Palladium-Catalyzed Head-to-Head Telomerization of Isoprene with Amines

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The palladium complex of tris(2,4,6-trimethoxyphenyl)phosphine (TTMPP) catalyzes the telomerization of isoprene with several secondary amines with unprecedented levels of selectivity for the head-to-head isomer. A mechanism based on stereoelectronic control by a Pd−monophosphine adduct is proposed.

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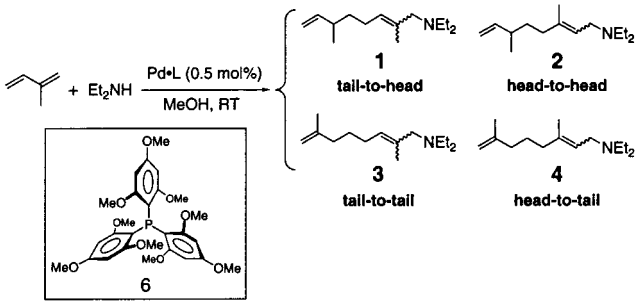
The palladium-catalyzed telomerization of 1,3-butadiene with nucleophiles to give linear octadienes was first reported in 1967.[1] Linear telomerization of isoprene with nucleophilic capture can occur in a head-to-head, head-to-tail, tail-to-head, or tail-to-tail manner, providing a potential route to terpenoid compounds. Regioselectivity is generally modest and can be influenced to some extent by solvent, choice of catalyst and cocatalyst, and temperature.[2−4] Here we report the results of a detailed survey of reaction conditions in the Pd(II)−phosphine-catalyzed telomerization of isoprene with amines and the discovery of a system highly selective for the production of the head-to-head isomer **2**.

Results and Discussion

The telomerization reaction of isoprene and diethylamine catalyzed by a 2:1 mixture of PPh_3 and $PdCl_2$ has been reported to give isomer **4** as the largest component (28%) of the product mixture (Scheme 1).[3d] We thought it likely that the assembly of isoprene and amine units around the catalytic center(s) would be sterically and/or stereoelectronically demanding, and therefore a survey of ligands was judged to be warranted in a search for selective pathways.[5,6]

Scheme 1



When the phosphine to $PdCl_2$ ratio is reduced from the previously reported 2:1 to 1:1, reaction rates are substantially increased and isomer **1** becomes the major component of the product mixture (Table 1, entry 1). Methanol proved to be a far better solvent/additive than other alcohols or organic solvents. Trialkylphosphines do not promote catalysis with $PdCl_2$, and the reaction proved to be somewhat sensitive to the steric and electronic nature of triarylphosphines. For example, tris(*o*-tolyl)phosphine provides no catalytic activity and tris(*p*-chlorophenyl)phosphine gives a sluggish catalyst relative to triphenyl and tris(*p*-tolyl)phosphine. Trialkyl and triaryl phosphites afford similar selectivities and thus manifest less sensitivity to steric and electronic factors (e.g., entries 2 and 3). The addition of CO_2 to telomerization reactions of both butadiene and isoprene has been reported to have dramatic effects on reaction time and selectivity.[2c,7] However, CO_2 had no significant influence on the triphenylphosphine reaction.

Faster telomerization reactions were observed with $[Pd(C_3H_5)(cod)]BF_4$ (**5**) as the precatalyst (cod = 1,5-cyclooctadiene), consistent with a previous report of high activities with cationic palladium complexes.[8] Thus,

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(5) See Experimental Section for details.

(6) Products were initially identified by preparative GC and their assignments confirmed by comparison of NMR spectra to literature data.[3c,d]

(7) (a) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *J. Chem. Soc., Chem. Commun.* **1971**, 330. (b) Kaneda, H.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1981**, *46*, 2356−2362. (c) Bianchini, J. P.; Waegell, B.; Gaydou, E. M.; Rzehak, H.; Keim, W. *J. Mol. Catal.* **1981**, *10*, 247−252.

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Table 1. Selected Telomerization Reactions Using Phosphine Ligands[a]

entry	ligand	Pd	P:Pd	time, h	conv, %	amt, % 1	2	3	4
1	PPh_3	$PdCl_2$	1:1	40	100	48.4	17.7	21.3	12.6
2	$P(OEt)_3$	$PdCl_2$	1:1	40	100	46.7	5.0	27.4	20.8
3	$P(OPh)_3$	$PdCl_2$	1:1	40	79	45.6	4.6	28.0	21.8
4	PCy_3	**5**	1:1	40	100	56.6	9.6	29.2	4.6
5	$P(p\text{-tolyl})_3$	**5**	1:1	40	100	50.6	10.1	27.3	12.0
6	$P(o\text{-tolyl})_3$	**5**	1:1	40	100	52.7	21.8	18.7	7.7
7	**6**	$PdCl_2$	1:1	40	9	18.4	81.0	<0.5	<0.5
8[b]	**6**	$PdCl_2$	1:1	168	100	10.8	88.4		<0.5
9[c]	**6**	$PdCl_2$	1.5:1	96	100	3.4	96.6		
10	**6**	**5**	1:1	40	100	15.2	83.5		1.3
11[c]	**6**	**5**	1.5:1	72	100	6.1	93.0		0.5

[a] Reaction conditions: Pd, 0.025 mmol; MeOH, 0.50 mL; isoprene, 0.50 mL (5 mmol); Et_2NH, 0.50 mL (4.8 mmol); room temperature; nitrogen atmosphere. [b] $T = 0$ °C. [c] Reaction conditions: MeOH, 1.0 mL; isoprene, 0.50 mL; Et_2NH, 0.50 mL.

trialkylphosphines, which showed no activity with $PdCl_2$, gave rise to substantial conversion with the cationic system, although these systems were still less active than most of those employing triarylphosphines. Tail-to-head isomer **1** was again the major product, with more **2** and less **4** than is observed for triarylphosphines; tricyclohexylphosphine provided the most selective example of this class (entry 4). Selectivity with triarylphosphines was similar to the results obtained with $PdCl_2$. While the more active Pd precursor allowed the participation of tris(*o*-tolyl)phosphine, the observed selectivity for **1** was similar to that for the less hindered *p*-tolyl analogue (entries 5 and 6). The highest selectivity for tail-to-tail coupling (giving a 49% yield of **3**) was observed with the hindered tris(2-*tert*-butylphenyl) phosphite, although the reaction was very slow.[9,10]

