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Article

Water-Soluble Complexes [(κ^2-*P,O*-Phosphinesulfonato)PdMe(L)] and Their Catalytic Properties

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Palladium(II) phosphinosulfonato methyl complexes [(P∧O)PdMeL] (P∧O=κ^2-*P,O*-2-(2-RC$_6$H$_4$)$_2$-PC$_6$H$_4$SO$_3$ with R = OMe (**a**), 2,6-(MeO)$_2$C$_6$H$_3$ (**b**)) rendered water-soluble by monodentate ligands L = tri(sodium phenylsulfonate)phosphine (TPPTS; **3a**) and L = H$_2$N(CH$_2$CH$_2$O)$_n$Me (n = ca. 52, **4a**, **4b**) were prepared. While aqueous solutions of **3a** are inactive toward ethylene, with **4a** and, particularly, **4b** very small particles of ca. 20 nm size of linear polyethylene are obtained, as anticipated. Catalyst activities and polymer molecular weights are low. This contrasts with the high polymerization activity of the amine complexes **4a**,**b** and polymer molecular weights obtained in nonaqueous polymerizations in toluene. NMR spectroscopic studies reveal that the inactivity of **3a** (also observed in nonaqueous polymerizations) is due to a lack of dissociation of the sulfonated phosphine from the Pd(II) center. The catalyst precursors **4a**,**b** are stable in aqueous solutions, also at elevated temperature (70 °C). Decomposition occurs upon addition of ethylene monomer in the presence of water. These findings are supported by polymerization experiments with known lipophilic analogues of **3** and **4**.

Introduction

Olefin polymerization by cationic complexes of d^8 metals (late transition metals) has been studied intensely in the past decade.[1] These catalysts are much more tolerant toward polar reagents in general by comparison to their highly oxophilic early transition metal counterparts. Thus, ethylene and 1-olefins can be copolymerized with electron-deficient vinyl monomers such as acrylates,[2] and polymerizations can be carried out in aqueous systems to afford dispersions of submicrometer particles.[3] In comparison to traditional free-radical routes,[4] which are applied on a large scale for the preparation of environmentally friendly coatings and paints, catalytic polymerizations enable a control of polymer microstructure. A general prerequisite for obtaining submicrometer particles is a high degree of dispersion of the initial reaction mixture. For the more common lipophilic catalyst precursors, this can be provided by mini-[3] or microemulsions.[5] An alternative approach are water-soluble catalyst precursors.[6] Due to an efficient nucleation, nanoparticles with sizes of only ca. 10 to 30 nm—a size range that is challenging to access by any given polymerization type[7]—and unique morphologies are obtained.[6d,8] These particles can, for example, contribute to a fundamental understanding of crystallization in confinement, crystallinity can be a

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source of anisotropy, and such particles can serve as crystalline mesoscopic building blocks for ultrathin films.[9,10] For these studies, Ni(II) salicylaldiminato complexes [(N∧O)NiMe(L)], which are rendered water-soluble by a highly hydrophilic ligand L, were employed as catalyst precursors.[6b,6c] The resulting catalysts possess a limited lifetime in highly disperse aqueous systems,[6b] and the polymerization of polar vinyl monomers such as acrylates suffers from either low effectivity or rapid catalyst deactivation.[11]

An interesting class of catalysts in this context are neutral Pd(II) complexes of chelating phosphinosulfonates.[1g,12−18] Due to a much decreased propensity for β-hydride elimination[19] by comparison to their cationic Pd(II) diimine counterparts,[20] they polymerize ethylene in a linear fashion. Acrylates and various other vinyl comonomers,[12,13,15,17] including even acrylonitrile,[16a] can be incorporated in linear copolymers, and multiple insertions of acrylate observed in acrylate homooligomerization possess the mechanistic characteristics of an insertion polymerization of an electron-deficient vinyl monomer.[18] Polymerizations with these catalysts in aqueous emulsions[13,17] have also been reported to afford dispersions of ethylene copolymers with acrylates[13b] or norbornene.[13a]

We now report the preparation and catalytic properties of water-soluble neutral κ^2-*P,O*-phosphinesulfonato Pd(II) complexes.

Results and Discussion

Synthesis and Characterization of Complexes. Reaction of the *o*-phosphinesulfonate **a**, and its more bulky substituted analogue **b**, respectively, with [(tmeda)PdMe$_2$] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) afforded the tmeda-bridged binuclear complexes **1a** and **1b**, respectively (Scheme 1).[13c] Both compounds are slightly soluble in CD_2Cl_2 and $CDCl_3$ and highly soluble in DMSO-d_6 (for which the tmeda ligand can be exchanged[18]). They are stable in the solid state but decomposed slowly in CD_2Cl_2 solution at room temperature. Pyridine complexes[13c,15b,18] **2a**,**b** were prepared for comparison of their catalytic and spectroscopic properties.

