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Water-Soluble Palladium(II) Compounds as Catalysts for the Alternating Copolymerization of Olefins with Carbon Monoxide in an Aqueous Medium

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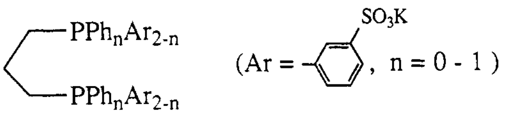
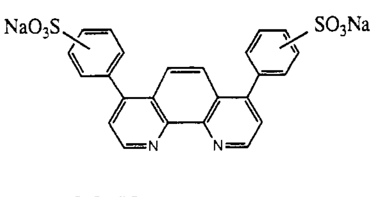
The use of water as a reaction medium in place of organic solvents is of great current interest from the standpoint of environmentally benign synthesis of organics and polymers since the use of the former would significantly decrease harmful emissions, as well as cut costs associated with solvent recycling. A number of important transition-metal-catalyzed reactions such as hydrogenation, hydroformylation, and olefin metathesis, have been reported to proceed in an aqueous medium.[1] Herein, we describe the synthesis of several new water-soluble palladium(II) complexes that catalyze the alternating copolymerization of olefins with carbon monoxide in water.

We and others have previously reported on the palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide in organic solvents.[2] These reports showed that many of the highly active catalysts for the reaction, such as $[Pd(dppp)(MeCN)_2](BF_4)_2$ (dppp = $Ph_2P(CH_2)_3PPh_2$) and $[Pd(phen)(MeCN)_2](BF_4)_2$ (phen = 1,10-phenanthroline), were tolerant to oxygen and moisture, indicating that the copolymerization reaction was compatible with an aqueous medium. Indeed, as described herein, by using the potassium salt of sulfonated dppp (dppp-SO_3K) and the disodium salt of 4,7-diphenyl-1,10-phenanthrolinedisulfonic acid (phen-SO_3Na) as ligands (see structures below), it is possible to synthesize water-soluble palladium(II) compounds that are effective catalysts for the alternating copolymerization of olefins with carbon monoxide in pure water.



dppp-SO_3K



phen-SO_3Na

The water-soluble chelating ligand, dppp-SO_3K, was prepared through direct sulfonation of dppp with fuming sulfuric acid followed by neutralization with an aqueous potassium hydroxide solution.[3] In a typical reaction, dppp (1.0 g) was dissolved in 20% fuming sulfuric acid (8.0 mL) while maintaining the temperature below 24 °C, and the reaction mixture was allowed to stir at ambient temperature for 3 days. At the end of this period, the formation of the water-soluble sulfonic acid derivatives was confirmed by adding the reaction mixture to water, which resulted in a clear solution without any precipitate. The $^{31}P\{^1H\}$-NMR spectrum of the mixture in D_2O showed a broad resonance at 4.97 ppm; no resonance for phosphine oxide was detected. Note that, although the sulfonation of the phenyl groups of dppp was faster at elevated temperatures (70 °C or above), such reaction conditions also caused substantial oxidation of the phosphine to the corresponding phosphine oxide.

The aqueous solution of the sulfonic acid derivatives of dppp obtained through the procedure described above was then cooled in an ice bath and slowly neutralized with an aqueous solution of KOH. After removal of water from the resultant mixture, the potassium salts of the sulfonated dppp, dppp-SO_3K (0.70 g), were isolated as a white solid through Soxhlet extraction with methanol followed by evaporation of the solvent under vacuum. The dppp-SO_3K obtained was a mixture of sulfonated derivatives, with major component being $Ar_2P(CH_2)_3PAr_2$($Ar = -C_6H_4$-*m*-SO_3K). The ^1H-NMR (D_2O) spectrum showed absorptions at 2.10 (4H, m) and 1.33 (2H, m) ppm due to the bridging $-CH_2CH_2CH_2-$ group and resonances at 7.17-7.61 ($\approx$17H, m) due to the phenyl and sulfonated phenyl groups. The $^{31}P\{^1H\}$-NMR (D_2O) spectrum exhibited one major absorption (singlet) at -15.22 ppm and two small resonances at -15.31 and -16.27 ppm. The latter two absorptions was due to the presence of $Ar_2P(CH_2)_3P(Ar)(Ph)$. This was supported by the results of elemental analysis, indicting a S/P molar ratio for dppp-SO_3K of 1.9. Note that the dppp-SO_3K synthesized was free of K_2SO_4 (no K_2SO_4 was obtained after extended extraction of pure K_2SO_4 with methanol).

