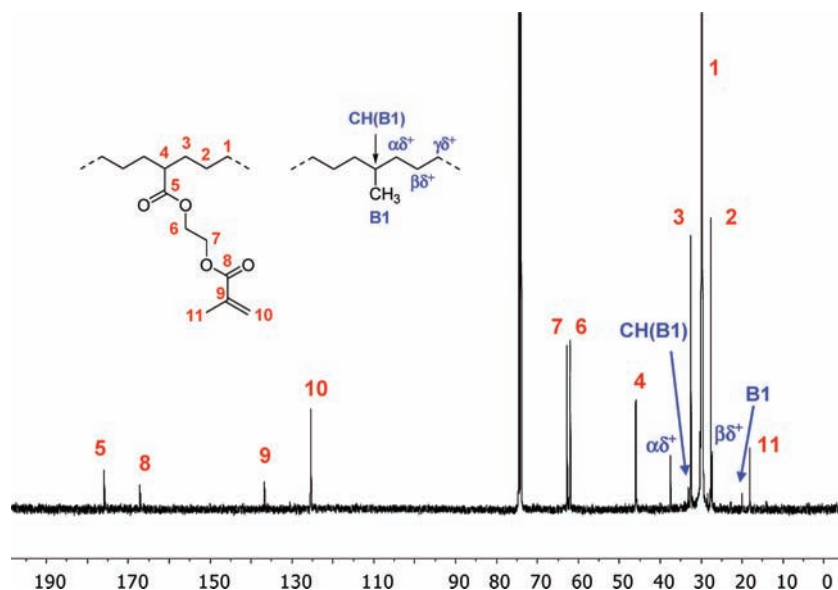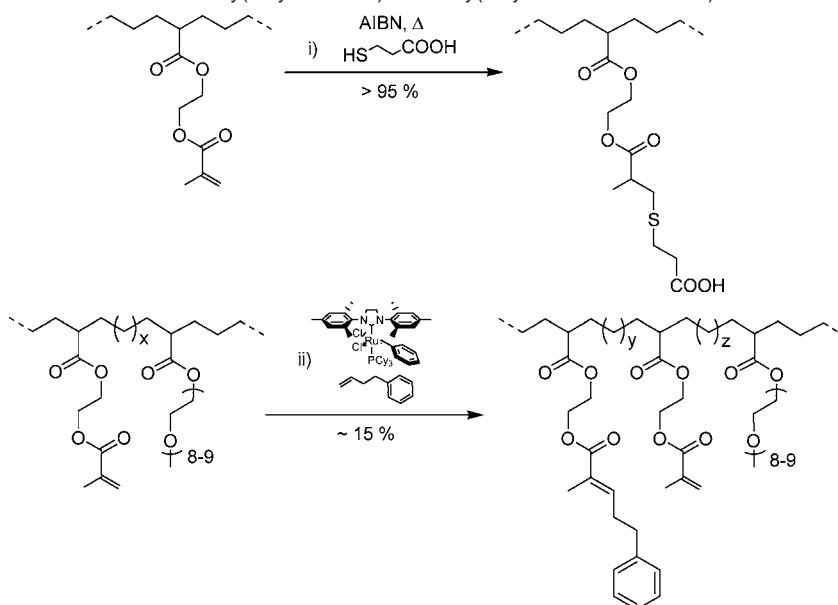
Figure 3. $^{13}C\{^1H\}$NMR spectrum of poly(ethylene-*co*-**8**) in $C_2D_2Cl_4$ at 130 °C.

Scheme 3. Post-polymerizaton Modification of Poly(ethylene-*co*-**8**) and Poly(ethylene-*co*-**8**-*co*-APEG)[a]

[a] Reaction conditions: (i) 100 mg of polymer, 10 mL of $C_2H_2Cl_4$, 40 equiv of thiol, 0.4 equiv of AIBN, 9 h, 80 °C. (ii) 100 mg of polymer, 10 mL of $C_2H_2Cl_4$, 10 equiv of 4-phenylbutene, 0.1 equiv of Ru−alkylidene complex, 12 h, 70 °C.

zation conditions, MMA is at least 10^2-fold less amenable to incorporation under polymerization conditions.