For the preparation of complexes of hydrophilic ligands L, DMF was found to be a suitable solvent that enables reaction of the starting materials despite their very different polarity and consequently solubility in most solvents. Displacement of tmeda from **1a** and **1b**, respectively, afforded complexes **3a**, **4a**, and **4b** of the water-soluble phosphine TPPTS (tri(sodiumphenylsulfonate)phosphine) and the amine $H_2N(CH_2CH_2O)_nMe$ (n = ca. 52). As anticipated, all three compounds are sufficiently water-soluble (solubility >200 μmol/L) and stable in the solid state. Their identity was established unambiguously by ^{1}H, ^{13}C, and ^{31}P NMR and elemental analysis (cf. Experimental Section). Only a single isomer was observed regarding the arrangement of ligands at the square-planar Pd(II) center for all three compounds.[21] Key spectroscopic features (Table 1) are a single doublet resonance for the Pd-CH_3 hydrogen atoms ($^3J_{PH}$ = 1.6 and 2.8 Hz, respectively) in **4a** and **4b** and accordingly a single ^{13}C NMR resonance originating from the Pd-CH_3 moiety ($^2J_{PC}$ 6.0 and 7.4 Hz, respectively) and a single ^{31}P NMR resonance at δ 19.18 (**4a**) and 20.51 (**4b**) ppm. Similarly, for the TPPTS adduct **3a**, a virtual triplet ^{1}H resonance at δ 0.04 ppm ($^3J_{PH}$ = 6.4 Hz) for the methyl group and two ^{31}P NMR doublet resonances at δ 8.19 and 29.14 ppm coupling with one another with $^2J_{PP}$ = 402 Hz were observed. The observed values of coupling constants $^3J_{PH}$ and $^2J_{PP}$ are in agreement with a *cis* arrangement of the metal-bound methyl moiety and the phosphine donors.

Reactivity toward Ethylene. The behavior of aqueous solutions of the novel water-soluble complexes toward ethylene (40 atm) was studied. For comparison, polymerization with these complexes in the absence of water, and nonaqueous and aqueous polymerizations with their lipophilic analogues **1a**,**b** and **2a**,**b** were carried out (Table 2). For polymerizations in aqueous emulsions, the lipophilic catalyst precursors were dispersed in the initial reaction mixture as a mini-emulsion of a solution of the catalyst precursor in a small amount of methylene chloride, analogous to refs 13a and 13c. Overall, results of these comparative experiments with the tmeda and pyridine complexes catalyst (entries 1 to 10) are in agreement with the previous notes of Claverie et al.[13] Polymerization in emulsion afforded polyethylene dispersions, along with a substantial portion of coagulated polymer. Formation of coagulate (amounting to half of the amount of polymer formed) occurred particularly with the tmeda-bridged complexes **1a**,**b**, which are much less soluble in methylene chloride versus their pyridine analogues. Polymer yields and corresponding catalyst activities in aqueous systems, as well as polymer molecular weights, are reduced considerably versus nonaqueous polymerizations in toluene.

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Scheme 1. Synthesis of Complexes

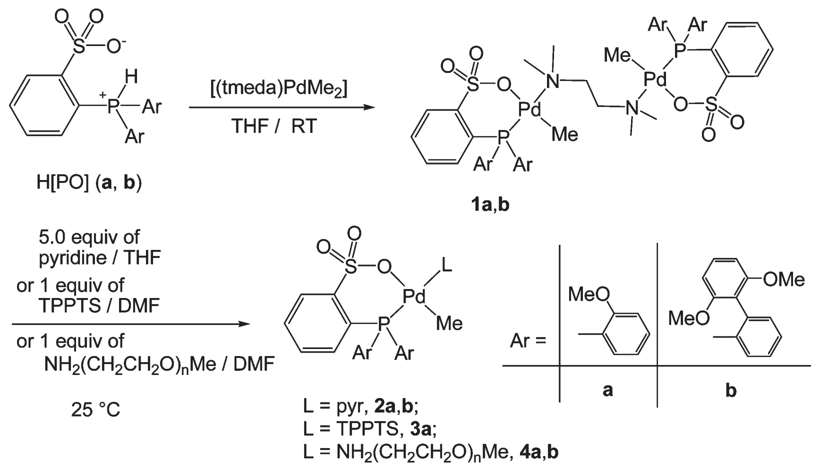


Table 1. Selected NMR Data of the Complexes[a]

complex	^{1}H NMR δ [ppm] Pd−C$\underline{H}_3$	^{13}C NMR δ [ppm] Pd−$\underline{C}$H$_3$	^{31}P NMR δ [ppm]	solvent and reference
1a	0.01	1.40		$CDCl_3$, this work
1b	0.10 (s)	1.24	10.15(s)	$CDCl_3$, 13c
2a	0.24 (s)	0.40 (d, J_{PC} = 4 Hz)	21.54 (s)	CD_2Cl_2, 18
2b	0.23 (d, J_{HP}=2.1 Hz)	1.30	16.90(s)	$CDCl_3$, 13c
3a	0.04 (vt, J_{HP}=6.4 Hz)	0.43 (d, J_{PC} = 4.3 Hz)	29.14 (d, J_{PP} = 402 Hz), 8.19 (d, J_{PP} = 402 Hz)	CD_3OD, this work
4a	0.04 (d, J_{HP}=2.8 Hz), 1.67 (br s, Pd-N$\underline{H}_2$)	−3.65 (d, J_{PC} = 6.0 Hz)	19.18 (s)	CD_2Cl_2, this work
4b	−0.06 (d, J_{HP}=1.6 Hz), 1.62 (br s, Pd-N$\underline{H}_2$)	−0.65 (d, J_{PC} = 7.4 Hz)	20.51 (s)	CD_2Cl_2, this work

[a] 25 °C; ^{1}H: 400 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.8 MHz.

