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## Efficient Bulky Phosphines for the Selective Telomerization of 1,3-Butadiene with Methanol

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**Abstract:** A series of bulky phosphines containing substituted biphenyl, 2-methylnaphthyl, or 2,7-di-*tert*-butyl-9,9-dimethylxanthene moiety were prepared. They were used in the preparation of new monophosphine–palladium(0)–dvdS complexes, which were employed as catalysts for the selective telomerization of 1,3-butadiene with methanol to obtain 1-methoxyocta-2,7-diene (1-MOD), the key intermediate in the Dow 1-octene process. Several ligands showed improved selectivity and yield compared to that of the benchmark ligand PPh<sub>3</sub>. Especially 2,7-di-*tert*-butyl-9,9-dimethylxanthene-4-yl-diphenylphosphine (**4**, “monoxantphos”) stands out as an excellent ligand in terms of yield, selectivity, and stability.

### Introduction

Selective synthesis of linear  $\alpha$ -olefins [C<sub>6</sub>–C<sub>20</sub>] gained considerable interest in both industry and academia due to the high demand in diverse markets such as polyolefins, synthetic lubricants, plasticizers, detergent intermediates, etc. Linear  $\alpha$ -olefins, especially 1-hexene and 1-octene, are key components for the production of LLDPE and the demand for 1-hexene and 1-octene has increased enormously in recent years.<sup>1</sup> Thus, several processes have been developed in the past decades to produce 1-hexene and 1-octene selectively.

In the late 1960s, Keim at Shell discovered a homogeneous phosphine [P,O] nickel catalyst that oligomerizes ethene selectively to higher homologues. This process is known as SHOP (Shell higher olefin process), but as a result of the Schulz–Flory distribution of the product formed, 1-hexene and 1-octene are produced in limited amounts.<sup>2</sup> Later on, other type of ligands such as diimine [N,N]<sup>3</sup> or [N,O]<sup>4</sup> and [P,N]<sup>5</sup> were also studied for this reaction.

Sasol’s coal-based high-temperature Fischer–Tropsch technology produces an Anderson–Schulz–Flory distribution of hydrocarbons with high  $\alpha$ -olefin content, and the desired olefins are separated by distillation.<sup>6</sup> Nowadays other technologies are

being considered for on-purpose 1-octene production: ethene tetramerization, the Sasol process based on hydroformylation of 1-heptene, and the Dow process based on the telomerization of 1,3-butadiene.

**Ethene Trimerization and Tetramerization.** 1-Hexene can be obtained by ethene trimerization, and to this end, industrial groups such as Phillips<sup>7</sup> or academic ones developed a family of catalysts that trimerize ethene to 1-hexene with high selectivity, based mainly on Cr<sup>8</sup> but also on Ti<sup>9</sup> and Ta.<sup>10</sup> To achieve such high selectivity to 1-hexene, a fundamentally different chemical pathway must be at work compared to “linear growth” oligomerization reactions.<sup>11</sup> The key difference between this catalyst system and conventional oligomerization catalyst is the propensity of the chromium-based catalyst to form seven-membered ring metallacycles.<sup>12</sup>

Until recently, it was thought unlikely that further ethene insertion to form metallacyclononane, which should eliminate selectively 1-octene, would take place.<sup>13</sup> However, researchers

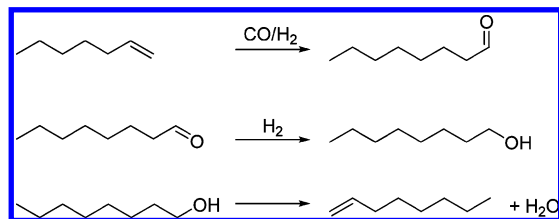
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**Scheme 1.** Sasol Process for the Production of 1-Octene from 1-Heptene



from Sasol have found catalyst systems and operating conditions that do indeed allow the formation of nine-membered metallacycle in large proportion relative to seven-membered ring formation.<sup>14</sup> This provides a fairly selective reaction to 1-octene. Sasol's catalysts gave good selectivity for octene-1 (up to 70% selectivity) and varying quantities of 1-hexene, along with higher olefins. In the near future commercialization of this route is expected.

**Octanol Process by Sasol.**<sup>15</sup> The chemistry of converting 1-heptene to 1-octene is shown in Scheme 1. To transform 1-heptene to 1-octene, three steps are required: (1) hydroformylation of 1-heptene to octanal, (2) hydrogenation of octanal to 1-octanol, and (3) dehydration of 1-octanol to 1-octene. This process is commercial.

**Dow Process.** The commercial route to produce 1-octene based on butadiene as developed by Dow Chemical is presented in Scheme 2.<sup>16</sup> It came on stream in Tarragona in 2008. The telomerization of butadiene with methanol in the presence of a palladium catalyst yields 1-methoxy-2,7-octadiene,<sup>17</sup> which is fully hydrogenated to 1-methoxyoctane in the next step. Subsequent cracking of 1-methoxyoctane gives 1-octene and methanol for recycle.

