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Large P−P Distance Diphosphines and Their Monophosphine Analogues as Ligands in the Palladium-Catalyzed Telomerization of 1,3-Butadiene and Methanol

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The potential of diphosphines based on a dibenzodioxocin or benzofurobenzofuran backbone possessing large P−P distances was studied for the selective telomerization of 1,3-butadiene with methanol under commercially relevant process conditions to obtain 1-methoxyocta-2,7-diene (1-MOD). They were found to act as monophosphines. New bulky monophosphine analogues of the same backbone and ferrocene were also evaluated. Several ligands showed improved selectivity and yield compared to the benchmark ligand PPh_3 and monoxantphos. Especially 1,6-bis-(diphenylphosphino)-5a,10b-dihydro-5a,10b-dimethyl-3,8-dimethylbenzofuro[3,2-*b*]benzofuran (**3**) and, 2,10-di-*tert*-butyl-4-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**7**), a diphosphine and a monophosphine, respectively, stand out as excellent ligands in terms of yield, selectivity, and stability.

Introduction

Linear α-olefins, especially 1-hexene and 1-octene, are key components for the production of highly desirable linear low-density polyethylene (LLDPE), and as a result the demand for 1-hexene and 1-octene has increased enormously in recent years.[1] To meet this demand, the Dow Chemical Company, which is one of the major consumers of 1-octene for the preparation of LLDPE, developed an industrial process for the production of 1-octene from butadiene. The process came on stream in Tarragona (Spain) in 2007.

The commercial route to produce 1-octene based on butadiene as developed by Dow is presented in Scheme 1.[2] The telomerization of butadiene with methanol in the presence of a palladium catalyst yields 1-methoxy-2,7-octadiene, which is fully hydrogenated to 1-methoxyoctane in the next step. Subsequent cracking of 1-methoxyoctane gives 1-octene and methanol, which is recycled.

Currently, the catalytic system used by Dow is composed of Pd/PPh_3. The reaction leads to the formation of 1-methoxy-2,7-octadiene (1-MOD) (Scheme 2). Main byproducts of the reaction are 3-methoxy-1,7-octadiene (3-MOD) and 1,3,7-octatriene (OCT).[3] The control of the selectivity in the first step of the process is crucial, and research efforts on catalyst design and tuning of the reaction parameters aim at this target. Thus, the palladium-catalyzed telomerization of 1,3-butadiene with nucleophiles to give 2,7-octadienes with 100% atom efficiency from simple starting materials is a clear target.[4]

The telomerization process has been intensively studied by many industrial and academic laboratories.[5] The important contribution of Jolly on mechanistic aspects has been crucial for further development.[6] Recently Beller and co-workers[4h,7] reported the most selective, active, and productive catalyst, an $(NHC)Pd^0$ complex.[7d−f] This outstanding performance,

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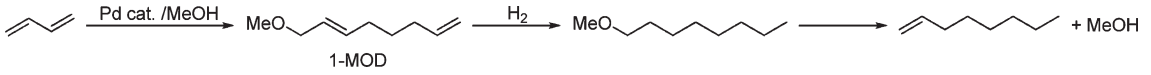
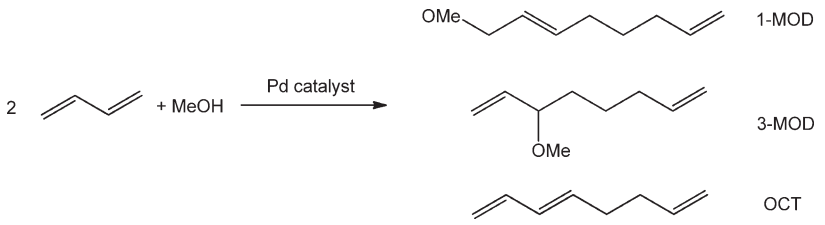
Scheme 1. Simplified Reaction Scheme of the Dow Process



Scheme 2. Telomerization of 1,3-Butadiene with Methanol To Produce 1-Methoxy-2,7-octadiene (1-MOD)



however, could not be achieved under the Dow production conditions using the industrial feed.[8]

Diphosphines were reported as ligands for the telomerization of dienes with amines, water,[9,10] and alcohols,[7f,g,11] but often diphosphine catalysts performed worse than monophosphine catalysts in terms of productivity and selectivity, especially when an alkyl spacer was used. An exception among the diphosphines is 2,2′-bis(1,4-cyclooctylenephosphinomethyl)-1,1′-biphenyl, which gave high selectivity to the linear telomer (up to 94% at 70 °C).[12]

Recently we reported on the successful use of moderately bulky monophosphines, for instance monoxantphos, for the telomerization of 1,3-butadiene with methanol to selectively produce 1-MOD under commercially relevant reaction conditions; the reactions were carried out with crude C4, containing ∼50% of 1,3-butadiene.[13] We continued our investigations using diphosphines having a large P−P distance, which might invoke bimetallic species or which might act as two independent monophosphines. Large backbones containing two phosphines acting independently are of interest, because per weight they are more effective than the monophosphines derived from the same backbone. Second, the interest for such diphosphines is also related to the expected costs of the syntheses of the ligands; obviously, using a symmetric backbone for the preparation of a diphosphine will be easier than the (always tricky) monofunctionalization of the same backbone to prepare the monophosphine.