Table 2. Polymerization Results

entry	n(Pd) (μmol)	solvent	T/°C	time/min	yield/g	solids content/wt %	TOF [d]	M_n[e,f]/g mol^{-1}	M_w/M_n[e]	T_m[g] [°C]	χ[g]	particle size [h]Φ [nm]
1	**1a** (100)	emuls.[a]	100	260	1.31	0.63[i]	110					97
2	**1a** (25)	toluene[b]	80	25	8.80		32000	13 900 [e]	9.27	137	75%	
3	**1b** (56)	emuls.[a]	80	60	0.42	0.25	473	1 070[f]				171 [k]
4	**1b** (8)	toluene[b]	80	10	9.57		274000	163000[e]	5.0	140	71%	
5	**2a** (110)	emuls.[a]	100	300	1.27	1.3	83	420[f]		53	57%	139
6	**2a** (20)	toluene[b]	80	60	9.97		17 800	18 800[e,]	2.48	134	77%	
7	**2b** (56)	emuls.[a]	100	120	1.60	1.6[i]	511	1 000 [e]/ 1 050[f]	4.50	124	75%	164
8	**2b** (30)	emuls.[a]	100	60	0.38	0.38	453	2 400 [e]	3.05	n.d.[j]	n.d. [j]	149
9	**2b** (30)	emuls.[a]	80	60	0.56	0.56	663	5 300 [e]	5.12	130	73%	159
10	**2b** (5)	toluene[b]	80	30	6.51		92 600			137	72%	
11	**3a** (100)	H_2O [c]	100	60	trace							
12	**3a** (50)	toluene[b]	80	60	trace							
13	**4a** (43)	H_2O [c]	100	60	0.040	0.021 [i]	33			142	66%	n.d.[j]
14	**4a** (41)	toluene[b]	100	65	2.55		2040					
15	**4b** (20)	H_2O [c]	100	60	0.020	0.020	36			115	68%	n.d.[j]
16	**4b** (20)	H_2O [c]	80	60	0.070	0.070	125	660[f]		76	53%	20
17	**4b** (20)	H_2O [c]	60	60	0.048	0.048	86			113	67%	24
18	**4b** (20)	H_2O [c]	40	60	0.011	0.011	19					
19	**4b** (40)	H_2O [c]	80	480	0.087	0.087	97	1 210[f]		123	62%	23
20	**4b** (13)	toluene[b]	100	45	16.50		57 800	20 400 [e]	2.24	135	78%	

[a] Polymerization conditions: 100 mL of H_2O, 2.0 mL of CH_2Cl_2, 0.25 mL of hexadecane, 750 mg of SDS, 40 bar of C_2H_4, polymer obtained as latex. [b] Polymerization conditions: 100 mL of toluene, 40 bar of C_2H_4. [c] Polymerization conditions: 100 mL of H_2O, 750 mg of SDS, 40 bar of C_2H_4, polymer obtained as nanoparticle dispersion. [d] mol[C_2H_4] × mol[Pd] $^{-1}$ × h^{-1}. [e] From GPC versus linear PE standards at 160 °C. [f] Determined by ^{1}H NMR. [g] Crystallinity, determined by DSC from the second heating cycle. [h] Volume average particle size determined by DLS. [i] Partial coagulation. [j] Not determined. [k] Bimodal particle size distribution.

Monitoring of the catalyst activity via the uptake of ethylene (determined by means of mass flow meters) revealed a maximum activity after 10 to 20 min, which ceased completely after ca. 1 h.

No polymerization activity was observed for an aqueous solution of the TPPTS complex, **3a** (entry 11). To shed light on the reactivity of **3a**, solutions of the complex in D_2O (Figure 1) and also H_2O/SDS were studied by NMR

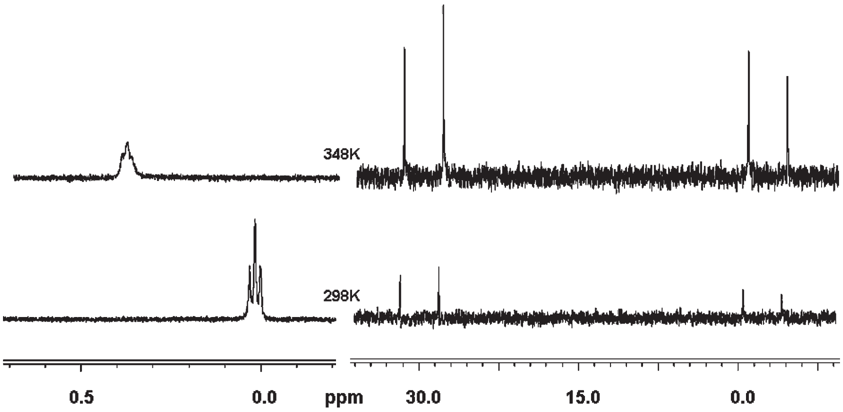


Figure 1. High-field region of ^1H NMR spectra (left) and ^{31}P NMR spectra (right) of D_2O solutions of **3a** acquired at 25 °C (bottom) and 75 °C (top). ^1H chemical shifts are referenced to residual solvent signal (δ 4.72 ppm).

