

Selective Telomerization of Butadiene with Various Nucleophiles Catalyzed by Polymer-Bound Palladium(0) Complexes

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The telomerization of butadiene with various nucleophiles such as alcohols, amines, carboxylic acids, phenol, water, and silane was carried out by using the phosphinated polystyrene-bound palladium(0) catalysts. In secondary amine reactions, 2:1 adducts of butadiene and amines are selectively formed, and the reactivities decrease with an increase in the steric bulk about nitrogen of the amines: morpholine > piperidine > diethylamine > diisopropylamine. Primary amines react with butadiene selectively to give 4:1 adducts depending on choice of reaction conditions. In carboxylic acid reactions, triethylamine is necessary as an additive to attain high yields of 2:1 adducts. The isomerization of linear to branched 2:1 adducts occurs easily. At high conversions of butadiene, the isomer ratios reach a thermodynamical equilibrium value, ca. 2.0. The reaction with formic acid gives exclusively 1,7-octadiene. In alcohol reactions, benzene must be used as a solvent to obtain high yields of telomers at fast rates, and the molecular size of alcohols strongly influences the telomer yields. The polymeric catalysts can be easily separated from a reaction mixture and reused with some loss of the activity.

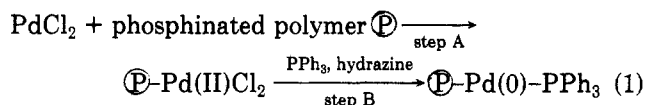
The transition-metal-catalyzed reaction of 1,3-dienes with nucleophiles such as alcohols, amines, carboxylic acids, and phenols yields various telomers. The selective 2:1 telomerizations are characteristic to palladium(0) compounds as catalysts and can scarcely be achieved by other metal compounds.¹ The application of the telomers to the synthesis of useful natural products has become of interest in recent years;^{2,3} Tsuji has synthesized steroids and macrolides using acetic acid telomers, ricifeiolide using nitroalkane telomers, royal jelly acid from malonic acid telomers, etc.²

Recently we have reported that a phosphinated polystyrene-bound and three-coordinated palladium(II) chloride complex could be reduced with hydrazine to give an unsaturated polymer-bound palladium(0) complex.⁴ The isolated palladium(0) complex is stable to air and moisture and is an efficient and recoverable catalyst for various carbon-carbon bond formation reactions. In order to expand the use of the catalysis of the palladium(0) complex to many other organic reactions, we have tried useful telomerizations of butadiene and nucleophiles using our polymeric palladium(0) complex. We describe herein the characteristic features of the polymeric palladium catalyst for various kinds of telomerizations as compared to those of homogeneous ones. Two groups have already reported on the catalysis of polymeric palladium(0) complexes: Pittman discussed effects of the phosphine loading in the polymeric palladium complexes on the telomerization reactivity,⁵ and Trost found that the polymeric palladium(0)

complexes showed high stereospecificity in allylic amination.⁶

Results and Discussion

In order to compare the telomerization reactivities of our polymer-bound palladium(0) catalysts with those of homogeneous palladium catalysts, we kept the reaction conditions, e.g., substrate concentration, catalyst concentration, and reaction temperature, as similar as possible to those of corresponding homogeneous systems already reported. Butadiene as a 1,3-diene was reacted with various kinds of nucleophiles such as alcohols, amines, carboxylic acids, phenol, silane, and water. Phosphine loading in the resin was 74%. The P/Pd ratios in the polymeric palladium(0) catalysts were controlled in both preparation steps of polymeric palladium(II) and palladium(0) complexes: (1) polymeric palladium(II) complexes were prepared by the reaction of palladium chloride and the phosphinated resin in an appropriate molar ratio (step A, eq 1), and, subsequently, triphenylphosphine was added



in the reduction of palladium(II) to palladium(0) (step B); (2) the ratios of P/Pd were controlled only in step A, followed by the reduction without triphenylphosphine. Except where noted, the polymeric palladium(0) complexes of P/Pd ratios of 2 and 4 prepared by the former method (1) were used as the catalysts.

Amines. In the telomerization of butadiene with morpholine using homogeneous and heterogeneous palladium(0) catalysts, the effect of solvents on the catalytic activity was examined. Pd(PPh₃)₄ was used as a representative homogeneous catalyst because its ligand environment was similar to that of the polymeric palladium(0) complex. The results are shown in Table I. Use of acetone, benzene, or THF solvent gave high conversions of butadiene in both catalyst systems. Acetone is the best solvent in the case of the polymeric palladium(0) complex (entry 1). So, we adopted acetone as a solvent in the telomerization with various kinds of amines. However,

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(2) (a) Tsuji, J.; Tsuruoka, K.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* 1976, 46, 1701. (b) Tsuji, J.; Kaito, M.; Takahashi, T. *Ibid.* 1978, 51, 547. (c) Tsuji, J.; Kaito, M.; Yamada, T.; Mandai, T. *Ibid.* 1978, 51, 1975. (d) Takahashi, T.; Kasuga, K.; Takahashi, M.; Tsuji, J. *J. Am. Chem. Soc.* 1978, 100, 7424. (e) Tsuji, J.; Shimizu, I.; Naito, Y. *Tetrahedron Lett.* 1978, 487. (f) Tsuji, J.; Yamakawa, T.; Mandai, T. *Ibid.* 1978, 565. (g) Tsuji, J.; Kobayashi, Y.; Takahashi, T. *Ibid.* 1980, 483.

(3) Byrom, N. T.; Grigg, R.; Koukathip, B. *J. Chem. Soc., Chem. Commun.* 1976, 216.

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





(6) Trost, B. M.; Keinan, E. *J. Am. Chem. Soc.* 1978, 100, 7778.

