Insertion Copolymerization of Difunctional Polar Vinyl Monomers with Ethylene

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S *Supporting Information*

ABSTRACT: A single-step synthesis, structural characterization and application of a neutral, acetonitrile ligated, palladium–phosphinesulfonate complex $[\{P^\wedge O\}PdMe(L)]$ ($P^\wedge O = \kappa^2$-P,O—$Ar_2PC_6H_4SO_2O$ with Ar = 2-$MeOC_6H_4$; L = CH_3CN) (3) in coordination/insertion copolymerization of ethylene with difunctional olefin is investigated. In a significant development, complex 3 was found to catalyze insertion copolymerization of industrially relevant 1,1-disubstituted difunctional vinyl monomers for the first time. Thus, insertion copolymerization of ethyl-2-cyanoacrylate (ECA or super glue) and trifluoromethyl acrylic acid (TFMAA) with ethylene produced the corresponding copolymers with 6.5% ECA and 3% TFMAA incorporation. Increasing the concentration of difunctional olefins led to higher incorporation but at the expense of lower activities. These observations indicate that complex 3 tolerates difunctional vinyl monomers and provides direct access to difunctional polyolefins that have not been attempted before.
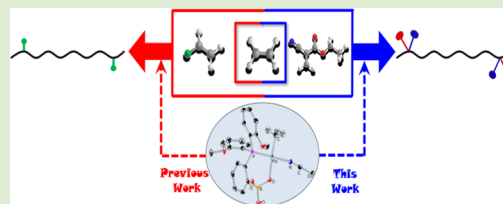
The seminal work of Karl Ziegler and Giulio Natta laid the foundation of coordination/insertion polymerization of olefins.[1] Tremendous progress has been made, and today the world produces roughly 145 million tons of polyolefins annually.[2] Polyethylene (PE) occupies the top position (in terms of production) among the polyolefins, and various grades of PE are commercially produced.[3] PE is inherently a long chain of hydrophobic methylene repeat units without any functional group on the backbone. This partly limits the potential application of PE in adhesives, binders, paints, printing ink, dying, etc. Incorporation of even a small amount of functional groups in PE can significantly enhance these material properties and can further broaden the PE application window. However, due to the high oxophilicity of early transition metal based Ziegler–Natta type catalysts, the functional group on the polar vinyl monomer coordinates to the metal (occupying the vacant site) that generally leads to catalyst poisoning. This limitation has been partly addressed by postfunctionalization of PE,[4] ADMET polymerization of functionalized dienes,[5] or OMRP of polar vinyl monomers with ethylene.[6] However, these strategies suffer from typical issues associated with free radical polymerization. Therefore, it has been a long cherished dream of organometallic chemists to synthesize functionalized PE in a single step via insertion (co)polymerization of ethylene with industrially relevant polar vinyl monomers.[7,8] Despite the significant progress in olefin polymerization, insertion (co)polymerization of functional olefins remained inaccessible until recently.[9]

Apart from a few random attempts, the insertion (co)-polymerization of functional olefins mainly explored two ligand classes, (a) α-diimine ligands[10] and (b) the phosphinesulfonate ligand system.[11] The Brookhart system mainly copolymerizes acrylates with high branching density due to extensive chain-walking.[12] However, the phosphine–sulfonate system displays broad functional group tolerance, and various polar vinyl monomers such as acrylate,[13] acrylonitrile,[14] vinyl acetate,[15] vinyl ethers,[16] acrylic acid,[17] and vinyl chloride[18] could be incorporated. The excellent performance of the phosphinesulfonate system further rose the scientific aspirations, and subsequent investigations focused on structural fine-tuning of the catalyst.[19] Three crucial positions as depicted in Figure 1 were identified, among which the effect of the donor group "D" has been extensively studied (see Figure 1: C1).[20]

The above investigations mainly focused on insertion copolymerization of monosubstituted polar vinyl monomers, wherein one functional group is introduced into the polymer
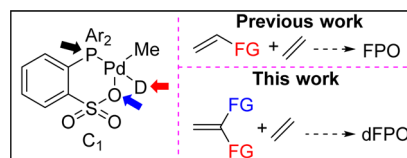

Figure 1. Structural tuning of C1 at designated positions and insertion copolymerization to (a) monofunctional polyolefin (FPO) and (b) 1,1-disubstituted difunctional polyolefin (dFPO).

chain per insertion. A paradigm shift could be achieved if two functional groups can be introduced in a polymer chain per insertion (of a functional olefin), resulting in a doubly polar polymer. Although highly desirable, there are no reports on insertion copolymerization of 1,1-disubstituted difunctional olefins to date.