spectroscopy at ambient and elevated temperature. A single resolved ^1H triplet resonance is observed for the Pd-Me moiety at room temperature; also a single set of ^{31}P resonances with a coupling constant typical for *trans*-arranged phosphines is observed. Heating to 75 °C does not result in any significant changes in the spectra. A slight broadening of the Pd-Me resonance is indicative of somewhat increased dynamics. Note that the apparent shift of the ^1H resonance with temperature results from referencing to the water solvent signal, which varies with temperature. This observed behavior of **3a** contrasts with corresponding salicylaldiminato Ni(II) complexes [(N∧O)NiMe(TPPTS)], for which a solvent-dependent dissociation of the phosphine was observed. Displacement occurred increasingly in the order CD_3OD < DMSO-d_6 < D_2O.[6b] For **3a**, no free phosphine (δ −4.9) was observed in either solvent. Upon addition of ethylene to D_2O solutions of **3a**, no evidence for chain growth or any other reaction, e.g., decomposition of the complex, was observed at either 25 or 75 °C. As a conclusion, the lack of any observable catalytic activity with **3a** in aqueous solution even under 40 atm of ethylene (entry 12) can be attributed to a hindered dissociation of the sulfonated phosphine ligand. Note that, while this likely also contributes to the lack of catalytic activity of **3a** in an attempted nonaqueous polymerization in toluene (entry 10), in this case the low solubility of **3a** in toluene even at high temperature additionally hinders polymerization from occurring.

By contrast, aqueous solutions of the water-soluble amine complexes **4a** and **4b** displayed an, albeit low, activity for ethylene polymerization (entries 13 and 15−19). A maximum activity of 10^2 turnovers h^{-1} was observed with **4b** at 80 °C in a 1 h polymerization experiment (entry 16). Optically transparent dispersions with a low content of ca. 20 nm particles composed of low molecular weight material were obtained. Comparison of experiments with different polymerization times reveals that the catalyst is largely deactivated within 1 h (entries 16 and 19). Accordingly, a black solid, presumably elemental metal, was observed in the reaction mixture after polymerization runs. The low productivity observed with aqueous solutions of **4a** and **4b** is primarily due to a rapid deactivation of the active species in the presence of water, rather than to an insufficient activation. Thus, a very high polymerization activity was observed with a nonaqueous toluene solution of **4b**, making the exothermic reaction difficult to control (entry 20). Monitoring of the ethylene consumption indicated stability of the catalyst over the period of 45 min studied. Catalyst activities and molecular weights of the polymers obtained resemble the observed behavior of the corresponding tmeda and amine complexes, **1** and **2**.

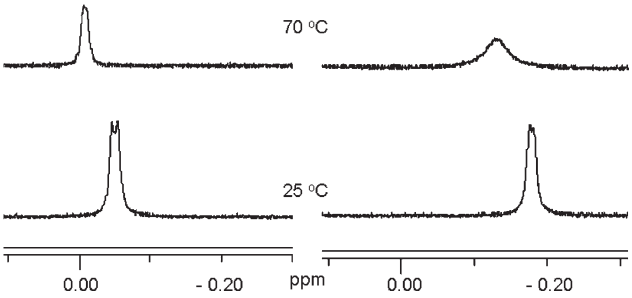


Figure 2. High-field region of the ^1H NMR spectra of compounds **4a** (left) and **4b** (right) in DMSO-d_6/D_2O (v/v 2:1) solutions at 25 and 70 °C. ^1H chemical shifts are referenced to residual undeuterated DMSO solvent signal (δ 2.54 ppm).

^1H NMR spectra of solutions of **4a** and **4b**, respectively, in solutions of DMSO-d_6/D_2O mixtures (v/v 2:1) at room temperature and 70 °C revealed no evidence for decomposition or other reactions of the catalyst precursors with water (Figure 2). Merely a very small amount of black solid, presumably palladium black, was observed in solutions of **4b** after acquisition of the NMR spectra.

Upon addition of ethylene to the NMR tubes at room temperature, no changes of the spectra were observed apart from the signal of free ethylene. However, upon keeping the NMR tube sample of **4b** for ca. 5 min at 70 °C, formation of palladium black was observed, along with the gradual disappearance of the Pd-Me signal and the ingrowth of weak signals of products of chain growth in the ^1H NMR spectra. **4a** reacted significantly slower than **4b**, while the half-life of **4b** based on disappearance of the Pd-Me signal was ca. 5 min at 70 °C; for **4a**, formation of an observable amount of palladium black and of chain growth products required ca. 20 min.