The reaction profile changed dramatically with both palladium precursors when tris(2,4,6-trimethoxyphenyl)phosphine[11] (**6**; Scheme 1) was employed. Under the standard $PdCl_2$ reaction conditions, **6** gave a very slow reaction but a dramatic increase in the relative production of head-to-head isomer **2** to 81% of the product mixture (entry 7). Allowing the original reaction with $PdCl_2$ to proceed for 1 week at 0 °C afforded a quantitative yield of an 8:1 ratio of **2** to **1** (entry 8). Selectivity proved to be sensitive to the amount of methanol in the reaction mixture: halving the methanol component caused a precipitous decline in **2** and, interestingly, a significant amount of telomerization products incorporating methanol, whereas doubling the amount of methanol improved the yield of **2** slightly. The addition of more methanol past this point resulted in a significant reduction in reaction rate. When a 1.5:1 ratio of phosphine to $PdCl_2$ was used along with the larger amount of methanol, a slow but very clean reaction with the maximum selectivity for **2** vs **1** of 28:1 was observed (entry 9). The same reaction with the cationic palladium precatalyst **5** provided similar selectivities for **2**. These

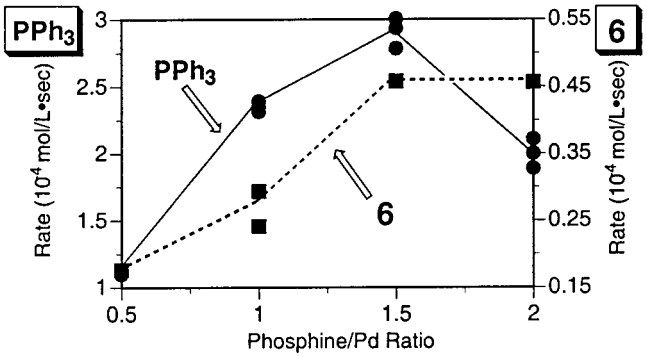

Figure 1. Rate vs P/Pd ratio for telomerization reactions with catalysts derived from cationic Pd precursor **5** and two different phosphines.

Scheme 2

$$\underset{\text{inactive}}{[Pd]} \overset{+L}{\underset{K_1}{\rightleftharpoons}} \underset{\text{active}}{[PdL]} \overset{+L}{\underset{K_2}{\rightleftharpoons}} \underset{\text{inactive}}{[PdL_2]}$$

reactions are somewhat faster than with $PdCl_2$ and not as sensitive to the amount of methanol, giving a maximum selectivity of 15:1:0.1 for **2**:**1**:**4** (entries 10 and 11). Similar head-to-tail selectivity was observed with **6** and morpholine or dimethylamine. Using the conditions of entry 9, diene **2** was prepared on a 75 mmol scale and isolated as an *E*/*Z* mixture in 78% yield. When catalyst (**5** + **6**) concentration is diminished to less than 0.2 mol %, a maximum of approximately 400 turnovers is observed before the reaction stops.

To determine the composition of the active catalyst, kinetics experiments were performed using **5** with PPh_3 or **6**.[12,13] The results are shown in Figure 1. For PPh_3, the reaction rate doubles as the P/Pd ratio is increased from 0.5:1 to 1:1. A smaller rate increase is observed on going to 1.5 equiv of phosphine, and the rate falls when 2 equiv is used. Although fewer runs were conducted with **6**, a similar trend is observed: the rate increases roughly linearly with phosphine concentration through a P:Pd ratio of 1.5:1 and then levels off at 2.0:1. These data are consistent with a first-order dependence on phosphine at low P:Pd ratios and thus with a *monophosphine* Pd complex as the active catalyst species. As more PPh_3 is added, $Pd(PPh_3)_2$ complexes are generated, which are relatively inactive compared with the monophosphine species, causing a drop in observed rate. Thus, the observed rate is determined by the relative concentrations of phosphine-free, PdL, and PdL_2 species, as well as their different catalytic efficiencies. For the highly hindered ligand **6**, one can expect the equilibrium constant for formation of PdL complexes to be much larger than that for the formation of PdL_2 species ($K_1 \gg K_2$; Scheme 2), and therefore the concentration of PdL (and thus the observed rate) reaches a plateau at a P:Pd ratio of about 1.5:1 and does not diminish in the presence of more phosphine.

(8) Röper, M.; He, R.; Schieren, M. *J. Mol. Catal.* **1985**, *31*, 335−343.

(9) In this case, as in all others examined, raising the temperature to 60 °C gave increasing amounts of other unidentified products, without substantial change in selectivity of the telomerization reaction.

(10) Note that interesting tail-to-tail selectivity has been achieved in a multicomponent diene coupling process: Kimura, M.; Matsuo, S.; Shibata, K.; Tamaru, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3386-3388.

(11) (a) Dunbar, K. R.; Haefner, S. C. *Polyhedron* **1994**, *13*, 727−736. (b) Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482−483. (c) The ligand is now commercially available.

(12) The $PdCl_2/PPh_3$ system is not completely homogeneous, requiring the use of the soluble cationic allylpalladium starting material for kinetics.

(13) The phosphine:Pd ratios were varied from 0.5:1 to 2:1 and the reaction rates determined by following the disappearance of isoprene relative to an internal standard by ^1H NMR spectroscopy. Graphs of the amount of isoprene remaining vs time provided straight lines through more than 50% completion, consistent with zero-order (saturated) kinetics, and the rates were calculated from the measured slopes of these lines.