The use of monodentate arylphosphines containing *o*-methoxy substituents was reported recently, and these catalysts gave a higher selectivity to 1-MOD than did PPh_3,[5a,14] as is also known for allylic alkylation reactions, for which a stronger donor trans to C3 gives more linear product.[15]

With regard to the potential formation of bimetallic species, in the rhodium-catalyzed carbonylation of methanol we found that, unexpectedly, bimetallic complexes gave much

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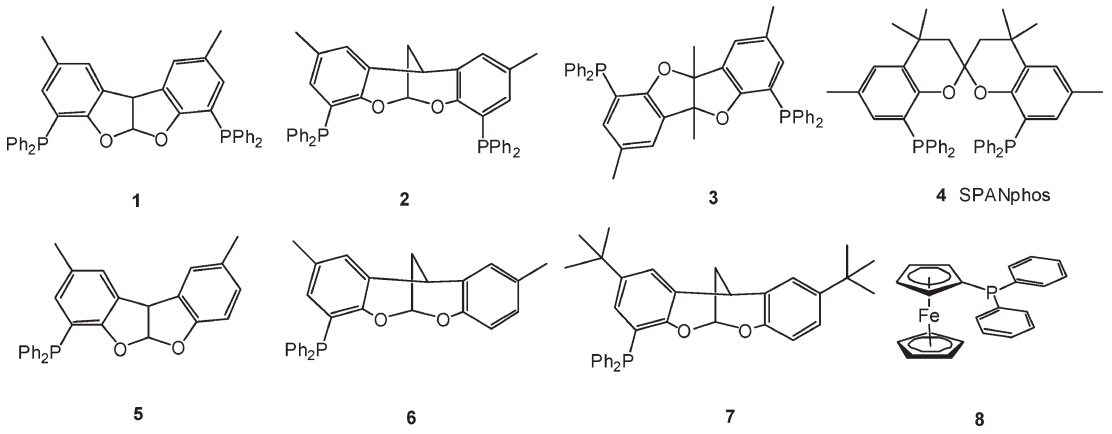

Figure 1. Phosphines.

faster catalysts: for instance, those based on SPANphos derivatives and related diphosphines.[16,17] Diphosphines that coordinate in a cis fashion give low selectivity to the linear product (vide supra), and these were not considered in this study.

A series of diphosphines, previously synthesized in our group, which contain oxygen in the ortho position with respect to phosphorus were tested in the telomerization reaction.[17,18] In addition to these diphosphines having distant phosphine groups, their monophosphine homologues were also investigated. The results are described in the present publication.

Results and Discussion

The phosphines used are shown in Figure 1: diphosphines **1**−**3**, SPANphos, and monophosphines **5**−**8**. We report here the synthesis of the new monophosphines **5**−**7**, while **8** is a known compound. Ligand **8** was included because the Fc moiety also behaves as a more bulky phenyl group in a phosphine. Unfortunately, SPANphos is insoluble in the reaction medium and will not be considered in the following.

Ligand Syntheses and Properties. From the series of ligands synthesized (Figure 1), diphosphines 4,7-Bis(diphenylphosphino)-5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran (**1**), 2,10-dimethyl-4,8-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**2**), 1,6-bis(diphenylphosphino)-5a,10b-dihydro-5a,10b-dimethyl-3,8-dimethylbenzofuro[3,2-*b*]benzofuran (**3**), and SPANphos (available from Strem) were prepared by previously described methods.[17,18] Phosphine **8** was prepared by the Friedel−Crafts reaction reported by Sollot, between ferrocene (Fc) and chlorodiphenylphosphine ($ClPPh_2$).[19] The new monophosphines 5a,10b-dihydro-2,9-dimethyl-4-diphenylphosphinobenzofuro[2,3-*b*]benzofuran (**5**), 2,10-dimethyl-4-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**6**), and 2,10-di-*tert*-butyl-4-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**7**) were prepared by direct lithiation of the corresponding new bromo compounds **9**−**11** at low temperature, which are further reacted with $ClPPh_2$ to give the desired phosphine. These backbones were investigated for the preparation of new ligands, first because of their similarity to the xanthene backbone of xantphos and the spirobischromane backbone of SPANphos and second because of their large steric bulk compared to PPh_3 (this is shown by the large P−P distances in the corresponding diphosphines compared to SPANphos and Xantphos).[17] As mentioned above, the preparation of a diphosphine will be easier than the synthesis of a monophosphine via the standard procedure of bromination, lithiation, and phosphorylation. Bromination does not stop at the monobrominated compound, and a statistical mixture of nonbrominated, monobrominated, and dibrominated backbones is usually obtained, which leads to loss of material during a cumbersome purification. For comparison and because of the expected efficiency of the ligands, the monophosphines were also synthesized, and it turned out that bromination often gave somewhat better results than might have been expected statistically.