By comparison, in neat DMSO-d_6 solutions in the absence of water, **4a** and **4b** were much less reactive toward ethylene also at 70 °C. Thus, disappearance of the Pd-Me signal of **4b** required ca. 1 h.

This decomposition in aqueous solutions contrasts with the properties of neutral salicylaldiminato Ni(II) alkyl complexes, for which detailed mechanistic studies revealed that

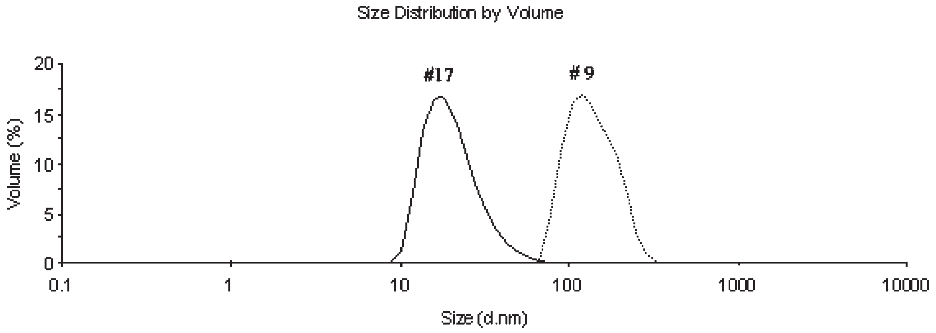
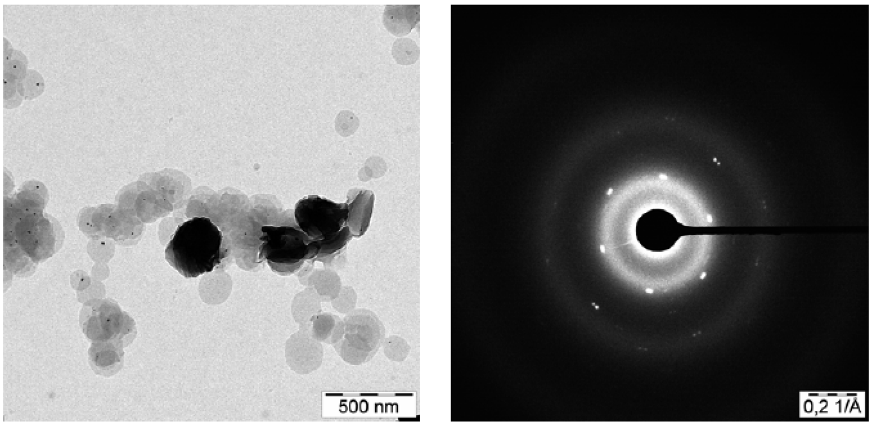


Figure 3. Particle sizes and size distribution of polymer dispersions as determined by dynamic light scattering (173° backscattering). Entry numbers refer to entries in Table 2.



(a) (b)

Figure 4. (a) TEM image of polymer particles (Table 1, entry 9). (b) Electron diffraction on a particle.

decomposition in the presence of water (by hydrolysis) of Ni−alkyl bonds is at most a minor deactivation pathway even under chain growth conditions.[22a] An accelerated decomposition in the presence of both ethylene *and* water has been observed previously also for cationic diiimine Pd(II) alkyl complexes.[22b,23] Theoretical studies suggest the possibility of Pd(II)−alkyl bond hydrolysis as well as Wacker-type reactions in this case.

Polymer Microstructure and Particle Morphology. ^{1}H and ^{13}C NMR spectroscopy of the polymeric materials prepared reveals an essentially linear structure, with a very low degree of methyl branches (ca. 1 per 1000 carbon atoms), as expected. Terminal as well as internal olefinic end groups are both observed, in roughly similar amounts or with a preference for the latter. The relatively low melting points of some samples obtained in aqueous systems are a result of low polymer molecular weight (e.g., entries 5 and 16).

DLS traces indicate a relatively broad particle size distribution both for the dispersion of very small particles obtained with aqueous catalyst precursor solutions and for large polyethylene particles originating from mini-emulsions of lipophilic catalyst precursors (Figure 3). TEM micrographs are in agreement with particle sizes determined by DLS. The larger particles obtained with lipophilic catalyst precursor mini-emulsions are very thin platelets (Figure 4). Apart from thicker aggregates (three more electron dense large particles in the center of Figure 4a), these platelets (which partially overlap in Figure 4a) appear to possess a very uniform thickness. This indicates that these are single lamella crystalline particles.[8] The small (<10 nm) electron dense spots observed are likely Pd(0) nanoparticles formed by decomposition of the catalyst. Electron diffraction of a single particle confirms its crystalline nature (Figure 4b). For the samples obtained with water-soluble catalyst precursors, the low polymer content relative to the surfactant and Pd(0) content in combination with the generally low contrast of very small polymer particles hindered a detailed analysis of particle structure from the TEM micrographs.

