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Articles

Polymerization of Phenylacetylene Catalyzed by Diphosphinopalladium(II) Complexes

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ABSTRACT: Cationic bis(phosphino)palladium complexes were generated in situ from the reaction of (dppf)PdCl(CH_3), (dippf)PdCl(CH_3), (dppe)PdCl(CH_3), (dppf)PdCl_2, (dippf)PdCl_2, and (dppe)PdCl_2 (dppf = bis(diphenylphosphino)ferrocene, dippf = bis(diisopropylphosphino)ferrocene, and dppe = bis(diphenylphosphino)ethane) with AgOTf. The dppf− and dippf−paladium complexes catalyzed the polymerization of phenylacetylene (PA) whereas the dppe analogues formed phenylacetylene oligomers. Solvent and temperature effects on polymerization were investigated and showed that best test polydispersity for phenylacetylene (PPA) formation was a 1:1 $CH_2Cl_2-CH_3CN$ solvent mixture and room temperature.

Introduction

A variety of substituted acetylenes are polymerized using transition metal complexes as catalysts forming polymers with alternating single and double bonds along the main chain, which brings about unique physical properties such as photoconductivity,[1] third-order nonlinear optical response (NLO),[2] liquid crystallinity,[3] magnetic susceptibility,[4] and gas permeability.[5] The majority of the catalysts reported for the polymerization of acetylenes can be divided into two main groups on the basis of the polymerization mechanism. namely, metathesis and insertion polymerization. Groups 5 and 6 transition metals are used for the polymerization of mono- and disubstituted acetylenes, which proceed via the metathesis polymerization mechanism. Catalysts for the polymerization of substituted acetylenes, especially for substituted phenylacetylenes, are mainly based on rhodium metal,[6] which form high molecular weight polymers quantitatively with low polydispersity through an insertion mechanism. There are however other acetylene polymerization catalysts based on group 4 metallocenes[7] such as Cp_2TiCl_2, Cp_2ZrCl_2, and Cp_2HfCl_2/R_xAlCl_{3-x}, as well as nickel[8] and palladium catalysts.[9] The only example of a palladium catalyst that forms high molecular weight ($M_n = 9000$) poly(phenylacetylene) (PPA) is $[Pd(NCCH_3)_4](BF_4)_2$.[10] This catalyst is also used for the copolymerization of phenylacetylene and CO.[11]

To the best of our knowledge, there have been no reports on the polymerization of acetylene derivatives using $[(P-P)Pd^{II}]^+$ and $[(P-P)Pd^{II}]^{2+}$ catalysts. In this paper, we report on polymerization of phenylacetylene (PA) catalyzed by $[(P-P)Pd(CH_3)(NCCH_3)]^+$ and $[(P-P)Pd(NCCH_3)_2]^{2+}$ to form poly(phenylacetylene). The effect of solvent and different catalysts as well as different temperatures on the polymerization of phenylacetylene is also reported.

Experimental Section

All manipulations were performed under a dry, deoxygenated nitrogen atmosphere using standard Schlenk techniques. IR spectra were recorded as KBr pellets on a Perkin Elmer Paragon 1000PC FT-IR spectrometer. NMR spectra were recorded on a Gemini 2000 instrument (^{1}H at 200 MHz, ^{13}C at 50 MHz). The chemical shifts are reported in δ (ppm) referenced to residual protons and ^{13}C signals of deuterated chloroform as internal standard. The number- and weight-average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) of polymers were determined by gel permeation chromatography (THF, 30 °C, rate = 1.0 cm^3/min) with PL-MIXED-C columns (2) using polystyrene standards. Dichloromethane was dried over P_2O_5, distilled, and stored under a nitrogen atmosphere. Acetonitrile was dried over A4 molecular sieves. The catalyst precursors (dppf)PdCl(CH_3),[12] (dppe)PdCl(CH_3),[12] (dippf)PdCl(CH_3),[12] and (dppf)PdCl_2[13] were prepared by literature methods. Phenylacetylene (98%) was obtained from Aldrich and used as received.

Polymerization of Phenylacetylene Using Solvent Mixture of CH_2Cl_2 and CH_3CN. A typical experiment (experiment 3, Table 1) is given as follows. A solution of silver triflate (0.036 g, 0.14 mmol) in 20 mL of $CH_2Cl_2-CH_3CN$ (1:1) was added to a solution of (dppf)PdCl(CH_3) (0.10 g, 0.14 mmol) in 20 mL of degassed CH_2Cl_2 for a final composition of (3:1). A white precipitate of AgCl appeared immediately. The mixture was stirred for 5 min and filtered to give a yellow solution (catalyst formed in situ), followed by the addition of 0.78 mL (7.0 mmol, 50 equiv) of phenylacetylene. The resultant solution was stirred for 24 h. The yellow solution changed to dark red with the formation of a yellow precipitate. The yellow precipitate was isolated by filtration (0.15 g). After evaporation, the filtrate was observed to give a dark red residue, which was recrystallized from CH_2Cl_2 and methanol to give 0.58 g of a yellow powder. The combined yield of the yellow product was 0.73 g; yield = 97%. The product was characterized by ^{1}H NMR, ^{13}C{^{1}H} NMR, FT-IR, and GPC analysis.