Detailed mechanistic studies with an appropriate precursor providing the reactive [(P^O)PdMe] fragment in solution reveal that methacrylate insertion into the Pd−Me bond is possible in principle. Insertion occurs in both 1,2- and 2,1-fashion, with a slight preference for the former. While the 1,2-insertion product, which lacks β-H atoms, could be isolated, the 2,1-insertion products are subject to facile β-H elimination under the reaction conditions of this insertion. In the 1,2-insertion product (**4**), the carbonyl unit of the inserted MMA binds to the metal center to form a five-membered chelate. This chelate is very stable, and opening requires harsher conditions than for the corresponding six-membered chelate formed by two consecutive 2,1-insertions of MA into the Pd−Me bond (ethylene polymerizations with the latter as a catalyst precursor are independent of ethylene

concentration already at p(ethylene) $\geq$ 5 bar, and the chelate is completely opened by 1 equiv of pyridine at room temperature).[12b] Eyring analysis yielded thermodynamic parameters $\Delta H^{\ddagger} = 69.0(3.1)$ kJ mol^{-1} and $\Delta S^{\ddagger} = -103(10)$ J mol^{-1} K^{-1} as the total average for 1,2- and 2,1-insertion of methacrylate. By comparison, for MA insertion, $\Delta H^{\ddagger}$ amounts to 48.5(3.0) kJ mol^{-1} and $\Delta S^{\ddagger} = -138(7)$ J mol^{-1} K^{-1}. These thermodynamic parameters are also in qualitative agreement with the lack of observation of any methacrylate incorporation in ethylene polymerization.

The huge difference in reactivity of acrylate vs methacrylate, and essential inertness of the latter under polymerization conditions, enables the generation of linear polyethylenes with intact methacrylate substituents by copolymerization with a mixed bifunctional acrylate−methacrylate (**8**). These polymers are attractive for post-polymerization reactions to materials

otherwise difficult to access. This was exemplified by thiol addition to provide a thiol and carboxylic acid-substituted polyethylene and by cross-metathesis.

Experimental Section

Materials and General Considerations. Unless noted otherwise, all manipulations of complexes were carried out under an inert atmosphere using standard Schlenk techniques. All glassware was dried at 80 °C for at least 48 h. Toluene was distilled from sodium and diethyl ether, THF, and dioxane were distilled from sodium/ benzophenone ketyl under argon. Methylene chloride, chloroform, and pentane were distilled from CaH₂. Dimethylsulfoxide p.a., acetone p.a., and methanol p.a. were degassed and used without further purification. Ethylene (3.5 grade) was supplied by Praxair. Methyl methacrylate and methyl acrylate, supplied by Sigma Aldrich (99%, GC), were degassed using freeze—pump—thaw cycles and stored at 4 °C. [2-di(2-methoxyphenyl)phosphino]ben-zenesulfonic acid,[7] 2-(acryloyloxy)ethyl methacrylate (**8**),[27] [(COD)-Pd(Me)Cl],[30] [(tmeda)PdMe₂],[31] **1-dmso**,[12] and **1**ₙ,[11] were prepared by known procedures. All deuterated solvents were supplied by Eurisotop. Galvinoxyl, purchased from ABCR, was stored at −28 °C.

NMR spectra were recorded on a Varian Unity INOVA 400 or a Bruker Avance DRX 600 spectrometer equipped with a cryoprobe head. ¹H and ¹³C NMR chemical shifts were referenced to the solvent signal. Multiplicities are given as follows (or combinations thereof): s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet. Coupling constants are given in hertz (Hz). The identity and purity of metal complexes were established by ¹H, ¹³C, and ³¹P NMR and elemental analysis. NMR assignments were confirmed by ¹H,¹H gCOSY, ¹H,¹³C gHSQC, and ¹H,¹³C gHMBC experiments. NMR probe temperatures were measured using an external anhy-drous methanol standard for temperatures <25 °C or anhydrous ethylene glycol standard for temperatures >25 °C. Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated according to the derivation of Girolami et al.,[32] with the estimated error in the temperature calibration measurement of ±1 K and a deviation of 5% for the pseudo-first-order rate constants k. High-temperature NMR measurements of polyethylenes were performed in 1,1,2,2-tetrachloroethane-d_2 at 130 °C. GPC measurements were carried out in 1,2,4-trichlorobenzene at 160 °C at a flow rate of 1 mL min⁻¹ on a Polymer Laboratories 220 instrument equipped with Olexis columns with differential refractive index, viscosity, and light-scattering (15° and 90°) detectors. Data reported were determined directly against PE standards. FAB mass spectra were obtained with a double-focusing Finnagan MAT 8200 mass spectrometer equipped with an ION TECH (Teddington, UK) FAB ion source. About 1 μL of the sample solution (CH₂Cl₂) and 1 μL of 3-nitrobenzyl alcohol (NBA) (and NaI if necessary) were mixed on the tip of the sample holder. X-ray analysis was performed at 100 K on a STOE IPDS-II diffractometer equipped with a graphite-monochromated radiation source (λ = 0.71073 Å) and an image plate detection system. A crystal mounted on a fine glass fiber with silicon grease was employed. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell dimensions by a least-squares fit of the 2Θ values, data reduction, LP correction, and space group determination were performed using the X-Area software package delivered with the diffractometer. A semiempirical absorption correction was performed. The structure was solved by direct methods (SHELXS-97), completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 minimizing $w(F_o^2 - F_c^2)^2$. Weighted R factor (wR) and the goodness of fit (GooF) are based on F^2.