Conclusions

The coordination of sulfonated phosphine (TPPTS) or poly(ethylene glycol)-substituted amine to the (κ^2-*P,O*-phosphinesulfonato)PdMe fragment affords stable water-soluble complexes, which were isolated in high yield and fully characterized by NMR spectroscopy. While the TPPTS complex is inactive toward ethylene due to hindered phosphine dissociation, aqueous solutions of the amine complexes polymerize ethylene to ca. 20 nm particles of low molecular weight linear polyethylene. Catalyst productivity is low, in contrast to polymerization with these catalyst

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precursors in the absence of water, due to a rapid deactivation in the aqueous system.

Experimental Section

Materials and General Considerations. Unless noted otherwise, all manipulations of metal complexes were carried out under an inert atmosphere using standard glovebox or Schlenk techniques. Toluene and diethyl ether were distilled from sodium/benzophenone, and methylene chloride and DMF from CaH_2 under argon. Hexadecane was degassed by sparging with argon. Demineralized water was distilled under a nitrogen atmosphere and degassed three times after distillation. Pyridine was distilled from CaH_2. TPPTS supplied by Fluka and $H_2N(CH_2CH_2O)_nMe$ (n = *ca.* 52) supplied by Aldrich were used as received. $[(TMEDA)PdMe_2]$,[24] the phosphinesulfonates **a**,**b**,[12,13] and their corresponding palladium complexes **1a**,**2a**[18] and **1b**,**2b**[13c] were prepared according to published procedures.

NMR spectra were recorded on a Varian Unity INOVA 400 spectrometer. Chemical shifts were referenced to the residual ^1H and ^{13}C solvent resonances and to external 85% H_3PO_4 (^{31}P), respectively. Elemental analyses were performed up to 950 °C on an Elementar Vario EL. For high-temperature NMR spectroscopy of polyethylenes, a mixture of polymer and $CDCl_2CDCl_2$ in an NMR tube was heated to 115 °C, affording a homogeneous solution. The tube was inserted into a preheated NMR probe at 115 °C, and NMR spectra were obtained after a 5 min temperature equilibration period. Methyl branches were quantified from ^{13}C NMR spectra according to ref 25. Number average molecular weights (M_n) were estimated from ^1H NMR spectra for lower molecular weight samples. Gel permeation chromatography (GPC) was carried out in 1,2,4-trichlorobenzene at 160 °C 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 via universal calibration (for samples with $M_n < 10^5$ g mol^{-1}) and triple detection ($M_n > 10^5$ g mol^{-1}). Both methods were in good agreement with one another. Differential scanning calorimetry (DSC) was performed on a Netzsch Phoenix 204 F1 at a heating and cooling rate of 10 K min^{-1}. DSC data reported are from second heating cycles. Polymer crystallinities were calculated on the basis of a melt enthalpy of 293 J g^{-1} for 100% crystalline polyethylene. Dynamic light scattering was carried out on a Malvern Nano Zeta Sizer. For the determination of particle size, a few drops of a latex sample were diluted with ca. 3 mL of water. TEM images were obtained on a Libra 120 Zeiss instrument. Samples were not contrasted.

Synthesis of Metal Complexes. [κ^2-*P*,*O*-2-{Di(2-methoxyphenyl)phosphino}benzenesulfonato]methyl{sodium tri(*m*-sulfonatophenyl)phosphine}palladium(II) (3a). To a mixture of **1a** (93 mg, 80 μmol) and TPPTS (90 mg, 160 μmol) in a septum-capped Schlenk tube (25 mL) was added DMF (5 mL) via syringe at 20 °C with stirring under argon. After stirring the resulting brown-yellow mixture for 1 h, the solvent was carefully removed under vacuum. The crude residue was washed with CH_2Cl_2 (3 × 10 mL) and diethyl ether (3 × 5 mL) and dried under vacuum to yield a white powder (166 mg, 152 μmol, 95% yield).

^1H NMR (400 MHz, 25 °C, CD_3OD): δ 0.04 (vt, J_{PH} = 6.4 Hz, 3H, Pd-CH_3), 3.70 (s, 6H, OCH_3), 7.04 (m, 4H, Ar-*H*), 7.31 (m, 1H, Ar-*H*), 7.41 (m, 3H, Ar-*H*), 7.50−7.59 (m, 6H, Ar-*H*), 7.83−7.87 (m, 3H, Ar-*H*), 7.97 (vt, *J* = 8.0 Hz, 4H, Ar-*H*), 8.16 (vt, *J* = 6.4 Hz, 3H, Ar-*H*). $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_3OD): δ 161.1 (d, J_{PC} = 2.6 Hz), 147.3 (d, J_{PC} = 15.4 Hz), 145.9 (d, J_{PC} = 15.4 Hz), 136.9 (br m), 136.6 (d, J_{PC} = 13.6 Hz), 135.4 (d, J_{PC} = 3.3 Hz), 133.3 (s), 131.2 (d, J_{PC} = 12.6 Hz), 130.4 (d, J_{PC} = 2.5 Hz), 130.1 (d, J_{PC} = 2.1 Hz), 130.0 (d, J_{PC} = 2.5 Hz), 129.5 (d, J_{PC} = 6.3 Hz), 129.1 (s), 128.8 (d, J_{PC} = 10.4 Hz), 128.4 (s), 127.1 (d, J_{PC} = 7.4 Hz), 120.7 (d, J_{PC} = 10.7 Hz), 115.4 (d, J_{PC} = 48.9 Hz), 111.3 (d, J_{PC} = 4.3 Hz), 55.0 (s, OCH_3), 0.43 (d, J_{PC} = 4.3 Hz, Pd-CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C, CD_3OD): δ 29.14 (d, J_{PP} = 402 Hz), 8.19 (d, J_{PP} = 402 Hz). Anal. Calcd for $C_{39}H_{33}Na_3O_{14}P_2PdS_4$ (M = 1091.27 g mol^{-1}): C 42.92, H 3.05. Found: C 41.81, H 2.98.

