Solid-Supported Single-Component Pd(II) Catalysts for Polar Monomer Insertion Copolymerization

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S *Supporting Information*

ABSTRACT: Heterogenized representatives of neutral phosphine sulfonato Pd(II) complexes for polar monomer insertion polymerization were prepared by two different approaches. $[\{\kappa^2\text{-}(P,O)\text{-}(2\text{-anisyl})_2PC_6H_4SO_2O\}Pd(Me)L]$ (L = pyr, dmso, or Cl) complexes were physisorbed on inorganic substrates, namely, clay or silica. In addition, new phosphine sulfonato complexes bearing hydroxyl linker groups at the nonchelating *P*-aryl moiety were prepared. These complexes were covalently tethered to cross-linked polystyrene. All immobilized palladium complexes are active in ethylene polymerization and ethylene/MA copolymerization without any additional cocatalyst. In addition, separation from the polymer solution formed and reutilization for another polymerization were demonstrated for polystyrene-bound complexes.

KEYWORDS: *insertion polymerization, polar monomer, palladium, supported, silica, montmorillonite clay, polystyrene beads*
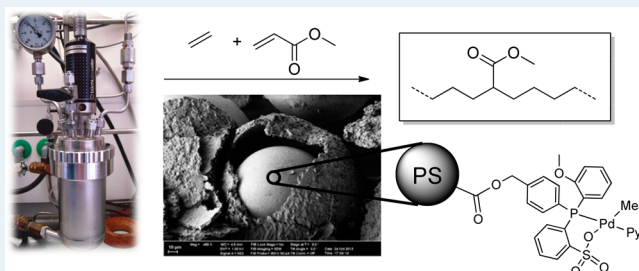
INTRODUCTION

Polymerization of ethylene and propylene is among the largest-scale synthetic chemical reactions performed. Polyolefin chain growth relies upon activation of the olefin, by π-coordination to an electrophilic metal center, for migratory insertion into a more or less polar metal alkyl. This electrophilicity, however, can go along with a sensitivity to any polar reagent present. In particular, the highly polymerization active early transition metal centers are also extremely oxophilic. More electron-rich late transition metals are more compatible with polar groups. This is reflected in their ability to (co)polymerize polar monomers like acrylates by an insertion mechanism.[1−7]

Solid-supported catalysts are commonly employed in olefin polymerization. In general, there are various motivations for supporting metal complexes for olefin polymerization.[8,9] The control of the morphology of the solid polymer formed is essential in slurry- and gas-phase polymerization processes. In cases in which a soluble polymer is formed, recycling of the catalyst can also become possible. Further, "site isolation" by binding to a support can suppress bimolecular deactivation reactions involving two metal sites. On the other hand, given a certain mobility of the active sites, the higher concentration on the support material can also promote such reactions.

Notably, virtually all support materials contain polar functionalities, such as hydroxyl or carboxyl groups. Compatibility with the electrophilic metal center is achieved only by a prior passivation, often by an excess of aluminum cocatalyst, which functions as a scavenger here. Even for late transition metals, supported catalysts were activated with excess aluminum alkyls.[10−13] This also prohibits polar monomer insertion polymerization, because of the reaction of the cocatalyst with the monomer.

We now report insights into the compatibility of a single-component polar monomer copolymerization catalyst toward various polar support surfaces.

RESULTS AND DISCUSSION

As a catalyst system, neutral Pd(II) phosphine sulfonato complexes were studied because of their unique compatibility of incorporating different types of functional polar monomers.[5,6] A variety of different phosphine sulfonato Pd(II) complexes have been reported recently.[5,14−16] However, none of these bear suitable reactive substituents on the bidentate ligand to bind them directly to a solid substrate. The prototypical $[\{2\text{-}(2\text{-anisyl})_2PC_6H_4SO_2O\}Pd\text{-L}]$ (**1-L**; L = pyr, dmso, or Cl)[2] and the $[\{2\text{-}(tert\text{-butyl})(phenyl)PC_6H_4SO_2O\}\text{-}Pd\text{-L}]$ system (**2-L**; L = lut) of Claverie et al.[15] perform well in terms of polymerization activity combined with a high degree of comonomer incorporation. Therefore, these complexes served as a model for new $(\hat{P\,O})$ chelated complexes ^{OH}**2-pyr**, ^{OH}**3-pyr**, and ^{OH}**4-pyr** with a hydroxyl group on the nonchelating *P*-aryl moiety for tethering to a polystyrene support (Figure 1).

Synthesis of New Phosphine Sulfonato Pd(II) Complexes. All three *P*-asymmetric complexes ^{OH}**2-pyr**, ^{OH}**3-pyr**, and ^{OH}**4-pyr** (Figure 1) were prepared by a procedure similar to the one depicted for ^{OH}**3-pyr** (Scheme 1). To prevent side reactions of the hydroxyl group, a tetrahydropyran (THP)
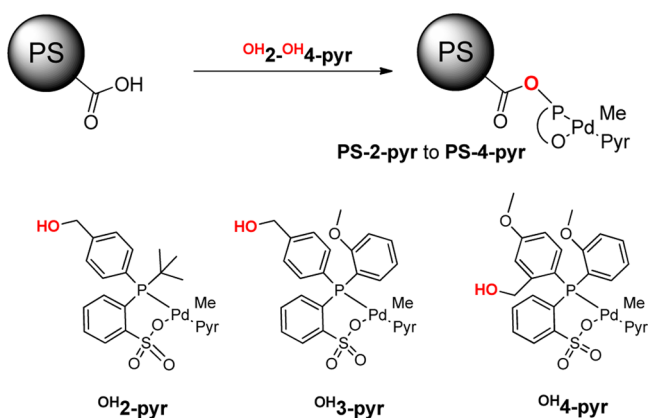
Figure 1. New linkable phosphine sulfonato Pd(II) complexes ^{OH}2-pyr, ^{OH}3-pyr, and ^{OH}4-pyr for an immobilization on functionalized polystyrene.