(30) Salo, E. V.; Guan, Z. *Organometallics* **2003**, *22*, 5033–5046.
(31) De Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907–2917.
(32) Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646–1655.

Ethylene Polymerization. Ethylene polymerization was carried out in a 250 mL stainless steel mechanically stirred (1000 rpm) pressure reactor equipped with a heating/cooling jacket supplied with a thermostat controlled by a thermocouple dipping into the polymerization mixture. A valve controlled by a pressure transducer allowed for applying and keeping constant ethylene pressure. Prior to a polymerization experiment, the reactor was heated under vacuum to the desired temperature for 60 min and then filled with argon. A stock solution of the catalyst precursor in methylene chloride was prepared. The required amount of complex was filled into a syringe. The reactor was vented, and in a slight argon/ethylene stream, the solvent and catalyst solution was transferred via cannula. The reactor was closed, and a constant ethylene pressure was applied. After the desired reaction time, the reactor was rapidly vented and cooled to room temperature. The reaction mixture was filled into a flask, and the solvent was removed in vacuum. The remaining polymer was dried in vacuum at 30 mbar and 50 °C for 48 h.

Polymerization of Ethylene in the Presence of Methyl Methacrylate and Methyl Isobutyrate, Respectively. A procedure identical to that for ethylene homopolymerization was applied. A mixture of toluene and MMA or MIB, respectively, with a total volume of 50 mL was transferred into the reactor under an argon counter stream. The catalyst precursor **1-dmso** was dissolved in 1 mL of dichloromethane and introduced by a syringe to the reactor. After the desired reaction time, the reactor was rapidly vented and cooled to room temperature. The reaction mixture was stirred with an excess volume of methanol. The polymer was isolated by filtration, washed several times with methanol, and dried in vacuo at 50 °C and 23 mbar for at least 48 h.

Sodium [2-(2-Methoxyphenyl)phosphino]benzenesulfonate ((P^O)Na). 500 mg (1.2 mmol) of [2-di(2-methoxyphenyl)phos-phino]benzenesulfonic acid and 33.6 mg (1.4 mmol) of sodium hydride were dispersed in 20 mL of THF for 24 h. The solvent was removed in vacuum. Adding 20 mL of methylene chloride and 20 mg of phenol (for scavenging excess sodium hydride) afforded a dispersion. The solid was isolated by filtration, washed with ether, and dried in vacuum to yield 480 mg (1.13 mmol, 94%) of a white powder still containing one-sixth of Et₂O.
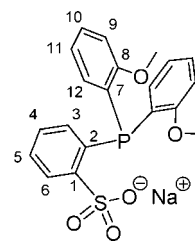
¹H NMR (400 MHz, CD₃OD) δ = 8.06 (ddd, $^4J_{HH}$ = 1.2, $^4J_{PH}$ = 4.0, $^3J_{HH}$ = 7.8, 1H, 6-H), 7.37 (dt, $^4J_{HH}$ = 1.2, $^3J_{HH}$ = 7.7, 1H, 5-H), 7.27 (vt, J = 7.8, 2H, 11-H), 7.21 (dt, $^4J_{HH}$ = 1.2, $^3J_{HH}$ = 7.5, 1H, 4-H), 6.96 (ddd, $^4J_{HH}$ = 1.2, $^3J_{PH}$ = 3.4, $^3J_{HH}$ = 7.6, 1H, 3-H), 6.91 (dd, $^3J_{PH}$ = 4.8, $^3J_{HH}$ = 8.1, 2H, 12-H), 6.77 (vt, J = 7.4, 2H, 10-H), 6.57 (d, $^4J_{PH}$ = 3.7, 2H, 9-H), 3.65 (s, 6H, OMe); ¹³C NMR (101 MHz, CD₃OD) δ = 162.66 (d, $^2J_{PC}$ = 16.3, C8), 151.22 (d, $^2J_{PC}$ = 27.6, C1), 136.96 (d, $^2J_{PC}$ = 1.7, C3), 136.72 (d, $^1J_{PC}$ = 22.7, C2), 135.04 (C9), 131.07 (C11), 130.90 (C4), 129.60 (s, C5), 128.71 (d, $^3J_{PC}$ = 4.9, C6), 127.68 (d, $^1J_{PC}$ = 14.6, C7), 122.00 (C10), 111.59 (C12), 56.11 (OMe); ³¹P NMR (161 MHz, CD₃OD) δ = −29.88 (s). Anal. Calcd for (C₂₀H₁₈NaO₅PS · ¹/₆Et₂O): C, 56.84; H, 4.54; S, 7.34. Found: C, 56.35; H, 4.57; S, 7.08.