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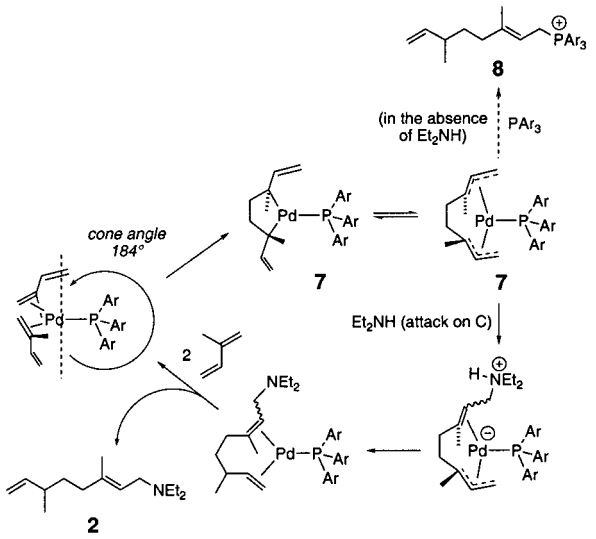
Scheme 3



Our working mechanistic hypothesis, based on previous proposals,[14] is shown in Scheme 3; we assume that Pd(II) is reduced to Pd(0) prior to the initiation of catalysis.[4b] The large size of **6** (cone angle 184°)[11] prevents bis(phosphine) complex formation and directs the loading of the two dienes on the Pd(0) center such that the more hindered ends of isoprene are away from the bulky phosphine. The dienes may then undergo oxidative coupling to generate the symmetric bis(allylic) species **7**; similar compounds have been isolated and characterized.[14a,15] The importance of electronic factors is demonstrated by the observation that tris(*o*-tolyl)-phosphine (of comparable size to **6**, cone angle 194°)[16] gives poor catalytic activity and poor selectivity; presumably, an electron-rich phosphine is required to support the oxidative C−C bond-forming step. Nucleophilic attack by amine occurs at one of the equivalent terminal carbons of **7**, followed by protonation of the remaining allyl group (perhaps via a Pd−hydride) at the internal position to give the more stable monosubstituted coordinated olefin fragment. Ligand substitution of the resulting diene completes the catalytic cycle. Attack of nucleophile at the metal as previously observed for β-keto esters[14b] is possible but is less likely due to the lack of an acidic residue in the present case. A bimetallic mechanism of the type proposed by Keim[2g,3b] can likewise not be ruled out but seems implausible for such a bulky phosphine. When amine is omitted from the reaction mixture, the same regiochemistry is established in diene coupling, but the C_8−bis(allyl)palladium intermediate system is intercepted by the labile and highly nucleophilic phosphine to give the corresponding phosphonium adduct **8**, which has been characterized by X-ray crystallography.

Similar direction to the 3,6-dimethyl (head-to-head) isomer has been reported in low-temperature nickel-catalyzed isoprene dimerizations in the presence of the bulky tricyclohexylphosphine.[17] Most importantly, Trost and Zhi have reported that isoprene telomerization with activated carbon nucleophiles is diverted from a 4:1 tail-to-tail selectivity to 6:1 selectivity in favor of the head-to-head isomer by the use of the hindered ligand tris(2,6-dimethoxyphenyl)phosphine.[18] It seems likely that the mechanism of this latter process closely resembles the one we describe here.

Metal-catalyzed diene coupling reactions remain important tools for the synthesis of highly useful olefinic frameworks. Our observation of unprecedented levels of regioselectivity in isoprene telomerization using a commercially available phosphine, along with the apparent simplicity of the coordination environment of the active species, suggests that further tailoring of the catalytic site with modified ligands may allow more complete control of this valuable family of C−C bond-forming processes.

Experimental Section

General Experimental Details. All catalytic experiments were carried out under dry nitrogen in an inert-atmosphere glovebox (Vacuum Atmospheres Co.) or using standard Schlenk techniques. Unless otherwise noted, all reactions were performed at room temperature. Infrared spectra were recorded on a Nicolet Impact-400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on General Electric QE 300 or GN-300 spectrometers at 300.15 and 75.5 MHz, respectively, and referenced to solvent peaks. Preparative GC was carried out on a GowMac instrument using a 0.25 in. × 3 ft Chromosorb-W packed column. Product ratios were obtained by direct analysis of reaction mixtures by GC/MS (Hewlett-Packard 1100 MSD instrument; 30 m DB-5 capillary column) following quenching of the catalyst by exposure to air. The detection efficiencies of each of the isomers **1**−**4** with respect to an internal standard were found to be very similar. Thus, the ratios of these products were derived directly from their relative peak areas measured in the GC/MS spectra. The percent conversion was measured by following the disappearance of isoprene by GC/MS; unless otherwise mentioned, no products other than the reported telomers were detected. Elemental analyses were obtained on a Perkin-Elmer PE-2400 Series II CHN analyzer, using acetanilide as calibration standard. Isoprene and methanol were dried over CaH_2 and distilled prior to use. Diethylamine (Aldrich) and all phosphines were used as received. $PdCl_2$ (Fisher) was used as received. [Pd(η^3-C_3H_5)(cod)]BF_4[19] and [Rh(cod)(BINAP)]BF_4[20] were prepared according to literature procedures.

Catalytic Screening Experiments: Results and Comments. Below is a complete description of experiments performed to test the influence of a variety of variables on the telomerization process, from which the results and conclusions reported above (including Table 1) are derived.

Table 2 shows the results of varying solvent in the $PdCl_2$:PPh_3 = 1:1 system. The dependence of the reaction on the steric and electronic nature of the phosphine ligand was probed with experiments summarized in Table 3. No conversion of isoprene was observed in the presence of trialkylphosphines, (entries 1−5) except for di-*tert*-butylphosphine (entry 6), for which the desired telomerization products constituted only about half the final mixture. Triarylphosphines (entries 7−9

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Table 2. Telomerization Using $PdCl_2/PPh_3$ in Different Solvents[a]

			amt, %				
entry	solvent	conv, %	**1**	**2**	**3**	**4**	other
1	MeOH	100	45.4	17.7	21.3	15.5	
2	EtOH	28	44.2	5.1	25.8	24.9	
3	MeCN	43	41.4	8.6	23.3	26.7	
4	MeCN[b]	100	25.9	3.2	34.6	33.6	2.7
5	DMF	0					
6	toluene	0					
7	THF	0					

[a] Reaction conditions: $PdCl_2$, 4.5 mg (0.0254 mmol); PPh_3, 6.6 mg (0.0252 mmol); solvent, 0.5 mL; isoprene, 0.5 mL (5 mmol); Et_2NH, 0.5 mL (4.8 mmol); time, 40 h. [b] Reaction conditions: reaction time, 18 h; reaction temperature, 69 °C.