The new monobrominated compounds (Figure 2) 4-bromo-5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran (**9**), 4-bromo-2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**10**), and 4-bromo-2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]-dioxocin (**11**) were prepared by reacting the corresponding backbone with *N*-bromosuccinimide (NBS) in DMF. Thus, backbone/monoBr/diBr mixtures were obtained in 2/75/23, 9/76/13, and 50/50/0 ratios for **9**−**11**, respectively; washing with methanol gave monoBr/diBr mixtures in 75/25 and 90/10 ratios for **9** and **10**, respectively. Compound **11** can be obtained in pure form, albeit in low yield (34%), by subsequent recrystallization from methanol. The mixtures of mono- and dibrominated compounds were used without further purification to prepare the desired ligands **5**−**7**.

The crude reaction mixture contains the corresponding hydrogenated backbones 5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran,[20] 2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-g][1,3]dioxocin,[21] 2,10-di-*tert*-butyl-6,12-methano-12H-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin,[21] the

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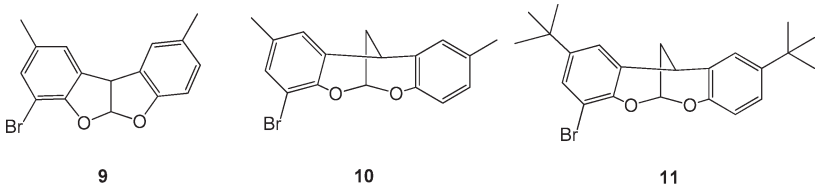

Figure 2. Monobrominated backbones.

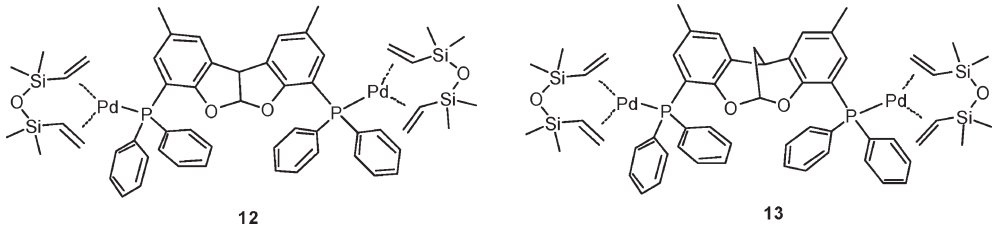

Figure 3. Pd−dvds complexes **12** and **13**.

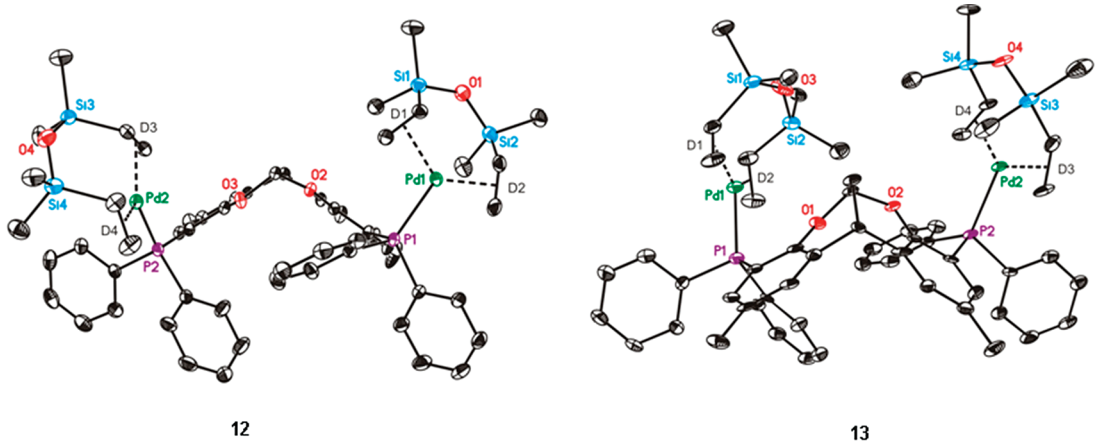

Figure 4. Ortep plots (thermal ellipsoids shown at the 50% probability level) of the complexes **12** (left) and **13** (right). Hydrogen atoms have been omitted for the sake of clarity. D1, D2, D3, and D4 denote C=C bond lengths.

desired monophophines **5**−**7**, and the corresponding diphosphines, respectively. The phosphines were obtained pure in 9, 31, and 3.5% yields from the corresponding hydrocarbons, but the synthesis has not been optimized. In the case of **5** and **6**, it seems that the phosphine decomposed during the purification by chromatography column over silica gel. In the case of **7**, an important amount of the intermediate compound **11** was lost during its purification by recrystallization.

Palladium−Diphosphine Complexes. In order to also have structural information on the type of phosphine−Pd−diolefin complexes that these large-backbone diphosphines will form under catalytic conditions, we synthesized the corresponding diphosphine−[Pd(dvds)]$_2$ (dvds = 1,1,3,3-tetramethyl-1,3-divinyldisiloxane) for diphosphines **1** and **2**. Attempts to obtain crystals of the palladium complex derived from **3** were unsuccessful.

The two different palladium complexes **12** and **13** (Figure 3) were prepared by the straightforward method reported by Pörschke, reacting 1 equiv of phosphine **1** and **2** with 1 equiv of (tmeda)PdMe$_2$[22] in dvds (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and were obtained in 60 and 75% yields, respectively.[23] Monocrystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a concentrated solution of **12** and **13** in diethyl ether at −25 °C. The molecular structures of **12** and **13** are presented in Figure 4 and selected bond lengths and angles in Table 1.