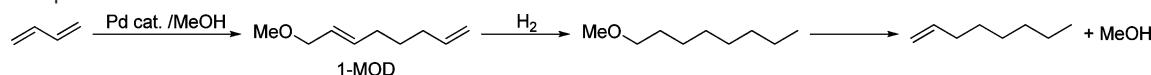
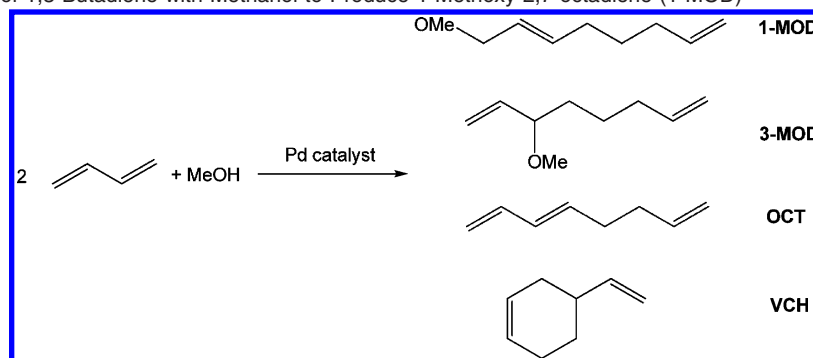
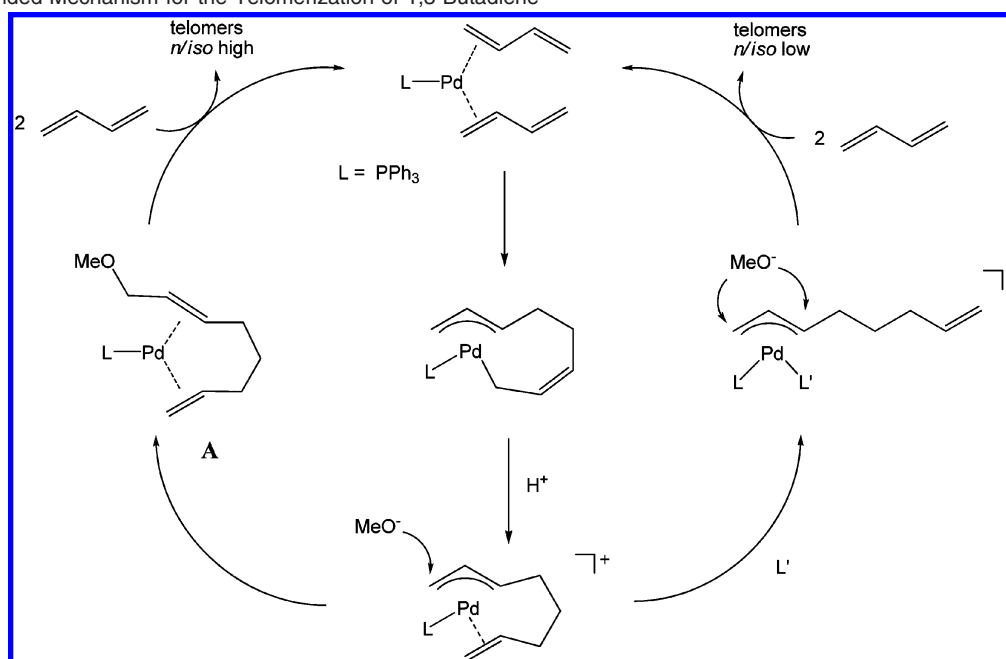
The control of the selectivity and optimization of the reaction is crucial in terms of the development of greener processes, and efforts on catalyst design and/or tuning of the reaction parameters aim at these targets.

Thus, the palladium-catalyzed telomerization of 1,3-diene with nucleophiles giving with 100% atom-efficiency substituted

2,7-octadienes from simple starting materials is a clear target.<sup>18</sup> 1,3-Butadiene and MeOH are attractive feedstocks because of their ample availability and low price. The reaction leads to

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**Scheme 2.** Simplified View of the Dow Process**Scheme 3.** Telomerization of 1,3-Butadiene with Methanol to Produce 1-Methoxy-2,7-octadiene (1-MOD)**Scheme 4.** Extended Mechanism for the Telomerization of 1,3-Butadiene

the formation of 1-methoxy-2,7-octadiene (1-MOD) (Scheme 3), which is for instance a useful precursor for 1-octene.<sup>19</sup> Main byproduct of the reaction are the 3-methoxyocta-1,7-diene (3-MOD), 1,3,7-octatriene (OCT), and less importantly 4-vinylcyclohexene (VCH) formed by a Diels–Alder reaction of two molecules of 1,3-butadiene.<sup>20</sup>

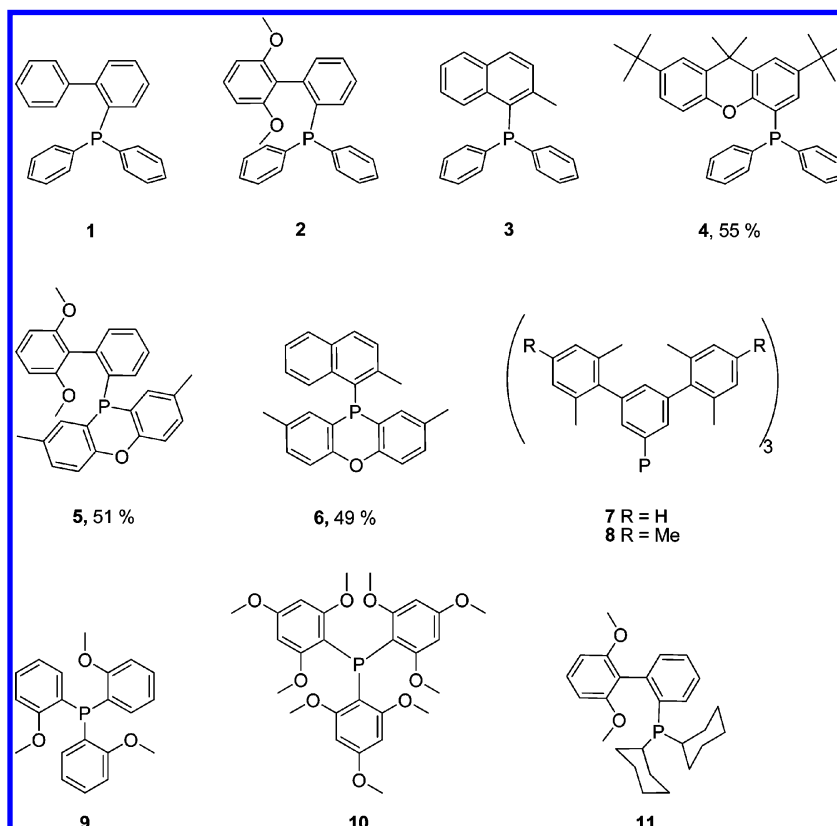
As a consequence of the increasing industrial use of 1-octene as a co-monomer for polyethylene,<sup>21</sup> the telomerization process has been intensively studied by many industrial and academic laboratories.<sup>22</sup> The important contribution of Beller's group in understanding and optimizing the reaction has been reviewed recently<sup>18h</sup> and has led to the development of the most active

and productive catalyst, a (NHC)Pd(0) complex, achieving TONs up to 1,500,000.<sup>23d,e</sup>

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**Figure 1.** Series of bulky phosphines.

The mechanism of the reaction has been carefully studied by Jolly,<sup>24</sup> but factors explaining the changes in chemo- and regioselectivity remain unraveled. Recent studies from Beller et al. performed on the  $\text{PPh}_3$ -based system showed that increasing the L/Pd ratio led to systems with high productivity (high TON) due to stabilization of the  $\text{Pd}(0)$  species, although it had a detrimental effect on selectivity. Mechanistic investigations indicated that a palladium complex containing two phosphines is responsible for the formation of the (undesired) branched telomers. The formation of this palladium-bisphosphine species is enhanced by higher L/metal ratios.<sup>23h</sup> The

extended reaction scheme as proposed by Beller, based on Jolly's original one, is depicted in Scheme 4.

As pointed out by Beller et al., monoligated palladium complexes are highly selective<sup>23d,f,h</sup> compared to catalysts containing two ligands. Additionally, high L/Pd ratios are required to increase TONs to guarantee metal stabilization. Phosphine is lost via catalytic oxidation during the course of the reaction and has to be replenished to avoid palladium aggregation and metal precipitation.