Table I. Telomerization of 1,3-Butadiene with Morpholine Catalyzed by Polymer-Bound Pd(0) and Pd(PPh₃)₄ Complexes in Various Solvents^a

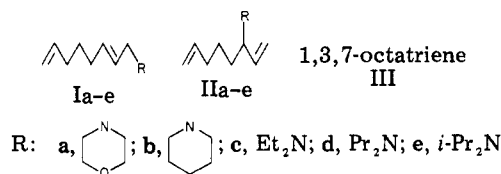
entry	solvent	catalyst	overall yield, ^b %	% products			selectivity (Ia/IIa)
				Ia	IIa	III	
1	acetone	Ⓢ-Pd(0)	97	92	6	2	15
2	acetone	Pd(PPh ₃) ₄	90	89	4	7	22
3	benzene	Ⓢ-Pd(0)	84	96	3	1	38
4	benzene	Pd(PPh ₃) ₄	92	50	11	39	4.8
5	THF	Ⓢ-Pd(0)	80	95	2	3	42
6	THF	Pd(PPh ₃) ₄	85	98	1	1	72
7	ethyl acetate	Ⓢ-Pd(0)	57	95	4	1	27
8	ethyl acetate	Pd(PPh ₃) ₄	79	98	1	1	59
9	cyclohexane	Ⓢ-Pd(0)	30	96	3	1	25
10	cyclohexane	Pd(PPh ₃) ₄	58	72	12	16	6.2
11	dioxane	Ⓢ-Pd(0)	27	56	11	33	5.0
12	dioxane	Pd(PPh ₃) ₄	58	57	12	31	4.8

^a Reaction conditions: palladium catalyst (P/Pd ratio of 4.0), 0.1 mmol; morpholine, 80 mmol; solvent, 20 mL; butadiene, 120 mmol; reaction temperature, 85 °C; reaction time, 5 h. ^b Based on butadiene used. Ia = 1-morpholino-2,7-octadiene, IIa = 3-morpholino-1,7-octadiene, and III = 1,3,7-octatriene.

Table II. Telomerization with Secondary Amines Catalyzed by Polymer-Bound Pd(0) Complexes^a

entry	P/Pd ratio	amine	temp, °C	time, h	overall yield, ^d %	% products			selectivity (I/II)
						I	II	III	
1	4.0		85	5	97	92	6	2	15
13	2.0		85	5	99	92	7	1	13
14 ^b	2.0		85	10	98	99	0	1	
15	4.0		85	2	11	94	5	1	19
16	2.0		85	3	42	94	5	1	20
17	4.0		90	10	93	92	2	6	43
18	4.0	Et ₂ NH	90	20	98	98	0	2	
19	4.0	Pr ₂ NH	90	20	9	100	0	0	
20	2.0	Pr ₂ NH	90	20	35	100	0	0	
21	4.0	<i>i</i> -Pr ₂ NH	95	20	12	75	0	25	
22 ^c	4.0	<i>i</i> -Pr ₂ NH	95	20	25	80	0	20	

^a Reaction conditions: polymeric catalyst, 0.1 mmol; amine, 80 mmol; acetone, 20 mL; butadiene, 120 mmol. ^b The catalyst was prepared without a PPh₃ additive. ^c The amount of *i*-Pr₃Al used was equivalent to the amount of palladium used. ^d Based on the amount of butadiene used.



since aromatic amines react easily with acetone to form imines, a dioxane solvent had to be used in the telomerization with aniline.

The reaction of butadiene with various secondary amines in the presence of the polymeric palladium(0) catalysts was carried out in an acetone solvent. The results are shown in Table II. Adduct telomers (2:1) of butadiene and amines were selectively obtained in all reactions, and 1,3,7-octatriene (III) was a minor product. Homogeneous nickel catalysts are prone to formation of 1:1 adduct telomers, vinylcyclohexene, and cyclooctadiene.⁷ Trace

amounts of these products could be observed in some of our reactions. These phenomena are also observed in homogeneous palladium-catalyzed reactions.^{8,9} Morpholine showed the highest reactivity for the telomerization. The reaction with diisopropylamine gave a 12% butadiene conversion even at 95 °C (entry 21). The reactivities of amines decrease along the order morpholine > piperidine > diethylamine > diisopropylamine. Similar reactivity orders have been found when homogeneous palladium

(8) Takahashi, S.; Shibano, T.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1968, 41, 454.

(9) Green, M.; Scholes, G.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1978, 309.

(7) Baker, R.; Cook, A. H.; Halliday, D. E.; Smith, T. N. *J. Chem. Soc., Perkin Trans 2*, 1974, 1511.

Table III. Telomerization with Primary Amines Catalyzed by Polymer-Bound Pd(0) Complexes^a

entry ^e	P/Pd ratio	amine	time, h	overall yield, ^b %	% products			4:1 adduct	selectivity (I/II)
					I	II	III		
23	2.0	BuNH ₂	10	94	11	10	9	70	1.1
24	4.0	BuNH ₂	20	97	27	8	5	60	3.3
25 ^c	4.0	BuNH ₂	20	38	3	3	3	91	1.0
26	4.0	CH ₂ =CHCH ₂ NH ₂	20	37	11	3	24	62	4.0
27 ^d	4.0	PhNH ₂	16	85	93	0	6	1	

^a Reaction conditions: polymeric catalyst, 0.1 mmol; acetone, 20 mL; butadiene, 120 mmol; H₂NR, 100 mmol. ^b Based on butadiene used. I = 2:1 linear adduct, II = 2:1 branched adduct, and III = 1,3,7-octatriene. ^c BuNH₂, 30 mmol. ^d Dioxane was used as a solvent. ^e The reaction temperature was 90 °C in all cases.

catalysts were used;^{8,9} in the Pd(cod)₂-catalyzed reaction, butadiene conversions are quantitative for morpholine, 80% for piperidine, and 20% for diethylamine, and no reaction is observed with diisopropylamine.⁹ These orders of the amine reactivities cannot be explained only in terms of their basicity.¹⁰ The steric bulk about nitrogen of the amines may play an important role in determining the yields. Stone also has reported that the particular effectiveness of morpholine was unrelated to the basicity; morpholine derives its high reactivity from stretching and weakening of the N-H bond via intramolecular hydrogen bonding to the oxygen in the boat configuration.⁹ Addition of Lewis acid Al(O-*i*-Pr)₃ or Al(O-*t*-Bu)₃ promotes the telomerization with amines in the presence of Pt(cod)₂ catalyst.⁹ So, Al(O-*i*-Pr)₃ was adopted as an additive in the reaction with diisopropylamine using the polymeric palladium(0) catalyst, and the conversion of butadiene was increased to 25% (entry 22).

