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Articles

Nickel(II)−Methyl Complexes with Water-Soluble Ligands L [(salicylaldiminato-κ^2N,O)NiMe(L)] and Their Catalytic Properties in Disperse Aqueous Systems

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Neutral (salicylaldiminato)nickel(II) methyl complexes [{6-C(H)=NAr-2,4-$I_2C_6H_2O$-κ^2N,O}NiMe(L)] (Ar = 2,6-{3,5-$(F_3C)_2C_6H_3$}$_2C_6H_3$) with different water-soluble ligands L (**2a**, L = 1,3,5-triaza-7-phosphaadamantane; **2b**, L = hexamethylenetetramine (urotropine); **2c**, L = tetraethylammonium pyridine-3-sulfonate; **2d**, L = amino-terminated poly(ethylene glycol) monomethoxy ether) were prepared. **2a**−**d** are potentially water-soluble catalyst precursors for ethylene polymerization, which form a water-insoluble active site [{κ^2-N,O}NiR(ethylene)] (R = growing chain). Only complex **2d** was found to be water-soluble (>2 mmol L^{-1}); **2c** is soluble in water/2-propanol mixtures. In toluene as a reaction medium, only the relatively weakly coordinated tertiary amine complex **2b** is polymerization active (1.7×10^4 TO). In aqueous systems **2c,d** are also active due to compartmentalization of the active site in the polymer particles and of L in the aqueous phase. Polyethylene particle sizes vary from 18 nm (dispersions formed with **2d**) to over 0.5 μm (**2c**) to suspensions (**2b**) depending on the initial state of the reaction mixture, correlated with catalyst solubility.

Introduction

Late transition metal catalysts for polymerization of olefins have been studied intensely recently.[1] Due to their functional group tolerance, polar monomers can be copolymerized.[2] Also, polymerizations can be carried out in aqueous emulsion to afford dispersions of submicron polymer particles.[3−6] By contrast to traditional free-radical emulsion polymerization, which is applied on a large scale for the synthesis of polymer dispersions for, e.g., environmentally friendly coatings, catalytic polymerization allows for a control of polymer microstructures and is also complimentary in terms of monomers polymerizable. Polyethylene dispersions have been prepared starting from aqueous mini-[3,4] or microemulsions[7] of a solution of lipophilic catalyst precursors in a small amount of hydrocarbon solvent.[8] This is attractive, as most types of catalyst precursors known are lipophilic compounds. Polymerization with water-soluble complexes is also of interest, however: the absence of organic solvent simplifies the initial catalyst system as well as the polymer dispersions obtained in terms of number of phases and compounds present. This is desirable for, e.g., studies of the unique particle formation processes in these systems or of thermal properties of dispersed particles or film formation. In this context, it is notable that unusually small polymer particles

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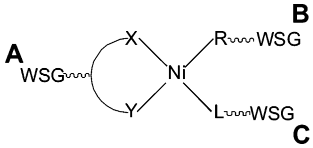
10.1021/om0607191 CCC: $37.00

Chart 1. Possible Generic Structures of Water-Soluble Neutral Ni(II) Complexes Suitable as Catalyst Precursors (WSG: Water-Soluble Group)



of 5−30 nm size can be prepared by catalytic polymerization.[7−10] Such particle sizes are challenging to prepare for any polymer type and preparation method.

Different generic structures are conceivable for water-soluble complexes suited as catalyst precursors for olefin polymerization (Chart 1). Water-solubility can be introduced by water-soluble groups covalently attached to the chelating ligand (**A** in Chart 1), which controls the catalytic properties of the active site and ideally stays coordinated to the metal site throughout the catalytic reaction. This would render the active site [(X^Y)-NiR(ethylene)] (R = growing polymer chain) permanently hydrophilic, and water-soluble when R is a short alkyl chain. Attachment of a water-soluble moiety to the alkyl group R (**B** in Chart 1) would render the catalyst precursor water-soluble. Upon chain growth by repeated insertion of monomer into the metal−alkyl bond, eventually a particle would form by collapse of the growing chain upon itself. The active site is lipophilic in this case. This is also the case if water solubility of the catalyst precursor is brought about by a water-soluble ligand L on the fourth coordination site (**C** in Chart 1). Note that the function of L in general is stabilization of the catalyst precursor but dissociation under polymerization conditions to provide a coordination site for monomer binding. By contrast to approach **B**, reversible coordination of water-soluble L vs monomer coordination could also intermittently convert the lipophilic active species into a hydrophilic dormant species, given that the growing chain is short and does not induce a strong lipophilicity of the overall complex [(N^O)NiR(L)]. Such dormant species as formed, e.g., after chain transfer, could leave an existing particle and initiate a new particle.