To fulfill both (apparently contradictory) demands, we considered the use of sterically demanding phosphine ligands. They should be able to stabilize the complex toward palladium aggregation and avoid or diminish coordination of a second ligand due to repulsive steric interactions.

There are some examples in the literature of sterically hindered phosphines that already serve this purpose, for instance, in cross-coupling catalysis, also using palladium.<sup>25</sup> Together with newly designed ligands, we tested some of the known bulky ligands for comparative purposes.

Concerning the metal precursor, palladium(0)-1,6-diolefin complexes, containing only one phosphine ligand, resembling the catalytic intermediate A (Scheme 2) seem ideal candidates.<sup>23d,f,h</sup> The  $\text{Pd}(0)$ -diolefin complexes of all of the ligands used in this study have been prepared, and their catalytic behavior has been tested in the telomerization of 1,3-butadiene with methanol.

## Results and Discussion

**Ligand Syntheses and Properties.** From the series of ligands synthesized (Figure 1), phosphines **1**, **2**, **3**, **7**, and **8** were

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**Table 1.** Phosphine Basicity and Coordination Induced Shift  $\Delta$  in Rh Complex

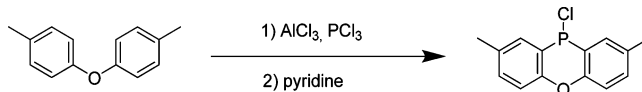
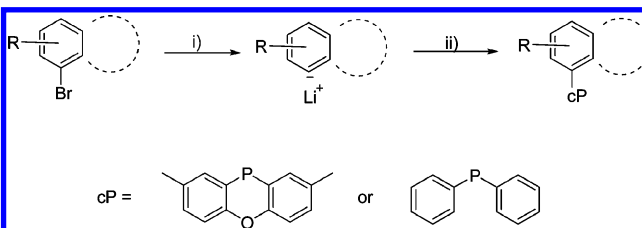
phosphine	Rh(CO)(phosphine) <sub>2</sub> Cl			
	<sup>31</sup> P{ <sup>1</sup> H} NMR $\delta$ (ppm); J (Hz)	$\nu$ (CO) (cm <sup>-1</sup> )	cone angle $\theta$ (deg)	$\Delta\delta$ <sup>31</sup> P{ <sup>1</sup> H} (complex-free ligand) (ppm)
<b>1</b>	32.2; $J_{\text{Rh-P}} = 129.5$	1961	191 <sup>26</sup>	42.5
<b>2</b>	31.8; $J_{\text{Rh-P}} = 129.2$	1966		41.3
<b>3</b>	25.2; $J_{\text{Rh-P}} = 124.1$	1960	223 <sup>26</sup>	42.6
<b>4</b>	28.4; $J_{\text{Rh-P}} = 128.7$	1969		38.5
<b>5</b>	-4.8; $J_{\text{Rh-P}} = 132.0$	1972		49.2
<b>6</b>	-24.2; $J_{\text{Rh-P}} = 122.2$	1972		34.8
<b>9</b>	nd	1948	200 <sup>41</sup>	nd
<b>10</b>	nd	1930	184 <sup>42</sup>	nd
<b>11</b>	52.3; $J_{\text{Rh-P}} = 96.7$	1954		60.9
PPh <sub>3</sub>	28.4; $J_{\text{Rh-P}} = 128$	1967	145 <sup>43</sup>	34.3

prepared by previously described methods,<sup>26–28</sup> whereas ligands **4–6** have been specifically designed for this work.

Phosphines **1** and **3** were *ortho*-substituted aryl phosphines initially developed to enhance the branched/linear ratio in hydroformylation reactions.<sup>26</sup> The related ligand **2**, published by Straub,<sup>27</sup> is the diphenyl analogue of the commercially available (dicyclohexyl) SPhos **11** (also tested in this study), which was developed by Buchwald and used in a wide range of coupling reactions (C–C and C–N bond formation).<sup>29</sup> To vary the electronic and steric properties of these ligands, the 2,7-phenoxaphosphine moiety was introduced instead of a diphenylphosphino group on ligands **2** and **3** to give the new phosphines **5** and **6**, respectively. These phosphines should be bulkier and less basic (see Table 1) than their diphenyl counterparts, because of the higher rigidity and extended  $\pi$ -system of the phenoxaphosphine moiety.<sup>30</sup>

The very bulky bowl-shaped phosphines (BSP) such as **7** and **8** developed by Goto<sup>28b,c</sup> and Tsuji,<sup>28a</sup> respectively, and successfully used for hydrosilylation of unsaturated substrates<sup>28a,31</sup> or Suzuki cross-coupling<sup>32</sup> were prepared and used in this study. Also the highly basic and bulky methoxy-substituted triphenylphosphines **9** and **10** developed by Wada were tested.<sup>33</sup>

We also designed a new bulky monophosphine based on the backbone used for the construction of the wide bite angle diphosphine Xantphos,<sup>34</sup> which has been extensively studied

**Scheme 5.** Synthesis of the Chlorophenoxaphosphine**Scheme 6.** Syntheses of Ligands **4**, **5**, **6**: (i) *n*-BuLi, -78 °C, (ii) Chlorophosphine, -78 °C

and used in homogeneous catalysis.<sup>35</sup> The availability of the xanthene skeleton in our group, combined with the fact that it forms *ortho*-substituted aryl phosphines, prompted us to prepare the new ligand **4** (“mono-xantphos”).

New phosphines **4**, **5**, and **6** were prepared by reacting the corresponding bromo reagent, after lithiation, with the desired chlorophosphine, namely, chlorodiphenylphosphine or 2,8-dimethyl-10-chlorophenoxaphosphine (POP). Chlorophenoxaphosphine was prepared by a Friedel–Crafts reaction between di-*p*-tolylether and phosphorus trichloride in the presence of aluminum trichloride (Scheme 5).<sup>36</sup>