The 2:1 adducts consist of two regioisomers of 1-amino-2,7-octadiene (Ia-e) and 3-amino-1,7-octadiene (IIa-e). 1-Amino-2,6-octadiene, which is obtained by using the nickel-triphenylphosphite catalyst,¹¹ could not be detected in our reactions. The linear adducts of Ia-e were the main products in all reactions. It seems that the steric bulk about the nitrogen also affects the isomer ratio of I/II; the selectivity for I increases with increasing the steric bulk. Morpholine, having low steric requirements, showed a selectivity of Ia/IIa of 15, while bulky diisopropylamine gave the only linear isomer Ie. It is notable that the catalyst with a P/Pd ratio of 2 from the preparation without a triphenylphosphine additive gave exclusively the linear Ia at a slow rate (entry 14). The product distribution was examined in the course of the morpholine reaction. The isomer selectivity did not change remarkably (entries 1, 15). Also, the linear product of Ia was recovered unchanged from the reaction of the isolated Ia in the presence of the polymeric palladium(0) catalyst. These phenomena are much different from those of the telomerization with carboxylic acids, which will be discussed in a later section.

Next, we carried out the reaction of butadiene with three primary amines in the presence of the polymeric palladium(0) catalysts (data are shown in Table III). The reaction with butylamine gave a mixture of 2:1 adducts, a 4:1 adduct, and the triene III. The product ratios (I/II) between the 2:1 regioisomers were much lower than those in secondary amine reactions. However, apparent anomalous phenomena can be explained easily in terms of the different reactivity between two 2:1 regioisomers with an

Table IV. Recycling of Polymer-Bound Pd(0) Catalyst^a

entry	catalyst	overall yield, ^b %	% products		
			Ia	IIa	III
1	fresh	97	92	6	2
28	recycle 1	99	98	1	1
29	recycle 2	72	98	1	1

^a Reaction conditions: polymeric catalyst (P/Pd ratio of 4.0), 0.1 mmol; morpholine, 80 mmol; 85 °C; 5 h. ^b Based on butadiene used. Ia = 1-morpholino-2,7-octadiene, IIa = 3-morpholino-1,7-octadiene, and III = 1,3,7-octatriene.

active palladium intermediate;¹² 3-(butylamino)-1,7-octadiene hardly attacks the palladium intermediate species because of its larger steric bulk about the nitrogen atom, while 1-(butylamino)-2,7-octadiene with a lower steric requirement may react smoothly with two molecules of butadiene to give the linear 4:1 adduct. Notably, the 4:1 adduct could be obtained exclusively when the amount of the amine was decreased (entry 25). Allylamine showed low reactivity for the telomerization. A prolonged reaction time of over 50 h increased the yield of telomers, but the product distribution became more complicated because allylamines were disproportionated to give di- and tri-allylamine and ammonia, followed by the reaction of butadiene with the diallylamine to form the 2:1 adducts. In contrast with the above two amines, the reaction with aniline gave exclusively 1-(phenylamino)-2,7-octadiene with trace amounts of another 2:1 regioisomer and 4:1 adducts. In the case of the homogeneous Pd(PPh₃)₄ and Pd-(PPh₃)₂(C₄H₂O₃) catalysts, the reaction with aniline gives a mixture of 2:1 and 4:1 adducts.⁸

The catalyst recycling study with a polymeric palladium complex of a P/Pd ratio of 4 was carried out in the reaction with morpholine (data are shown in Table IV). The polymeric palladium complex could be reused with some loss of its catalytic activity. The remarkable change in the product distribution could not be observed during each run.

Carboxylic Acids and H₂O. Since the telomerization of butadiene with acetic acid provides not only a convenient synthetic method for octadienyl alcohols but also very useful materials for the synthesis of natural products,² it is important to obtain either of two regioisomers in a pure

(10) Hagihara⁸ has reported that the reaction with morpholine gave a high yield of the 2:1 adducts, whereas a weak base such as carbazole gave a low conversion, and electron donating substituents in aniline derivatives increased the yield of telomers. Therefore, he has suggested that there was a relationship between the reactivity and the basicity of amines in the telomerization of butadiene.

(11) Heimbach, P. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 882.

(12) Three mechanisms for the linear telomerization have been proposed at present: (a) a mononuclear di- π -allylpalladium mechanism: Wilke, G.; Bogdavic, B.; Hardt, P.; Kein, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, G.; Walker, D.; Zimmerman, H. *Angew. Chem., Int. Ed. Engl.* 1966, 5, 151; Takahashi, S.; Yamazaki, H.; Hagihara, N. *Bull. Chem. Soc. Jpn.* 1968, 41, 254. (b) A stepwise mechanism involving the primary formation of a Pd(II)-hydride complex: Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol 2, p 45. (c) A bridged bimetallic π -allylpalladium mechanism, Smutny, E. J. *Ann. N. Y. Acad. Sci.* 1973, 214, 125.

Table V. Telomerization with Carboxylic Acids and Water Catalyzed by Pd(0) Complexes^a