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Table 1. Polymerization of Phenylacetylene Catalyzed by (P−P)Pd^{II} Complexes^a

		reaction conditions					
exp	cat	solvent	*t* (h)	temp (°C)	yield (%)	M_n	M_w/M_n
1	**1a**	CH_2Cl_2:CH_3CN = 1:1	24	r.t.	81	12000	1.58
2	**1a**	CH_2Cl_2:CH_3CN = 5:3	24	r.t.	91	10000	2.55
3	**1a**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	97	7275	2.10
4	**1a**	CH_2Cl_2:CH_3CN = 7:1	24	r.t.	100	4500	2.33
5	**2a**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	78	3582	2.50
6	**3a**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	28	500	1.40
7	**1b**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	90	17707	1.70
8	**2b**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	49	4321	1.55
9	**3b**	CH_2Cl_2:CH_3CN = 3:1	24	r.t.	22	627	1.13
10	**1a**	CH_2Cl_2:CH_3CN = 3:1	24	40	100	3500	6.86
11	**2a**	CH_2Cl_2:CH_3CN = 3:1	24	40	94	3896	1.60
12	**3a**	CH_2Cl_2:CH_3CN = 3:1	24	40	28	715	1.02
13	**1a**	CH_2Cl_2	24	r.t.	49	600	1.67
14	**1a**	THF	24	r.t.	100	4500	1.71
15	**1a**	toluene	24	r.t.	100	6700	1.64
16	**1a**	toluene	2	40	80	4000	2.00

^{a} All reactions were run in 40 mL of solvent: [Pd] = 3.5×10^{-3} mol/L; Pd/PA = 1:50. Here r.t. = room temperature.

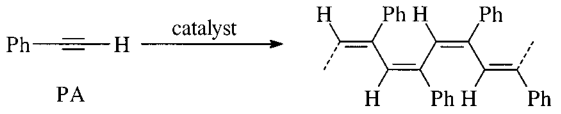
General Procedure for Polymerization of Phenylacetylene Using Pure Solvent (CH_2Cl_2, THF, or Toluene). To a solution of (dppf)PdCl(CH_3) (0.10 g, 0.14 mmol) in 20 mL of degassed CH_2Cl_2, was added a solution of silver triflate (0.036 g, 0.14 mmol) in 20 mL of CH_2Cl_2−CH_3CN (1:1) (experiment 15, Table 1). A yellow solution was obtained after the removal of AgCl. The solvent was removed under high vacuum, and 40 mL of toluene was added to form a homogeneous solution. Phenylacetylene (0.78 mL, 7.0 mmol, 50 equiv) was added and the reaction stirred for 24 h. The yellow solution changed to dark red. The solvent was removed to give a dark red residue, and recrystallization from CH_2Cl_2 and methanol gave 0.74 g of a yellow powder, which was characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, FT-IR, and GPC analysis.

The major products of experiments 1−5, 7, 8, 10, 11, and 14−16 were polymers. ^1H NMR ($CDCl_3$): δ 6.955 (s, Ph), 6.645 (d, Ph), 5.843 (s, vinyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.88 (s, quaternary C of the main chain), 139.34 (s, *ipso*-C of Ph), 131.82 (s, vinyl), 127.78 (s, *o*-C of Ph), 127.57 (s, *m*-C of Ph), 126.70 (s, *p*-C of Ph). FT-IR (KBr, cm^{-1}): 3076 (s), 3053 (s), 3020 (s), 1595 (s), 1573 (s), 1487 (vs), 1442 (s), 1073 (s), 1027 (s), 882 (br, s) 753 (s), 735 (s). For GPC, see Table 1.

The major product of experiments 6, 9, 12, and 13 were oligomers. ^1H NMR ($CDCl_3$): δ 6.746−7.579 (m) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 128.28 (m). FT-IR (KBr, cm^{-1}): 3055 (m), 3021 (m), 1684 (s), 1597 (s), 1572 (s), 1491 (vs), 1073 (s), 1029 (vs), 882 (m), 756 (br, s). For GPC, see Table 1.