In early work, Flood reported that an aqueous solution of the water-soluble cationic rhodium complex $[(N^\wedge N^\wedge N)RhMe(OTf)_2]^+$ polymerizes ethylene to low molecular weight material ($M_w = 5 \times 10^3$ g mol^{-1}) with very low activities (average activity ca. 1 turnover/day), the polymer separating macroscopically from the aqueous phase (N^N^N = triazacyclononane; in terms of the above classification, this example is analogous to case **A**).[12]

Polymerizations in aqueous emulsions, which afforded polyethylene dispersions, have been studied briefly with four-coordinate, square-planar complexes of types **A** and **B**.[13,14] This contribution studies concept **C**. A practical advantage of route **C** is that existing lipophilic chelating ligands, e.g., salicylaldimines, can be employed and developed organometallic routes can be adopted for complex synthesis. Darensbourg et al. have reported a (salicylaldiminato-$\kappa^2 N,O$)nickel(II)−phenyl complex with the water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) coordinating the fourth site, [(N^O)NiPh(PTA)]. The complex was found to be inactive toward ethylene in a biphasic toluene/water system.[15] We have recently communicated studies of ethylene polymerization by aqueous solutions of water-soluble (salicylaldiminato)nickel(II) methyl complexes [(N^O)NiMe(L)] of sulfonated phosphines (L = triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt (TPPTS) or triphenylphosphine-3,3′-disulfonic acid disodium salt (TPPDS)) or polyethylene glycol-substituted primary amine (L = $H_2N(CH_2CH_2O)_nMe$).[10] Aqueous dispersions of particles as small as 4 nm, as determined by single-angle dynamic light scattering (DLS), were obtained. Dissociation of the water-soluble ligand L was found to be enhanced in water due to a compartmentalization of L into the aqueous phase and of the active sites into the particles formed. We now give a full account of the synthesis, solubilities, and catalytic properties of a series of complexes with a range of water-soluble ligands L.

Results and Discussion

Synthesis and Characterization of Complexes. Four (salicylaldiminato-$\kappa^2 N,O$)nickel(II)−methyl complexes [(N^O)-NiMe(L)], **2a**−**d**, with various P- and N-coordinating water-soluble ligands L were prepared, L = 1,3,5-triaza-7-phosphaadamantane (PTA), hexamethylenetetramine (urotropine), tetraethylammonium pyridine-3-sulfonate, and amino-terminated poly(ethylene glycol) monomethoxy ether (Scheme 1). All complexes are based on salicylaldimine **1**. Nickel−methyl complexes of this salicylaldimine (with L = pyridine or tmeda) polymerize ethylene to linear, high-molecular weight polyethylene at high rates, and polymerization starting from aqueous mini- or microemulsions of these lipophilic complexes affords polymer dispersions.[16]

The synthesis of **2a**−**d** requires the reaction of a water-soluble ligand (L) with the lipophilic salicylaldimine and $[(tmeda)NiMe_2]$. The latter is also temperature sensitive, which prohibits elevated reaction temperatures to increase solubilities and reaction rates. For this reason, water-soluble ligands L which are also soluble in toluene were employed. To solid $[(tmeda)NiMe_2]$ and L, a cold toluene solution (−50 °C) of the salicylaldimine was added. Gradual warming of the reaction mixture to 0 °C afforded clear solutions of **2a**−**c**. Notably, also the ionic complex **2c** is soluble in toluene at the typical concentrations of complex synthesis, 2.5×10^{-2} mol L^{-1}. Complex **2d** was synthesized from $[(tmeda)NiMe_2]$, salicylaldimine, and PEG amine in benzene, as reported.[10] Compounds **2a**−**d** were isolated in 63−83% yield as red solids. Of the complexes active for catalysis (vide infra), **2b** is stable to oxygen and moisture; even after 1 year in air no decomposition was observed by ^{1}H NMR spectroscopy. **2c**,**d** are hygroscopic and both decompose within days in air at room temperature.

In ^{1}H NMR and ^{13}C NMR spectra of all four complexes a singlet can be observed between −1 and −1.5 ppm and between

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(13) References 3a,b. The sulfonated phosphinoenolato complex (cf.: Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134) possesses a very low activity in neat aqueous solutions, hampering detailed studies.