entry ^k	P/Pd ratio	RCOOH and H ₂ O	time, h	overall yield, ^b %	% products			selectivity (IV/V)
					IV	V	III	
30	4.0	CH ₃ COOH	20	83	52	25	23	2.0
31 ^c	4.0	CH ₃ COOH	20	71	63	27	10	2.3
32 ^d	4.0	CH ₃ COOH	20	53	89	9	2	9.4
33	4.0 ^e	CH ₃ COOH	20	56	66	25	9	2.7
34 ^c	4.0 ^e	CH ₃ COOH	20	76	71	26	3	2.8
35 ^d	4.0 ^e	CH ₃ COOH	20	91	64	24	12	2.6
36 ^f	4.0	CH ₃ COOH	20	35	73	26	1	2.5
37 ^g	4.0	CH ₃ COOH	20	88	66	23	11	2.9
38 ^h	4.0	CH ₃ COOH	20	57	74	25	1	3.1
39	2.0	CH ₃ COOH	20	83	55	27	18	2.1
40 ⁱ	2.0	CH ₃ COOH	20	50	75	24	1	3.0
41	4.0	CH ₃ COOH	1	10	79	20	1	5.0
42	2.0	CH ₃ COOH	1	36	77	22	1	3.5
43	4.0	C ₂ H ₅ COOH	20	87	48	25	27	1.9
44	4.0	C ₂ H ₅ COOH	1	18	85	14	1	6.2
45	2.0	C ₂ H ₅ COOH	1	36	83	16	1	5.5
46	4.0	C ₅ H ₁₁ COOH	20	99	47	22	31	1.9
47	4.0	C ₅ H ₁₁ COOH	1	22	86	13	1	8.4
48	2.0	C ₅ H ₁₁ COOH	1	54	76	22	2	3.5
49	4.0	HCOOH	1	88	l			
50 ^j	4.0	H ₂ O	20	70	m			10

^a Reaction conditions: polymeric catalyst, 0.1 mmol; carboxylic acid, 60 mmol; Et₃N, 30 mmol; acetone, 20 mL; butadiene, 120 mmol. ^b Based on butadiene used. III = 1,3,7-octadiene, IVa-c = H₂C=CH(CH₂)₃CH=CHCH₂R₁ and Va-c = H₂C=CH(CH₂)₃CHRCH=CH₂. R: a, CH₃COO; b, C₂H₅COO; c, C₅H₁₁COO. ^c Benzene was used as a solvent. ^d THF was used as a solvent. ^e The homogeneous Pd(PPh₃)₄ catalyst was used. ^f Et₃N was not added. ^g 30 mmol of triethylenediamine was added. ^h 0.2 mmol of NaOAc was used. ⁱ The catalyst was prepared without a PPh₃ additive. ^j CO₂, 10 atm, H₂O 240 mmol. ^k The reaction temperature was 95 °C in all cases. ^l Products: 99% H₂C=CH(CH₂)₄CH=CH₂ and 1% H₂C=CH(CH₂)₃CH=CHCH₂. ^m Products: 86% H₂C=CH(CH₂)₃CH=CHCH₂OH, 9% H₂C=CH(CH₂)₃CH(OH)CH=CH₂, and 6% III.

form. Previous researchers have paid attention to the improvement of selectivity between two octadienyl acetates;^{5d,13,14} addition of *o*-alkyl or aryl-substituted triarylphosphites on the Pd(acac)₂ catalyst increases the selectivity for linear 1-acetoxy-2,7-octadiene (IVa).¹³

We carried out the reaction of butadiene with acetic acid using the polymeric palladium(0) catalysts. The results are summarized in Table V. In the presence of triethylamine, 83% of the butadiene reacted to give IVa (52%), 3-acetoxy-1,7-octadiene (Va, 25%), and the triene III (23%) at 95 °C. Butenyl acetates could not be detected. In the absence of the amine, the palladium catalyst showed low activity (entry 36). Similarly, in the case of homogeneous catalysts such as PdCl₂(PPh₃)₂^{5d} and Pd(acac)₂-PPh₃,¹⁴ the triethylamine additive must be used to increase both the reaction rate and the selectivity for octadienyl acetates.¹⁵ Comments regarding the role of the amine additive are largely speculative in our reaction system. Probably the amine might assist the ionic dissociation of acetic acid and/or increase the electron density of palladium through its coordination. Acetone was a suitable solvent for the telomerization with acetic acid as well as for the amine reactions described in a former section. Use of benzene or THF in the place of acetone gave moderate conversions of butadiene (entries 31, 32). On the other hand, the homogeneous Pd(PPh₃)₄ complex showed higher catalytic activity in a THF solvent than in acetone or benzene (entry 35).

Walker has reported that 1-acetoxy-2,7-octadiene (IVa) was formed by a kinetically controlled reaction and that 3-acetoxy-1,7-octadiene (Va) was an isomerization product from IVa in the case of the Pd(acac)₂-PPh₃-tertiary amine

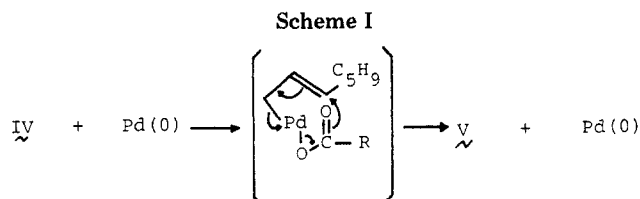
system.¹⁴ The equilibrium value of the IVa/Va ratio is 70:30 at 100 °C. In retrospect, in our heterogeneous system, the 52:25 isomer ratio of IVa/Va attains a near-equilibrium value. In an initial stage, the linear adduct of IVa was mainly formed, and the ratio of IVa/Va fell to about 2.0 as the reaction progressed (entries 30, 41). It was also confirmed by control experiments that the reaction from either the isolated IVa or Va reached the equilibrium composition at fast rates in the presence of the polymeric palladium(0) catalyst. In the homogeneous Pd(acac)₂-phosphite catalyst systems, the presence of NaOAc favors high isomer ratios of IVa/Va.¹³ However, the present combination catalyst of the polymeric palladium(0) complex and NaOAc did not show high selectivity for IVa (entry 38).

Little is known concerning the telomerization with carboxylic acids other than acetic acid. We carried out the reaction with propionic acid under the same conditions as with acetic acid. After 20 h, a mixture of 1-(propionyl-oxy)-2,7-octadiene (IVb, 48%), 3-(propionyl-oxy)-1,7-octadiene (Vb, 25%), and III (27%) was obtained at 87% butadiene conversion. In an initial stage of the reaction, the linear product of IVb was formed selectively (entry 44). The reaction with hexanoic acid showed a tendency for the product distribution similar to those with the above two acids (entries 46, 47). Although the polymeric palladium(0) catalyst with a low P/Pd ratio (=2) was used in the place of the catalyst with a P/Pd ratio of 4, a profound effect on the isomer distribution could not be observed (entries 39, 42, 45, 48). It seems that varying the P/Pd ratio of the catalyst resins may have little influence on the rate of the isomerization to branched products. In order to obtain high yields of the linear products, one must stop the reaction before butadiene is largely consumed. As mentioned in a previous section, the yield of amine telomers strongly decreases with an increase in the molecular size of the nucleophiles, but it is notable that the remarkable size effect is not observed in the telomerization with carboxylic

(13) Rose, D.; Lepper, H. *J. Organomet. Chem.* 1973, 49, 473.