The single-crystal X-ray structure analysis of complexes **12** and **13** reveals that both diphosphines formed dinuclear palladium complexes as expected, due to the large P−P distance. The palladium atom has a trigonal-planar coordination environment, created by the phosphorus atom and the two C=C bonds of the dvds ligand. As observed by Pörschke, the Pd(1,6-diene) moiety adopts a stable chairlike conformation.[23]

As observed by us in the case of monophosphine−Pd−dvds[13] and by Beller in the case of (NHC)−Pd−dvds,[7d] the trigonal-planar geometry around both palladium atoms of each complexes is highly distorted, as revealed by the value, far from the expected 120°, of the three angles (deg) D1−Pd1−D2 (**12**, 130.10(7); **13**, 131.7(3)), D3−Pd2−D4 (**12**, 128.53(7); **13**, 132.6(3)), D1−Pd1−P1 (**12**, 116.28(5); **13**,

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113.9(2)), D2−Pd1−P1 (**12**, 113.22(5); **13**, 114.2(2)), D3−Pd2−P2 (**12**, 113.23(5); **13**, 116.4(2)), and D3−Pd2−D4 (**12**, 118.20(5); **13**, 111.0(2)).[7] Similarly to previously reported structures, the C═C bonds lie exactly in the coordination plane and the C═C bond length (1.40 Å) is lengthened as compared with a typical C═C bond distance (1.34 Å), indicating a weak back-donation by Pd.

Catalytic Results. All phosphines were tested for the telomerization of 1,3-butadiene with MeOH at 90 °C, working in crude C4 with a NaOMe/Pd ratio of 5 (NaOMe is used as promoter), and the results are presented in Table 2 together with the results previously reported for PPh_3 and monoxantphos under the same conditions.[13] Catalysts were formed in situ, as no differences were obtained using a phosphine−Pd−dvds or $Pd(acac)_2$/2L mixture for the telomerization.[13,7d] Thus, precatalyst stock solutions were used for catalysis prepared from palladium(II) acetylacetonate and 2 equiv of the phosphine; acetic acid was added to increase the storage stability of the complex in solution (see the Experimental Section).

Diphosphines were tested in two different ligand/Pd ratios: 1 and 2; the results are presented in Table 2 and the rate of formation of 1-MOD in the presence of these ligands is shown in Figure 5 (ligand **2** was not tested at L/Pd = 2 because of its low solubility). Diphosphine **1** gave moderate results: viz., a higher selectivity to 1-MOD but a lower productivity (entry 3, Table 2) compared to triphenylphosphine. The addition of 2 equiv of diphosphine per Pd increased the conversion of butadiene (entry 4, Table 2) and reaction rate (Figure 5) but did not influence significantly the selectivity to 1-MOD. Dioxocin diphosphine **2** gives results similar to those for **1** and exhibits lower productivity with higher selectivity than PPh_3. To our surprise, diphosphine **3** gave impressive results comparable to those for monoxantphos (entry 6, Table 2) in a comparison of productivity and selectivity to 1-MOD; adding 2 equiv of diphosphine **3** per Pd lowered the Pd loss from 17 to 6%. With regard to the activity, the catalyst derived from **3** appears promising, but in this case no increase of reaction rate was observed by adding 2 equiv of **3**, in contrast to the case for **1** (Figure 5).

The good results obtained with **3** could be explained by the fact that the two phosphorus atoms are trans to one another, as opposed to the case for **1** and **2**. Thus, no unfavorable steric interactions between the two phosphine−palladium−octadienyl moieties during the catalysis can occur, as might happen with a diphosphine possessing the two P atoms in a cis fashion. In other words, the steric bulk of the backbone in **3** exerts the same beneficial effect as does xanthene in monoxantphos compared to triphenylphosphine.

With regard to the monophosphines, ligand **5** gave a more selective but less productive catalyst for the production of 1-MOD than triphenylphosphine (entry 8, Table 2) under the same conditions, but the Bd conversion and 1-MOD selectivity are higher than those of its diphosphine analogue **1**. Unfortunately, Pd loss was very high (entry 8, Table 2). The dioxocin-based monophosphines **6** and **7** gave very good results in terms of conversion, selectivity in comparison to PPh_3, and also stability (entries 9 and 10, Table 2) in comparison to **5**. The *t*-Bu substituents in **7** seem to increase the catalyst performance compared to that for **6**. The results obtained for **7** are even superior to those reported for monoxantphos (entry 2; conversion 93%, 1-MOD 89%, Pd loss 6%).[13] Ferrocenylphosphine **8** gave poor results (entry 11, Table 2).