(14) Reference 9. The in situ catalyst prepared may contain a water-soluble sulfonated phenyl group either attached to the nickel center (approach **B** in Chart 1) or incorporated in the chelating phosphinoenolato ligand (approach **A** in Chart 1).

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Scheme 1. General Synthetic Pathway and Complexes Prepared

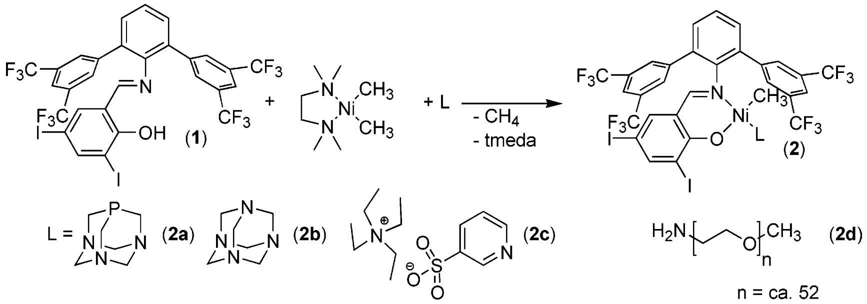

Table 1. Polymerization Results

entry	catal (amt (μmol))	reacn medium	physical state before polymerizatn	time (h)	yield (g)	TON ($\times 10^3$)	M_n ($\times 10^5$ g mol^{-1})[j] (M_w/M_n)	colloidal state after polymerizatn	particle size[k] (nm)
1	**2b** (10)	toluene[a]	solution	2	4.71	16.8	2.0 (2.6)	suspension	n/a
2	**2b** (10)	H_2O[b]	suspension	1	0.75	2.7	1.9 (2.1)	suspension	n/a
3	**2b** (10)	$H_2O/{}^iPrOH$[c]	suspension	1	2.6	9.4	3.2 (2.3)	latex + suspension[d]	
4	**2c** (10)	toluene[a]	solution	1	−	n/a	n/a	n/a	n/a
5	**2c** (5)	H_2O[b]	suspension	1	0.17	0.6	1.3 (2.5)	latex + suspension[e]	500
6	**2c** (10)	$H_2O/{}^iPrOH$[c]	solution in ^{i}PrOH	3.5	9.0	32.3	2.5 (2.2)	latex[f]	700
7	**2d** (10)	toluene[a]	solution	1		n/a	n/a	n/a	n/a
8	**2d** (10)	H_2O[b]	solution	1	2.7	9.6	0.88 (1.7)	latex[g]	18
9	**2d** (20)	H_2O[b]	solution	3.5	9.4	16.8	0.94 (2.5)	latex[h]	230

[a] Polymerization conditions: 20 °C; 40 bar of C_2H_4; 100 mL of toluene. [b] Polymerization conditions: 20 °C; 40 bar of C_2H_4; 100 mL of H_2O; 0.75 g of SDS. [c] Polymerization conditions: 20 °C; 40 bar of C_2H_4; 98 mL of H_2O; 2 mL of 2-propanol; 0.75 g of SDS. [d] Polymer in form of latex/coagulate (3:1). [e] Latex/coagulate (1:1). [f] 6% coagulate. [g] No coagulate. [h] 95% as latex. [j] Determined by GPC vs linear PE standards at 160 °C in trichlorobenzene. [k] Volume average particle sizes determined by DLS.

−6 and −18 ppm, respectively. This shift is characteristic for nickel(II)-bound methyl groups. For complex **2a** no coupling between phosphorus and the Ni-bound methyl group is detected. The ^{31}P NMR resonance is shifted from −100.3 ppm for free PTA to −51.7 ppm for coordinated PTA. Observation of only one Me signal for all four complexes indicates that only one isomer with respect to arrangement of L and the methyl ligand at the square planar nickel center is present. Solid-state structures of related complexes revealed coordination of the methyl group trans to oxygen,[15,16a,17] and the similar spectroscopic properties of the compounds studied in this work suggest that this also the case for **2a**−**d**. Both bis(trifluoromethyl)phenyl rings are equivalent in solution, most likely due to rotation around the aryl−aryl bond. The high fluorine content disturbs elemental analysis, and satisfactory analyses were obtained only in some cases.