protecting group was introduced. Isolated (anisyl)-(diethylamino)phosphorus chloride (**7**) proved to be advantageous for a clean reaction to the phosphorus chloride **8**. The anticipated cleavage of the THP protecting group from the phosphine sulfonate (**9**) with HCl or TFA in methanol did not proceed cleanly. However, the desired pyridine complex ^{OH}3-pyr can be obtained by reaction of the phosphine sulfonate (**9**) with [(COD)PdMeCl] and pyridine to yield ^{OTHP}3-pyr, followed by subsequent deprotection under acidic conditions in methanol.

The phosphine sulfonato Pd(II) complexes obtained were fully characterized by one- and two-dimensional nuclear magnetic resonance (NMR) techniques (cf. the Supporting Information). X-ray structure analysis confirmed the identity and molecular structure of complexes ^{OH}4-pyr, [{^{OH}3-μLiCl}$_2$], ^{OTHP}3-pyr, and ^{OH}3-pyr (Figure 2). All palladium

complexes exhibit a distorted square planar coordination sphere around the palladium center, and the methyl group is located mutually *cis* to the phosphorus atom.

Tethering of Complexes to Polystyrene. Commercial cross-linked, carboxyl-functionalized polystyrene was activated by treatment with oxalyl chloride, and the isolated and deprotected palladium pyridine complexes ^{OH}2-pyr–^{OH}4-pyr were subsequently bound to this carboxylic acid chloride under basic conditions (Et$_3$N and pyridine in CH$_2$Cl$_2$). ^{31}P magic angle spinning NMR spectra of insoluble **PS(12)-2-pyr** (12 μmol of ^{OH}2-pyr/100 mg of PS) exhibit one resonance at 45 ppm (see Figure S6 of the Supporting Information), which agrees with the solution spectrum of ^{OH}2-pyr, exhibiting a ^{31}P resonance at 43.2 ppm. The same coupling conditions were also used to synthesize a soluble reference complex ^{Ester}2-pyr (Scheme 2).

The exact degree of functionalization (given as Y in micromoles per 100 mg) of PS(Y) with the palladium complexes was determined indirectly by ^{31}P NMR spectroscopy (see Figure S8 of the Supporting Information). Because phosphines coordinate considerably stronger to the palladium center than pyridine, they will displace the latter. This results in depletion of a PPh$_3$ solution upon exposure to the supported catalyst. For quantification, a known amount of trioctylphosphine oxide served as an internal standard.[17] Further, to ensure a quantitative integration of the ^{31}P NMR spectra, the spin–lattice relaxation times of PPh$_3$ and Oct$_3$P=O were determined (see Figure S7 of the Supporting Information). The quantitative feasibility of this method was evaluated by reference experiments with the soluble complex **1-pyr**. Further proof of covalent binding is obtained from polymerization studies (*vide infra*).

Ethylene and MA (Co)polymerization with PS-Bound Complexes. The polystyrene-bound phosphine sulfonato Pd(II) complexes **PS(Y)-2-pyr**–**PS(Y)-4-pyr** are active ethyl-