Herein we report synthesis of the Pd–phosphinesulfonate acetonitrile complex (3) and its implications in insertion copolymerization of ethylene with industrially relevant 1,1-disubstituted difunctional vinyl monomers (see Figure 1; dFPO-difunctional polyolefin) for the first time.

In our pursuit to realize this goal, we attempted synthesis of acetonitrile complex 3 (Scheme 1). Ligand 1 was treated with

Scheme 1. Synthesis of the Acetonitrile-Ligated Pd–Phosphinesulfonate Acetonitrile Complex (3)
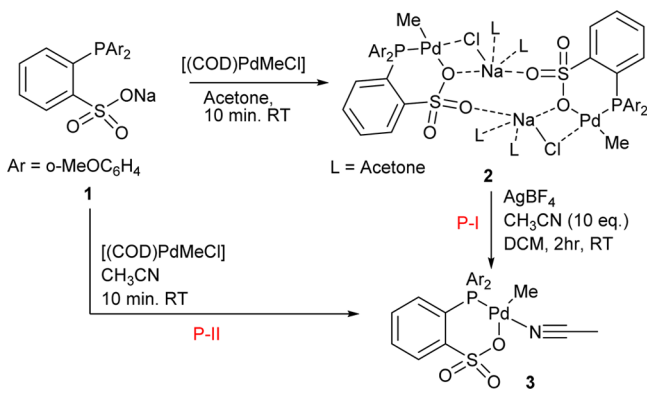
[[(COD)PdMeCl]], and within 10 min the acetone dimer 2 (78%) was obtained.[21] Treatment of AgBF$_4$ in the presence of acetonitrile (10 equiv) afforded the anticipated complex 3 which was isolated in good yield (92%) (Scheme 1, P-I).

An alternative, one-step synthesis was also explored. Reaction of 1 with [(COD)PdMeCl] in acetonitrile directly produced complex 3 (Scheme 1, P-II) in excellent yield (91%). The existence of palladium complex 3 was unambiguously ascertained from spectroscopic and analytical data.[22] ^{31}P NMR of complex 3 displayed a characteristic resonance at 21.1 ppm (SI, S1). In a typical proton NMR, the palladium-bound methyl protons (Pd–CH$_3$) appeared at 0.18 ppm, whereas the corresponding methyl carbon (Pd–CH$_3$) appeared at −2.4 ppm in a ^{13}C NMR spectrum.[23] The NMR findings were further corroborated by electrospray ionization mass spectrum (ESI-MS +ve mode) which displayed a pseudomolecular ion peak at m/z = 544.97 [M-ACN + Na]$^+$ (SI S6). A single-crystal X-ray structure of complex 3 displayed slightly distorted square planar geometry at palladium (Figure 2) which is crystallized in the orthorhombic Pbca space group. The phosphine and the methyl group are mutually cis to each other, whereas the acetonitrile is situated trans to the phosphine.[24]

To shed light on the relative binding strength of donor solvents, 1 equiv of DMSO was added to complex 3, and the changes were tracked using proton and phosphorus NMR. Addition of 1 equiv of DMSO led to complete disappearance of a characteristic Pd–Me (in 3) resonance at 0.18 ppm; concomitantly a new signal at 0.39 ppm appeared in the ^{1}H NMR spectrum (SI S8 and Table S1). The new resonance (at 0.39) can be readily assigned to a previously reported DMSO-coordinated Pd–Me complex.[13] These experiments indicate
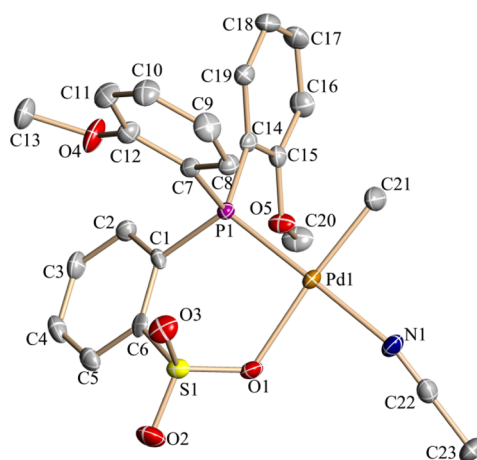
Figure 2. Molecular structure of complex 3. Solvent molecules and H atoms are omitted for clarity, and thermal ellipsoids are drawn at the 50% probability level.

that acetonitrile binding strength is lower or as good as DMSO binding strength.