Table 3. Telomerization Using $PdCl_2$ and Various Phosphorus Ligands[a]

			conv,	amt, %				
entry	phosphine	solvent	%	**1**	**2**	**3**	**4**	other
1	PEt_3	MeOH	0					
2	P(*n*-Bu)$_3$	MeOH	0					
3	P(*t*-Bu)$_3$	MeOH	0					
4	PCy_3	MeOH	0					
5	P(CH_2CH_2-CN)$_3$	MeOH	0					
6	P(*t*-Bu)$_2$H	MeOH	23	30.7	2.2	17.1	3.4	46.5
7	PPh_3	MeOH	100	48.4	17.7	21.3	12.6	
8	dppp	MeOH	100	51.0	27.5	10.7	10.7	
9	P(4-Cl-C_6H_4)$_3$	MeOH	41	44.8	3.3	27.2	24.7	
10	P(4-Cl-C_6H_4)$_3$	CH_3CN	11	37.5	20.7	12.5	29.3	
11	P(*p*-tolyl)$_3$	MeOH	100	50.7	12.3	24.6	12.4	
12	P(*o*-tolyl)$_3$	MeOH	0					
13	P(2-furyl)$_3$	MeOH	0					
14	P(C_6F_5)$_3$	MeOH	0					
15	PPh_3/CO_2	MeOH	100	51.9	28.2	8.2	11.7	
16	P(OMe)$_3$	MeOH	58	54.5	8.0	23.9	13.5	
17	P(OEt)$_3$	MeOH	100	46.7	5.0	27.4	20.8	
18	P(OEt)$_3$	CH_3CN	11	44.5	12.6	17.5	25.3	
19	P(OBu)$_3$	MeOH	100	45.9	4.8	28.4	20.9	
20	P(OBu)$_3$[b]	MeOH	100	35.5	12.2	21.8	29.7	
21	P(OBu)$_3$	CH_3CN	<1					
22	P(OCH_2CF_3)$_3$	MeOH	60	50.1	3.1	27.4	19.3	
23	P(OPh)$_3$	MeOH	79	45.6	4.6	28.0	21.8	
24	P(OPh)$_3$	CH_3CN	0					
25	P($OSiMe_3$)$_3$	MeOH	19	35.5	22.9	33.9	7.6	
26	P($OSiEt_3$)$_3$	MeOH	0					
27	P($SiMe_3$)$_3$	MeOH	0					
28	P(NMe_2)$_3$	MeOH	0					
29	$AsPh_3$	MeOH	0					

[a] Reaction conditions: $PdCl_2$, 4.5 mg (0.0254 mmol); phosphine, 0.025 mmol;"solvent", 0.5 mL; isoprene, 0.5 mL (5 mmol); Et_2NH, 0.5 mL (4.8 mmol); time, 40 h. [b] Reaction conditions: reaction time, 18 h; reaction temperature, 69 °C.

and 11) and trialkyl phosphites (entries 16, 17, 19, 20, 22, and 23) led to the production of **1** as the major isomer in 40−50% yield (entries 1−3 and 5). Tris(2,2,2-trifluoroethyl) phosphite (entry 22), which is more electron-deficient than its nonfluorinated counterpart (entry 17), is a bit less reactive but affords nearly identical selectivity. Triphenyl phosphite (entry 23) shows behavior similar to that of trialkyl phosphites under similar conditions (entries 16, 17, and 19). Thus, electronic factors do not seem to play a dominant role.

More rapid telomerization reactions using [Pd(C_3H_5)(cod)]-BF_4 as the precatalyst are summarized in Table 4. Trialkylphosphines, which showed no activity with $PdCl_2$, gave rise to substantial conversion with the cationic allylpalladium complex. As above, tail-to-head isomer **1** is again the major product, with more **2** and less **4** than is observed for triarylphosphines (entries 1−6). The selectivity was likewise similar to that of either palladium precursor in the presence of triarylphosphine and phosphite ligands, although the greater activity of the cationic system allowed several cases

Table 4. Telomerization Using [Pd(C_3H_5)(cod)]BF_4 and Various Phosphorus Ligands[a]