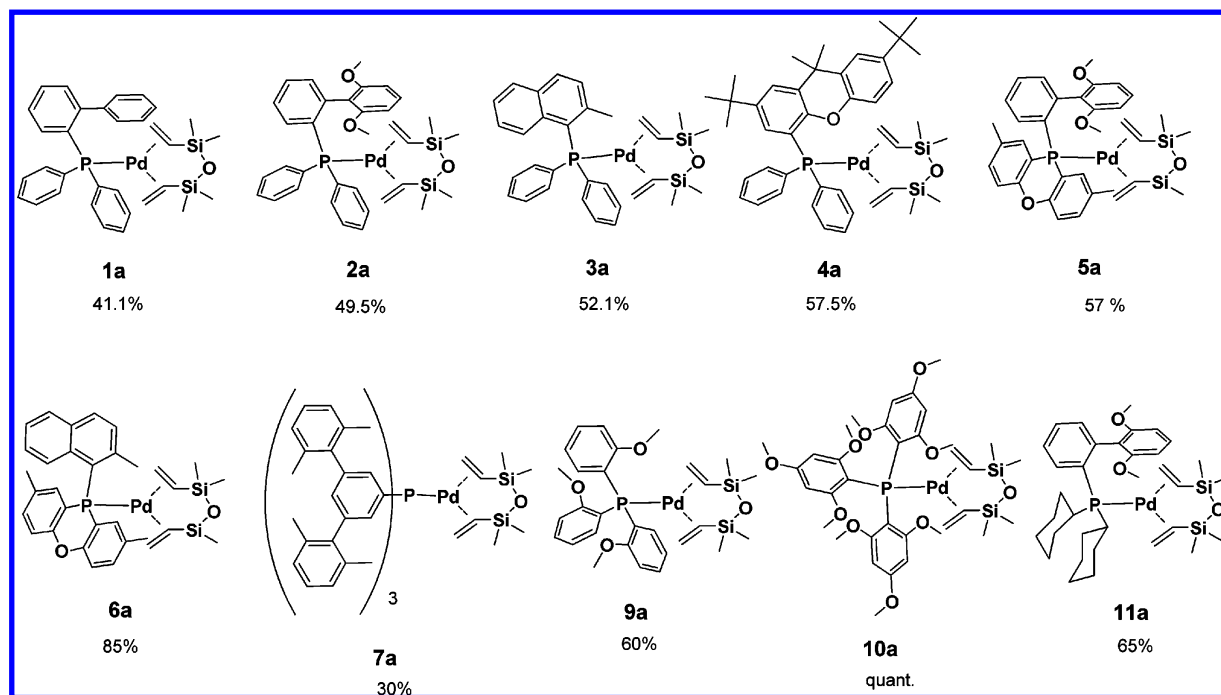
Bromides such as 2'-bromo-2,6-dimethoxybiphenyl or 1-bromo-2-methylnaphtyl were commercially available. For the synthesis of phosphine **4**, a new brominated compound **12**, 5-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene, was prepared by selective bromination of the *ortho*-position of the desired backbone with *N*-bromosuccinimide in a DMF/THF mixture. Compound **12** was used to synthesize the phosphine without further purification. The mixture contains, apart from the desired monobrominated derivative, the starting material and the dibrominated derivative in a molar ratio of 90/7/3, respectively, and can be used without further purification to prepare the desired phosphine **4** (Figure 1).

Typically, the phosphines were prepared by lithiation of the brominated backbone at -78 °C with *n*-BuLi followed by the reaction with the respective chlorophosphine, and they were obtained in moderate yields (Scheme 6).

Tolman introduced the cone angle  $\theta$  (deg) and the  $\chi$  value to describe the steric and electronic properties of phosphines.<sup>37</sup> Both parameters have been used extensively as a measure of ligand properties.<sup>38</sup> To evaluate the relative basicity of our ligands, we synthesized the corresponding Rh(phosphine)<sub>2</sub>(CO)Cl complexes by reacting 4 equiv of phosphine with the rhodium dimer [Rh(CO)<sub>2</sub>Cl]<sub>2</sub>. The multiplicity of the signals (only one doublet in all cases) and the value of the coupling constants  $J_{\text{Rh-P}}$  are consistent with the formation of Rh complexes in which the two phosphine ligands are

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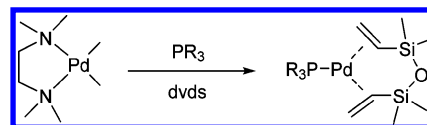
**Figure 2.** Phosphine–palladium–dvds complexes.

arranged in a *trans* fashion, as expected due to steric reasons and the *trans* influences.<sup>39</sup> The fact that along the series the same type of complex is formed validates the construction of the electronegativities series based on the comparison of their carbonyl IR frequencies,  $\nu(\text{CO})$ , Table 1. According to these data, the series follows the following basicity order trend: **10** > **9** > **11** > **3** > **1** > **2** >  $\text{PPh}_3$  > **4** > **5** = **6**. As expected methoxy-substituted triphenylphosphines are the most basic<sup>33,40</sup> of the series, and the POP-based ones are located at the opposite end.<sup>30</sup> Sphos **11** is also rather basic, thanks to the presence of two cyclohexyl moieties, and phosphines **2** and **4** are electronically similar to triphenylphosphine.

**Phosphine–Palladium–dvds Complexes.** Phosphine–palladium–diolefin complexes were synthesized and studied as they represent a model of the catalytic intermediate A in the telomerization reaction (Scheme 4). The synthesis of the complexes was achieved using the elegant method developed by Pörschke et al.<sup>44</sup> by reacting  $[(\text{TMEDA})\text{Pd}(\text{CH}_3)_2]$  (TMEDA = 1,2-bis(dimethylamino)ethane) with 1 equiv of the phosphine in the presence of an excess of the diolefin. Tetramethyldivinylsiloxane (dvds) is used as the diolefin ligand because it stabilizes the palladium(0) diolefin complex thanks to its increased  $\pi$ -acceptor ability (Scheme 7).

Thus, we prepared a series of new palladium complexes, obtained in moderate to good yield (30–100%) following the procedure described in Scheme 7. The new complexes are depicted in Figure 2.

**Scheme 7.** Synthesis of Phosphine–Pd–dvds Complexes



In the case of the BSP phosphine **8**, the palladium(0) complex does form but is not stable and decomposes with time and/or during the workup. The main difference between the two BSP phosphines **7** and **8** is the depth (*d*) of the bowl, which is 2.1 and 2.8 Å for **7** and **8**, respectively,<sup>28</sup> which could account for the instability of **8a** compared to **7a**. In complex **8a**, the steric repulsion between the *m*-terphenyl moieties and dvds should be larger than in **7a** and could destabilize the corresponding Pd-complex.

Single crystals suitable for X-ray diffraction have been obtained for complexes **1a**, **2a**, and **3a** by crystallization from a concentrated solution of the complex in diethyl ether at  $-25^\circ\text{C}$ . The molecular structures are presented Figure 3.

The X-ray structure analysis of complexes **1a**, **2a**, and **3a** reveals that 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 chair like conformation.<sup>46</sup> On the one hand, we can observe that in the case of **1a** and **2a** the biphenyl moiety pointed over the Pd atom because of favorable interactions between the aromatic  $\pi$ -system and the palladium center as observed by Buchwald for SPhos.<sup>29b,c</sup> On the other hand, because such interaction is not possible in **3a**, the naphthyl moiety is inside the “cone” of the phosphine ligand and the methyl substituent points to the Pd atom.