The performance of 3 in ethylene-functional olefin copolymerization was evaluated, and representative polymerization experiments are summarized in Table 1. The Pd-complex 3 catalyzes copolymerization of acrylonitrile and ethylene at 95 °C. After polymerization, the volatiles were evaporated under reduced pressure to obtain solid material. Insertion copolymerization of acrylonitrile and ethylene produced the desired copolymer with 9.2% acrylonitrile incorporation (Table 1, run 1−1). The performance of 3 in another industrially important monomer, methyl acrylate, was tested. An incorporation of 9.6% was observed at 0.6 mol/L concentration, and the polymer molecular weight was 3100 g/mol (run 1−2). Thus, catalyst 3 tolerated the cyano- as well as acrylate functional groups and produced functional copolymers with reasonable molecular weights. Ethyl-2-cyanoacrylate (ECA) was chosen as a representative 1,1-disubstituted difunctional olefin as both the cyano- and acrylate group are installed within the same olefin. It should be noted that cyanoacrylates are commonly sold under the trade name "Super Glue or Krazy Glue", and the polymers thereof are commercially produced and find applications in various adhesives. It is one of the largest adhesives produced worldwide.[25] Interestingly though, very little information exists on the reactivity of such an industrially highly relevant 1,1-disubstituted difunctional olefin in insertion (co)-polymerization reaction.[26]

Having known that the probability of functional group coordination (acrylate or cyano) to the metal and subsequent catalyst deactivation is increased by 2-fold in ethyl-2-cyanoacrylate, we begin our exploration with a very low (0.03 mol/L) ECA concentration at 5 bar ethylene pressure (Table 1, run 1−3). After polymerization, the reactor content was transferred to a Schlenk flask; volatiles were stripped off; and the solid mass was washed with excess chloroform to yield solid polymeric material.[27,28] The proton NMR of the solid was recorded in deuterated tetrachloroethane at 130 °C in a 10 mm NMR tube, and the amount of incorporation was determined (see Figure 3).[29] Typically, ^{1}H NMR of the copolymer displayed distinct signals at 4.47 (H$_c$), 2.87−2.30 (H$_a$), 1.49, and 1.38 (H$_b$) ppm suggesting ECA incorporation. The proton NMR findings were further corroborated by ^{13}C NMR, which

Table 1. Insertion Copolymerization of Ethylene with Functional Olefins Catalyzed by Complex 3[a]

R = CN/CF₃; FG = COO-Et/H

run	FO (mol/L)	C₂H₄ (bar)	% incor.[b]	yield (g)	Mn (10³ g/mol)[c]	M_w/M_n[c]
1−1	AN (1.2)	5	9.2[d]	0.13	ND	ND
1−2	MA (0.60)	5	9.6[d]	0.39	3.1	1.3
1−3	ECA (0.03)	5	0.3	0.90	4.7	1.5
1−4	ECA (0.06)	5	2.1	0.79	8.2	1.4
1−5	ECA (0.12)	5	4.9	0.87	6.4	1.7
1−6	ECA (0.06)	1	6.5	0.20	5.8	1.6
1−7	ECA (0.06)	10	1.9	1.09	8.3	1.4
1−8[d]	ECA (0.06)	1	2.01	0.21	4.9	1.2
1−9[e]	TFMAA (0.06)	1	0.7	0.37	ND	ND
1−10[e]	TFMAA (3.0)	1	3.0	0.07	2.8	1.2

[a]Reaction conditions: **3** = 20 μmol in DCM, toluene = 50 mL (toluene + functional olefin); temperature = 95 °C, time = 1 h, AN = acrylonitrile, MA = methyl acrylate, ECA = ethyl-2-cyanoacrylate, TFMAA = trifluoromethyl acrylic acid. [b]Incorporation was determined by high-temperature ¹H NMR in C₂D₂Cl₄ at 130 °C. [c]Determined by high-temperature GPC at 160 °C in trichlorobenzene against PS standard; ND = not determined. [d]DMSO complex of type **3** was used as a catalyst. [e]Toluene = 5/3 mL, TFMAA incorporation was determined by high-temperature ¹H NMR in C₂D₂Cl₄ at 130 °C (for run 1−9) and C₆D₆ + TCB (10:90) mixture at 120 °C (for run 1−10).
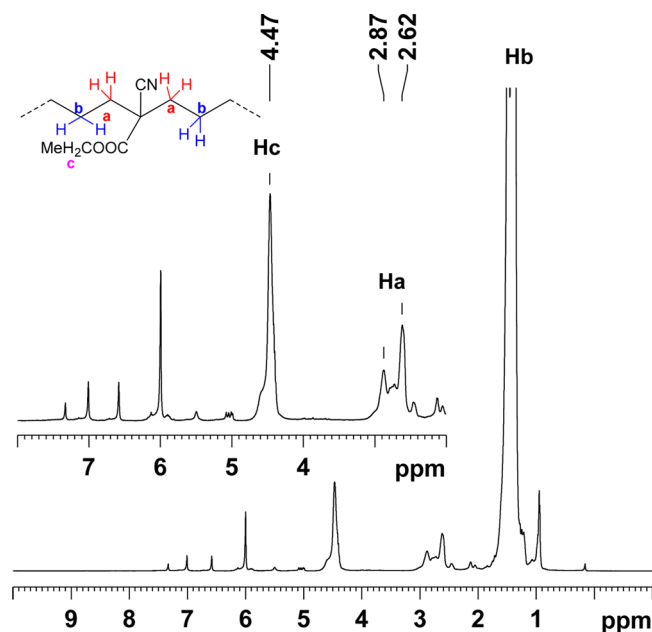