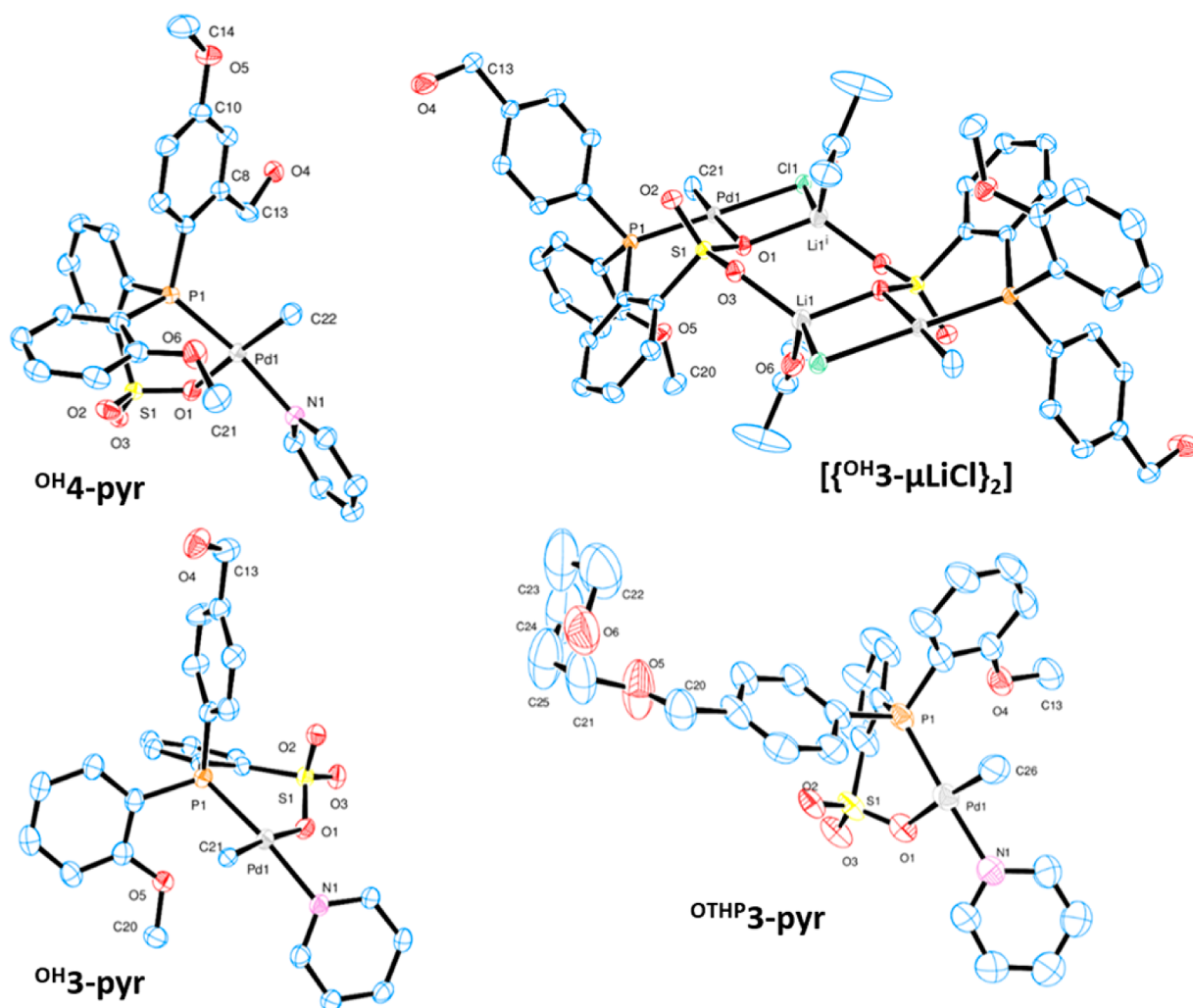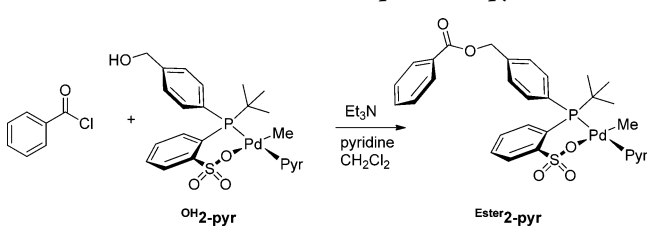**Scheme 1. Stepwise Synthesis of the Phosphine Sulfonato Pd(II) Complex ^{OH}3-pyr**
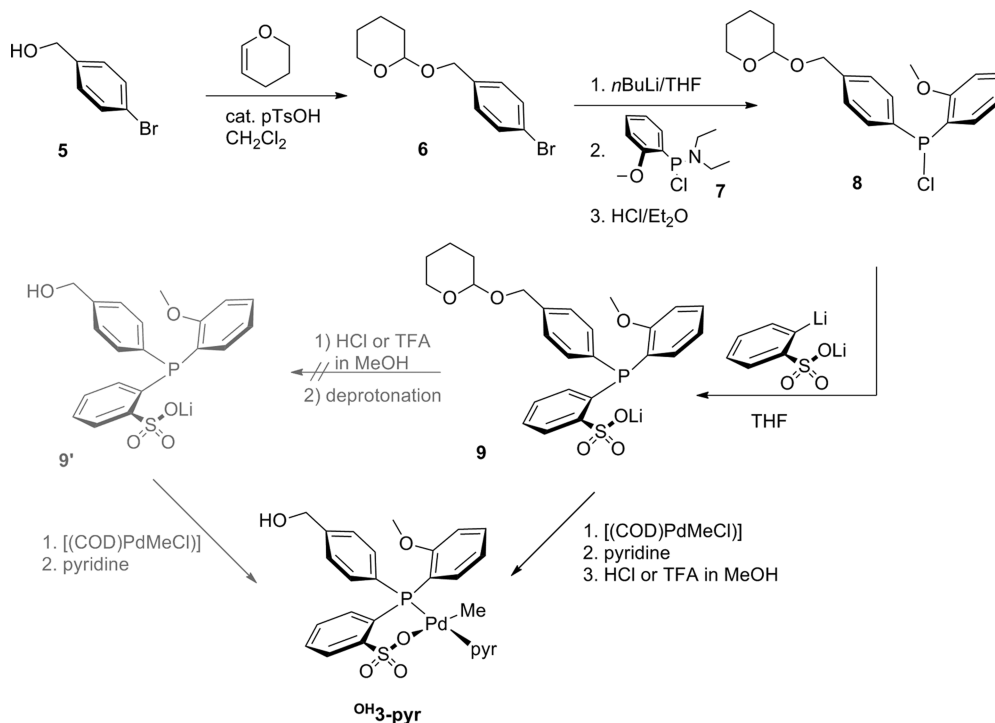
Figure 2. ORTEP plots of complexes ^{OH}**4-pyr**, [{^{OH}**3-μLiCl**}$_2$], ^{OH}**3-pyr**, and ^{OTHP}**3-pyr**. Ellipsoids are drawn with 50% probability, and hydrogen atoms have been omitted for the sake of clarity.

Scheme 2. Soluble Reference Complex ^{Ester}2-pyr

ene polymerization catalysts (Table 1). Activities, however, are significantly lower than those of the unbound complexes. This is ascribed mainly to a hindered diffusion of the ethylene substrate or polyethylene product in the macroporous polystyrene beads. The polymers obtained exhibit molecular weights of ~10^4 g mol^{-1}, which is approximately half of the molecular weight obtained with the free complexes (compare, e.g., entries 1-15 and 1-19). Further, all polyethylenes exhibit a highly linear microstructure with fewer than one methyl branch per 1000 carbon atoms.