2a,**b** are insoluble in water (<0.0003 mmol L^{-1}). Solubility of **2c** in water is very low (<0.1 mmol L^{-1}), but it is soluble in 2-propanol (>10 mmol L^{-1}). Complex **2d** was found to be water-soluble; solubility in neat water exceeds 2 mmol L^{-1} (>6 g L^{-1}).

The stability of **2d** in aqueous solution was monitored by UV/vis spectroscopy. In the absence of oxygen,[18] a freshly prepared solution of the complex in neat water shows a clear absorption spectrum below 600 nm without scattering (see Figure S1 in the Supporting Information). With time, the broad absorption band is shifted hypsochromic; correspondingly the color of the solution changes from bright red to pale yellow. The appearance of an isosbestic point indicates that a reaction is occurring. At 342 nm, the wavelength of the largest change of absorption, a first-order decay curve can be fitted with a half-life of $3^1/_2$ h. With progressing decomposition, an increasing scattering of light and formation of a yellow precipitate is observed. These phenomenological observations show that an irreversible decomposition reaction occurs, possibly hydrolysis of the Ni−Me bond.[19] The observed half-life of several hours shows that handling of aqueous solutions of **2d** in preparation of polymerization experiments, which usually takes a few minutes, is uncritical.

Polymerization Studies. All complexes are soluble in toluene, enabling a systematic study of their catalytic behavior in this solvent in addition to studies in aqueous systems (Table 1). In accordance with Darensbourg's studies, the phosphine (PTA) complex **2a** was found to be inactive under all reaction conditions studied. This differs from the behavior of related triphenylphosphine complexes.[2b,10] Apparently, the alkylphosphine PTA, which also has a rather low steric bulk, does not dissociate from the metal center. By contrast, the nitrogen analogue, urotropine, dissociates rather readily. **2b** is a precursor to a very active polymerization catalyst at a mild temperature of 20 °C (entry 1). This behavior of **2b** in toluene solution is in line with previous observations for complexes with L = tmeda, that is, complexes also coordinated by a tertiary amine ligand L.[16] Complex **2c**, which is soluble in toluene as well, affords only traces of polymer under identical conditions (20 °C, 40 atm of ethylene) (entry 4). This again is in line with previous studies of pyridine complexes, which were found to require slightly elevated temperatures of 50 °C for activation.[16a] Notably, the primary amine-coordinated complex **2d** was found to be entirely inactive toward ethylene at 20 °C in toluene solution (entry 7).

Polymerizations in aqueous systems were carried out in the presence of sodium dodecylsulfate (SDS) as a surfactant to

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(17) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Comm.* **2003**, 2272−2273.

(18) The measurements were carried out in a cuvette with a septum. This same setup was successfully used for investigations of triplet lifetimes of organic compounds, which would be detoriated by any oxygen present. Thus, the absence of oxygen in the experiments described in this paper can be safely assumed.

(19) Hristov, I. H.; DeKock, R. L.; Anderson, G. D. W.; Göttker-Schnetmann, I.; Mecking, S.; Ziegler, T. *Inorg. Chem.* **2005**, *44*, 7806−7818.

stabilize polymer particles formed. The state of the initial reaction mixtures differed with the solubility properties of the catalyst precursor. Water-insoluble complexes were suspended in aqueous SDS solutions, supported by ultrasound. For water-insoluble complexes, which are soluble in a water-miscible alcohol, suspending in water in a fine fashion was facilitated by introducing them as a solution in a small volume of alcohol.

From a suspension of **2b** in aqueous SDS solution, immediately after stoppage of the ultrasound treatment, a bright red precipitate visibly separated, with a colorless supernatant aqueous phase. This catalyst precursor suspension is active for polymerization of ethylene (entry 2). The activity is about one-third vs the activity observed in toluene (entry 1). This lowered activity is not surprising, ethylene solubility in water as well as in the semicrystalline polymer (not swollen by any solvent) being rather low, such that mass transfer limitations may occur.[20,21] The activity can be increased by adding 2-propanol as a cosolvent. Upon sonication of **2b** in pure 2-propanol a red solid precipitates again immediately when sonication is stopped; however, the liquid phase stays red, indicating a slight solubility of the complex. On addition of aqueous SDS solution to the mixture and exposure to ethylene, the polymer is partly formed as a latex (entry 3).