(14) Walker, W. E.; Manyik, R. M.; Atkins, K. E.; Farmer, M. L. *Tetrahedron Lett.* 1970, 3817.

(15) Pittman^{5d} has also reported that Pd(OAc)₂-PPh₃ and its polymer-anchored catalysts were very active for the telomerization with acetic acid in the absence of triethylamine.



acids. The facile isomerization may be rationalized on the basis of the allylic inversion process as shown in Scheme I, which is derived from the oxidative addition of the linear telomer to palladium(0).¹⁶

The telomerization was applied to formic acid. (Formyloxy)octadienes of 2:1 adducts could not be detected, and 1,7-octadiene was exclusively formed (entry 49). In contrast, it has been reported that 1,6-octadiene was exclusively obtained in the presence of the homogeneous Pd(OAc)₂ catalyst, and other homogenous palladium catalysts gave a mixture of 1,6-octadiene and the triene III.^{17,18} The highly selective formation of 1,7-octadiene may be explained by a mechanism involving a (formato)palladium intermediate proposed by Heck,¹⁹ evolution of CO₂ in a formato complex affords a π -allylpalladium hydride, followed by reductive elimination, and then a preferential attack of hydrogen on C-3 of an allylic moiety occurs to give 1,7-octadiene (Scheme II).²⁰

Use of H₂O in the place of carboxylic acids can lead to a simple synthesis of octadienyl alcohols. The reaction with H₂O in an acetone solvent was carried out under 10 atm of CO₂. 1-Hydroxy-2,7-octadiene was formed as a main product, accompanied by small amounts of 3-hydroxy-1,7-octadiene and III. In the absence of CO₂, small amounts of III were formed without octadienyl alcohols. The acceleration effect with CO₂ has been also reported in the homogeneous Pd(acac)₂-PPh₃ and Pd(PPh₃)₄ catalysts.²¹

Alcohols, Phenol, and Silane. In the catalysis of organic polymer-bound metal complexes, the degree of swelling of catalyst resins in solvents must especially be considered in addition to common solvent effects in homogeneous systems. Since contraction of polymers with alcohols decreases the diffusion rate of substrates into polymer channels, addition of benzene as a good swelling solvent²² may improve the degree of swelling of the polymeric palladium catalysts to give high reactivity. We carried out the reaction of butadiene with methanol in various volume of benzene at 80 °C. The results are shown in Table VI. Decreasing the amount of benzene increases the yield of 2:1 adduct telomers (VIa and VIIa), but in the absence of benzene, the reaction rate was slow (entry 54). So, a suitable volume of a benzene additive must be chosen to obtain a high reaction rate and high selectivity for the telomers. A similar acceleration of reaction rates with the benzene additive can be observed in the hydrogenation of olefins catalyzed by the polymeric palladium(II) catalysts.²³

Table VI. Telomerization with Methanol in Various Volumes of Benzene^a

entry	mL of CH ₃ OH	mL of C ₆ H ₆	q ^c	overall yield, ^b %	% products		
					VIa	VIIa	III
51	6	14	2.6	97	59	6	35
52	10	10	2.0	94	77	12	11
53	16	4	1.3	98	86	8	6
54	20	0	1.1	79	92	4	4

^a Reaction conditions: polymeric catalyst (P/Pd ratio of 4.0), 0.1 mmol; butadiene, 120 mmol; 80 °C; 5 h.

^b Based on butadiene used. VIa = 1-methoxy-2,7-octadiene, VIIa = 3-methoxy-1,7-octadiene, and III = 1,3,7-octatriene. ^c q is the degree of swelling and is calculated as described in ref 22.

It is notable that use of acetone in the telomerization with alcohols gave the triene III without the telomers, while acetone is a good solvent for two kinds of telomerization with amines and carboxylic acids. This may reflect a greater degree of swelling with benzene compared to acetone.

The results in various alcohol reactions are summarized in Table VII. Ethanol reacted with butadiene at a slow rate, and the reaction was complete at 90 °C. 2-Propanol, a steric bulky alcohol, gave only III in very low yield even at 95 °C. Addition of NaOPh to the reaction with 2-propanol did not make a profound difference (entry 61). The yield of telomers remarkably decreases with an increase in the molecular size of alcohols as nucleophiles, and the portion of III among the products increases. The similar size effects of alcohols are observed in homogeneous palladium-catalyzed telomerizations;^{7,24} in comparison to the homogeneous Pd(acac)₂-PPh₃ catalyst, the polymeric palladium(0) catalyst causes lower reactivity for sterically bulky alcohols.²⁵

Furthermore, we think that the telomerization with alcohols shows greater sensitivity to the steric factors of nucleophiles than the amine reactions.

In the case of telomerization with phenol, acetone in the place benzene as solvent was used because phenol is less soluble in benzene. In the homogeneous palladium-catalyzed reactions, NaOPh, a strong base, is necessary to attain high yields of phenol telomers.²⁶ The telomerization with the polymeric palladium catalyst, however, occurred at a fast rate even in the absence of NaOPh. After 2 h of reaction, butadiene was consumed completely, and the products were 1-phenoxy-2,7-octadiene (VIId, 73%), 3-phenoxy-1,7-octadiene (VIIId, 22%), and III (5%). As the reaction was continued further, the yields of VIIId and III increased, respectively (entry 63). Treatment of the isolated VIId with the polymeric palladium(0) catalyst gave both III (32%) and VIIId (18%). In comparison to alcoholic telomers, the telomer of VIId is converted easily to III in the presence of the polymeric palladium catalyst.²⁷ It can be said that III is mainly formed not by a direct route but

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(17) Gardnev, S.; Wright, D. *Tetrahedron Lett.* 1972, 163.