While the polyethylene yield increases slightly with prolonged polymerization time, the turnover frequencies show a significant loss of activity over time (Table 1, entries 1-2−1-4 or 1-15−1-17). This demonstrates that these PS-

bound complexes are amenable to some decomposition. One explanation might be that Pd(0) clusters or precipitates formed after reductive elimination are not amenable to reaction with the immobile phosphonium sulfonate and therefore do not undergo the reverse reaction (oxidative addition) to re-form an active catalyst.[18]

A physisorption rather than the anticipated covalent tethering in the synthesis of the supported catalyst described above could result in catalysis by nonbound complexes in solution. To this end, polymerization studies are instructive. Physical adsorption of the complex can be excluded by a comparative experiment (entry 1-11) with complex **2-pyr**,[15] which possesses no hydroxyl linker. The supporting procedure and washing steps used to tether the other complexes to PS were conducted with **2-pyr**. Subjecting the resulting solid support to ethylene in the pressure reactor yielded no polymer. This shows that complexes **PS-2-pyr**−**PS-4-pyr** are indeed covalently bound to PS. NMR analysis of the filtrates of reaction mixtures from polymerization experiments (entry 1-16), however, indicates that the complexes might be partly cleaved to a small extent under polymerization conditions because a weak ^{31}P resonance at −4.2 ppm, which would match with a phosphine sulfonate, and traces of aromatic signals in the ^{1}H NMR spectrum were found. The identity of this species

Table 1. Ethylene Polymerization with Polystyrene-Bound Complexes PS(Y)-2-pyr−PS(Y)-4-pyr and Soluble Reference Complexes[a]

entry	PS-bound catalytic precursor	Pd (μmol)	time (min)	yield (g)	TOF[b]	TON[c]	M_n (NMR) (g mol^{-1})[d]
1-1	**PS(31)-2-pyr**	31	90	0.343	263	395	10.0×10^3
1-2	**PS(20)-2-pyr**	20	10	0.288	3144	524	9.4×10^3
1-3	**PS(20)-2-pyr**	20	90	1.287	1562	2344	13.0×10^3
1-4	**PS(20)-2-pyr**	20	450	5.688	1381	10364	16.1×10^3
1-5	**PS(12)-2-pyr**	12	90	0.470	910	1365	14.3×10^3
1-6	**PS(12)-2-pyr**[e]	12	90	1.849	3578	5368	14.0×10^3
1-7	**PS(12)-2-pyr**[f]	12	90	−	−	−	−
1-8	**PS(05)-2-pyr**	5	90	0.300	1428	2143	0.1×10^3
1-9	**Ester2-pyr**	7	90	3.973	13138	19707	21.0×10^3
1-10	**Ester2-pyr**	8	450	14.074	8274	62055	14.0×10^3
1-11	PS and **2-pyr**[g]	−	90	0.001	−	−	−
1-12	**PS(12)-2-pyr**[h]	24	120	0.838	1247	2494	10.2×10^3
1-13	**PS(12)-2-pyr**[h]	24	(120+)120	0.769	1144	2289	10.1×10^3
1-14	**PS(12)-2-pyr**[h]	24	(240+)120	0.256	381	762	10.2×10^3
1-15	**PS(18)-3-pyr**	18	30	0.666	2628	1314	8.6×10^3
1-16	**PS(18)-3-pyr**	18	90	0.811	1067	1601	12.7×10^3
1-17	**PS(18)-3-pyr**	18	450	1.036	273	2045	8.1×10^3
1-18	**PS(18)-3-pyr**[i]	18	90	0.858	1128	1693	8.2×10^3
1-19	**OTHP3-pyr**	7.0	90	7.954	27056	40584	19.4×10^3
1-20	**OH3-pyr**	8.0	90	10.405	30967	46450	15.1×10^3
1-21	**PS(07)-4-pyr**	6.6	30	traces	−	−	−
1-22	**PS(07)-4-pyr**	6.6	90	0.180	706	471	11.7×10^3
1-23	**THP4-pyr**	7.3	90	16.775	54713	82069	26.7×10^3
1-24	**OH4-pyr**	7.7	90	12.632	39061	58591	22.3×10^3

[a]Reaction conditions: 100 mg of **PS(Y)-2-pyr−PS(Y)-4-pyr**, 100 mL of toluene, 10 bar of ethylene, reaction temperature of 90 °C, 250 mL stainless steel reactor. [b]In moles of E per mole of Pd per hour. [c]In moles of E per mole of Pd. [d]Determined by ^{1}H NMR spectroscopy at 130 °C in C$_2$D$_2$Cl$_4$. [e]At 40 bar of ethylene. [f]In 100 mL of heptane, without toluene. [g]Identical pretreatment of PS with **2-pyr** without a hydroxyl linker. [h]Catalyst recycling experiment: 200 mg of **PS(12)-2-pyr**, 20 bar, decanted and reused. [i]Addition of 1 equiv of B(C$_6$F$_5$)$_3$.