			conv,	amt, %			
entry	phosphine	solvent	%	**1**	**2**	**3**	**4**
1	PEt_3	MeOH	100	55.9	16.7	21.5	5.8
2	P(*n*-Bu)$_3$	MeOH	37	45.8	32.4	16.5	5.3
3	P(*t*-Bu)$_3$	MeOH	32	43.6	12.8	36.4	7.2
4	PCy_3	MeOH	100	56.6	9.6	29.2	4.6
5	P(CH_2CH_2CN)$_3$	MeOH	48	45.9	19.5	23.8	10.8
6	PEt_2H	MeOH	100	53.8	27.9	13.7	4.5
7	PPh_3	MeOH	100	45.9	9.9	27.1	17.1
8	dppp	MeOH	43	46.9	5.3	31.3	16.5
9	P(4-Cl-C_6H_4)$_3$	MeOH	100	41.7	4.7	26.8	26.8
10	P(4-Cl-C_6H_4)$_3$[b]	MeOH	72	16.4	19.0	34.7	29.8
11	P(4-Cl-C_6H_4)$_3$	toluene	100	27.8	2.0	38.1	32.1
12	P(4-Cl-C_6H_4)$_3$	THF	100	31.2	2.0	34.2	32.6
13	P(*p*-tolyl)$_3$	MeOH	100	50.6	10.1	27.3	12.0
14	P(*o*-tolyl)$_3$	MeOH	100	52.7	21.8	18.7	7.7
15	P(2-furyl)$_3$	MeOH	80	40.4	8.2	24.0	27.4
16	P(2-furyl)$_3$	toluene	12	20.8	2.6	40.9	35.8
17	P(2-furyl)$_3$	THF	54	38.8	3.3	27.9	29.9
18	P(C_6F_5)$_3$	MeOH	0				
19	P(OMe)$_3$	MeOH	100	39.8	3.4	29.1	27.5
20	P(OMe)$_3$	toluene	100	19.5	21.3	18.6	40.6
21	P(OMe)$_3$	THF	100	27.8	2.4	31.3	38.5
22	P(OCH_2CF_3)$_3$	MeOH	100	50.5	13.2	24.0	12.3
23	P(OPh)$_3$	MeOH	100	43.1	5.1	27.9	23.9
24	P(OPh)$_3$	toluene	23	13.4	5.3	56.0	25.3
25	P(OPh)$_3$	THF	16	15.4	4.1	45.4	35.0
26	P($OSiMe_3$)$_3$	MeOH	73	13.5	76.1	0.0	10.3
27	P($OSiEt_3$)$_3$	MeOH	28	41.2	19.6	29.7	9.2
28	P($SiMe_3$)$_3$	MeOH	<1				
29	$AsPh_3$	MeOH	71	26.7	32.6	31.1	9.6
30	P(O-2-*t*-BuC_6H_4)$_3$	MeOH	28	20.2	15.2	49.3	15.2
31	P(2-OMe-C_6H_4)$_2$Ph	MeOH	100	52.3	18.2	22.4	6.9
32	P[2,4,6-($OMe)_3$-C_6H_2]$_3$	MeOH	100	15.2	83.5	0.0	1.3

[a] Reaction conditions: [Pd(C_3H_5)(cod)]BF_4, 4.2 mg (0.012 mmol); phosphine, 0.012 mmol; "solvent", 0.25 mL; isoprene, 0.25 mL (2.5 mmol); Et_2NH, 0.25 mL (2.4 mmol); time, 40 h. [b] Reaction conditions: reaction time, 20 h; reaction temperature, 60 °C.

to be measured for the first time (entries 14−17, 27, and 29). For example, the increased steric bulk of P(*o*-tolyl)$_3$ relative to P(*p*-tolyl)$_3$ gave rise to more **2**, less **3**, and less **4** (entry 13 vs 14), but the changes are modest. While the use of toluene or THF shuts down the $PdCl_2$-catalyzed process, [Pd(C_3H_5)-(cod)]$^+$ gave observable, although slower, reactions (entries 11−12, 16−17, 20−21, and 24−25) that show small changes in selectivity when compared to methanol.

Reactions using tris(2,4,6-trimethoxyphenyl)phosphine (**6**) are shown in Table 5. In addition to the comments in the text, the following trends were observed. The reaction rate increases at the expense of selectivity at increased temperature (entries 3 and 4). Bis(2-methoxyphenyl)phenylphosphine gives selectivity characteristic of a "normal" triarylphosphine (entries 13 and 14; compare to Table 3, entry 7), and the very hindered tris(2-*tert*-butoxyphenyl)phosphine is ineffective.

Larger Scale Production of 2 and Confirmation of Structure. Diene **2** was prepared on a 75 mmol scale and isolated as an *E*/*Z* mixture in 78% yield. To confirm its structure, 3,6-dimethyloct-7-enal (**9**) was prepared from **2** as a mixture of diastereomers by Rh−BINAP-catalyzed isomerization to the enamine,[20] followed by acidic hydrolysis (Scheme 4). Similarly, a mixture of (*E*)- and (*Z*)-3,6-dimethylocta-2,7-dienal (**10**) was prepared from **2** by oxidative rearrangement.[21] The aldehydes **9** and **10** were spectroscopically characterized, and elemental analysis was successfully performed on their 2,4-dinitrophenylhydrazone derivatives.

***N,N*-Diethyl-3,6-dimethyl-2,7-octadienylamine (2).** $PdCl_2$ (0.155 g, 0.874 mmol), P[2,4,6-($OMe)_3$Ph]$_3$ (0.698 g, 1.311

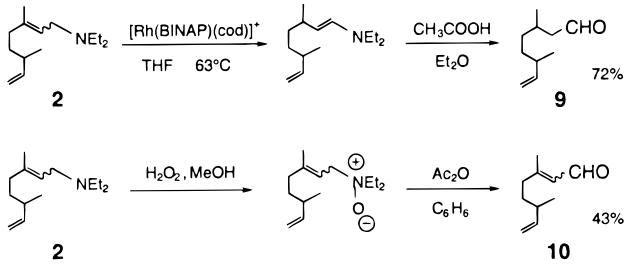
(21) Takabe, K.; Yamada, T.; Katagiri, T. *Chem. Lett.* **1982**, 1987−1988.

Table 5. Telomerization Using *o*-Alkoxy-Substituted Triarylphosphines[a]

entry	ligand	Pd	P:Pd	time, h	conv, %	amt, % 1	2	3	4	others[b]
1	**6**	$PdCl_2$	1:1	40	9	18.4	81.0	<1.0	<1.0	
2	**6**	$[Pd]^+$	1:1	40	100	15.2	83.5		1.3	
3[c]	**6**	$PdCl_2$	1:1	18	95	32.1	66.8		1.0	5.9
4[d]	**6**	$[Pd]^+$	1:1	18	100	19.4	77.8		2.8	
5[e]	**6**	$PdCl_2$	1:1	168	100	10.8	88.4		<1.0	
6	**6**	$PdCl_2$	1.5:1	84	100	8.2	86.0	<1		4.8
7	**6**	$PdCl_2$	2:1	84	50	9.0	88.7		<1.0	1.3
8[f]	**6**	$PdCl_2$	1:1	84	88	36.0	52.0		0.3	11.7
9[g]	**6**	$PdCl_2$	1:1	90	100	6.9	90.7	1.2	1.3	1.1
10[g]	**6**	$PdCl_2$	1.5:1	96	100	3.4	96.6			
11	**6**	$[Pd]^+$	1.5:1	72	100	15.2	83.5		1.3	
12[g]	**6**	$[Pd]^+$	1.5:1	72	100	6.1	93.0		0.5	
13	$P(2\text{-}OMe\text{-}C_6H_4)_2Ph$	$PdCl_2$	1:1	40	72	55.5	27.3	11.1	6.1	
14	$P(2\text{-}OMe\text{-}C_6H_4)_2Ph$	$[Pd]^+$	1:1	40	100	52.3	18.2	22.4	6.9	
15	$P(O\text{-}2\text{-}t\text{-}BuC_6H_4)_3$	$PdCl_2$	1:1	40	0					
16	$P(O\text{-}2\text{-}t\text{-}BuC_6H_4)_3$	$[Pd]^+$	1:1	40	28	20.2	15.2	49.3	15.2	