(18) Roffia, R.; Gregorio, G.; Conti, F.; Pregaglia, G. F.; Ugo, R. *J. Organomet. Chem.* 1973, 55, 405.

(19) Neilan, J. P.; Laine, R. M.; Cortese, N.; Heck, R. F. *J. Org. Chem.* 1976, 41, 3455.

(20) In a separate experiment, treatment of III with the polymeric palladium(II) catalyst under H₂ gave a mixture of 1,6- and 1,7-octadienes. So, 1,7-octadiene does not arise by a specific hydrogenation of primarily formed III. Intermediacy of 1-(formyloxy)-2,7-octadiene may be also ruled out since 1-(formyloxy)-2,7-octadiene is easily converted into 1,6-octadiene in the presence of the Pd(OAc)₂ catalyst.¹⁷

(21) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *J. Chem. Soc., Chem. Commun.* 1971, 330.

(22) Regen, S. L. *J. Am. Chem. Soc.* 1974, 96, 5275.

(23) Although alcohols as compared to benzene are much better solvents for the olefin hydrogenations using the polymeric palladium(II) catalysts, use of a mixed solvent of ethanol and benzene shows the highest hydrogenation rate: (a) Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *J. Catal.* 1978, 51, 406. (b) Terasawa, M.; Yamamoto, H.; Kaneda, K.; Imanaka, T.; Teranishi, S. *Ibid.* 1979, 57, 315.

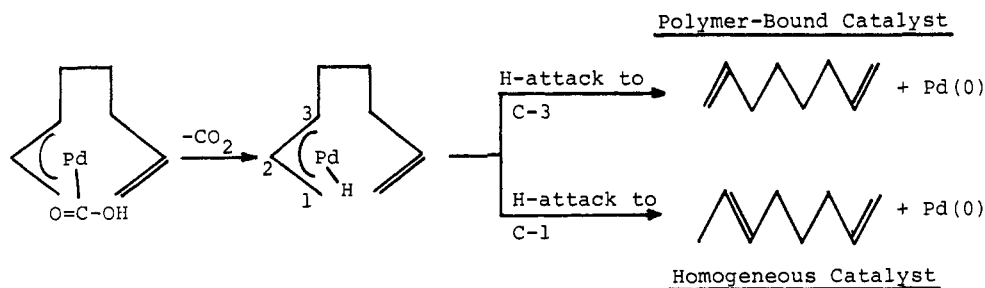
(24) Beger, J.; Reichel, H. *J. Prakt. Chem.* 1973, 315, 1067.

(25) These phenomena about the steric effect are often observed in many polymer-bound metal catalyst reactions. See, for example: (a) Grubbs, R. H.; Kroll, L. C. *J. Am. Chem. Soc.* 1971, 93, 3062. (b) Kaneda, K.; Uchiyama, T.; Terasawa, M.; Imanaka, T.; Teranishi, S. *Chem. Lett.* 1976, 446.

(26) Smutny, E. J. *J. Am. Chem. Soc.* 1967, 89, 6793.

(27) The elimination of allylic acetates and phenyl ethers easily occurs to give 1,3-dienes in the presence of the Pd(OAc)₂-PPh₃ catalyst: Tsuji, J.; Yamakawa, T.; Kaito, M.; Mandai, T. *Tetrahedron Lett.* 1978, 2075.

Scheme II

Table VII. Telomerization with Alcohols and Phenol Catalyzed by Polymer-Bound Pd(0) Complexes^a

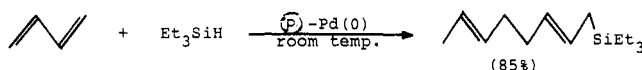
entry	P/Pd ratio	ROH	temp, °C	time, h	overall yield, ^b %	% products			selectivity (VI/VII)
						VI	VII	III	
53	4.0	MeOH	80	5	98	85	8	7	11
55	4.0	MeOH	80	0.5	90	87	6	7	13
56	4.0	EtOH	90	18	99	74	11	14	7
57 ^c	4.0	EtOH	90	18	99	64	2	33	32
58	4.0	EtOH	90	2	23	83	4	13	20
59	2.0	EtOH	90	1	34	91	6	3	24
60	4.0	<i>i</i> -PrOH	95	18	4	1	0	99	
61 ^c	4.0	<i>i</i> -PrOH	95	18	16	6	0	94	
62 ^d	4.0	PhOH	95	2	99	73	22	5	3.4
63 ^d	4.0	PhOH	95	18	99	48	24	28	2.1
64	4.0	HOC ₂ H ₄ OH	95	18	72	89	7	4	13
65	4.0 ^e	HOC ₂ H ₄ OH	95	18	61	92	3	5	16
66 ^f	4.0	CH ₃ NHC ₂ H ₄ OH	90	20	88	^g			

^a Reaction conditions: polymeric catalyst, 0.1 mmol; alcohol, 16 mL; benzene, 4 mL; butadiene, 120 mmol. ^b Based on butadiene used. VIa-e = H₂C=CH(CH₂)₃CH=CHCH₂R; VIIa-e = H₂C=CH(CH₂)₃CHRCH=CH₂; III = 1,3,7-octatriene. R: a, MeO; b, EtO; c, *i*-PrO; d, PhO; e, HOC₂H₄O. ^c 0.2 mmol of NaOPh was used. ^d PhOH, 100 mmol; acetone, 20 mL. ^e The homogeneous Pd(PPh₃)₄ catalyst was used. ^f CH₃NHC₂H₄OH, 80 mmol; acetone, 20 mL. ^g H₂C=CH(CH₂)₃CH=CHCH₂N(C₂H₄OH)CH₃ (99%), III (1%), and H₂C=CH(CH₂)₃CH[N(C₂H₄OH)CH₃]CH=CH₂ (trace).

by the decomposition of the 2:1 adducts.

