Ruthenium phosphine complexes as catalysts of alternating copolymerization of ethylene and carbon monoxide

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The properties of the ruthenium(II) phosphine complexes $[Ru(dppe)_2(OTs)_2]$ and $[Ru\{PhP(CH_2CH_2CH_2PPh_2)_2\}(OTs)_2]$ as catalysts of alternating copolymerization of ethylene and carbon monoxide were studied. The catalytic activity of these complexes in the absence of cocatalysts is low, but it is substantially increased in the presence of trifluoroacetic acid or 1,4-benzoquinone. These compounds are the first ruthenium complexes which catalyze copolymerization of ethylene and CO.

Key words: ruthenium complexes, copolymerization, ethylene, carbon monoxide.

Alternating copolymerization of olefins and carbon monoxide is an extensively developing field of the modern chemistry of high-molecular-weight compounds.[1,2] Cationic palladium(II) complexes which contain two tertiary phosphine ligands in the *cis* positions and weakly coordinated anions are generally used as catalysts of these reactions. It was reported that nickel and rhodium compounds also exhibit catalytic activity, but the reaction rates and the molecular weights of the resulting polymers were low and the numbers of catalytic cycles in these processes were small.[2–7] Data on the use of ruthenium catalysts in copolymerization of olefins and CO are lacking. A search for catalysts based on ruthenium compounds shows promise because octahedral ruthenium complexes have substantially greater possibilities for modification than planar-square palladium complexes. In addition, in this case approaches to the preparation of statistical copolymers can probably be developed. From the practical standpoint, the latter copolymers are of as great interest as alternating copolymers.

Analysis of the published data made it possible to state the criteria for choosing potential catalysts among ruthenium complexes. Presumably, the most promising ruthenium(II) compounds with di- and polyphosphine ligands are those which satisfy the following requirements: first, the complexes should be dicationic and contain weakly coordinated counterions; and second, the complexes should have at least two vacant coordination sites in the *cis* positions with respect to each other. The problem is that transoid structures are more typical of compounds of the $[Ru(diphos)_2X_2]$ type.[8] The ruthenium complexes *cis*-$[Ru(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)_2(OTs)_2]$ (**1**) and $[Ru\{\eta^3\text{-}Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2\}(OTs)_2]$ (**2**) meet the above-stated requirements. The cisoid structure of compound **1** is realized due to the ability of tosylate anions to be coordinated to the Ru atom in a bidentate fashion through two oxygen atoms,[9] whereas the presence of two vacant coordination sites in the *cis* positions in complex **2** results from the structure of the phosphine ligand $Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2$.[10] For these reasons, compounds **1** and **2** were chosen for studies of their catalytic properties in alternating copolymerization of ethylene and CO.

Compound **1** was synthesized according to a known procedure.[9] Complex **2** was prepared analogously by the exchange reaction of $[Ru\{PPh(CH_2CH_2CH_2PPh_2)_2\}Cl_2]$ with AgOTs. The ^{31}P NMR spectrum of complex **1** has two pseudotriplets at δ 46.0 and 59.5 with a spin-spin coupling constant of 18 Hz, which corresponds to an AA'XX' spin system. The ^{31}P NMR spectrum of complex **2** has one very broad signal at δ 36.2, which is, apparently, indicative of interchange of the tosylate groups.

Copolymerization of an equimolal mixture of ethylene and carbon monoxide was carried out at 90 °C in MeOH or in a MeOH–toluene mixture (Table 1; the reaction times were determined by the necessity of preparing the copolymer in quantities sufficient for analysis*). The corresponding kinetic curves are shown in Fig. 1.

The copolymer was identified based on the data from elemental analysis and ^{13}C NMR spectroscopy, which unambiguously confirmed the alternating structure of the copolymer.[2]

* Presently, the catalytic system is being studied in more detail.

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Table 1. Conditions of copolymerization of C_2H_4 with CO and the viscosities of the resulting copolymers

Run*	Ru complex (mol L^{-1})	Cocatalyst (mol L^{-1})	[Cocatalyst]/[Ru]	Reaction time /min	Consumption of the monomer mixture/L	Yield of copolymer/g	Total yield of products /g_{Ru}^{-1} h^{-1}	[η] /dL g^{-1}
1	**1** ($2.5 \cdot 10^{-3}$)	—	—	240	0.4	Traces	1.32	—
2	**1** ($2.5 \cdot 10^{-3}$)	CF_3COOH ($6.25 \cdot 10^{-2}$)	25	80	1.2	1.0	198	0.22
3	**1** ($2.5 \cdot 10^{-3}$)	CF_3COOH($6.25 \cdot 10^{-1}$)	250	47	3.5	2	924	0.32
4	**2** ($2.3 \cdot 10^{-3}$)	—	—	60	0	—	—	—
5	**2** ($2.3 \cdot 10^{-3}$)	CF_3COOH($1 \cdot 10^{-2}$)	5	60	0.1	Traces	~1.5	
6	**2** ($2.3 \cdot 10^{-3}$)	CF_3COOH($4 \cdot 10^{-2}$)	20	360	2.8	1.6	66.7	0.73
7	**2** ($2.3 \cdot 10^{-3}$)	1,4-Benzoquinone ($1.5 \cdot 10^{-2}$)	7.5	70	2.35	1.9	455	0.6

* Solvent: Toluene—MeOH (1 : 19, 100 mL), runs *1—3*; MeOH (100 mL), runs *4—7*.

The results of our studies demonstrate that complexes **1** and **2** used without cocatalysts exhibit lower catalytic activity compared to palladium(II) phosphine complexes[1,2] (see Table 1, runs *1* and *4*), complex **2** being less active than complex **1**.