[κ^2-*P*,*O*-2-{Di(2-methoxyphenyl)phosphino}benzenesulfonato]methyl{monoaminomonomethoxypoly(ethyleneoxide)}palladium(II) (4a). To a mixture of **1a** (54 mg, 46 μmol) and $H_2N(CH_2CH_2O)_nMe$ (200 mg, 100 μmol) in a septum-capped Schlenk tube (25 mL) was added DMF (5 mL) via syringe at 20 °C with stirring under argon. After stirring the resulting brown-yellow mixture for 1 h, the solvent was carefully removed under vacuum. The crude residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum to afford a yellow powder (213 mg, 84 μmol, 91% yield).

^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 0.04 (d, J_{HP} = 2.8 Hz, 3H, Pd-CH_3), 1.67 (br s, 2H, NH_2), 2.80 (br s, 2H,CH_2C$H_2$$NH_2$), 3.08 (br s, 2H, C$H_2$$CH_2$-$NH_2$), 3.34 (s, 3H, CH_2CH_2OCH_3), 3.57−3.63 (m, (CH_2CH_2)$_n$ and OCH_3), 3.75 (m, 4H, CH_2C$H_2$$OCH_3$), 6.93 (m, 2H, Ar-*H*), 7.00 (m, 2H, Ar-*H*), 7.26 (m, 2H, Ar-*H*), 7.44 (m, 1H, Ar-*H*), 7.51(m, 4H, Ar-*H*), 8.03 (m, 1H, Ar-*H*). $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ 160.7 (d, J_{PC} = 2.5 Hz), 148.6 (d, J_{PC} = 15.4 Hz), 137.7 (br s), 134.8 (d, J_{PC} = 2.1 Hz), 133.2 (d, J_{PC} = 1.8 Hz), 130.1(d, J_{PC} = 2.3 Hz), 128.5 (d, J_{PC} = 7.0 Hz), 128.0 (d, J_{PC} = 48.8 Hz), 127.6 (d, J_{PC} = 8.4 Hz), 120.6 (d, J_{PC} = 11.7 Hz), 116.4 (d, J_{PC} = 55.5 Hz), 111.4 (d, J_{PC} = 4.5 Hz), 72.1 (s), 71.1 (s), 70.7 (br m), 58.8 (s), 55.3 (s), 42.9 (d, J_{PC} = 1.6 Hz, H_2NCH_2−), −3.65 (d, J_{PC} = 6.0 Hz, Pd-CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C, CD_2Cl_2): δ 19.18 (s). Anal. Calcd. for $C_{126}H_{234}NO_{57}PPdS$ (M = 2844.64 g mol^{-1}): C 53.20, H 8.29, N 0.49. Found: C 52.88, H 8.89, N 0.54.

[κ^2-*P*,*O*-2-{Di(2-(2,6-dimethoxyphenyl)phenyl)phosphino}-benzenesulfonato]methyl{monoaminomonomethoxypoly(ethyleneoxide)}palladium(II) (4b). To a mixture of **1b** (80 mg, 50 μmol) and $H_2N(CH_2CH_2O)_nMe$ (200 mg, 100 μmol) in a septum-capped Schlenk tube (25 mL) was added DMF (5 mL) via syringe at 20 °C with stirring under argon. After stirring of the resulting brown-yellow mixture for 1 h, the solvent was carefully removed under vacuum. The crude residue was washed with diethyl ether (3 × 10 mL) and dried under vacuum to afford a yellow powder (243 mg, 89 μmol, 89% yield).