Furthermore, the telomerization was applied to multifunctional active hydrogen compounds. Ethylene glycol reacted with butadiene to give exclusively a linear 2:1 adduct (VIe) without 4:1 successive reaction products. The homogeneous reaction using the Pd(PPh₃)₄ catalyst also gave VIe as a major product (entry 65). The telomerization with (methylamino)ethanol occurred chemoselectively to give 1-[(2-hydroxyethyl)methylamino]-2,7-octadiene in high yield. The hydroxyl group did not react with butadiene under the present reaction conditions (entry 66). Similarly, the homogeneous Pd(acac)₂PPh₃ catalyst gives exclusively the octadienylamino alcohol.²⁸ These phenomena may be explained in terms of greater nucleophilicity of the amine group compared to that of the alcohol function.

The hydrosilylation of butadiene with an organosilicon hydride by using homogeneous palladium catalysts gives a complicated mixture of 1:1 adducts, a 2:1 adduct, and disilylated compounds.²⁹ The product distribution is strongly dependent on reaction conditions, the structure of the silicon hydrides, and the catalysts. The reaction of butadiene and triethylsilane with the polymeric palladium(0) catalyst was carried out at room temperature. After 20 h, 1-(triethylsilyl)-2,6-octadiene was formed exclusively. The positions of the two double bonds are different from those of above linear 2:1 adducts. This indicates that the mechanism for the hydrosilylation may be different from that of other telomerizations.



(28) Umpleby, E. J. D. *Helv. Chim. Acta* 1978, 61, 2243.

(29) (a) Langová, J.; Hetflejš, J. *Collect. Czech. Chem. Commun.* 1975, 40, 420. (b) *Ibid.* 1975, 40, 432.

In conclusion, our polymer-bound palladium(0) complex is an active catalyst not only for carbon-carbon bond formation reactions involving the oxidative addition of organic halides⁴ but also for the telomerization of butadiene with various kinds of nucleophiles. The polymeric catalyst can be easily separated from a reaction mixture and reused with some loss of activity.

Experimental Section

General Methods. PdCl₂ was purchased from Nakarai Chemicals Ltd. Solvents and reagents were dried and distilled prior to use. Butadiene was obtained from Wako Pure Chemical Industries, Ltd., and dried by passage through a calcium chloride tube before use. Pd(PPh₃)₄ was prepared by the method of Coulson.³⁰ GC analyses were run on a Shimadzu GC-6A gas chromatograph using the following stainless-steel columns: 3-m, OV-17 (3%); 3-m, DC-550 (25%); 3-m, PEG-20M (20%). Infrared spectra were recorded by using a JASCO Model IR-E spectrometer. Proton magnetic resonance spectra were recorded on HNM-4-100 and Hitachi R-600 spectrometers. Chemical shifts are reported on the δ scale relative to Me₄Si as internal standard, and coupling constants are in hertz. Elemental analyses were run on a Yanagimoto CNH-CORDER, Type 2.

Preparation of Polymer-Bound Pd(0) Complexes. A polymer-bound Pd(0) complex with a P/Pd ratio of 4 was given for a representative example. The procedure was similar to that in a previous report.⁴ The polystyrene resin with a 100% chloromethylated aromatic ring was treated with LiPPh₂ at 25 °C for 48 h. The analysis showed the following: C, 81.54%; H, 6.23%; Cl, 3.51%; P, 8.71%. This corresponds to 74% phosphination of chloromethyl moieties. The reaction of the phosphinated resin (5.00 g) with PdCl₂ (0.75 g) in a molar ratio of P/Pd of 3 was carried out to give a yellow polymeric Pd(II) complex. The Pd(II) complex (5.00 g, 3.71 mmol of Pd) was added to ethanol (50 mL) containing triphenylphosphine (2.09 g, 7.42 mmol). The mixture

(30) Coulson, P. R. *Inorg. Synth.* 1972, 13, 121.

was stirred at room temperature for 3 h. Then hydrazine hydrate (1.87 g, 3.71 mmol) was added to the mixture, and stirring was continued for 2 h. The resulting polymer was filtered, washed with ethanol and ether, and dried under vacuum to give a dark green polymeric complex. All above procedures were carried out under a nitrogen atmosphere. The analysis showed the following: C, 74.47%; H, 5.63%; Cl, 2.75; P, 9.13%. This corresponds to a ratio of P/Pd of 3.9, where the palladium content was calculated by difference. The polymeric Pd(0) complex with a P/Pd ratio of 2 was the same as that in a previous paper.⁴

General Procedure for Telomerization of Butadiene with Nucleophiles. The polymeric Pd(0) complex was weighed in a 100-mL glass autoclave. A nucleophilic compound, except for the reaction with H₂O, and solvent were added. The reaction system was flushed with nitrogen three times, and then butadiene was introduced into the reaction vessel. The reaction mixture was heated to an appropriate temperature with stirring. After the reaction, the catalyst was separated from the mixture by centrifugation. The homogeneous solution was treated with a usual workup. The yields of products were determined by GC analysis. The products were collected by the preparative GC method and/or identified by comparisons with authentic samples (retention time in GC, IR, and NMR). For new compounds, the structures were supported by the elemental analysis, IR, and NMR.

1-(Propionyloxy)-2,7-octadiene (IVb): IR (film) 1745 (C=O), 1645 (C=C), 970 (*trans*-CH=CH), 990, 910 cm⁻¹ (CH=CH₂); NMR (CDCl₃) δ 1.12 (t, *J* = 7 Hz, 3 H, CH₃), 1.4–1.8 (m, 2 H, CH₂), 1.8–2.5 (complex, 6 H, =CCH₂ and CH₂CH₃), 4.25 (d, *J* = 5 Hz, 2 H, =CCH₂O), 4.75–5.3 (m, 2 H, =CH₂), 5.5–6.0 (complex, 3 H, =CH).

3-(Propionyloxy)-1,7-octadiene (Vb): IR (film) 1745 (C=O), 1645 (C=C), 990, 910 cm⁻¹ (CH=CH₂); NMR (CDCl₃) δ 1.14 (t, *J* = 7 Hz, 3 H, CH₃), 1.4–1.9 (complex, 4 H, CH₂), 1.9–2.6 (complex, 5 H, =CCH₂, CH₂CH₃, and CHO), 4.8–6.2 (complex, 6 H, olefinic).