Results and Discussions

Polymerization of Phenylacetylene Catalyzed by (P−P)Pd^{II} Complexes. The polymerization of phenylacetylene (PA) was examined with a variety of (P−P)Pd^{II} catalysts: $[(dppf)Pd(CH_3)(NCCH_3)]^+OTf^-$ (**1a**), $[(dippf)Pd(CH_3)(NCCH_3)]^+OTf^-$ (**2a**), $[(dppe)Pd(CH_3)(NCCH_3)]^+OTf^-$ (**3a**), $[(dppf)Pd(NCCH_3)_2]^{2+}OTf^-$ (**1b**), $[(dippf)Pd(NCCH_3)_2]^{2+}(OTf)_2^-$ (**2b**), and $[(dppe)Pd(NCCH_3)_2]^{2+}(OTf)_2^-$ (**3b**) (P−P = 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,1′-bis(diisopropylphosphino)ferrocene (dippf), and 1,2-bis(diphenylphosphino)ethane (dppe)). In all cases the active catalysts were generated by the removal of one or two chloride atoms with the silver triflate in a CH_2Cl_2−CH_3CN mixture, followed by the weak coordination of acetonitrile. Even in experiments where the polymerization was performed in single solvents, the active catalysts were first generated as described above and the CH_2Cl_2−CH_3CN mixture was removed before the single solvent was added. Hence even in the nonpolar toluene, the active catalyst is stabilized by remnants of CH_3CN from the CH_2Cl_2−CH_3CN solvent mixture which was used to generate the active catalyst, though it should be easy for the CH_3CN to be displaced by the monomer. The polymerization reactions were performed with catalyst/monomer ratios of 1:50 either in CH_2Cl_2−CH_3CN solvent mixtures or neat CH_2Cl_2, THF, or toluene. In all reactions, the dark brown solids, which represent the combined yield of both polymers and oligomers, were obtained generally high yields (Table 1). The brown solids contained a yellow methanol-insoluble component, which was the major product in most reactions, and a brown methanol-soluble component. Recrystallization of the initial brown solids from CH_2Cl_2−methanol gave yellow solids of poly(phenylacetylene), and hence the polymerization can be described by eq 1.



(1)

PA

PPA

Polymers from experiments 1−5, 7, and 11−13 showed two sharp absorption peaks in the infrared spectra at 753 and 735 cm^{-1} and a broad peak at 882 cm^{-1} characteristic of *cis*-poly(phenylacetylene).[14] The ^1H NMR spectra of the polymers also showed a sharp singlet due to the vinylic protons in the polymer at δ 5.84 in addition to a set of broad peaks at δ 6.64 (2H, ortho) and δ 6.96 ppm (3H, meta and para), which are associated with a regular head to tail structure of a cis−transoidal structure.[6b,14] The high stereoregularity of the polymer is also supported by the $^{13}C\{^1H\}$ NMR spectra, in which only one set of signals of PPA was observed. Furlani[15] et al. have assigned a cis−transoidal structure to PPA from Rh(I)-catalyzed PA based on a similar ^{13}C NMR spectrum.

In reactions that were catalyzed by **1a**, **2a**, and **3a**, ^1H and ^{13}C NMR of products showed the presence of weak methyl peaks, indicative of methyl end groups in these products. For example poly(phenylacetylene) obtained from **1a** had methyl peaks at 1.258 and 30.85 ppm in the ^1H and ^{13}C NMR, respectively. On the basis of the NMR data the mechanism for the polymerization would involve an initial coordination of phenylacetylene monomer and subsequent insertion of the coordinated phenylacetylene into the Pd−C bond. A similar mechanistic route is known for the reaction of acetylenes with cationic palladium(II) methyl complexes.[16]

Effect of Catalysts on Polymerization. Two types of catalysts were used. The first type was $[(P{-}P)Pd(CH_3)(NCCH_3)]^+OTf^-$ and the second was $[(P{-}P)Pd(NCCH_3)_2]^{2+}(OTf)_2^-$. There were variations in the bidentate phosphine ligands as well (Table 1). Catalysts **1a**, **2a**, **1b**, and **2b** showed high activity toward the polymerization of PA; however, **3a** and **3b** only showed low activity toward polymerization and the main products were oligomers (Table 1). In general, catalytic activity decreased in the following order: **1a** > **2a** >**1b** > **2b** ≫ **3a** > **3b**. The order of decreasing catalytic activity by these catalysts is associated with the nature of the diphosphino ligands. The steric bulk and flexibility of the diphosphino ligand backbone would contribute to the degree of catalytic activity if the polymerization proceed via an insertion mechanism. Two