[a] Reaction conditions: Pd, 0.025 or 0.0124 mmol; phosphine; MeOH, 0.50 or 0.25 mL; isoprene, 0.50 or 0.25 mL; Et_2NH, 0.50 or 0.25 mL; temperature, 25 °C. Legend: **6**, $P[2,4,6\text{-}(OMe)_3C_6H_2]_3$; **5**, $[Pd(C_3H_5)(COD)][BF_4]$. [b] Principally dimethyloctadienyl methyl ethers from telomerization incorporating methanol. [c] Reaction conditions: temperature, 69 °C. [d] Reaction conditions: temperature, 63 °C. [e] Reaction conditions: temperature, 0 °C. [f] Reaction conditions: MeOH, 0.25 mL; isoprene, 0.50 mL; Et_2NH, 0.50 mL. [g] Reaction conditions: MeOH, 1.0 mL; isoprene, 0.50 mL; Et_2NH, 0.50 mL.

Scheme 4



mmol), MeOH (30 mL), isoprene (15 mL, 150 mmol), and diethylamine (15 mL, 145 mmol) were stirred for 7 days at room temperature. The resulting gray solid was filtered away, and the methanol and excess diethylamine were removed by distillation. Further distillation gave **2** (12.2 g, 78%) as a clear liquid of 88% regioisomeric purity (GC analysis), which was used in the preparation of **9** without further purification.

3,6-Dimethyl-7-octenal (9). THF (15 mL), **2** (3.7 g, 17.6 mmol), and $[Rh(cod)(BINAP)]BF_4$ (0.032 g, 0.342 mmol) were heated at 60 °C for 23 h under nitrogen. The THF was then evaporated, and the remaining mixture was purified by bulb-to-bulb (Kugelrohr) distillation (200 °C, 9 mm) to provide the intermediate enamine (2.3 g, 62%). This compound was diluted with ether (5 mL), and a 1:4 mixture of glacial acetic acid and water (5.4 mL) was added dropwise at 0 °C. The solution was stirred at 0 °C for 5 min and then for 25 min at room temperature. The ether layer was collected, washed with water (5 mL), saturated $NaHCO_3$ (2 × 5 mL), water (5 mL), and saturated NaCl (5 mL), and then dried over Na_2SO_4 and filtered. The ether was removed by evaporation, and the product was distilled at 147 °C/25 mm to give **9** as a colorless oil (1.2 g, 72%). IR (neat): 1727 cm^{-1} ν(C=O). ^1H NMR (300 MHz, $CDCl_3$): δ 9.75 (s, 1H, CHO); 5.66 (m, 1H, =CH); 4.93 (m, 2H, H_2C=); 2.39 (m, 1H, *H*CCHO); 2.21 (m, 1H, *H*CCHO); 2.04 (m, 2H, *H*CCH_3); 1.28 (m, 4H, CH_2); 0.98 (d, 3H, ^3J(HH) = 7.3 Hz, CH_3); 0.95 (d, 3H, ^3J(HH) = 7.7 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.0 (s, CO); 144.5 (s, =C); 112.6 (s, C=); 51.0 (s, *C*CO); 37.9 (s, =C*C*); 34.4 (s, CH_2); 33.8 (s, CH_2); 28.2 (*C*CO); 20.1 (s, CH_3); 20.0 (s, CH_3). Elemental analysis of this oil was unsatisfactory; therefore, its 2,4-dinitrophenyl hydrazone was prepared as an immediate precipitate upon reaction of 2,4-dinitrophenylhydrazine (0.25 g, 1.26 mmol) with **9** (0.14 g, 0.09 mmol) in MeOH (5 mL) in the presence of concentrated H_2SO_4 (0.4 mL). The solid was collected, washed with a small amount of cold methanol, and recrystallized from ethanol to give 0.15 g of the hydrazone (49% yield). ^1H NMR (250 MHz, $CDCl_3$): δ 11.01 (s, 1H, NH); 9.11 (d, 1H, ^3J(HH) = 2.6 Hz, Ph H); 8.27 (dd, 1H, ^3J(HH) = 10.2 Hz, ^3J(HH) = 2.6 Hz, Ph H); 7.91 (d, 1H, ^3J(HH) = 9.4 Hz, Ph H); 7.50 (t, 1H, ^3J(HH) = 5.8 Hz, C(H)=N); 5.64 (m, 1H, =CH); 4.91 (m, 2H, H_2C=); 2.34 (m, 2H, C*H*CN); 1.95 (m, 2H, *H*CCH_3); 1.32 (m, 4H, CH_2); 0.99 (d, 6H, ^3J(HH) = 6.4 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2 (s, C=N); 145.0 (s, =C); 144.5 (s, Ph); 137.6 (s, Ph); 129.8 (s, Ph); 128.6 (s, Ph); 123.4 (s, Ph); 116.4 (s, Ph); 112.6 (s, C=); 39.5 (s, *C*C=N); 37.9 (s, =C*C*); 34.5 (s, CH_2); 33.8 (s, CH_2); 31.4 (s, *C*CCN); 20.2 (s, CH_3); 19.7 (s, CH_3). Anal. Calcd for $C_{16}H_{22}N_4O_2$: C, 57.47; H, 6.63; N, 16.76. Found: C, 57.39; H, 6.64; N, 16.69.