Table 2. Copolymerization of MA and Ethylene with PS-Bound and Free Phosphine Sulfonato Pd(II) Complexes[a]

entry	PS-bound catalytic precursor	Pd (μmol)	time (min)	yield (g)	χ(MA)[b] (mol %)	M_n (NMR) (g mol^{-1})[b]
2-1	**PS(12)-2-pyr**	12	90	0.29	0.2	3.1×10^3
2-2	**PS(12)-2-pyr**	12	90	0.24	0.3	3.0×10^3
2-3	**PS(05)-2-pyr**	05	10	0.23	0.8	3.8×10^3
2-4	**PS(05)-2-pyr**	05	450	0.35	0.7	3.2×10^3
2-5	**PS(18)-3-pyr**	18	10	0.14	2.2	3.4×10^3
2-6	**PS(18)-3-pyr**	18	90	0.16	2.7	2.5×10^3
2-7	**PS(18)-3-pyr**	18	450	0.22	2.5	2.2×10^3
2-8	**PS(18)-3-pyr**[c]	54	90	0.23	2.4	3.0×10^3
2-9	**PS(18)-3-pyr**[c]	54	90(+90)	traces	−	−
2-10	**OH3-pyr**	25	90	1.51	3.5	6.2×10^3
2-11	**THP4-pyr**	24	90	5.26	1.9	4.3×10^3
2-12	**OH4-pyr**	23	90	0.65	2.0	3.5×10^3
2-13	**1-pyr**	23	90	6.81	2.5	6.6×10^3

[a]Reaction conditions: 100 mg of **PS(Y)-2-pyr** and **PS(Y)-3-pyr**, 0.2 M MA, total volume (MA and toluene) of 100 mL, 200 mg of BHT, 10 bar of ethylene, reaction temperature of 90 °C. [b]Determined by ^{1}H NMR spectroscopy at 130 °C in C$_2$D$_2$Cl$_4$. [c]Recycling experiment: 300 mg of **PS(18)-3-pyr**, 90 min each run.

could not be evaluated further because of its low concentration. AAS analysis of this solution (cf. the Supporting Information for details) also suggests that <1% of the metal complex has leached from the support.

Successful recycling experiments (Table 1, entries 1-12−1-14) with complex **PS(12)-2-pyr** further demonstrate that the deactivation and any leaching are not quantitative under polymerization conditions within 2 h. After decantation of the polyethylene solution, the polystyrene beads were washed with toluene, dried under vacuum, and reused to polymerize

ethylene again. The second run again yielded PE amounting to 91% of the PE yield of the first run. Note that the palladium−methyl complex activation in the first run will likely afford a PS-bound palladium−hydride complex upon workup. Also, the nature of the labile ligand at the fourth coordination site is not known, which influences the catalyst activity and stability. A third polymerization run produced an additional 30% of the PE yield of the first run. The polyethylene molecular weights remain constant (10^4 g mol^{-1}) over these recycling experiments. This shows again that some decomposition or
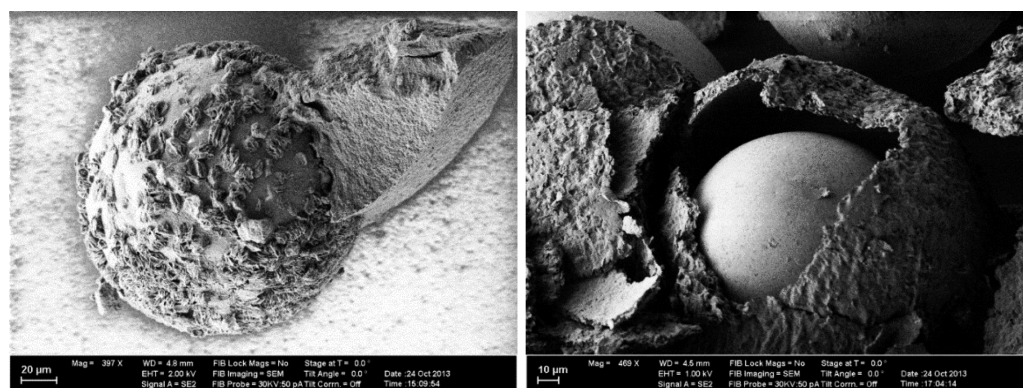
Figure 3. SEM images of a polystyrene bead [**PS(12)-2-pyr**] after ethylene polymerization (left, Table 1, entry 1-6) and MA−ethylene copolymerization (right, Table 2, entry 2-2).
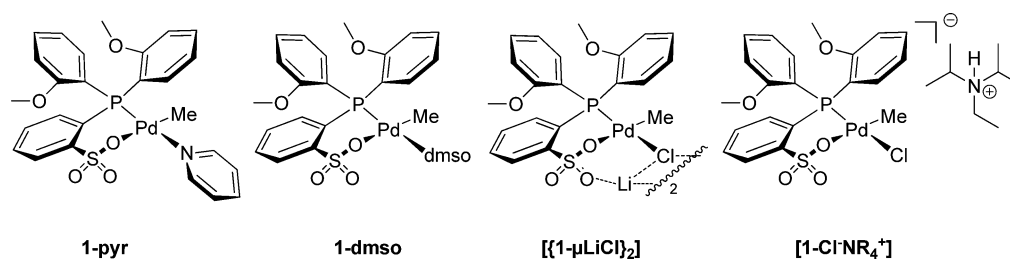

1-pyr   **1-dmso**   **[{1-μLiCl}₂]**   **[1-Cl⁻NR₄⁺]**

Figure 4. Phosphine sulfonato Pd(II) complexes [H]1-L utilized for immobilization on inorganic substrates.