From a suspension of **2c** in aqueous SDS solution, after stoppage of the ultrasound treatment, **2c** also precipitated visibly. However, the aqueous phase was orange, indicating that to some degree the complex remained in the liquid phase. Exposure of this mixture to ethylene resulted in polymerization (entry 5). This contrasts to the inactivity observed in toluene solution (entry 4). As observed previously for water-soluble complexes [(N^O)NiMe(L)] (L = water-soluble phosphine or amine), an incipient compartmentalization of the lipophilic active species generated by dissociation of L into the polymer particle formed and of the ligand L into the aqueous phase retards recombination of the latter with the active species and, thus, enhances activity.[10]

As outlined, **2c** is soluble in 2-propanol. Upon addition of a solution of **2c** in 2-propanol (2 mL) to an aqueous SDS solution (98 mL), no formation of precipitate was visibly observed. Attempts to elucidate the nature of these "solutions" by DLS failed; unreproducable results were obtained for a given sample. Possibly, absorption of light by the colored solution interfered with the measurement, or decomposition of the complex may have occurred due to contact with air, which cannot be excluded completely with the setup used. Exposure to ethylene resulted in polymerization with a high rate to afford a polymer dispersion along with a small amount of coagulate. Latex particle sizes were rather large (500 and 700 nm, respectively) with a broad distribution (Figure 1); accordingly, the intransparent dispersions were with a milky white appearance.

By contrast to **2a**−**c**, complex **2d** is water-soluble and dissolves in neat water upon stirring to form a homogeneous solution. Exposure of an aqueous SDS solution of **2d** to ethylene pressure resulted in polymerization to form a colloidally stable dispersion. The observation that **2d** is catalytically active in water but not in toluene is due to incipient compartmentalization of the lipophilic active sites into the polymer particles and of L into the aqueous phase. Location of the active sites and PEG amine in different phases (particle phase vs aqueous phase) retards recombination and enhances activity. Solvation of the coordinating amino function of the PEG amine by water could also contribute to enhanced dissociation and polymerization activities in water.

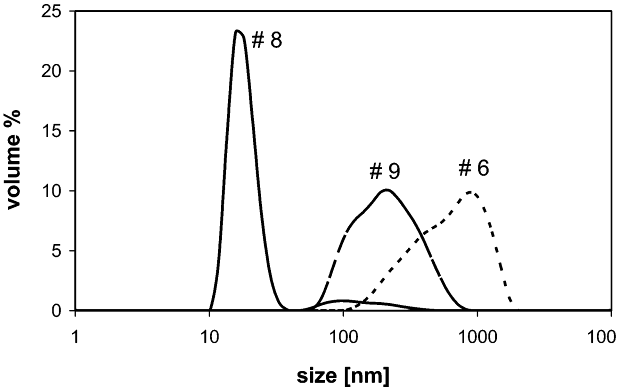

Figure 1. Particle sizes and size distributions of polymer dispersions as determined by dynamic light scattering (173° backscattering). Numbers refer to entries in Table 1.

In more detail, for the experiment with the lower catalyst concentration (entry 8), after 1 h the ethylene consumption had decreased to the detection limit of the mass flow system. For entry 9 with a higher catalyst concentration, monomer consumption was detected for 3.5 h (cf. Supporting Information, Figure S2, for mass flow traces). We assume that the decay in polymerization activity in these experiments is based on the decomposition of **2d** by hydrolysis (vide supra).

At the lower catalyst concentration (entry 8), a dispersion with extremly small particles with a volume average size of 18 nm was obtained (Figure 1). The calculated number of particles/nickel center added to the reaction mixture is ca. 0.2 in this case. Given the inaccuracies in particle size determination, this is relatively close to unity on an order of magnitude scale. A single given active site can generate a polymer particle (for detailed studies and discussion, cf. ref 10).

At the higher catalyst concentration (entry 9) a dispersion with a polymer solids content of 9 wt % was obtained, corresponding to a catalyst productivity of 1.7×10^4 TO. In this case, a small amount of coagulate was formed, likely due to an insufficient stabilization of the high area of the large number of small particles formed by the surfactant. Accordingly, particle sizes of the dispersion were also significantly higher with a volume average 230 nm (Figure 1). Presumably, formation of the final particles involves coagulation of already existing particles.

As expected from previous polymerization studies with nickel(II) complexes of salicylaldimine **1**, the polymers obtained possess a high molecular weight on the order of 10^5 g mol^{-1}. Molecular weight distributions M_w/M_n around 2 show that molecular weights are chain transfer controlled and indicate a single site nature of the active species. Branching of the polymers, prepared at a reaction temperature of 20 °C, is well below 10 methyl branches/1000 carbon atoms as observed by ^{13}C NMR spectroscopy. As observed previously for other polymerizations in aqueous systems and comparative studies in nonaqueous solutions with Ni(II) catalysts, the reaction medium has no significant effect on the microstructure of the polymer formed.