[{((P^O)Pd(Me)Cl)-μ-Na}₂·4acetone] (P^O = κ²-(P,O)-2-(2-MeOC₆H₄)₂PC₆H₄SO₃)) (2). 100 mg (0.33 mmol) of [(COD)-Pd(Me)Cl] and 177.6 mg (0.42 mmol, 1.3 equiv) of sodium[2-di(2-methoxyphenyl)phosphino]benzenesulfonate were added to 30 mL of acetone, and the mixture was shaken until the dispersion became clear. The solution was filtered right after the mixture became clear.

Remaining solids were washed repetitively with acetone. After removal of the solvent from the collected filtrates in vacuum, the residual solid was washed with ether and dried under reduced pressure to yield 87% of a white powder.

Ar:
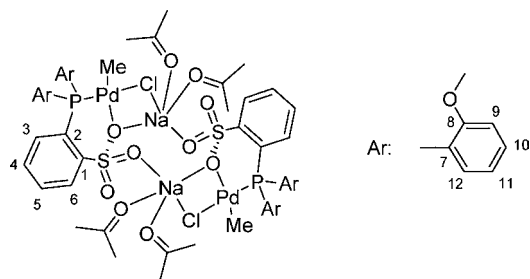
^{1}H NMR (400 MHz, acetone-d_6) δ = 7.96 (m, 1H, 6-H), 7.73 (br, 2H, 12-H), 7.54 (vt, J = 7.8, 2H, 10-H), 7.45 (m, 1H, 5-H), 7.37 (m, 2H, 4-H and 3-H), 7.02 (m, 4H, 9-H, 11-H), 3.62 (s, 6H, Ar-OMe), 0.20 (d, $^3J_{HP}$ = 3, 3H, Pd-Me). Anal. Calcd for ($C_{42}H_{42}Cl_2Na_2O_{10}P_2Pd_2S_2$): C, 43.39; H, 3.64; S, 5.52. Found: C, 43.85; H, 4.09; S, 5.06.

[{(P^O)Pd{CH$_2$CMe$_2$COOMe}}] (P^O = κ^2-(P,O)-2-(2-MeO-C$_6$H$_4$)$_2$PC$_6$H$_4$SO$_3$)) (4). 40 mg (0.077 mmol) of 1_n was dispersed in 7 mL of chloroform. After addition of 50 mg of methyl methacrylate, the dispersion was heated to 90 °C for 2.5 h. The resulting yellow dispersion was filtered, and the solvent was removed. The resulting yellow powder was dissolved in 10 mL of methanol. After evaporation and repetitive washing with ether, a yellow powder was obtained. Yield 28.8 mg (0.046 mmol, 60%).
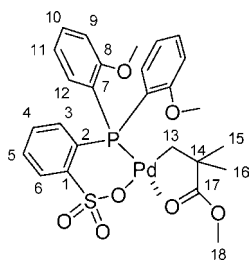
^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ = 8.07 (m, 1H, 6-H), 7.61 (br, 2H, 12-H), 7.54 (vt, J = 7.7, 2H, 10-H), 7.46 (m, 1H, 5-H), (m, 2H, 4-H and 3-H), 7.03 (vt, J = 7.5, 2H, 11-H), 6.95 (m, 2H, 9-H), 3.94 (s, 3H, 18-H), 3.62 (s, 6H, Ar-OMe), 1.15 (s, 6H, 15-H and 16-H), 1.09 (d, $^3J_{PH}$ = 2.6, 2H, 13-H); ^{13}C NMR (101 MHz, CD$_2$Cl$_2$) δ = 192.74 (C17), 160.85 (d, $^2J_{PC}$ = 2.0, C8), 149.21 (d, $^2J_{PC}$ =15.5, C1), 138.06 (C12), 134.70 (d, $^3J_{PC}$ = 2.8, C4), 134.08 (C10), 130.88 (d, $^4J_{PC}$ = 2.4, C5), 128.83 (d, $^2J_{PC}$ = 7.5, C3), 128.10 (d, $^3J_{PC}$ = 8.8, C6), 127.45 (d, $^1J_{PC}$ = 54.5, C2), 121.04 (d, $^3J_{PC}$ = 12.4, C11), 116.35 (d, $^1J_{PC}$ = 59.6, C7), 111.81 (d, $^3J_{PC}$ = 4.8, C9), 55.67 (ArOCH$_3$), 55.61 (C18), 49.93 (C14) 32.50 (C13), 28.22 (C15 and C16); ^{31}P NMR (161 MHz, CD$_2$Cl$_2$) δ = 23.57 (s); FAB-MS: calcd 622.96 g mol^{-1}, found 622.4 g mol^{-1} [M + H]$^+$, 506.4