The catalyst, $[Pd(dppp\text{-}SO_3K)(H_2O)_2](BF_4)_2$ (**1**), was formed in situ by dissolving a 1:1 molar mixture of $[Pd(MeCN)_4](BF_4)_2$[4] and dppp-SO_3K in pure water. Compound **1** was found to catalyze the alternating copolymerization of ethylene and carbon monoxide. Typically, 3.4×10^{-2} mmol of **1** in 7.0 mL of water was placed in a 125-mL Parr bomb, which was charged with 500 psi of ethylene and 500 psi of carbon monoxide. The reaction mixture was allowed to stir at 50 °C for 22 h. At the end of this period, the remaining gases were vented and the formed insoluble ethylene-carbon monoxide (E-CO) copolymer (1.7 g) was filtered, washed with water, and dried under vacuum. Productivity: 470 g of copolymer/g of Pd. The NMR spectra indicated that the E-CO copolymer had a strictly alternating structure. ^1H-NMR (CF_3COOD): δ 3.02 (s). $^{13}C\{^1H\}$-NMR (CF_3COOD): δ 217.02, 38.03.

The compound $[Pd(phen\text{-}SO_3Na)(H_2O)_2](BF_4)_2$ (**2**), prepared by dissolving a 1:1 molar mixture of $[Pd(MeCN)_4](BF_4)_2$ and commercially available phen-SO_3Na in water, was also found to be an active catalyst for the alternating

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copolymerization of ethylene with carbon monoxide in an aqueous solution. The catalytic activity of **2** was, however, lower than that of **1**. Productivity with **2**: 80 g of copolymer/g of Pd under the same reaction conditions.

Compound **1** was also an effective catalyst for the alternating copolymerization of propylene with carbon monoxide and the terpolymerization of ethylene, propylene, and carbon monoxide in an aqueous solution. Employing 36 g of propylene and 1000 psi of carbon monoxide, the productivity of the catalyst at 60 °C in 18 h for the copolymerization of propylene and carbon monoxide was 200 g of copolymer/g of Pd. The formed propylene–carbon monoxide (P–CO) copolymer had a molecular weight of 1.4×10^4 versus polystyrene standards. It had an atactic alternating structure with a mixture of 20% head-to-head, 60% head-to-tail, and 20% tail-to-tail arrangements in the polymer backbone, which was essentially the same as the P–CO copolymer formed using $[Pd(dppp)(MeCN)_2](BF_4)_2$ as the catalyst.[5] ^1H-NMR ($CDCl_3$): δ 2.90–3.21 (2H, br), 2.33–2.50 (1H, br), 1.01–1.10 (3H, br). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 215.41, 211.80, 207.57, 44.53, 40.24, 16.25 (all multiplets).

The ethylene–propylene–carbon monoxide (E–P–CO) terpolymer, prepared using 38 g of propylene, 500 psi of ethylene, and 500 psi of CO, consisted of alternating E–CO and alternating P–CO units randomly distributed in the polymer backbone.[5] Productivity: 170 g of copolymer/g of Pd in 44 h at 50 °C. The ratio of E–CO units to P–CO units was 9.0 based on the ^1H-NMR spectrum. ^1H-NMR (CF_3COOD): δ 2.93 (s), 2.6–3.2 (br), 1.19 (d, $J = 6.5$ Hz). $^{13}C\{^1H\}$-NMR (CF_3COOD): δ 219.31, 217.23, 47.63, 42.87, 38.22, 17.54. The terpolymer was insoluble in common organic solvents such as chloroform, methylene chloride, and THF but dissolved in acidic solvents such as trifluoroacetic acid and 1,1,1,3,3,3-hexafluoroisopropyl alcohol.