The trigonal planar geometry around the palladium for the three complexes is highly distorted as revealed by the value of the three angles (deg) D1–Pd1–D2 (**1a** 132.72(4), **2a** 130.48(7),

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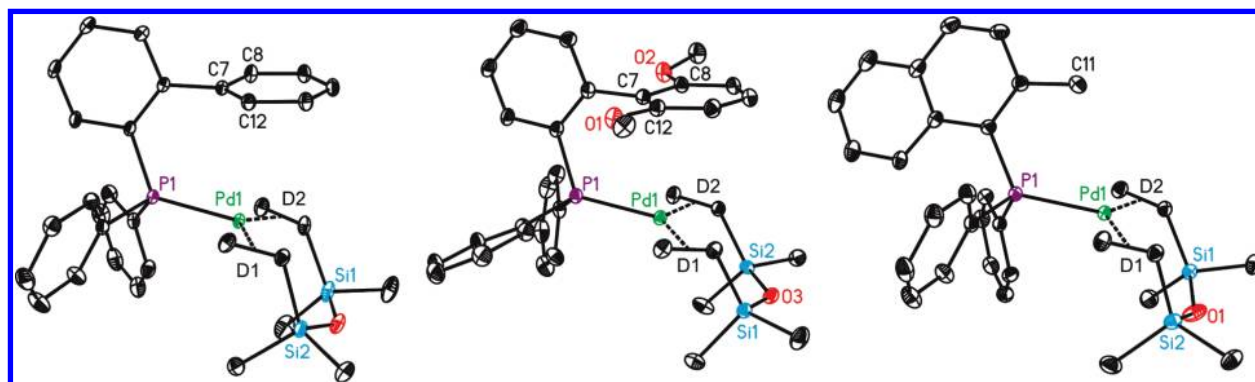
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**Figure 3.** Ortep plots (thermal ellipsoids shown at 50% probability level) of the complexes **1a**, **2a**, and **3a**. Hydrogen atoms have been omitted for the sake of clarity. D1: C27=C28 (left), C27=C28 (center), C26=C27 (right). D2: C25=C26 (left), C29=C30 (center), C24=C25 (right).

**Table 2.** Selected Bond Length and Bond Angles for Complexes **1a**, **2a**, and **3a**

	<b>1a</b>	<b>2a</b>	<b>3a</b>
Pd1–P1 (Å)	2.2975(6)	2.3192(5)	2.3255(3)
Pd1–D1 (Å)	2.0621(11)	2.068(2)	2.0733(13)
Pd1–D2 (Å)	2.0620(11)	2.088(2)	2.0622(13)
D1 (Å)	1.3922(15)	1.401(3)	1.399(2)
D2 (Å)	1.3910(15)	1.402(2)	1.3987(19)
D1–Pd1–D2 (deg)	132.72(4)	130.48(7)	132.78(5)
D1–Pd1–P1 (deg)	114.09(3)	119.91(5)	112.36(4)
D2–Pd1–P1 (deg)	113.03(3)	109.60(5)	114.72(4)
Pd1···C7 or C11 (Å)	3.38	3.27	3.30
Pd1···C8 (Å)	3.09	3.56	
Pd1···C12 (Å)	4.01	3.50	

**3a** 132.78(5)); D1–Pd1–P1 (**1a** 114.09(3), **2a** 119.91(5), **3a** 112.36(4); D2–Pd1–P1 (**1a** 113.03(3), **2a** 109.60(5), **3a** 114.72(4)) (Table 2), which are far from 120° as observed by Beller in the case of (NHC)–Pd–dvds complexes (D1–Pd–D2 ≈ 130°, D1–Pd1–P1 ≈ D2–Pd1–P1 ≈ 115°).<sup>23d</sup> Moreover, the C=C bond lies exactly in the coordination plane and the C=C bonds length (1.40 Å) is lengthened as compared with a typical C=C bond distance (1.34 Å), indicating a weak backbonding of the Pd. By contrast to **2a**, the phenyl ring covering the Pd in **1a** is tilted, as reflected by comparison of the Pd1–C8 and Pd1–C12 bond lengths in **1a** and **2a**.

In **1a** and **2a**, as observed by Buchwald in (SPhos)<sub>2</sub>Pd complexes,<sup>29a,c</sup> no Pd–C<sub>ipso</sub> interaction is observed as shown by the large distance of Pd1–C7 (3.27 Å); this is in contrast with (SPhos)Pd(dba) in which the Pd–C<sub>ipso</sub> bond length is around 2.37 Å.

In the case of phosphine rhodium complexes, Shaw observed a linear correlation between the chemical shift of the free phosphine and the coordination induced shift Δ, which was attributed to the widening of the cone angle of the ligand upon coordination.<sup>47</sup> The magnitude of Δ tends to be less for larger ligands than for smaller ligands, as ligands with large substituents generally open less on coordination, as the C–P–C angles are already large in the free ligand.<sup>37</sup> In this work, neither in the case of rhodium nor in the case of palladium complexes was such a correlation found (cf. PPh<sub>3</sub> is the least bulky phosphine and gives one of the lowest Δ in the case of rhodium (Table 1)).

A linear relation has also been found between the basicity of the phosphines and Δ, suggesting that Δ is related to the P–M

**Table 3.** Coordination Induced Shift Δ for the Phosphine–Pd–dvds Complexes

free ligand	δ <sup>31</sup> P{ <sup>1</sup> H} chemical shift (ppm)	complex	δ <sup>31</sup> P{ <sup>1</sup> H} chemical shift (ppm)	Δ δ <sup>31</sup> P{ <sup>1</sup> H} (complex–free ligand) (ppm)
<b>1</b>	−10.3	<b>1a</b>	27.1	37.4
<b>2</b>	−9.5	<b>2a</b>	24.1	33.6
<b>3</b>	−17.4	<b>3a</b>	15.5	32.9
<b>4</b>	−10.1	<b>4a</b>	26.9	37.0
<b>5</b>	−54.0	<b>5a</b>	−10.1	43.9
<b>6</b>	−59.0	<b>6a</b>	−27.8	31.2
<b>7</b>	−4.4	<b>7a</b>	29.8	34.2
<b>9</b>	−36.4	<b>9a</b>	17.7	54.1
<b>10</b>	−66.7	<b>10a</b>	−21.6	45.1
<b>11</b>	−8.6	<b>11a</b>	35.8	44.4
PPh <sub>3</sub>	−5.9	PPh <sub>3</sub> –Pd–vds	30.2	36.1 <sup>44</sup>