1-(Hexanoyloxy)-2,7-octadiene (IVc): IR (film) 1745 (C=O), 1645 (C=C), 970 (*trans*-CH=CH), 990, 910 cm⁻¹ (CH=CH₂); NMR (CDCl₃) δ 0.9 (t, *J* = 5 Hz, 3 H, CH₃), 1.2–1.9 (complex, 8 H, (CH₂)₃CH₃ and CH₂), 1.9–2.5 (complex, 5 H, =CCH₂ and OCOCH₃), 4.52 (d, *J* = 5 Hz, 2 H, =CCH₂O), 4.8–5.3 (m, 2 H, =CH₂), 5.4–6.1 (complex, 3 H, =CH).

3-(Hexanoyloxy)-1,7-octadiene (Vc): IR (film) 1740 (C=O), 1645 (C=C), 990, 910 cm⁻¹ (CH=CH₂); NMR (CDCl₃) δ 0.9 (t, *J* = 5 Hz, 3 H, CH₃), 1.1–1.9 (complex, 10 H, (CH₂)₃CH₃ and CH₂), 1.9–2.6 (complex, 5 H, =CCH₂, OCOCH₂, and CHO), 4.8–6.2 (complex, 6 H, olefinic).

1-(Triethylsilyl)-2,6-octadiene: IR (film) 1670 (C=C), 1390 (CH₃CH=), 970 cm⁻¹ (*trans*-CH=CH), no band assignable to the terminal C=C bond; NMR (CDCl₃) δ 0.2–1.2 (complex, 17 H, (C₂H₅)₃SiCH₂), 1.3–1.8 (complex, 4 H, =CCH₂), 2.05 (br s, 3 H,

=CCH₃), 5.2–5.7 (complex, 4 H, =CH).

1-(2-Hydroxyethoxy)-2,7-octadiene (VIe): IR (film) 1670 (internal C=C), 1638 (terminal C=C), 1115 (CH₂O), 970 (*trans*-CH=CH), 990, 910 (CH=CH₂); NMR (CDCl₃) δ 1.3–1.8 (m, 2 H, CH₂), 1.8–2.4 (complex, 4 H, =CCH₂), 2.74 (s, 1 H, OH), 3.3–3.9 (complex, 4 H, C₂H₄OH), 3.98 (d, *J* = 4 Hz, 2 H, OCH₂C=), 4.7–5.3 (m, 2 H, =CH₂), 5.7–6.0 (complex, 3 H, =CH).

The stereochemistry of the double bond of 2:1 adducts was assigned as *trans* on the basis of strong absorption in the 970-cm⁻¹ region of the IR and the lack of band between 650 and 700 cm⁻¹.

Reaction of Butadiene with H₂O. The polymeric Pd(0) complex (0.134 g, 0.1 mmol) was weighed into a 100-mL stainless-steel autoclave. H₂O (2.15 mL) and acetone (20 mL) were added. The system was flushed with nitrogen three times in a manner similar to that for other nucleophilic compounds, and then butadiene (60 mmol) was added. The reaction mixture was pressurized to 10 atm with CO₂, and after 20 h at 95 °C, the mixture was subjected to centrifugation. The GC analysis of the resulting solution showed 86% of 1-hydroxy-2,7-octadiene, 9% 3-hydroxy-1,7-octadiene, and 6% III at 70% conversion of butadiene.

Reaction of 2:1 Adduct Telomers with Pd(0) Complex under an N₂ Atmosphere. The following is a typical procedure used for 1-phenoxy-2,7-octadiene (VIId). In a test tube were placed the diene VIId (0.5 g, 2.5 mmol), the polymeric Pd(0) catalyst with a P/Pd ratio of 2 (5.8 mg, 0.36 mmol of Pd), and acetone (2 mL) under a nitrogen atmosphere. The tube (ca. 3 mL) was sealed, and the mixture was stirred at 95 °C for 18 h. The GC analysis showed the triene III (32%), 3-phenoxy-1,7-octadiene (VIIId, 18%), and the unreacted diene VIId (50%).

Registry No. Ia, 35755-84-1; Ib, 67732-44-9; Ic, 64596-17-4; Id, 35755-79-4; Ie, 76927-73-6; I (R = Bu), 76946-76-4; I (R = allyl), 76927-74-7; I (R = Ph), 35755-82-9; IIa, 40931-39-3; IIb, 64579-51-7; II (R = Bu), 69873-63-8; II (R = allyl), 76927-75-8; III, 1002-35-3; IVa, 30460-73-2; IVb, 76927-76-9; IVc, 76927-77-0; Va, 3491-26-7; Vb, 28720-92-5; Vc, 76927-78-1; VIa, 35702-75-1; VIb, 51586-85-7; VIc, 51650-42-1; VIId, 15972-89-1; VIe, 75320-42-2; VIIa, 20202-62-4; VIIb, 30566-41-7; VIIId, 15972-91-5; VIIe, 42954-39-2; 1,3-butadiene, 106-99-0; morpholine, 110-91-8; piperidine, 110-89-4; diethylamine, 109-89-7; dipropylamine, 142-84-7; diisopropylamine, 108-18-9; butylamine, 109-73-9; allylamine, 107-11-9; aniline, 62-53-3; acetic acid, 64-19-7; propanoic acid, 79-09-4; hexanoic acid, 142-62-1; formic acid, 64-18-6; water, 7732-18-5; 1,7-octadiene, 3710-30-3; 1,6-octadiene, 3710-41-6; 2,7-octadien-1-ol, 23578-51-0; 1,7-octadien-3-ol, 30385-19-4; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; phenol, 108-95-2; 1,2-ethanediol, 107-21-1; 2-(methylamino)ethanol, 109-83-1; *N*-(2-hydroxyethyl)-*N*-methyl-2,7-octadien-1-amine, 76927-79-2; (*E*)-1-(triethylsilyl)-2,6-octadiene, 76927-80-5; triethylsilane, 617-86-7; Pd, 7440-05-3; Pd(PPh₃)₄, 14221-01-3; polystyrene, 9003-53-6.