Summary and Conclusions

A series of (salicylaldiminato)nickel(II)−methyl complexes [(N^O)NiMe(L)] with different water-soluble ligands L has been prepared. All complexes, **2a**−**d**, are soluble in toluene. **2a**−**c**

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[20] For ethylene solubility in water, cf.: Plöcker, U.; Knapp, H.; Prausnitz, J. *Ind. Eng. Chem Process Des. Dev.* **1978**, *17*, 324−332.

[21] van Krevelen, D. W. *Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions*; Elsevier: Amsterdam, 1994; pp 535−84.

are insoluble in water; however, **2c** is soluble in 2-propanol. In contrast, **2d** is soluble in water.

In toluene solution, only complex **2b** coordinated by the tertiary amine L = urotropine is catalytically active for ethylene polymerization under the reactions conditions studied (20 °C, 40 atm of ethylene), with a productivity of 1.7×10^4 turnovers. By contrast, in aqueous systems, pyridine and primary amine complexes **2c**,**d** (L = tetraethylammonium pyridine sulfonate or amino-terminated polyethylene glycol) are also catalytically active. Incipient comparmentalization of the lipophilic active species into the polymer particle formed and of L into the aqueous phase appears to retard recombination and thus enhance activity, as observed previously for similar complexes.[10] Complex **2a** with the water-soluble alkylphosphine PTA is inactive in aqueous suspension as well as toluene solution due to the strong coordination of phosohine, in accordance with a previous report on a similar compound.[15]

Polymerization of ethylene by an aqueous SDS solution of the water-soluble complex **2d** affords dispersions with very small particle sizes of 18 nm. Exposure of suspensions of the water-insoluble **2b** to ethylene pressure (in the presence of surfactant to potentially stabilize polymer particles formed) affords polymer suspensions. When **2c** is introduced to an aqueous surfactant solution as a solution in 2-propanol, no visible precipitate is formed. Exposure to ethylene results in formation of polymer particles in the form of a latex, with large particle size. These findings underline that the size of polyethylene particles obtained by catalytic polymerization in aqueous systems is correlated to the degree of dispersion of the catalyst in the initial reaction mixture.

Experimental Section

Methods and Materials. Unless noted otherwise, all syntheses of organometallic compounds were carried out under an argon atmosphere (99.999% pure argon supplied by Messer). Toluene, benzene, and diethyl ether were distilled from sodium, and pentane was distilled from calcium hydride under argon. Demineralized water was deoxygenated by distillation under nitrogen. NMR analysis were conducted on a Varian Unity INOVA 400. Chemical shifts were referenced to the residual solvent signal or, in the case of ^{31}P NMR, to an external standard of 85% H_3PO_4. Elemental analysis were performed up to 950 °C on an Elemental Vario EL. GPC analyses were carried out on a Polymer Laboratories PL220 instrument equipped with Mixed B columns at 160 °C in 1,2,4-trichlorobenzene. Data are referenced to linear polyethylene standards. Dynamic light scattering (DLS) was performed using a Malvern nano ZS (173° backscattering). UV/vis studies were performed on a Carey 50.

1,3,5-Triaza-7-phosphaadamantane (PTA) was prepared according to Daigle.[22] Complex **2d** was synthesized as reported previously.[10]

Synthesis of 2a. In a Schlenk tube, 50 mg (0.244 mmol) of [(tmeda)Ni(CH_3)$_2$] and 41 mg (0.244 mmol) of PTA were combined, and a toluene solution (5 mL) of 213 mg (0.244 mmol) of salicylaldimine **1** was added at −50 °C. The orange solution was allowed to warm to 0 °C gradually over the course of 3 h. The solvent was evaporated under vacuum. The remaining solid was washed three times with 3 mL of pentane at −30 °C, and residual solvent was again removed in vacuum. To remove any unreacted PTA, the complex was washed in air with 10 mL of water. After drying of the sample in vacuo, 170 mg (63%) of an orange solid was isolated.