Table 3. Ethylene Polymerization with Phosphine Sulfonato Pd(II) Complexes 1-L, Supported on Clay or Silica[a]

entry	substrate and pretreatment	complex	time (min)	yield (g)	TOF[b]	TON[c]	M_n (NMR) (g mol^{-1})[d]
3-1	—	**1-pyr**	30	4.77	3.4×10^4	1.7×10^4	8.2×10^3
3-2	clay	**1-pyr**	30	5.45	3.9×10^4	1.9×10^4	4.5×10^3
3-3	clay	**1-pyr**	180	16.22	1.9×10^4	5.8×10^4	5.4×10^3
3-4	clay, washed	**1-pyr**	30	2.37	1.7×10^4	0.8×10^4	3.4×10^3
3-5	clay, MAO	**1-pyr**	30	—	—	—	—
3-6	—	**1-dmso**	30	13.26	9.5×10^4	4.7×10^4	7.4×10^3
3-7	clay	**1-dmso**	30	13.24	9.5×10^4	4.7×10^4	1.0×10^3
3-8	—	**[1-Cl⁻NR₄⁺]**	30	—	—	—	—
3-9[e]	—	**[1-Cl⁻NR₄⁺]**[e]	30	11.88	8.5×10^4	4.2×10^4	8.2×10^3
3-10	clay	**[1-Cl⁻NR₄⁺]**	30	4.11	2.9×10^4	1.5×10^4	5.6×10^3
3-11	clay	**[1-Cl⁻NR₄⁺]**	180	17.67	2.1×10^4	6.3×10^4	7.2×10^3
3-12[e]	clay	**[1-Cl⁻NR₄⁺]**[e]	30	1.74	1.2×10^4	0.6×10^4	2.1×10^3
3-13	silica	**1-pyr**	60	5.07	1.8×10^4	1.8×10^4	2.3×10^3
3-14	silica, iw[g]	**1-pyr**	5	0.80	3.6×10^4	0.3×10^4	4.0×10^3
3-15	silica, iw[g]	**1-pyr**	15	2.39	3.4×10^4	0.9×10^4	4.6×10^3
3-16	silica, iw[g]	**1-pyr**	60	4.82	1.7×10^4	1.7×10^4	2.4×10^3
3-17	silica, iw[g]	**1-pyr**	240	11.37	1.0×10^4	4.1×10^4	3.7×10^3
3-18[f]	silica, iw[g]	**1-pyr**[f]	60	0.80	0.3×10^4	0.3×10^4	0.9×10^3
3-19	silica, iw,[g] washed	**1-pyr**	60	5.21	1.9×10^4	1.9×10^4	2.3×10^3

[a]Polymerization conditions: 10 μmol of **1-L**, 120 mg of clay (montmorillonite, treated with a 6 M H₂SO₄/1 M Li₂SO₄ mixture) or 200 mg of silica in 100 mL of toluene, 7 bar of ethylene for clay or 10 bar of ethylene for silica, reaction temperature of 90 °C. [b]In moles of E per mole of Pd per hour. [c]In moles of E per mole of Pd. [d]Determined by ¹H NMR spectroscopy at 130 °C in C₂D₂Cl₄. [e]Addition of 1 equiv of AgBF₄. [f]Polymerization in 100 mL of *n*-heptane. [g]Incipient wetness.

leaching occurs during polymerization but that some catalyst remains active over at least 6 h and the identity of the active species is not altered.

The polystyrene-bound phosphine sulfonato Pd(II) complexes **PS(Y)-2-pyr** and **PS(Y)-3-pyr** were also found to be active for copolymerization of MA and ethylene (Table 2). Interestingly, the levels of incorporation of MA (0.2−0.8 mol %) into the copolymers produced with **PS(Y)-2-pyr** are

considerably lower than that of free complex **2-L**.[15] Under identical conditions, **PS(18)-3-pyr** was able to incorporate larger amounts of MA (~2.5 mol %), only slightly smaller than that with the corresponding unbound complex (3.5 mol % MA, entry 2-10). It is well established from studies of soluble catalysts that bulky substituents on the *P*-donor can reduce the level of MA incorporation.[19] Possibly, this effect is further amplified by the sterically demanding environment provided in
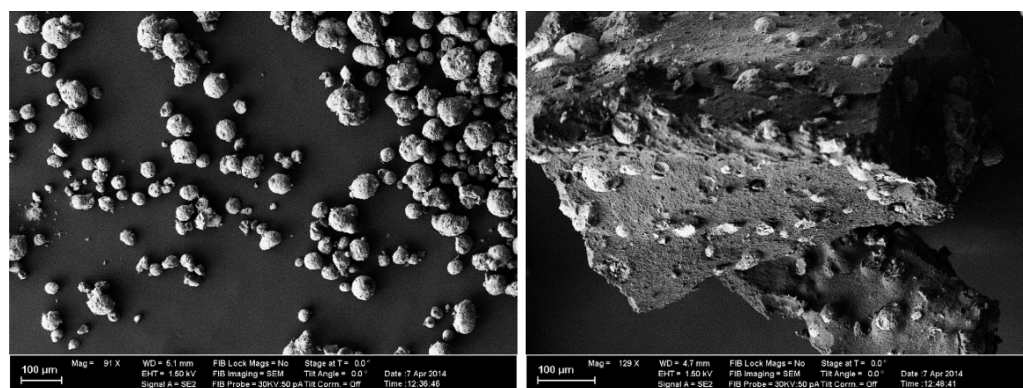
Figure 5. SEM images before (left) and after (right) ethylene polymerization with silica-supported catalyst **1-pyr** (Table 3, entry 3-14).

the cross-linked polystyrene support, particularly for the case of **PS(Y)-2-pyr** with its already bulky *tert*-butyl substituents.