**Table 4.** Telomerization of 1,3-Butadiene in the Presence of Phosphine–Palladium–dvds Complex<sup>a</sup>

entry	Pd complex	conv Bd (%)	TON	1-MOD (%)	3-MOD (%)	OCT (%)
1	<b>1a</b>	58	11600	89	4	7
2	<b>2a</b>	99	19800	90	8	2
3	<b>3a</b>	24	4800	94	4	2
4	<b>4a</b>	99	19800	93	5	2
5	<b>5a</b>	99	19800	87	10.5	2.5
6	<b>6a</b>	14	2800	90	4	6
7	<b>7a</b>	96	19200	76.5	12.5	11
8	<b>9a</b>	99	19800	96	3	1
9	<b>10a</b>	10	2000	72.5	1.5	26
10	<b>11a</b>	90	18000	83.5	9.5	7
11	Pd(OAc) <sub>2</sub> /PPh <sub>3</sub> (1/2)	90	18000	87.5	7.5	5
12	Pd(OAc) <sub>2</sub> /4 (1/2)	99	19800	93	5	2

<sup>a</sup> Reaction conditions: 60 °C, 16 h, MeOH/1,3-butadiene 2/1 (molar ratio), Pd complex (0.005 mol % vs 1,3-Butadiene), NaOMe (1 mol %).

bond strength, meaning the stronger the metal phosphine bond, the larger Δ.<sup>40</sup> Unfortunately, no such relation can be found here either (cf. Table 3), pointing out the unusual steric properties of “Buchwald-type” phosphines, containing two substituents such as phenyl or cyclohexyl and one very bulky moiety such as substituted biphenyl, xanthene, or 2-methylnaphthyl.

**Catalytic Studies.** The complexes prepared were tested in the telomerization of 1,3-butadiene with MeOH. The conditions used are 60 °C, 16 h, MeOH/1,3-butadiene (2 mol/mol), NaOMe (1 mol % vs butadiene), catalyst (0.005 mol % vs butadiene) to evaluate their overall productivity and selectivity to the linear product. The results obtained are presented in Table 4. The standard triphenylphosphine system was tested as a reference, and the results found are similar to those found by Beller.<sup>23g,h</sup> We observed that complexes **2a**, **4a**, and **9a** are highly selective

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toward linear 1-MOD and more productive and selective toward the linear product than the triphenylphosphine system under these conditions.

Concerning the productivity, ligands **3** and **6** render the less productive catalysts, exhibiting a TON of only 4560 and 2700, respectively (Table 4, entries 3, 6). Both ligands containing the 2-methylnaphthyl moiety are probably among the bulkier phosphine of the series (the cone angle of **3** is  $\theta = 223^\circ$ ). Thus, it seems that, as observed by Beller in the case of NHC ligands, although bulky ligands could activate the catalyst by destabilizing the diolefin complex, it does not always translate into an increased catalytic activity, maybe because decomposition takes place.<sup>23d</sup> By contrast, complexes **2a**, **4a**, and **5a** are the most productive catalysts of the series, showing nearly complete conversions (TON of 20,000) under such conditions. The commercially available tris(*o*-methoxyphenyl)phosphine **9** is the more selective catalyst, yielding 96% of 1-MOD (with 99% chemoselectivity and 97% regioselectivity). Unfortunately, the productivity of the catalyst with **9a** is strongly dependent on the quality of the methanol, because **9** is more sensitive to oxidation than **4** or **PPh<sub>3</sub>**.<sup>48</sup> It seems also difficult to find a trend concerning the properties of ligand and the productivity/selectivity of the catalyst as ligands **2**, **4**, and **9**, which are electronically and sterically different, give the most promising results. We also observed that in situ preparation of the catalyst has no detrimental effect on the productivity and on the selectivity of the catalyst (Table 4, entry 12).

Thus, we decided to study in detail the best phosphines (**2**, **4**, **5**, **9**, and **11**) compared to **PPh<sub>3</sub>** under different reaction conditions, such as scale-up (from 7 g of pure 1,3-butadiene to 150 g of C4 crude fraction containing 47.5 wt % of 1,3-butadiene), MeOH/1,3-butadiene ratio, and temperature. We also studied the activity of the catalyst by following the rate of formation of 1-MOD and/or butadiene conversion with time. Palladium loss at the end of the catalytic reaction was also evaluated. For these experiments 0.0025 mol % of Pd and 0.0125 mol % of NaOMe (vs butadiene) were used, and the catalysts were prepared in situ (TPP = **PPh<sub>3</sub>**, Bd = 1,3-butadiene, w/w = weight ratio, reaction time = 2.5 h, ligand/Pd = 2/1; see Supporting Information). The results obtained for **2**, **4**, **5**, **9**, **11**, and **PPh<sub>3</sub>** at different temperature and MeOH/Bd weight ratio are summarized in Table 5.

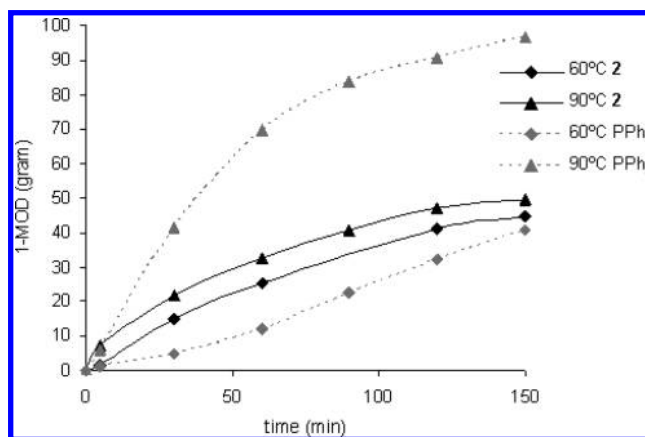
In the case of TPP at 60 °C, when only 0.0025 mol % of Pd loading is used, higher selectivity is obtained compared to previous results (1-MOD selectivity up to 92.4%; Table 5, entries 16 and 17). As observed by Beller et al., the concentration of 1,3-butadiene influences the yield of 1-MOD: decreased concentration of butadiene increases the yield of the linear telomer (cf. increase the regioselectivity) and increasing the temperature decreases the yield to 1-MOD (cf. decrease of the chemoselectivity) but increases butadiene conversion (Table 5, entries 16–19).<sup>23h</sup> Palladium precipitation at 90 °C is about 17% (Table 5, entries 18 and 19).