Previous studies of palladium catalysts have demonstrated that their activities can be substantially enhanced by introducing quinone or strong protic acids as cocatalysts.[1] We found that the use of 1,4-benzoquinone as a cocatalyst (the molar ratio **2** : quinone = 1 : 7.5) resulted in a substantial increase in the activity of complex **2** (see Table 1, run *7*; Fig. 1, curve *7*), and the activity of **2** became comparable with the activities of such catalysts as nickel compounds[11] and palladium complexes which do not contain phosphine ligands.[11,12]

An increase in the activity of catalysts **1** and **2** was also observed upon addition of trifluoroacetic acid to the reaction mixture (see Table 1, runs *2*, *3*, and *6*; Fig. 1, curves *2*, *3*, and *6*, respectively). It should be noted that the activity of the catalysts increased as the concentration of the acid increased. Along with the high-molecular-weight alternating copolymer, soluble products were formed which are apparently low-molecular-weight oligomers.[13]

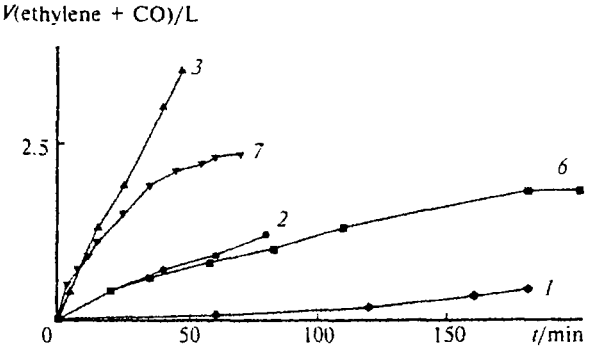

Fig. 1. Effect of the nature of the cocatalysts on the kinetics of copolymerization of ethylene and CO. The numbering of the curves corresponds to the numbering of the runs.

Therefore, we demonstrated that phosphine ruthenium(II) complexes can in principle be used as catalysts of alternating copolymerization of ethylene and carbon monoxide.

Experimental

The kinetics of copolymerization of ethylene and carbon monoxide was studied according to a procedure described previously.[14] An equimolal mixture of ethylene and CO was used. The intrinsic viscosities of the copolymers were determined in *m*-cresol at 30 °C. The melting points were measured by differential scanning calorimetry on a DSM-2M instrument at a heating rate of 16 °C min^{-1}. The ^{13}C NMR spectra of the copolymers were recorded on a Bruker AM-360 spectrometer in 1,1,1,3,3,3-hexafluoropropan-2-ol with addition of C_6D_6; the chemical shifts (δ) are given relative to Me_4Si.

The ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer. The chemical shifts (δ) are given relative to 85% H_3PO_4. The complexes *trans*-[$Ru(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)_2Cl_2$] and $Ru\{\eta^3\text{-}Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2\}Cl_2$] were prepared according to known procedures.[9,10]

Copolymerization was carried out in a 0.5-L stainless steel reactor at 90 °C at a pressure of 4 MPa of an equimolal mixture of ethylene and CO. The resulting copolymer was filtered off, washed with methanol, and dried at 120 °C; m.p. 252—258 °C. ^{13}C NMR, δ: 36.6 (CH_2); 212.2 (CO). Found (%): C, 63.88; H, 7.10. Calculated for the ratio C_2H_4 : CO = 1 : 1 (%): C, 64.27; H, 7.19.

Synthesis of *cis*-bis(P,P′-1,2-bis(diphenylphosphino)ethane)ruthenium(II) ditosylate, *cis*-[$Ru(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)_2(OTs)_2$] (1). AgOTs (0.20 g, 0.72 mmol) was added to a solution of *trans*-[$Ru(\eta^2\text{-}Ph_2PCH_2CH_2PPh_2)_2Cl_2$] (0.29 g, 0.30 mmol) in CH_2Cl_2 (50 mL). The reaction solution was stirred at ~20 °C for 3 days. The precipitate that formed was filtered off. The solution was concentrated to 5 mL. Then Et_2O (~30 mL) was added and the mixture was kept at 0 °C. The finely crystalline yellow precipitate was filtered off and dried *in vacuo*. The yield was 0.25 g (67%). ^{31}P NMR ($CDCl_3$), δ: 46.0 (t, $J_{PP'}$ = 18.0 Hz); 59.5 (t, $J_{PP'}$ = 18.0 Hz).

Synthesis of (P,P,′P′′-bis(3-(diphenylphosphino)-propyl)phenylphosphine)ruthenium(II) ditosylate, $[Ru\{\eta^3\text{-}Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2\}(OTs)_2]$ (2). AgOTs (0.42 g, 1.50 mmol) was added to a solution of $[Ru\{\eta^3\text{-}Ph_2P(CH_2)_3PPh(CH_2)_3PPh_2\}Cl_2]$ (0.43 g, 0.67 mmol) in CH_2Cl_2 (50 mL) and the reaction mixture was stirred at −20 °C for 10 h. The precipitate was filtered off, the filtrate was concentrated to 5 mL, and then Et_2O (~50 mL) was added. The precipitate that formed was filtered off and recrystallized from hot benzene. The yield was 0.53 g (76%). ^{31}P NMR ($CDCl_3$), δ: 36.2 (br.s). Found (%): C, 57.38; H, 5.29. $C_{50}H_{51}O_6P_3RuS_2 \cdot 2H_2O$. Calculated (%): C, 57.63; H, 5.32.

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