The activity of the catalysts derived from monophosphines **5** and **8** is low (Figure 6). Phosphine **6** formed a catalyst similar in terms of activity to the catalyst derived from monoxantphos and is thus a more active and selective system than the diphosphine **2** catalyst. Therefore, we can conclude that bulky monophosphines are better ligands than their large P−P distance diphosphine counterparts (cf. **5** and **1** or **6** and **2**; Table 2, Figures 4 and 5). As can be observed in Figure 6, the initial reaction rate, reflected by the larger amount of 1-MOD formed with the Pd/**7** system, surpassed that of monoxantphos at 90 °C; after 30 min the

Table 1. Bond Lengths (Å) and Bond Angles (deg) for 12 and 13

	13	**12**
Pd1−P1	2.318(2)	2.3026(4)
Pd2−P2	2.315(2)	2.3154(5)
Pd1−D1	2.054(7)	2.064(2)
Pd1−D2	2.056(8)	2.072(2)
Pd2−D3	2.056(7)	2.071(2)
Pd2−D4	2.056(7)	2.069(2)
P1−P2	7.310(11)	7.648(3)
D1	1.397(11)	1.390(3)
D2	1.408(11)	1.392(2)
D3	1.396(11)	1.398(2)
D4	1.416(11)	1.401(3)
D1−Pd1−D2	131.7(3)	130.10(7)
D3−Pd2−D4	132.6(3)	128.53(7)
D1−Pd1−P1	113.9(2)	116.28(5)
D2−Pd1−P1	114.2(2)	113.22(5)
D3−Pd2-P2 (deg)	116.4(2)	113.23(5)
D4−Pd2-P2 (deg)	111.0(2)	118.20(5)

Table 2. Catalytic Results Obtained for Ligands 1−7 at 90 °C for 2.5 h[a]

			conversn (%)						
entry	ligand	L/Pd	Bd	1-MOD	3-MOD	OCT	*l*/*b* ratio (%)	chemo (%)[c]	Pd loss (%)[b]
1	PPh_3	2	85	83	5	13	94/6	87	17
2	monoxantphos	2	93	89	5	6	94/6	94	6
3	**1**	1	63	86	4	9	95/5	91	
4	**1**	2	74	87	5	8	94/6	92	
5	**2**	1	79	86	5	9	94/6	91	12
6	**3**	1	91	88	5	7	95/5	93	18
7	**3**	2	91	89	5	6	95/5	94	7
8	**5**	2	80	88	5	7	95/5	93	43
9	**6**	2	92	89	5	6	95/5	94	22
10	**7**	2	96	90	5	5	95/5	95	23
11	**8**	2	76	80	5	15	94/6	85	

[a] Reaction conditions: Pd (0.0025 mol %), NaOMe (0.0125 mol %), MeOH/Bd = 2.6. [b] Palladium loss was estimated by ICP-AES measurements (see the Experimental Section); measurement error ±5% absolute. [c] Chemoselectivity (%) = (1-MOD + 3-MOD)/(1-MOD + 3-MOD + OCT) × 100.

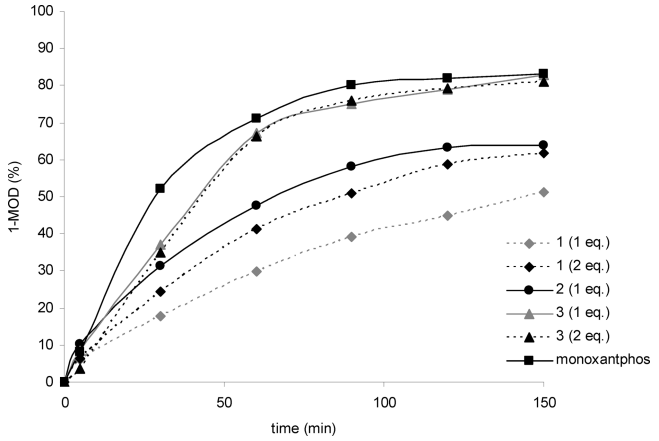

Figure 5. Rate of formation of 1-MOD (90 °C, "Pd" (0.0025 mol %), NaOMe (0.0125 mol %), MeOH/Bd = 2.6).

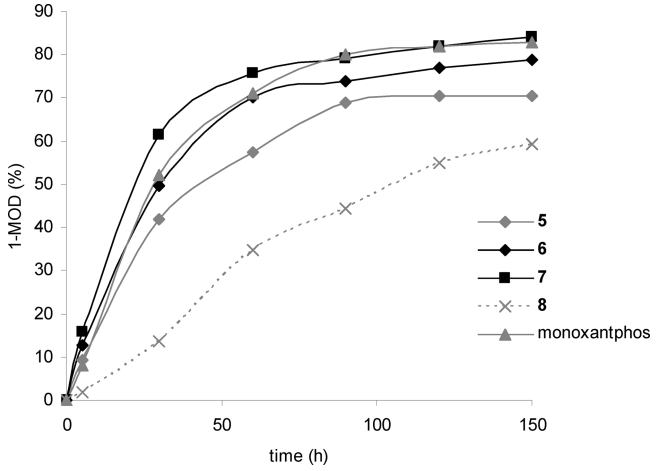

Figure 6. Rate of formation of 1-MOD (90 °C, "Pd" (0.0025 mol %), NaOMe (0.0125 mol %), MeOH/Bd = 2.6).

formation of 1-MOD is 10% higher with **7** in comparison to monoxantphos.

Conclusion

New bulky monophosphines containing dibenzodioxocin and benzofurobenzofuran backbones were prepared in moderate to good yield. Diphosphines based on the same backbones possessing large P−P distances and the monophosphines were used as ligands in the palladium-catalyzed selective telomerization of 1,3-butadiene.