3,6-Dimethyl-2,7-octadienal (10). To a solution of **2** (3.5 g, 16.7 mmol) in MeOH (13 mL) was added H_2O_2 (6 mL of 30%) in a dropwise fashion. The reaction mixture was stirred for 23 h, and the excess H_2O_2 was decomposed with $FeBr_3$. The solution was filtered, and the methanol was removed under reduced pressure. To the residue was added benzene (10 mL) and then acetic anhydride (6.0 mL, 63.6 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature, and then 10% HCl (70 mL) was added. The crude octadienal was extracted with ether (3 × 50 mL), and the ether solution was neutralized with saturated $NaHCO_3$ solution, dried over Na_2SO_4, and filtered. The organic solvents were removed by evaporation, and the product was distilled at 133 °C/7 mm (1.1 g, 43%). IR (neat): 1676 ν(C=O) (major); 1633 cm^{-1} ν(C=O) (minor). ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (d, ^3J(HH) = 7.8 Hz, 0.67H, CHO); 9.90 (d, ^3J(HH) = 8.3 Hz, 0.33H, CHO); 5.86 (m, 1H, C*H*CHO); 5.65 (m, 1H, =CH); 4.97 (m, 2H, H_2C=); 2.54 (t, ^3J(HH) = 8.0 Hz, 0.67H, H_2CC=); 2.16 (m, 4.33H, H_2CC=, =CCH, H_3CC=); 1.96 (d, ^4J(HH) = 0.9 Hz, 1H, H_3CC=); 1.50 (m, 2H, CH_2); 1.03 (d, ^3J(HH) = 6.9 Hz, 1H, =CCHC*H*$_3$); 1.01 (d, ^3J(HH) = 6.9 Hz, 2H, =CCHC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.3 (s, CO); 164.4 (s, H_3CC=); 143.6 (s, =C); 127.2 (s, =*C*CO); 113.5 (s, H_2C=); 38.3 (s, CH_2); 37.5 (s, =C*C*H); 33.8 (s, CH_2); 20.2 (s, CH_3); 17.6 (s, CH_3) (major). δ 190.8 (s, CO); 164.9 (s, H_3CC=); 143.4 (s, =C); 128.1 (s, =*C*CO); 113.9 (s, H_2C=); 37.9 (s, =C*C*H); 35.6 (s, CH_2); 30.4 (s, CH_2); 24.9 (s, CH_3); 20.2 (s, CH_3) (minor). As with **9**, conversion to the 2,4-dinitrophenyl hydrazone (as above, yield 74%) was required to obtain adequate elemental analysis. ^1H NMR (250 MHz, $CDCl_3$): δ 11.14 (s, 1H, NH); 9.12 (d, 1H, ^3J(HH) = 2.6 Hz, Ph H); 8.29 (dd, 1H, ^3J(HH) = 9.5 Hz, ^3J(HH) = 2.6 Hz, Ph H); 8.06 (d, 1H, ^3J(HH) = 9.9 Hz, C(H)=N); 7.92 (d, 1H, ^3J(HH) = 9.5 Hz, Ph H); 6.14 (d, 1H, ^3J(HH) = 9.8 Hz, C*H*CHN); 5.66 (m, 1H, =CH); 5.00 (m, 2H, H_2C); 2.20 (m, 3H,

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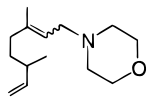
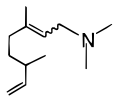
=CHC*H*, CH_2C=); 1.96 (s, 3H, CH_3); 1.52 (m, 2H, CH_2); 1.04 (d, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.1 (s, C=N); 147.4 (s, =*C*CN); 144.6 (s, Ph); 143.9 (s, =C); 140.2 (s, H_3CC=); 137.6 (s, Ph); 129.8 (s, Ph); 128.6 (s, Ph); 123.4 (s, Ph); 120.6 (s, C=N); 116.5 (s, Ph); 113.2 (s, H_2C=); 37.9 (s, CH_2); 37.4 (s, =C*C*); 34.2 (s, CH_2); 20.2 (s, CH_3); 17.6 (s, CH_3). Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.79; H, 6.01; N, 16.73.

Telomerization with Amines Other than Diethylamine. Similar selectivity for head-to-tail telomerization was observed with ligand **6** when morpholine or dimethylamine was used to give 4-(3,6-dimethylocta-2,7-dienyl)morpholine (**11**) and (3,6-dimethylocta-1,7-dienyl)dimethylamine (**12**),[2j] respectively. Propylamine, dibenzylamine, and diisopropylamine each gave significant amounts of other products as well as the desired telomers. Product mixtures rich in the other isomeric isomers were not converted to **2** when subjected to the telomerization reaction conditions.



11



12

4-(3,6-Dimethylocta-1,7-dienyl)morpholine (11). [Pd(η^3-C_3H_5)(cod)]BF_4 (0.034 g, 0.101 mmol), P[2,4,6-$(OMe)_3Ph$]$_3$ (0.080 g, 0.150 mmol), MeOH (4 mL), isoprene (2.0 mL, 10.0 mmol), and morpholine (1.2 mL, 13.8 mmol) were stirred for 3 days at room temperature. The solution was filtered, the solvent was removed under reduced pressure, and the solution was filtered again. Compound **11** was thus obtained in 93% yield by GC analysis relative to an internal standard and was then purified by preparative GC (200 °C) to provide a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 5.64 (m, 1H, H_2C=C*H*); 5.21 (m, 1H, =CH); 4.90 (m, 2H, H_2C=); 3.69 (m, 4H, $(CH_2)_2O$); 2.94 (m, 2H, CH_2N); 2.42 (br s, 4H, $(CH_2)_2N$); (1.97 (m, 3H, =CHC*H*, CH_2C=); 1.61, 1.60 (s, 3H, CH_3C=); 1.37 (m, 2H, CH_2); 0.96, 0.95 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.4 (s, H_2C=*C*); 139.5 (s, H_3CC=); 119.9 (s, =CH); 112.6 (s, H_2C=); 67.0 (s, CH_2O); 56.4 (s, NCH_2); 53.6 (s, CH_2N); 37.5 (s, CH_2 or *C*HCH_3); 37.4 (s, CH_2 or *C*HCH_3); 34.8 (CH_2CH_2); 20.2 (s, CH_3); 16.5 (s, CH_3). Anal. Calcd for $C_{14}H_{25}NO$: C, 75.28; H, 11.28. Found: C, 75.29; H, 11.32.