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ/ppm = 7.88 (s, 4H), 7.82 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 7.70 (s, 2H), 7.05 (m, 1H), 6.96 (m, 2H), 6.86 (s, 1H), 6.75 (d, $^4J_{HH}$ = 2.3 Hz, 1H), 4.1 (m, 6H, PTA), 3.9 (b, 6H, PTA), −1.50 (s, 3H).

^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ/ppm = 167.0, 163.4, 150.9, 149.2, 142.7, 141.2, 133.6, 131.8 (q, $^2J_{CF}$ = 33 Hz), 130.8, 130.6, 126.9, 123.8 (q, $^1J_{CF}$ = 273 Hz), 121.5, 119.3, 96.9, 73.5, 73.2, 50.0, −18.1. ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ/ppm = −51.7. Anal. Calcd for $C_{36}H_{27}F_{12}I_2N_4NiOP$: C, 39.20; H, 2.47; N, 5.08. Found: C, 40.37; H, 2.77; N, 4.85.

Synthesis of 2b. In a Schlenk tube 30.8 mg (0.15 mmol) of [(tmeda)Ni(CH_3)$_2$] and 21.0 mg (0.15 mmol) of hexamethylentetramine were combined and a cold toluene solution (5 mL) of 131 mg (0.15 mmol) of salicylaldimine **1** was added at −50 °C. Over 3 h the red solution was allowed to warm to 0 °C. The solvent was evaporated under vacuum. The solid was washed at −30 °C three times with 3 mL of pentane, and residual solvent was again evaporated under vacuum. To remove excess hexamethylentetramine, the complex was washed in air with 10 mL of water. After drying of the sample in vacuo, 135 mg (83%) of a red solid was isolated.

^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ/ppm = 7.87 (s, 4H), 7.83 (s, 2H), 7.79 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 6.98 (m, 1H), 6.88 (m, 2H), 6.64 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 6.33 (s, 1H), 4.3 (b m, 9H), 3.9 (b m, 3H), −1.40 (s, 3H). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ/ppm = 167.8, 163.0, 150.6, 150.4, 141.5, 141.4, 132.9, 132.0 (q, $^2J_{CF}$ = 33 Hz), 130.7, 130.4, 126.7, 123.6 (q, $^1J_{CF}$ = 273 Hz), 121.4, 120.0, 95.9, 75.0, 73.2, 73.1, −14.7. Anal. Calcd for $C_{36}H_{27}F_{12}I_2N_5NiO$: C, 39.81; H, 2.51; N, 6.45. Found: C, 40.38; H, 2.95; N, 5.88.

Synthesis of 2c. A 1 g amount of 3-pyridinesulfonic acid was dissolved in a mixture of 35 mL of water and 5 mL of methanol, and three drops of a 1% solution of bromothymol blue were added. An aqueous solution of tetraethylammonium hydroxide was added dropwise until the color changed to green. After addition of an equal volume of ethanol, the solvents were removed azeotropically on a rotary evaporator at 50 °C. The residual solid was first dried in vacuum and then stored over phosphorus pentoxide. Tetraethylammonium 3-pyridinesulfonate was obtained quantitatively as a white, hygroscopic solid.

^{1}H NMR (250 MHz, CD_3OD, 25 °C): δ/ppm = 8.93 (dd, $^4J_{HH}$ = 2.2 Hz, $^5J_{HH}$ = 0.8 Hz, 1H), 8.59 (dd, $^3J_{HH}$ = 4.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.19 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 7.51 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.9 Hz, $^5J_{HH}$ = 0.8 Hz, 1H), 3.27 (q, $^3J_{HH}$ = 7.3 Hz, 8H), 1.26 (tt, $^3J_{HH}$ = 7.3 Hz, $^3J_{HN}$ = 1.9 Hz, 12H). ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ/ppm = 150.5, 146.8, 142.5, 134.8, 124.2, 52.4 (t, $^1J_{NH}$ = 3.1 Hz), 6.7.

A 40 mg (0.195 mmol) amount of [(tmeda)Ni(CH_3)$_2$] and 56 mg (0.195 mmol) of tetraethylammonium 3-pyridinesulfonate were placed in a Schlenk tube. A cold solution of 170 mg (0.195 mmol) of the salicylaldimine **1** in 8 mL of toluene was added at −50 °C. The red solution was allowed to warm to 0 °C in 3 h, and the solvent was removed under vacuum. The solid was washed under argon with 20 mL of degassed water. A 67 mg (70%) amount of the red complex was isolated.