The tests of the phosphines under commercially relevant production conditions, using a crude C4 mixture containing ~50% of 1,3-butadiene, revealed the high potential of diphosphine **3** and monophosphine **7**. Both ligands emerged as very promising alternatives for PPh_3, giving a more active and selective catalyst than PPh_3 under the optimized standard conditions. The results obtained in terms of selectivity (up to 90% in favor of 1-MOD at 90 °C), activity, and stability are comparable or even superior to those for monoxantphos.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere using Schlenk techniques. Deuterated chloroform was distilled over phosphorus pentoxide under argon prior to use. MeOH was degassed by Ar bubbling. Chlorodiphenylphosphine was purchased from Fluka and distilled under an inert atmosphere prior to use. Palladium acetylacetonate was purchased from Strem and used as received. 5a,10b-Dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran,[19] 2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin,[20] 2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin[20] phosphines **8**,[19] **1**,[17] **2**,[17] **3**,[17] and **4**,[16] and (tmeda)$PdMe_2$ were prepared by previously described methods. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm and were calibrated using residual ^1H and ^{13}C resonances of deuterated solvents. Coupling constants (J) are expressed in hertz. X-ray structure analyses were done at the Research Support Unit of the ICIQ (Tarragona, Spain). Analyses of the catalytic reactions have been performed on a GC-FID equipped with an HP-5 (5% phenyl methyl siloxane; 30 m × 320 m × 0.25) capillary column. Elemental analyses were performed at the Unidad de Análisis Elemental of the Universidad de Santiago de Compostela (Spain).

Synthesis of 5a,10b-Dihydro-2,9-dimethyl-4-diphenylphosphinobenzofuro[2,3-*b*]benzofuran (5). A solution of 4-bromo-5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-*b*]benzofuran (**9**; 1.5 g, containing 3.55 mmol of monobromo backbone) in THF (40 mL) was cooled to −78 °C. Then, *n*-BuLi (2.5 M in hexane, 2.8 mL) was added slowly. The mixture was stirred at −78 °C for 2 h, and $ClPPh_2$ (1.065 mL) was added. The mixture was stirred at −78 °C for 2 h and at RT overnight. Then the solvent was evaporated and degassed water was added. The product was extracted with dichloromethane (DCM). The organic layer was separated and dried over $MgSO_4$. Evaporation of the solvent gave a crude product which was purified by a chromatography column on silica gel (eluent gradient DCM/hexane 1/3 to 1/1). The product was isolated impure as a white solid from the fourth fraction. Then, the product was purified by preparative thin-layer chromatography on silica (eluent hexane/DCM 1/1.5) and recovered as a white solid from the first fraction (0.23 g, 0.544 mmol, 15%).

^1H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.37−7.26 (m, 10H, *H* arom), 7.19 (br s, 2H, H arom), 6.97 (m, 1H, H arom), 6.83 (d, J = 6.8 Hz, 1H, H arom), 6.78 (d, J = 8.1 Hz, 1H, H arom), 6.47 (m, 1H, O−C*H*−O), 4.95 (d, J = 6.8 Hz, 1H, $CH_{methynic}$), 2.32 (s, 3H, CH_3), 2.19 (s, 3H, CH_3). ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 158.4 (d, J = 16.0 Hz), 155.8, 135.9 (d, J = 10.1 Hz), 136.0 (d, J = 11.6 Hz), 135.9 (d, J = 10.1 Hz), 133.8 (d, J = 19.6 Hz), 133.6 (d, J = 19.6 Hz), 133.3 (d, J = 2.6 Hz), 129.3, 128.7, 128.5, 128.4, 128.3, 128.3 (d, J = 10.0 Hz), 127.1, 126.8 (d, J = 3.0 Hz), 125.3, 124.3, 118.1 (d, J = 16.0 Hz), 112.5, 109.8, 50.2, 20.9, 20.8. $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, $CDCl_3$): δ −15.33. Anal. Calcd for $C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.85; H, 5.43.

Synthesis of 2,10-Dimethyl-4-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (6). A solution of 4-bromo-2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*]-[1,3]dioxocin (**10**; 1.5 g, containing 4.07 mmol of monobromo backbone) in THF (40 mL) was cooled to −78 °C. Then, *n*-BuLi (2.5 M in hexane, 2.4 mL) was added slowly. The mixture was stirred at −78 °C for 2 h, and $ClPPh_2$ (1.0 mL) was added. The mixture was stirred at −78 °C for 2 h and at room temperature overnight. Then the solvent was evaporated and degassed water was added. The product was extracted with DCM. The organic layer was separated and dried over $MgSO_4$. The product was purified by a chromatography column on silica gel (eluent gradient DCM/hexane 1/3 to 1/1) and obtained as a white solid from the third fraction (0.80 g, 1.83 mmol, 45%). ^1H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.38−7.20 (m, 10H, *H* arom), 7.04 (dd, J = 4.5, 1.9 Hz, 2H, H arom), 6.93 (ddd, J = 7.8, 2, 0.5 Hz, 1H, H arom), 6.79 (d, J = 8.2 Hz, 1H, H arom), 6.31 (ddd, J = 5, 2, 0.5 Hz, 1H, H arom), 6.02 (q, J = 2.1 Hz, 1H, O−C*H*−O), 3.91 (br s, 1H, $CH_{methynic}$), 2.30 (s, 3H, CH_3), 2.20 (m, 2H, $CH_{methylenic}$), 2.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, 25 °C, $CDCl_3$): δ 150.7 (d, J = 14.7 Hz), 148.8, 136.4 (d, J = 9.4 Hz), 136.2 (d, J = 9.4 Hz), 134.1