We observed that under the new reaction conditions, ligand **2** gives low selectivity compared to previous results (85% vs 89% 1-MOD selectivity at 60 °C) and compared to **PPh<sub>3</sub>** under the same conditions (85% vs 91% 1-MOD selectivity for ligand **2** and **PPh<sub>3</sub>**, respectively (Table 5, entries 1 and 16)). At 90 °C,

**Table 5.** Telomerization of 1,3-Butadiene<sup>a</sup>

entry	ligand	T (°C)	MeOH/Bd w/w ratio	conv Bd (%)	1-MOD (%)	Pd loss <sup>b</sup> (%)
1	<b>2</b>	60	2	38	85	0
2	<b>2</b>	90	2	50	70	35
3	<b>4</b>	60	2	40	94	0
4	<b>4</b>	60	2.6	36	94	2
5	<b>4</b>	90	2	89	88	2
6	<b>4</b>	90	2.6	93	89	6
7	<b>4</b>	100	2	91	84	2
8	<b>5</b>	90	2.6	87	82	30
9	<b>9</b>	70	0.6	57	95	
10	<b>9</b>	70	2.6	38	92	
11	<b>9</b>	90	0.6	82	92	
12	<b>9</b>	90	2.6	53	89	
13	<b>11</b>	60	2	10	75	0
14	<b>11</b>	60	2.6	10	61	4
15	<b>11</b>	90	2	30	76	32
16	<b>PPh<sub>3</sub></b>	60	2	32	91	0
17	<b>PPh<sub>3</sub></b>	60	2.6	29	92	0
18	<b>PPh<sub>3</sub></b>	90	2	82	80	16
19	<b>PPh<sub>3</sub></b>	90	2.6	85	83	17

<sup>a</sup> Reaction conditions Pd (0.0025 mol % vs butadiene), NaOMe (0.0125 mol % vs butadiene), 2.5 h, ligand/Pd 2/1. <sup>b</sup> Measurement error  $\pm 5\%$ .



**Figure 4.** Rate of formation of 1-MOD (MeOH/Bd (w/w) = 2/1, Pd (0.0025 mol % vs butadiene); comparison of ligand **2** and **PPh<sub>3</sub>**.

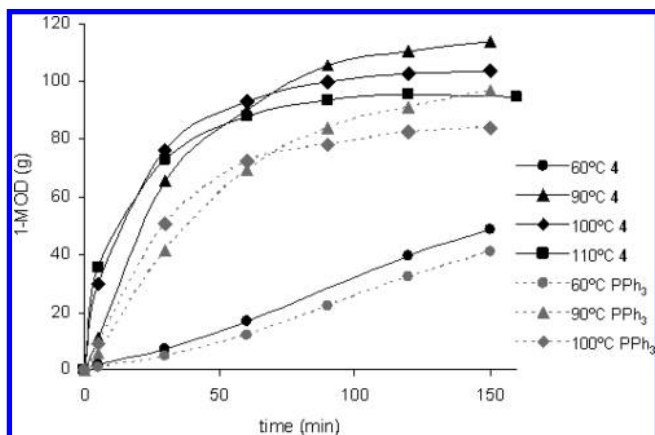
significant decrease of selectivity is observed for **2** (1-MOD = 70% vs 80% for **PPh<sub>3</sub>**; Table 5, entry 2).

Concerning the reaction rate, at 60 °C **2** gives a more active catalyst (see Figure 4) than **PPh<sub>3</sub>**. However at 90 °C, the reaction rate decreases strongly after 10 min (initial reaction rates for **PPh<sub>3</sub>** and **2** seem equivalent at 90 °C), meaning that the catalyst derived from **2** is unstable. High palladium loss was measured in the case of **2** at 90 °C (up to 35%), which is in favor of this hypothesis.

As observed previously (Table 4, entry 8) for ligand **9**, high selectivity to 1-MOD was obtained (up to 92% at 90 °C; see Supporting Information), but in this case low MeOH/Bd ratio (0.6 instead of 2.7) enhances the selectivity and the butadiene conversion (53% with MeOH/Bd = 2.6 and 82% with MeOH/Bd = 0.5). In this case, this could be explained by the fact that degassed commercially available methanol was used for these experiments, pointing out the high sensitivity of **9** to oxidation.<sup>48</sup>

The system based on **5** shows similar performance in terms of productivity, selectivity, and activity as the one using **PPh<sub>3</sub>**, except that the palladium loss is higher (up to 30%). Ligand **11** gives very bad results in term of selectivity, conversion, and a very high Pd precipitation (see Supporting Information).

(48) For example, we observed that butadiene conversion drops to 50% instead of 99% if non-degassed commercially available extra dry methanol (ACROS) is used as received (amount of water in degassed and distilled methanol at the bench being around 10 ppm).



**Figure 5.** Rate of formation of 1-MOD (MeOH/Bd (w/w) 2/1, Pd (0.0025 mol % vs butadiene); comparison of ligand **4** (monoxantphos) and PPh<sub>3</sub>.

Phosphine **4**, which is the most promising ligand of the series, has been studied in more detail. In all conditions tested, ligand **4** gives better results than PPh<sub>3</sub> (Table 5, entries 3–7) concerning productivity and selectivity to 1-MOD, which stays constant during the course of the reaction, meaning that formation of byproduct such as 3-MOD and OCT is directly dependent on the catalyst features and is not a consequence of catalyst decomposition. At 60 °C with **4**, the selectivity to 1-MOD is 2–3% higher than the one observed with PPh<sub>3</sub> and butadiene conversion increases from ~30% to ~38% (Table 5, entries 3, 4, 16, and 17), but the largest differences are observed at 90 °C. Selectivity to 1-MOD and butadiene conversion are 6–8% and 8% higher, respectively, than PPh<sub>3</sub>. Moreover, Pd-loss is significantly lower in the presence of ligand **4**, decreasing from 17% to 6% under the same conditions (Table 5, entries 6 and 18).

The high potential of monoxantphos **4** is also demonstrated by the kinetics depicted in Figure 5. At 60 °C the rate of formation of 1-MOD is slightly higher than with PPh<sub>3</sub>. At 90 °C after 30 min of reaction, a max TOF of ~40,000 and of 25,500 h<sup>-1</sup> (Beller reported a TOF 25,000 after 30 min for PPh<sub>3</sub>)<sup>23g</sup> is reached in the case of **4** and PPh<sub>3</sub>, respectively. The most impressive result is obtained at 100 °C: after 5 min of reaction, a TOF of ~140,000 h<sup>-1</sup> is observed for **4**; in the case of PPh<sub>3</sub>, TOF (5 min) ≈ 41,600 h<sup>-1</sup>. Only in the case of an NHC ligand has such a high TOF (up to 100,000 h<sup>-1</sup> at 90 °C) been observed, although this was not achieved under the conditions of the commercial process.<sup>23d</sup>

## Conclusions and Outlook

In addition to several published sterically hindered phosphines, new ones possessing different electronic and steric properties were prepared in moderate to good yield. The xanthene backbone, well-known for its diphosphine Xantphos, as well as the phenoxaphosphine moiety, have been used to prepare new phosphines.