The catalyst productivity observed in water was much lower than that usually observed in nonaqueous solvents. For example, using $[Pd(dppp)(MeCN)_2](BF_4)_2$ as catalyst, a productivity of 28 kg of copolymer/g of Pd was observed for the alternating copolymerization of ethylene and carbon monoxide carried out at 70 °C for 19 h in a 2:1 (v/v) $MeNO_2$–MeOH mixture as solvent (compound **1** itself could not be employed in the latter solvent system because of its insolubility).[6] Similarly, the productivity for the propylene–carbon monoxide copolymerization at 50 °C using this system was 4–5 times higher than that observed for the water-based system.[6] Two factors may be responsible for the significantly lower polymerization rates observed in an aqueous medium. First, water coordinates more strongly to the Pd(II) ion than do alcohols, nitriles, or nitroalkanes[7] that are commonly present in organic solvent-based copolymerization systems.[2] Thus, in water, the catalyst center is less accessible to the incoming monomers. Second, and more importantly, the solubilities of the nonpolar monomers are much lower in water than in organic solvents.

The generally accepted mechanism for the palladium(II)-catalyzed alternating copolymerization of olefins with carbon monoxide involves alternate insertions of olefin and carbon monoxide into an initial Pd–H bond.[2a] In the present case, it appears that the initial palladium hydride was formed from water via the water–gas shift reaction (eq 1).[8] Metal hydrides are known to be intermediates in this reaction. Thus, we observed the deuteration of the terminal group of the E–CO copolymer when the copolymerization was carried out in D_2O instead of H_2O. The ^2H-NMR spectrum of the resultant copolymer in $(CF_3)_2CHOH$ showed a resonance at 1.12 ppm due to the terminal methyl of the ethyl end group. In addition, the formation of $^{13}CO_2$ was observed when ^{13}CO alone was allowed to react with D_2O in the presence of **1**. ^{13}C-NMR (D_2O) of $^{13}CO_2$: δ 124.68.

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{1}$$

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References and Notes

(1) Reviews: (a) Herrmann, W. A.; Kohlpainter, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524. (b) Kalck, P.; Monteil, F. *Adv. Organomet. Chem.* **1992**, *34*, 219. (c) Barton, M.; Atwood, J. D. *J. Coord. Chem.* **1991**, *24*, 43. Also: (d) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

(2) (a) Review: Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. More recent publications: (b) Bronco, S.; Consiglio, G.; Hutter, R.; Batistini, A.; Suter, U. W. *Macromolecules* **1994**, *27*, 4436. (c) Jiang, Z.; Adams, S. E.; Sen, A. *Macromolecules* **1994**, *27*, 2694. (d) Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. *J. Am. Chem. Soc.* **1994**, *116*, 3641. (e) Borkowsky, S. L.; Waymouth, R. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 792. (f) Xu, F. Y.; Zhao, A. X.; Chien, J. C. W. *Makromol. Chem.* **1993**, *194*, 2579. (g) Busico, V.; Corradini, P.; Landriani, L.; Trifuoggi, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 261. (h) Liaw, D.-J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 309. (i) Wong, P. K.; van Doorn, J. A.; Drent, E.; Sudmeijer, O.; Stil, H. A. *Ind. Eng. Chem. Res.* **1993**, *32*, 986. (j) Drent, E.; Van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235 and references to patents therein.

(3) See refs 1a–c for a discussion on the sulfonation of phosphines.

(4) Thomas, R. R.; Sen, A. *Inorg. Synth.* **1989**, *26*, 128; **1990**, *28*, 63.

(5) Previous reports on the $[Pd(dppp)(MeCN)_2](BF_4)_2$-catalyzed synthesis of propylene–carbon monoxide copolymer and ethylene–propylene–carbon monoxide terpolymer: (a) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999. (b) Xu, F. Y.; Zhao, A. X.; Chien, J. C. W. *Makromol. Chem.* **1993**, *194*, 2579.

(6) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999.

(7) Sen, A.; Lai, T.-W.; Thomas, R. R. *J. Organomet. Chem.* **1988**, *358*, 567.

(8) Reviews: (a) Laine, R. M.; Wilson, R. B. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, The Netherlands, 1984; p 217. (b) Ford, P. C. *Acc. Chem. Res.* **1981**, *14*, 21.