(d, J = 19.9 Hz), 133.8 (d, J = 19.4 Hz), 132.4 (d, J = 1.9 Hz), 130.6, 130.5 (d, J = 13.1 Hz), 128.9, 128.7, 128.5, 128.3 (d, J = 7.4 Hz), 128.1 (d, J = 6.6 Hz), 127.6, 126.2 (d, J = 12.7 Hz), 126.1, 124.1 (d, J = 12.7 Hz), 116.3, 92.0, 31.9, 20.6, 20.5. $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, $CDCl_3$): δ −12.52. Anal. Calcd for $C_{29}H_{25}O_2P$: C, 79.80; H, 5.77. Found: C, 79.62; H, 5.86.

Synthesis of 2,10-Di-*tert*-butyl-4-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (7). At −78 °C *n*-butyllithium (1.7 mL, 1.6 M in hexanes, 2.72 mmol) was added dropwise to a stirred solution of 4-bromo-2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (**11**; 1.07 g, 2.58 mmol) in dry THF (70 mL). The reaction mixture was stirred for 1 h and then was warmed to −40 °C. At this temperature chlorodiphenylphosphine (0.50 mL, 2.68 mmol) was added and the reaction mixture was warmed to room temperature overnight. The solvent was removed in vacuo, the resulting solid was dissolved in dry CH_2Cl_2, and the solution was washed with deoxygenated water. The organic layer was removed in vacuo and recrystallized from deoxygenated methanol to afford the product (0.2 g, 15%) as an air-stable white solid. ^1H NMR (400 MHz, 25 °C, $CDCl_3$): δ 7.37−7.26 (m, 10H, *H* arom), 7.20 (dd, J = 2.3, 6.2 Hz, 1H, *H* arom), 7.14 (dd, J = 2.3, 8.5 Hz, 1H, *H* arom), 6.82 (d, J = 8.5 Hz, 1H, *H* arom), 6.49 (dd, J = 2.3, 5.4 Hz, 1H, *H* arom), 6.01 (br d, J = 1.7 Hz, 1H, O−C*H*−O), 3.96 (br s, 1H, $CH_{methynic}$), 2.20 (m, 2H, $CH_{methylenic}$), 1.31 (s, 9H, $C(CH_3)_3$), 1.09 (s, 9H, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, $CDCl_3$): δ −11.63. Anal. Calcd for $C_{35}H_{37}O_2P$: C, 80.74; H, 7.16. Found: C, 80.70; H, 7.12. HR-MS: $(M + Na)^+$ for $C_{35}H_{38}O_2P$ m/z calcd 521.2609, found 521.2598.

Synthesis of 4-Bromo-5a,10b-dihydro-2,9-dimethylbenzofuro-[2,3-*b*]benzofuran (9). 5a,10b-Dihydro-2,9-dimethylbenzofuro-[2,3-*b*]benzofuran (1.5 g, 6.3 mmol) and *N*-bromosuccinimide (NBS; 2.016 g, 11.3 mmol) were dissolved in DMF (100 mL) and stirred at room temperature for 1 day (the flask is covered with aluminum foil). The conversion was monitored by GC/MS. If necessary, more NBS can be added. After 3 days, a monobromo/dibromo/starting material mixture was formed in a 75/23/2 ratio. The solvent was evaporated to dryness, and the solid was washed with water and extracted with DCM. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The solid obtained was washed with ethanol to give a white solid (1.5 g, containing a 75/25 monobromo/dibromo mixture). The mixture was used without further purification to prepare the phosphine.

Synthesis of 4-Bromo-2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (10). 2,10-Dimethyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (1.5 g, 5.95 mmol) and NBS (1.477 g, 8.29 mmol) were dissolved in DMF (100 mL) and stirred at room temperature for 1 day. The conversion was monitored by GC/MS. If necessary, more NBS can be added. After 3 days, a monobromo/dibromo/starting material mixture was formed in a 76/9/13 ratio. The solvent was evaporated to dryness, and the solid was washed with water and extracted with DCM. The organic layer was dried over $MgSO_4$ and evaporated to dryness. The solid obtained was washed with ethanol to give a white solid (1.5 g, containing a 90/10 monobromo/dibromo mixture). The mixture was used without further purification to prepare the phosphine.

Synthesis of 4-Bromo-2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin (11). To a stirred solution of 2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*]-[1,3]dioxocin (3.70 g, 11.0 mmol) in DMF (125 mL) was added NBS (1.98 g, 11.0 mmol). The reaction mixture was monitored by GC chromatography. Once a 1/1 mixture of starting material and monobromo derivative was obtained, we decided to stop the reaction (to avoid formation of dibromo derivative). Then DMF was removed by evaporation. The residue was dissolved in H_2O and the solution extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated. After recrystallization with methanol, 4-bromo-2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-*d*:1′,2″-*g*][1,3]dioxocin was obtained as a white solid (1.07 g, 34%). ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (9H, s, *t*Bu), 1.27 (9H, s, *t*Bu), 2.24−2.29 (2H, m, CH_2), 3.95 (1H, m, C*H*), 6.23 (1H, m, C*H*), 6.84 (1H, d, $^3J_{H,H}$ = 8.6 Hz, Ar), 7.12−7.18 (3H, m, Ar), 7.33 (1H, d, $^4J_{H,H}$ = 2.2 Hz, Ar).