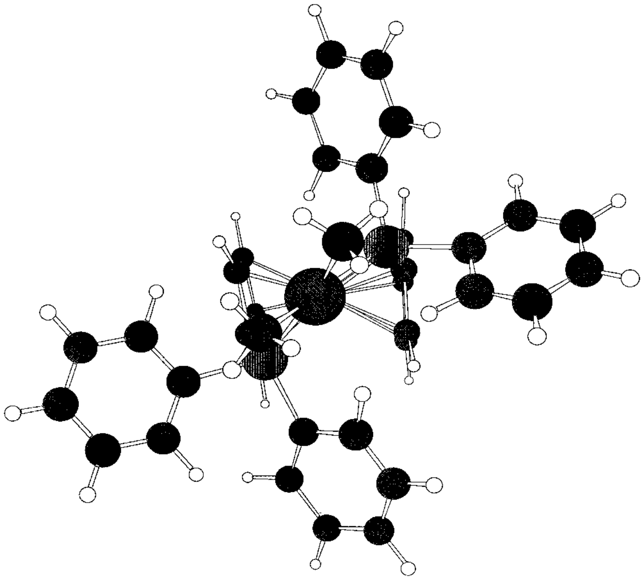


Figure 1. View of Sybyl force field minimized structure for dimethyl analogue of **1a** looking at the dimethylpalladium center (ferrocene iron hidden).

mechanistic pathways are known for PA polymerization, namely metathesis and insertion of an alkyne into a metal−alkyl bond. The latter is readily diagnosed by NMR spectroscopy if the active catalyst contains a metal-alkyl bond. For catalysts **1a** and **2a**, ^{13}C NMR spectra of polymers and oligomers isolated from our reactions showed alkyl peaks at 1.258 and 30.85 ppm, respectively, indicating that polymerization proceeds via an insertion mechanism. The steric bulk of dippf compared to dppf means initial coordination of PA to Pd before insertion into a Pd−C bond is more facile for **1a** compared to **1b**. The lower activity of **3a** and **3b**, compared to the other catalysts, can be attributed to the flexibility of the diphosphine backbone. A more flexible backbone for dppf and dippf ligands compared to dppe makes the dppe complexes less accessible for PA coordination. Literature reports indicate that diphosphino ligands such as dppp (1,3-bis(diphenylphosphino)-propane) and dppb (1,4-bis(diphenylphosphino)butane), with flexible backbones, have phenyl groups that can bend away from coordination sites of incoming ligands.[15] Theoretical calculations[17] on model compounds also indicate that ligand backbone flexibility could enhance insertion reactions.

As shown in Figure 1, for a dimethyl palladium analogue of **1a**, the only stable conformer (based on molecular mechanics using the Sybl force field[18]) has pseudo-C_2 symmetry. As dppe has a skew conformation[19] access to **3a** and **3b** by PA would be hindered. Hence, the nature of the bidentate phosphine determines both the mechanism of reaction and the activity of the catalyst.

Effect of Reaction Conditions on Polymerization. The polymerization was performed in several mixtures of CH_2Cl_2/CH_3CN in different ratios and in neat CH_2Cl_2 and THF as well as toluene (Table 1). At room temperature, the optimum solvent mixture was found to be 7:1, which gave a 100% yield. Increasing the proportion of CH_3CN gave both high molecular weight polymers and low polydispersity. When single solvents were used for polymerization, both THF and toluene gave high activities, but the activity in CH_2Cl_2 was poor and only oligomers were found. The presence of coordinating solvents like CH_3CN and THF is crucial in stabilizing the cationic active catalyst before coordination with PA. It is, however, not clear why polymerization in the noncoordination toluene was high activity. Generally polymerization in pure solvents yielded low molecular weight polymers as well as polymers of high polydispersity. A reasonable explanation for this phenomenon is that the cationic palladium center requires coordinating solvent for stability, but if that solvent is in excess, the rate of monomer π-complex formation is insufficient for polymerization to proceed at a reasonable rate. Further studies are underway to resolve these issues.

When polymerization reactions were performed at 40 °C, they were faster and always quantitative. The polymers produced were of low molecular weight and high polydispersity. In the case of **3a**, higher temperature produced only oligomers. It therefore shows that to produce high molecular weight polymers the use of pure solvents and operation at high temperature must be avoided.

Conclusions

Two types of cationic palladium catalysts, $[(P{-}P)Pd(CH_3)(NCCH_3)]^{+}OTf^{-}$ and $[(P{-}P)Pd(NCCH_3)_2]^{2+}(OTf)_2^{-}$, were readily generated in situ which catalyzed the polymerization and oligomerization of phenylacetylene. The highest moleculat weight polymer was obtained from a 1:1 $CH_2Cl_2{-}CH_3CN$ mixture at room temperature and appears to be the best conditions for polymerization. Complexes with dppe-ligand-catalyzed oligomer formation under all conditions, but the other phosphine−palladium complexes also catalyzed oligomer formation when the pure CH_2Cl_2 was used as solvent.

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