(3,6-Dimethyloctadienyl)dimethylamine (12). [Pd(η^3-C_3H_5)(cod)]BF_4 (0.034 g, 0.101 mmol), P[2,4,6-$(OMe)_3Ph$]$_3$ (0.080 g, 0.150 mmol), Me_2NH (12 mL of a 2.5 M solution in methanol, 30 mmol), and isoprene (2.0 mL, 20 mmol) were stirred for 3 days at room temperature. The solvent was removed under reduced pressure, and the solution was filtered; **12** was then isolated in 64% yield as a colorless oil by preparative GC (130 °C). ^1H NMR (300 MHz, $CDCl_3$): δ 5.66 (m, 1H, H_2C=C*H*); 5.24 (m, 1H, =CH); 4.93 (m, 2H, H_2C=); 2.87 (d, ^3J(HH) = 6.6 Hz, 2H, CH_2N); 2.21 (s, 6H, NCH_3); 2.15 (m, 3H, =CHC*H*, CH_2C=); 1.63 (s, 3H, CH_3C=); 1.41 (m, 2H, CH_2); 0.99 (d, ^3J(HH) = 6.6 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5 (s, H_2C=*C*); 138.5 (s, H_3CC=); 121.4 (s, =CH); 112.5 (s, H_2C=); 57.0 (s, CH_2N); 45.2 (s, NCH_3); 37.4 (s, CH_2 or *C*HCH_3); 37.3 (s, CH_2 or *C*HCH_3); 34.7 (s, CH_2CH_2); 20.2 (s, CH_3); 16.4 (s, CH_3). Anal. Calcd for $C_{12}H_{23}N$: C, 79.49; H, 12.79. Found: C, 79.24; H, 12.87.

Kinetics Experiments. In a typical experiment CD_3OD (0.375 mL), benzene (0.10 mL, 1.13 mmol) (internal standard), isoprene (0.19 mL, 1.90 mmol), diethylamine (0.19 mL, 1.84 mmol), [Pd(η^3-C_3H_5)(cod)]BF_4 (0.0032 g, 0.0094 mmol), and PPh_3 (0.0025 g, 0.0095 mmol) were placed in an NMR tube under a nitrogen atmosphere. The mixture was shaken well to dissolve the phosphine. Eight minutes later the first spectrum was obtained, and subsequent spectra were recorded every 4 min to a maximum of 30 spectra (approximately every 30 min for reactions involving **6**). The amount of isoprene remaining as a function of time was measured by integration relative to the internal standard, providing linear plots (R^2 > 0.99) well beyond 50% completion in each case.

Preparation of {$C_{10}H_{17}P$[2,4,6-$(OMe)_3Ph$]$_3$}PF_6 (8). $PdCl_2$ (0.150 g, 0.846 mmol), P[2,4,6-$(OMe)_3Ph$]$_3$ (0.540 g, 1.014 mmol), and isoprene (0.5 mL, 5.0 mmol) were stirred in methanol (25 mL) overnight. The resulting deep red solution was exposed to air, filtered through Celite, and treated with a solution of KPF_6 (0.58 g, 3.15 mmol) in methanol (30 mL). After a few minutes, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 and filtered. The solvent volume was reduced to a minimum and the mixture chromatographed on silica gel (1.5 × 9 cm), with CH_2Cl_2/EtOH (18:1) as eluent. Compound **8** elutes before two highly colored fractions and was collected and recrystallized by addition of ether to a concentrated dichloromethane solution. An additional crop of **8** was obtained by repeat chromatography of the combined colored fractions collected from the first column; the total yield of **8** was 0.285 g (35%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.10 (d, ^4J(HP) = 4.6 Hz, 6H, Ph H); 5.54 (m, 1H, H_2C=C*H*); 5.00 (m, 1H, =CH); 4.84 (m, 2H, H_2C=); 3.87 (s, 9H, OCH_3); 3.77 (d, ^3J(HH) = 7 Hz, 2H, =CHCH_2); 3.60 (s, 18H, OCH_3); 1.77 (m, 3H, CH_2, C*H*CH_3); 1.44 (s, 3H, CH_3); 1.00 (m, 2H, CH_2); 0.84 (dd, ^3J(HH) = 6.9 Hz, ^4J(HH) = 1.2 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4 (s, Ph); 163.5 (s, Ph); 144.3 (s, H_2C=*C*); 140.8 (d, ^3J(CP) = 17 Hz, H_3CC=); 114.4 (d, ^2J(CP) = 6 Hz); 112.4 (s, H_2C=); 92.7 (d, ^1J(CP) = 105 Hz, Ph); 90.7 (d, ^3J(HH) = 7 Hz, Ph); 55.7 (s, OCH_3); 55.6 (s, OCH_3); 37.1 (d, ^5J(CP) = 2 Hz, CH_2); 36.6 (s, *C*HCH_3); 34.7 (d, ^4J(CP) = 3 Hz, CH_2); 28.8 (d, ^1J(CP) = 58 Hz, H_2CP); 19.9 (s, CH_3); 16.0 (d, ^4J(CP) = 2 Hz). Anal. Calcd for $C_{37}H_{50}F_6O_9P_2$: C, 54.55; H, 6.19. Found: C, 54.81; H, 6.28.

The X-ray crystal structure of **8** and associated data are reported in the Supporting Information. Isolated **8** is unchanged upon incubation with a large excess of diethylamine and, thus, is not part of the catalytic cycle.

Acknowledgment. We are grateful to Union Camp Corp. for support of this work and to Dr. Walter Frank of Union Camp for helpful discussions.

Supporting Information Available: An ORTEP diagram and tables giving details of the X-ray crystallographic analysis of compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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