The molecular weights are lower (3×10^3 g mol^{-1}) than that of neat PE formed with the same supported catalysts. This is not surprising because incorporation of polar comonomers increases the likelihood of β-hydride elimination and therefore enhances chain transfer. All copolymers obtained possess a highly linear microstructure with fewer than one methyl branch per 1000 carbon atoms. As during ethylene polymerization, polymerization experiments with different reaction times imply a significant decomposition of these immobilized complexes because the isolated polymer yield did not increase much after the first few minutes.

Scanning electron microscopy (SEM) images (Figure 3) of the polystyrene beads [**PS(12)-2-pyr**] after ethylene (co)-polymerization show that the PS beads are still intact and that the polymerization process does not break up the cross-linked polystyrene. Under (co)polymerization conditions (90 °C in toluene), the ethylene−MA copolymer and also the poly-ethylene formed are completely dissolved in the reaction medium. The (co)polymer precipitates only during the workup [precipitation of the dissolved (co)polymer by excess methanol and drying under vacuum] and is thus found as a matrix in which the polystyrene beads are embedded.

Clay and Silica Supports. We further investigated a possible immobilization of phosphine sulfonato Pd(II) complexes **1-L** (Figure 4) on common inorganic substrates, clay[20] and silica.

Montmorillonite clay was treated with a 6 M H$_2$SO$_4$/1 M Li$_2$SO$_4$ mixture for 6 h at 100 °C, washed, and dried under vacuum before complexes **1-L** (L = pyridine, dmso, or Cl) were adsorbed from an excess volume of a solution of the complex. The precatalyst **1-pyr** was also adsorbed on calcined silica (GRACE XPO-2326) by treatment of the silica with a toluene or methylene chloride solution of the complex. Here, the catalyst was supported by the incipient wetness (iw) method, using 300 μL of a catalyst solution (6 mg in CH$_2$Cl$_2$) with 200 mg of silica, just enough solvent volume to fill the pores (pore volume of 1.54 mL g^{-1}).[21]

The activities of clay-supported complexes **1-pyr** and **1-dmso** compare to those of the unsupported single-site catalysts (compare entries 3-1 and 3-2 or entries 3-6 and 3-7 in Table 3). Longer reaction times give significantly more polyethylene; however, the turnover frequency is also reduced over time, which is likely caused by some decomposition.

The reduced yield of entry 3-4, where the clay-supported complex was washed repeatedly with toluene before it was

applied for polymerization, suggests that the complex can leach from the clay support to some extent. It remains unclear if clay-supported phosphine sulfonato complexes **1-L** are active in their immobilized form or if polymerization occurs solely in solution and therefore which possible decomposition pathways remain accessible.

Pretreatment of the clay with MAO results in an inactive catalyst (entry 3-5). The degradation of the palladium complex is already evident by the rapid formation of palladium black when the catalyst solution is added to the MAO-pretreated clay slurry.

Surprisingly, polymerization with clay-supported palladate complex [**1-Cl$^-$NR$_4$$^+$**] yields polyethylene in good yield, even without addition of silver salts (entries 3-10 and 3-11). This contrasts with the reactivity of the unsupported complex, which is inactive unless it is activated by silver-mediated chloride abstraction (entries 3-8 and 3-9). Such an addition of silver salts is even disadvantageous for the clay-supported complex (entry 3-12). Possibly, chloride abstraction is promoted by the ionic nature of the support by attraction to the cation-containing layers in the anionic aluminate framework.

The polyethylene microstructure is only slightly altered when using clay-supported complexes. Molecular weights are decreased to ~4000 g mol^{-1} by comparison to the unsupported catalyst (8000 g mol^{-1} without clay). In addition, all polyethylenes obtained are still highly linear (<2 Me/1000 C).

The immobilization on silica has a slightly more pronounced effect on the polymer molecular weight. Whereas activities remain high and the linear microstructure of the polymer obtained is not altered significantly, M_n values are further decreased to ~3000 g mol^{-1}. The method of preparation of the silica-supported complexes (incipient wetness, or mixing with excess solvent volume and drying in vacuum) has no observable effect on the catalyst activity or the PE microstructure. Further, it appears that the catalyst precursor is adsorbed well on the silica substrate and does not leach easily in toluene because repetitive washing of the substrate with toluene after immobilization does not reduce activity in a subsequent polymerization experiment (entry 3-19).

AAS analysis of the supernatant solution after polymerization indicates that ≤10% of the Pd has leached (cf. the Supporting Information). Given that polymer yields are similar to those with the unsupported catalyst, this further confirms that catalysis occurs for the longest part or entirely by supported active species. Apparently, the neutral catalyst is adsorbed efficiently on silica. This is notable, as in the well-studied supporting of metallocenes (or also late transition metal

Table 4. Copolymerization of Ethylene and MA with Clay- and Silica-Supported Complexes 1-L[a]

entry	substrate and pretreatment	complex	time (min)	yield (g)	$\chi(MA)^b$	M_n (NMR) (g mol^{-1})^b
4-1	–	**1-pyr**	30	0.93	3.4	4.9×10^3
4-2	clay	**1-pyr**	30	0.49	3.2	2.1×10^3
4-3	clay	[**1-Cl$^-$NR$_4^+$**]	30	0.56	2.2	1.8×10^3
4-4	clay	[**1-Cl$^-$NR$_4^+$**]^c	30	0.71	4.3	4.7×10^3
4-5	silica, iw^d	**1-pyr**	15	0.24	2.5	3.7×10^3
4-6	silica, iw^d	**1-pyr**	60	0.76	2.5	2.6×10^3
4-7	silica, iw^d	**1-pyr**	240	2.20	2.3	2.7×10^3