g mol^{-1} [M − C$_6$H$_{12}$O$_2$]$^+$. Anal. Calcd for (C$_{26}$H$_{29}$O$_7$PPdS): C, 50.13; H, 4.69; S, 5.15. Found: C, 50.09; H, 4.76; S, 4.79

Key NMR Resonances of Complexes 5 and 6. 5: ^{1}H NMR (in parentheses: correlated ^{13}C resonance identified by a gHSQC experiment) (600 MHz, CD$_2$Cl$_2$) δ = 3.92 (55.60) (s, 3H, OMe), 3.04 (45.64) (m, 1H, 2-H), 1.44, 1.24 (26.51) (m, 2H, 1-H), 1.09 (d, $^3J_{HH}$ = 7.6 Hz, 3H, 4-H); ^{13}C NMR (150 MHz, CD$_2$Cl$_2$) δ = 191.0 (C=O), 55.60 (OMe), 45.64 (C2), 26.51 (C1), 18.24 (C4); ^{31}P NMR (161 MHz, CD$_2$Cl$_2$): δ = 20.04 (s).
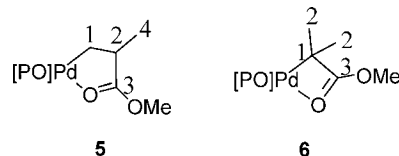
6: ^{1}H NMR (600 MHz, CD$_2$Cl$_2$) δ =3.85 or 3.78 (s, 3H, OMe), 2.13 (s, 6H, 2-H); ^{13}C NMR (150 MHz CD$_2$Cl$_2$) δ = (208.26) (C=O), 55.73 or 55.41 (OMe), 31.47 (C2), C1 n.d.; ^{31}P NMR (161 MHz, CD$_2$Cl$_2$) δ = 24.88 (s).

[{(P^O)Pd{C(Et)HC(O)OCH$_2$CH$_2$OC(O)C(Me)CH$_2$}(dmso)] (9). **1-dmso** (22 mg, 0.0366 mmol) was dissolved in 0.6 mL of CH$_2$Cl$_2$. After addition of 80 mg of **8** (0.48 mmol, 13 equiv), the solution was kept for 2.5 h at room temperature. The solvent was then removed in vacuum, and the complex was washed thrice with 7 mL of ether. After drying in vacuum, a yellow powder was obtained (25.8 mg, 0.033 mmol, 90%).
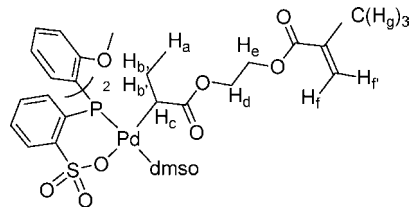
^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ = 8.74 (br, 1H), 7.97 (m, 1H), 7.55 (m, 2H), 7.44 (m, 2H), 7.29 (m, 2H), 7.14 (m, 1H), 6.99 (m, 2H), 6.87 (m, 1H), 6.11 (s, 1H, H$_{f'}$), 5.57 (s, 1H, H$_f$), 4.31 (m, 4H, H$_d$ and H$_e$), 3.50 and 3.64 (s, 6H, ArOCH$_3$), 2.76 (s, 6H, dmso), 1.91 (s, 3H, H$_g$), 1.70 (vt, J = 8.8, 1H, H$_c$), 1.38 and 0.74 (2 × m, 1H each, H$_b$, H$_{b'}$), 0.24 (t, $^3J_{HH}$ = 7.2, 3H, H$_a$); ^{31}P NMR (161 MHz, CD$_2$Cl$_2$) δ = 25.10 (s).

Supporting Information Available: Additional experimental procedures, analytical data, and CIF file for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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