Figure 3. ¹H NMR of the ET−ECA copolymer in C₂D₂Cl₄ at 403 K (Table 1, run 1−6).

revealed a very characteristic signal at 113.7−117.3 ppm that can be assigned to in-chain CN incorporation.[30]

A representative HMBC spectrum (SI, S16D) of a low molecular weight copolymer fraction revealed cross-peaks that can be assigned to −CH₂ protons (diastereotopic in nature) of ECA (2.20−2.80 ppm) and −CH₂ carbons originating from ethylene repeat units (28−30 ppm) (SI sect. 5.2).[22] The 2D C−H correlation spectra displayed cross peaks that established the connectivity between "a" type protons to "a" carbons; "a" protons to "b" type carbon; and vice versa (see Figures S16B−D). In addition to these 2D-NMR experiments, MALDI-ToF-MS (SI S17A−E) also indicated ECA incorporation, and various copolymer fragments could be identified. This was further confirmed by comparing the reported ET−ECA copolymer produced by the radical polymerization method[30]

as well as control experiments.[31] Thus, ¹H NMR of a copolymer obtained in run 1−3 revealed a very low incorporation of 0.32%. Increasing the concentration of ECA resulted in increased incorporation (run 1−3 to 1−5). On the other hand, increasing ethylene pressure (from 1 to 10 bar) led to decreased ECA incorporation (run 1−6, 1−4, and 1−7). Thus, the highest incorporation of 6.5% could be achieved at ambient ethylene pressure and 0.06 mol/L ECA concentration. The rigorous washing protocol may wash out the low molecular weight fraction and might lead to lower polydispersity in some cases. The DMSO complex of type **3** displayed similar reactivity in the insertion copolymerization of 1,1-disubstituted functional olefin, along with ca. 2.% incorporation (run 1−8). It is most likely that ethylene insertion in the Pd−Me bond leads to chain propagation, or the 2,1-/1,2-insertion of ECA in the Pd−Me bond initiates the polymerization, as the three initiating groups (IG-1, IG-2, and IG-3) could be detected by ¹³C NMR (SI section 6). To further strengthen our hypothesis, we investigated insertion copolymerization of another 1,1-disubstituted functional olefin (trifluoromethyl acrylic acid: TFMAA). About 0.7% TFMAA incorporation was observed at a very low TFMAA concentration (0.06 mol/L run 1−9). However, increased incorporation of 3% could be achieved at higher TFMAA concentration (3.0 mol/L run 1−10). A characteristic proton resonance at 2.1 ppm indicated formation of an ethylene−TFMAA copolymer (SI S48). Furthermore, the absence of characteristic proton resonance at 3.4 ppm ruled out the presence of a TFMAA homopolymer (SI S50).[32] An ¹⁹F NMR spectrum (Figure 4) of the oligomeric fraction (accessed by suspending the copolymer in excess chloroform) revealed characteristic signals at −65.1, −66.1, −66.7, and −68.4 ppm. These chemical shifts are similar to those reported for ethylene−trifluoropropene copolymers (the closest copolymer known)[33] and can be readily assigned to ET−TFMAA oligomers. The absence of a characteristic splitting pattern and signal broadening hampered further analysis, and the resonances can be tentatively assigned to structure A−D (SI S51). The NMR findings were further supported by IR, which revealed a characteristic (C=O) band at 1710 cm⁻¹ (SI S49), that can be ascribed to acidic CO and is in line with earlier
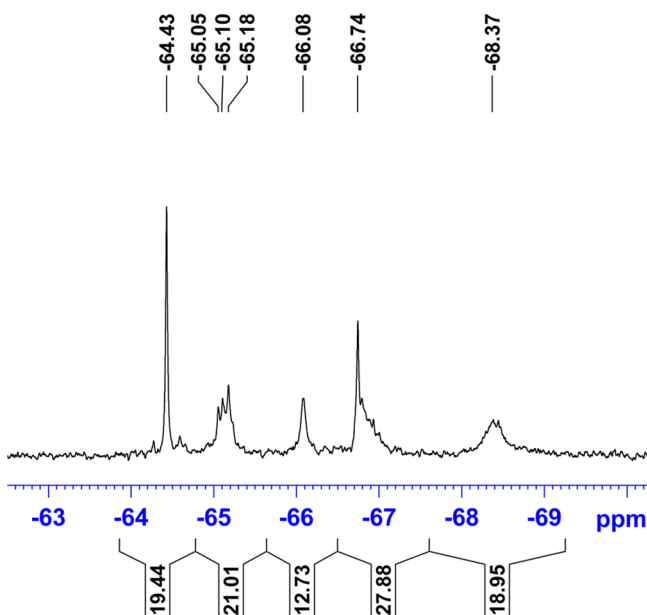
Figure 4. ^{19}F NMR (^1H decoupled) of the ET–TFMAA oligomeric fraction recorded at 343 K in $C_2D_2Cl_4$.