^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ/ppm = 8.80 (s, 1H), 8.38 (s, 4H), 8.35 (m, 1H), 8.16 (s, 2H), 8.02 (m, 1H), 7.84 (m, 1H), 7.70 (m, 2H), 7.58 (m, 1H), 7.31 (m, 1H), 7.25 (m, 1H), 3.50 (q, $^3J_{HH}$ = 7.2 Hz, 8H), 1.26 (tt, $^3J_{HH}$ = 7.2 Hz, $^3J_{HN}$ = 1.2 Hz, 12H), −1.00 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6, 25 °C): δ/ppm = 170.6, 165.2, 152.3, 151.7, 150.9, 150.8, 143.6, 143.4, 136.9, 135.0, 133.1 (q, $^2J_{CF}$ = 33 Hz), 133.0, 132.6, 130.4, 129.0, 125.5 (q, $^1J_{CF}$ = 273 Hz), 124.5, 123.1, 121.8, 98.2, 73.2, 54.0 (t, $^1J_{NH}$ = 2.9 Hz), 8.7, −6.3. Anal. Calcd for $C_{43}H_{39}F_{12}I_2N_3NiO_4S$: C, 41.84; H, 3.18; N, 3.40. Found: C, 39.96; H, 3.25; N, 3.37.

Polymerization experiments were carried out in a 250 mL stainless steel pressure reactor with mechanical stirrer (500 rpm) and a heating/cooling jacket controlled by a thermostat connected

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[22] Daigle, D. J.; Pepperman, A. B.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407−408.

to a thermocouple dipping into the reaction mixture. The reactor is connected to a gas supply, which allows for application of constant ethylene pressure and monitoring of the ethylene uptake via mass flow meters.

Polymerization in Toluene. A 90 mL volume of toluene was transferred via cannula into the reactor under an ethylene atmosphere. A 10 μmol amount of the respective complex was dissolved in 10 mL of toluene, affording a homogeneous orange to red solution. This solution was transferred into the reactor, which was then closed and rapidly pressurized with 40 bar of ethylene. The temperature was adjusted to 20 °C. Under a constant pressure of ethylene, the reaction was allowed to proceed. After 60 or 120 min, the ethylene feeding was stopped and the reactor was carefully vented. The content of the reactor was poured into 250 mL of vigorously stirred methanol. After 1 h, the precipitated polymer was filtered out, washed three times with 30 mL of methanol, and dried at 50 °C under vacuum.

Polymerization in Aqueous Media. Due to the different solubility of the complexes in water, the preparation varied for each complex. For suspension-type polymerization, 10 μmol (5 μmol) of the water-insoluble complex **2b**,**c**, respectively, and 0.75 g of SDS were sonicated in 3 mL of water for 10 min. The resulting red slurry and an additional 97 mL of water were transferred via cannula into the reactor under an ethylene atmosphere. For polymerization with complex **2c** with 2-propanol as a cosolvent, 2 mL of 2-propanol was added to 10 μmol of complex **2c**, affording a red, transparent solution. On addition of 10 mL of water, no precipitate was observed. This mixture and a solution of 0.75 g of SDS in 88 mL of water were transferred to the reactor under an ethylene atmosphere. For polymerization with complex **2b** with 2-propanol as a cosolvent, 2 mL of 2-propanol was added to 10 μmol of complex **2b**. After 10 min of sonication, complex **2b** partly dissolved affording an orange solution with an orange precipitate. This mixture and a solution of 0.75 g of SDS in 98 mL of water were transferred to the reactor under an ethylene atmosphere. For polymerization with the water-soluble complex **2d**, a solution of 0.75 g of SDS in 90 mL of water was transferred into the reactor under an ethylene atmosphere. A 10 μmol (20 μmol, respectively) amount of the complex was dissolved in 10 mL of water, affording a homogeneous red solution, and also transferred into the reactor.

The temperature was adjusted to 20 °C, and the reactor was pressurized with 40 bar of ethylene. After 60 or 210 min, respectively, the ethylene feeding was stopped, the reactor was vented, and the latex was filtered through glass wool. An aliqout of 10 mL was poured in 50 mL of vigorously stirred methanol, resulting in precitipation of the polymer. The preciptiate was filtered through a nylon membrane, washed twice with 10 mL of methanol and twice with 10 mL of water, and dried at 50 °C under vacuum.

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Supporting Information Available: Figure S1, giving UV−vis spectra of complex **2d** in water, and Figure S2, giving plots of ethylene consumption over time for polymerization with **2d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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