^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ −0.06 (d, J_{HP} = 1.6 Hz, 3H, Pd-CH_3), 1.62 (br s, 2H, NH_2), 1.92 (br s, 2H, CH_2C$H_2$$NH_2$), 2.82 (br s, 2H, C$H_2$$CH_2NH_2$), 3.34 (s, 3H, CH_2CH_2OCH_3), 3.40 (s, 6H, OCH_3), 3.56 − 3.65 (m, (CH_2CH_2)$_n$), 3.69 (s, 6H, OCH_3), 6.28 (d, J_{HP} = 8.4 Hz, 2H), 6.41 (d, *J* = 8.4 Hz, 2H), 6.99 (t, J_{HP} = 8.0 Hz, 1H), 6.99−7.15 (m, 5H), 7.30 (t, J_{HP} = 8.0 Hz, 2H), 7.42 (t, J_{HP} = 8.0 Hz, 2H), 7.55 (t, J_{HP} = 8.0 Hz, 1H), 7.61−7.71 (m, 3H). $^{13}C\{^1H\}$ NMR (100.5 MHz, 25 °C, CD_2Cl_2): δ 157.6 (s), 148.7 (d, J_{PC} = 36.9 Hz), 141.1 (d, J_{PC} = 1.7 Hz), 140.0 (s), 136.2 (d, J_{PC} = 8.3 Hz), 135.1 (s), 133.8 (d, J_{PC} = 8.8 Hz), 129.9 (d, J_{PC} = 2.2 Hz), 129.7 (s), 128.7 (s), 127.9−127.8 (m), 127.5, 126.1 (d, J_{PC} = 9.1 Hz), 119.0 (d, J_{PC} = 2.1 Hz), 103.2 (s), 72.1 (s), 71.7 (s), 70.7 (br m), 58.8 (s), 55.2 (s), 54.9 (s), 42.4 (s), −0.65 (d, J_{PC} = 7.4 Hz, Pd-CH_3). $^{31}P\{^1H\}$ NMR (162 MHz, 25 °C, CD_2Cl_2): δ 20.51 (s). Anal. Calcd for $C_{140}H_{246}NO_{59}PPdS$ (M = 3056.88 g mol^{-1}): C 55.01, H 8.11, N 0.46. Found: C 54.75, H 7.79, N 0.55.

Variable-Temperature NMR Experiments. J. Young NMR tubes were charged with solid complexes in a glovebox. Generally, 6 mg of **3a** or 10 mg of **4a** and **4b** was dissolved in 500 μL of solvent. The tube was sealed, taken out of the box, and inserted into a preheated NMR probe at the desired temperature. NMR spectra were obtained after a 5 min temperature

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equilibration period. For NMR experiments with ethylene, the J. Young NMR tube was charged with the solid complex and solvent in the glovebox and closed. The tube was removed from the box and connected with a three-way stopcock to the Schlenk line and to the ethylene gas supply. The tube was cooled to −78 °C in a dry ice/2-propanol bath and charged with ca. 1 atm of ethylene by several pump−fill cycles. The NMR tubes was sealed, warmed to room temperature, and shaken briefly prior to recording NMR spectra. For NMR experiments at elevated temperature, the tube was inserted into a preheated NMR probe at the desired temperature and NMR spectra were obtained after a 5 min temperature equilibration period.

Ethylene Polymerizations. Ethylene polymerizations were performed in a 100 mL stainless steel mechanically stirred (750 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. This setup enabled control of polymerization temperature with an exotherm of <5 °C. A valve controlled by a pressure transducer allowed for applying and keeping up a constant ethylene pressure. The required flow of ethylene, corresponding to ethylene consumed by polymerization, was monitored by a mass flow meter and recorded digitally. Prior to a polymerization experiment, the reactor was heated under vacuum to the desired reaction temperature for 30−60 min and then backfilled with argon. After the desired reaction time the reactor was rapidly vented and cooled to room temperature.

For nonaqueous polymerizations, 90 mL of dry toluene was added to the reactor, heated to the desired temperature with stirring, and flushed and pressurized with ethylene three times. The catalyst precursor, previously weighed into a Schlenk tube in the glovebox, was dissolved in 10 mL of toluene and injected into the reactor with a syringe. The reactor was closed, and a constant ethylene pressure was applied. After the desired reaction time, the reactor was cooled to room temperature and vented. The reaction mixture was stirred with an excess volume of methanol. The precipitated polymer was isolated by filtration, washed several times with methanol, and dried overnight under vacuum at 50 °C.

For polymerization in aqueous emulsion, 80 mL of degassed water was introduced to the reactor and heated to the desired temperature with stirring, and ethylene pressure was applied in order to presaturate the solution. The catalyst precursor, previously weighed into a Schlenk tube in the drybox, was dissolved in 2 mL of dichloromethane and 0.25 mL of hexadecane (the latter functions as a hydrophobe). This solution was added to 20 mL of an aqueous solution of 0.75 g of SDS. The biphasic mixture was homogenized under an argon atmosphere by means of an ultrasonic homogenizer (Bandelin HD2200 with KE76 tip, operated at 120 W, 2 min). The resulting mini-emulsion was cannula-transferred to the pressure reactor. The reactor was flushed with ethylene, a constant ethylene pressure was then applied, and the reaction mixture was brought rapidly to the desired temperature. After the specified reaction time, the reactor was vented and cooled. The emulsion was filtered through glass wool. For determination of yields and for further polymer analysis, a specified portion of the latex was precipitated by pouring into excess methanol. The polymer was washed three times with methanol, H_2O, and acetone and dried overnight under vacuum at 50 °C.

For polymerization in aqueous solution, 100 mL of an aqueous solution of the catalyst precursor and 0.75 g of SDS were introduced to the reactor, and the pressure reactor was flushed with ethylene and further subjected to an identical procedure to that described in the previous paragraph for polymerization in emulsion.

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