General Procedure for the Synthesis of the Phosphine−Palladium−dvds Complexes. A suspension of (tmeda)$Pd(CH_3)_2$ (0.05 g, 0.20 mmol) and of the desired phosphine (0.5 equiv, 0.010 mmol, 0.060 g for **1**, 0.061 g for **2**) in degassed and dried tetramethyldivinyldisiloxane (dvds, 2 mL) was stirred at room temperature overnight. Then, the solvent was removed under vacuum and the white solid obtained was washed with a small portion of pentane at −60 °C to remove small quantities of unreacted reagents. Yield: 60 and 75% for **12** and **13**, respectively. Due to their low stability at room temperature, the phosphine−palladium−dvds complexes have been characterized only by ^1H and ^{31}P NMR spectroscopy and should be stored as solids under an inert atmosphere at −20 °C.

4,7-Bis(diphenylphosphino)-5a,10b-dihydro-2,9-dimethylbenzofuro-[2,3-*b*]benzofuran{Pd[(η^2-H_2C=CHSiMe_2)$_2$O]}$_2$ (12). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 7.45−7.14 (m, 22H, *H* arom), 6.83 (br d, J = 10.8 Hz, 2H, *H* arom), 6.36 (d, J = 6.6 Hz, 1H, O−C*H*−O), 4.76 (d, J = 6.6, 1H, $CH_{methynic}$), 3.43−2.85 (m, 12H, dvds), 2.25 (s, 6H), 0.26 (s, 12H, dvds), −0.27 (s, 6H, dvds), −0.28 (s, 6H, dvds). $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, $CDCl_3$): δ −25.05.

2,10-Dimethyl-4,8-diphenylphosphino-6,12-methano-12*H*-dibenzo-[2,1-*d*:1′,2″-*g*][1,3]dioxocin{Pd[(η^2-H_2C=CHSiMe_2)$_2$O]}$_2$ (13). ^1H NMR (400 MHz, 25 °C, CD_2Cl_2): δ 7.36−7.1 (m, 22H, *H* arom), 6.71 (br d, J = 9.7 Hz, 2H, *H* arom), 5.09 (br s, 1H, O−C*H*−O), 3.90 (s, 1H, $CH_{methynic}$), 3.26−2.85 (m, 12H, dvds), 2.17 (s, 2H, $CH_{methylenic}$), 2.16 (s, 6H), 0.20 (s, 12H, dvds), −0.27 (s, 6H, dvds), −0.28 (s, 6H, dvds). $^{31}P\{^1H\}$ NMR (160 MHz, 25 °C, $CDCl_3$): δ −27.19.

Precatalyst Solution. The catalyst was prepared with palladium acetylacetonate ($Pd(acac)_2$) plus 2 mol equiv of the phosphine. One molar equivalent of acetic acid may be added to increase storage stability. The catalyst was prepared in methanol by dissolving all three components such that the palladium concentration in methanol equals about 500 ppm.

Catalytic Reaction. The reaction was carried in a 1 L (L) Parr reactor made from electropolished stainless steel. For each reaction, the Parr reactor's autoclave was filled with specified amounts of methanol, promoter (sodium methoxide, at a promoter to palladium molar ratio of 5/1) and inhibitor (diethyl hydroxyl amine, approximately 20 parts by weight per million parts by weight (ppm) based on total weight of methanol plus crude C4 load, ∼50% of 1,3-butadiene). The autoclave was closed, and purged twice with low-pressure nitrogen (6 bar or 600 kilopascals (kPa)) to substantially remove oxygen contained in the autoclave. A stainless steel sample cylinder was filled with a crude C4 stream that contains approximately 50 wt % of 1,3-butadiene, based upon total crude C4 stream weight and pressure. The content was added to the autoclave with low-pressure nitrogen (6 bar or 600 kPa). The temperature in the autoclave was raised to the desired work temperature (90 °C or otherwise indicated).

An amount of the catalyst solution was weighed, such that the palladium concentration in the reactor after addition of all raw materials was 10 ppm based upon the total weight of raw materials, into a drybox, and then the catalyst solution was placed into a stainless steel sample cylinder. The catalyst solution was added to the autoclave using high-pressure nitrogen (19−20 bar, or 1900−2000 kPa). Following catalyst addition, the reaction began, producing the final product. Samples were taken from the autoclave at set times (5 min after catalyst addition and at 30 min intervals thereafter), and gas and liquid phases of the samples were analyzed via GC (internal standard *m*-xylene).

Palladium Precipitation Measurement. Palladium precipitation in the reactor was determined by measuring the palladium

concentration in the liquid phase after the reaction and comparing that to a theoretical number based on the total amount of palladium added and the total liquid volume, which includes liquids added at the beginning of the reaction and liquids formed due to the butadiene conversion. Palladium concentration in the liquid was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

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Supporting Information Available: Text, a table, and CIF files giving details on data collection and crystallographic data for the structure analyses of **12** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.