reports. Furthermore, a typical –OH band was observed at 3368 cm^{-1}, which, together with CO band, indicates the existence of a carboxylic group in the copolymer. MALDI-ToF-MS spectra of the copolymer also indicated TFMAA incorporation and various copolymer fragments could be identified (see Table S6 and SI S52A–C). Interestingly, TFMAA does not homopolymerize under the current polymerization conditions and thus rules out the possibility of homopolymer contamination.[22] The reduced polymer yields with increasing ECA/TFMAA concentration and low molecular weights indicate reversible inhibition of polymerization, due to the coordination of functional groups located on the 1,1-disubstituted olefin to the metal. However, the fact that the copolymers could be obtained suggests that the presence of 1,1-disubstituted functional olefins does not necessarily lead to detrimental catalyst decomposition.

In summary, a single-step synthetic protocol to access an acetonitrile-ligated Pd–phosphinesulfonate complex (**3**) was established. Our investigations demonstrate that insertion copolymerization of ethylene with 1,1-disubstituted difunctional olefin is possible. Complex **3** tolerates the two functional groups located within the same polar vinyl monomer and successfully copolymerizes ECA and TFMAA with ethylene. A combination of multinuclear NMR, MALDI-ToF-MS, and control experiments suggest in-chain ECA incorporation. High-temperature NMR investigations revealed an unprecedented 6.5% incorporation of ethyl-2-cyanoacrylate and 3% incorporation of TFMAA in a copolymer. These copolymers represent a novel class of functional polyolefins with two functional moieties (cyanoacrylate or fluoro-acrylic acid) incorporated at a time. Investigations on the insertion copolymerization of other industrially relevant 1,1-disubstituted polar vinyl monomers and the mechanism are currently in progress.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.5b00562.

Synthetic protocols, text, figures, tables, method to determine percentage functional olefin incorporation, spectroscopic and analytical data, CIF files, and crystallographic data/processing method for **3** (CCDC 1012218) (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(22) See Supporting Information for spectroscopic, analytical data, and more details.

(23) Similar chemical shift values (^{31}P, ^{1}H, ^{13}C NMR) have been observed for pyridine, lutidine, DMSO complexes; see for example reference 13.

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(28) To avoid radical polymerization of ethyl-2-cyanoacrylate, radical scavenger BHT was added to the polymerization reactor. See Supporting Information.

(29) The functional olefin incorporation was determined by ^{1}H NMR; a detailed calculation method is presented in the Supporting Information (SI, section 5).

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(32) First radical homopolymerization of TFMAA was reported in 2013 by Patil et al. The chemical shift for -CH$_2$- protons next to the quaternary carbon was reported to be 3.4 ppm. See: Patil, Y.; Hori, H.; Tanaka, H.; Sakamoto, T.; Ameduri, B. *Chem. Commun.* **2013**, *49*, 6662.

(33) Ethylene−trifluoropropene copolymerization has been recently reported by Lanzinger et al. ^{19}F NMR of the copolymer displayed a resonance at −71.4 ppm, which is assigned to in-chain −CF$_3$ groups. Given the similarity between this copolymer and the herein investigated ET−TFMAA oligomers, the observed chemical shift can be assigned to groups A−D. See: Lanzinger, D.; Giuman, M. M.; Anselment, T. M. J.; Rieger, B. *ACS Macro Lett.* **2014**, *3*, 931.