[a]Polymerization conditions: 10 μmol of **1-L** on 120 mg of clay (montmorillonite, treated with a 6 M H$_2$SO$_4$/1 M Li$_2$SO$_4$ mixture) or 200 mg of silica, 0.2 M MA, total volume (MA and toluene) of 100 mL, polymerization temperature of 90 °C. [b]Determined by ^{1}H NMR spectroscopy at 130 °C in C$_2$D$_2$Cl$_4$. [c]Addition of 1 equiv of AgBF$_4$. [d]Incipient wetness.

diimine catalysts) on silica, the active species are cationic and bound by electrostatic interactions with their aluminum alkyl counterion, which have reacted to form covalent bonds to the support.[8,9]

SEM images of the catalyst-charged silica support before and after polymerization show that no fragmentation of the support occurs under polymerization conditions (Figure 5 and Figures S9–S16 of the Supporting Information). The spherical, microporous silica particles (10–100 μm in diameter) are unaltered and embedded in the polymer matrix after precipitation of polyethylene during workup.

Time-dependent polymerization experiments also show that silica-supported complex **1-pyr** remains active over some hours but is still slowly deactivated over a prolonged polymerization time (entries 3-14–3-17).

Montmorillonite clay- and silica-supported complexes **1-L** further allow a copolymerization of ethylene and methyl acrylate without any cocatalysts such as MAO (Table 4). Whereas both substrates do not influence the degree of MA incorporation significantly (2.5–4 mol % MA), productivity and molecular weights are both slightly reduced in the presence of silica or clay. Silica-supported complex **1-pyr** is less active than the free complex (entry 4-1 vs entry 4-6) but retains its activity over some hours and is only deactivated slowly (entries 4-5–4-7).

CONCLUSION

Both, adsorption on inorganic substrates and tethering to polystyrene for neutral phosphine sulfonato Pd(II) complexes afford active (co)polymerization catalysts without any additional scavenger or cocatalysts. Covalent binding to functionalized polystyrene has a stronger influence on activity, which decreases by ∼1 order of magnitude. This is likely due to a limited diffusion of the monomer substrate and the polymer product in the macropores of these microbeads (∼0.1 mm in size).

Clay and microporous silica as supports have a less pronounced impact on the catalyst activity. **1-pyr** on silica is quite stable under copolymerization conditions. While the possible occurrence of a leaching of small portions of the catalyst is difficult to rule out, results clearly show that catalysis occurs predominantly by supported species. To the best of our knowledge, this is the first demonstration of ethylene–acrylate insertion copolymerization by supported solid catalysts.

For all supported catalysts, polymer microstructures are not dramatically different from those of polymers obtained with soluble catalysts. Highly linear polymers are obtained in all cases. Differences in acrylate comonomer incorporation can be ascribed to steric congestion imparted by the support. Overall,

this shows that the nature of the active single-site species is advantageously retained upon supporting.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplemental data and figures, CIF files, general experimental procedures, synthesis, additional NMR spectra, and crystal structures. 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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REFERENCES

(1) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267–268.

(2) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899.

(3) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745.

(4) Guironnet, D.; Caporaso, L.; Neuwald, B.; Göttker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418–4426.

(5) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215–5244.

(6) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438–1449.

(7) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1203.

(8) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friedrichs, N. *Chem. Rev.* **2005**, *105*, 4073–4147.

(9) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347–1376.

(10) Ma, Z.; Sun, W.-H.; Zhu, N.; Li, Z.; Shao, C.; Hu, Y. *Polym. Int.* **2002**, *51*, 349–352.

(11) Bahuleyan, B. K.; Oh, J. M.; Chandran, D.; Ha, J. Y.; Hur, A. Y.; Park, D.-W.; Ha, C. S.; Suh, H.; Kim, I. *Top. Catal.* **2010**, *53*, 500–509.

(12) Kurokawa, H.; Hayasaka, M.; Yamamoto, K.; Sakuragi, T.; Ohshima, M.; Miura, H. *Catal. Commun.* **2014**, *47*, 13–17.

(13) Schrekker, H. S.; Kotov, V.; Preishuber-Pflugl, P.; White, P.; Brookhart, M. *Macromolecules* **2006**, *39*, 6341–6354.

(14) Allen, N. T.; Goodall, B. L.; McIntosh, L. H., III. U.S. Patent US7833927(B2), 2010.

(15) Piche, L.; Daigle, J.-C.; Rehse, G.; Claverie, J. P. *Chem.—Eur. J.* **2012**, *18*, 3277−3285.

(16) Neuwald, B.; Falivene, L.; Caporaso, L.; Cavallo, L.; Mecking, S. *Chem.—Eur. J.* **2013**, *19*, 17773−17788.

(17) Note that phosphine oxides were found to bind relatively weakly to phosphine sulfonato Pd(II) complexes, which makes them feasible as an internal ^{31}P NMR standard: Neuwald, B.; Ölscher, F.; Göttker-Schnetmann, I.; Mecking, S. *Organometallics* **2012**, *31*, 3128−3137.

(18) Rünzi, T.; Tritschler, U.; Roesle, P.; Göttker-Schnetmann, I.; Möller, H. M.; Caporaso, L.; Poater, A.; Cavallo, L.; Mecking, S. *Organometallics* **2012**, *31*, 8388−8406.

(19) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033−2038.

(20) A recent patent reports montmorillonite clay enhances the activities of phosphine sulfonato Pd(II) and Ni(II) complexes and decreases their lifetimes: Scott, S. L.; Campos, M. A. C. U.S. Patent US8268946(B2), 2012.

(21) Fantinel, F.; Mihan, S.; Karar, R.; Fraaije, V. International Patent Application WO2011147573(A2), 2011.