A series of phosphine–palladium–dvds complexes, containing those ligands, were synthesized and tested as catalyst for the selective telomerization of 1,3-butadiene with methanol. In comparison with PPh<sub>3</sub>, monoxantphos **4** emerged as a very promising alternative giving a more active and selective catalyst than PPh<sub>3</sub> in the standard system optimized for PPh<sub>3</sub>.

The testing of phosphines under “Dow production conditions” (scale-up, crude C4 fraction, high temperature) reveals the high potential of **4**. Remarkably, ligand **4** gives a highly active

catalyst, reaching TOF up to 140,000 h<sup>-1</sup> at 100 °C with high selectivity (up to 84%) for the production of 1-MOD. Surprisingly, ligand **4** also highly stabilizes the catalytic active species as the loss of palladium during the catalytic reaction is much lower than that of the catalyst based on PPh<sub>3</sub>.

Further studies on the structure–reactivity relationship and new derivatizations of monoxantphos **4** are currently carried out to understand the steric and electronic influence of the phosphine on the telomerization reaction and to optimize the systems accordingly.

## Experimental Section

**General Procedures.** All reactions were carried out under an argon atmosphere using Schlenk techniques. Deuterated chloroform was distilled over calcium hydride under argon prior to use. MeOH was dried by distillation over Mg under Ar and degassed twice by a freeze, pump, and thaw cycle. Tetramethyldivinylsiloxane (dvds) was purchased from Aldrich, dried over molecular sieves 4 Å, and degassed with argon. 2'-Bromo-2,6-dimethoxybiphenyl, 1-bromo-2-methylnaphthyl, phosphorus trichloride, *n*-BuLi solutions in hexane, and tetramethylethylenediamine (TMEDA) were purchased from Aldrich and used as received. Chlorodiphenylphosphine was purchased from Fluka and distilled under inert atmosphere prior to use. Tetracarbonyl-μ-chlorodirrhodium was purchased from Acros and used as received. Palladium dichloride was purchased from Strem and used as received.

Phosphines **1**,<sup>26</sup> **2**,<sup>27</sup> **3**,<sup>26</sup> **7**,<sup>28</sup> and **8**<sup>28</sup> were prepared by previously described methods, and commercially available phosphines **9**–**11** were purchased from Aldrich and used without further purifications. (TMEDA)Pd(Me)<sub>2</sub> was prepared by following the published procedure.<sup>45</sup> NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm and were calibrated using residual <sup>1</sup>H and <sup>13</sup>C resonances of deuterated solvents. Coupling constants (*J*) are expressed in Hertz. Mass spectra and X-ray structure analysis 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 a HP-5 (5% phenyl methyl siloxane; 30 m × 320 m × 0.25) capillary column. Elemental analysis were performed at the Unidade de Análise Elemental of the Universidade de Santiago de Compostela (Spain).

**Synthesis of 4-Diphenylphosphino-2,7-di-*tert*-butyl-9,9-dimethylxanthene (**4**).** To a solution of 4-bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (90%) (**12**) (1.53 g, containing 3.44 mmol of **12**) in THF (30 mL) at –78 °C was added slowly *n*-BuLi 2.5 M in hexane (1.52 mL), and the mixture was stirred for 1 h at –78 °C. Then, chlorodiphenylphosphine (3.8 mmol, 0.82 g, 0.67 mL) was added at –78 °C, and the mixture was stirred 1 h at –78 °C and 1 h at rt. Then, the solvent was evaporated under vacuum, dichloromethane (20 mL) was added, the solution was filtered off in order to eliminate the inorganic salts formed during the reaction, and the solvent was removed under reduced pressure. The product was purified by column chromatography over silica gel using as eluent hexane/dichloromethane (4:1). Compound **4** is obtained as white solid (0.95 g, 55%). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>) δ 7.41–7.31 (m, 12H, *H* arom.), 7.05 (dd, 1H, *J* = 2.3 Hz, *J* = 8.5 Hz, *H* arom.), 6.65 (dd, 1H, *J* = 2.3 Hz, *J* = 5.8 Hz, *H* arom.), 6.52 (d, 1H, *J* = 8.5 Hz) 1.64 (s, 6H, CH<sub>3</sub>), 1.29 (s, 9H, C(CH<sub>3</sub>)), 1.14 (s, 9H, C(CH<sub>3</sub>)); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, 25 °C, CDCl<sub>3</sub>) δ 150.4 (d, *J*(P,C) = 13.5 Hz), 148.5, 145.6, 145.3, 137.0 (d, *J*(P,C) = 10.2 Hz), 134.1 (d, *J*(P,C) = 20.0 Hz), 129.6, 129.5, 129.1, 129.0, 128.69, 128.4 (d, *J*(P,C) = 7.0 Hz), 124.2, 123.7 (d, *J*(P,C) = 14.0 Hz), 123.41, 121.9, 115.9, 34.9, 34.6, 34.5, 31.9, 31.7, 31.5; <sup>31</sup>P{<sup>1</sup>H} (160 MHz, 25 °C, CDCl<sub>3</sub>) δ –10.18. Anal. Calcd for C<sub>35</sub>H<sub>39</sub>OP: C, 82.97; H, 7.76. Found: C, 82.77; H, 7.74.

**Synthesis of 2-(2,8-Dimethylphenoxaphosphino)-2',6'-dimethoxybiphenyl (**5**).** To a solution of 2-bromo-2',6'-dimethoxybiphenyl (0.88 g, 3 mmol) in 20 mL of THF cooled at –78 °C was added

*n*-BuLi (1.1 equiv, 3.3 mmol, 1.32 mL, 25 M in hexane) dropwise via syringe. The resulting mixture was stirred at  $-78^{\circ}\text{C}$  for 0.5 h. Then 10-chloro-2,8-phenoxaphosphine (1 equiv, 3 mmol, 0.80 g) dissolved in 10 mL of THF was added via syringe. The mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h and then allowed to slowly warm to rt. The solvent was removed under vacuum. The resulting solid was dissolved in dichloromethane (20 mL) and filtered off through Celite in order to eliminate the inorganic salts formed during the reaction. Then the solvent was removed under reduced pressure to afford a yellow solid. Recrystallization from ethanol (20 mL) provided the phosphine as a white solid (0.68 g, 51%).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.42 (t,  $J = 8.3$  Hz, 1H, *H* arom.), 7.28 (brt,  $J = 7.9$  Hz, 1H, *H* arom.), 7.15–7.10 (m, 2H, *H* arom.), 7.07–6.98 (m, 5H, *H* arom.), 6.82 (brd,  $J = 9.8$  Hz, 2H, *H* arom.), 6.72 (d, 2H,  $J = 8.3$  Hz, *H* arom.), 3.77 (s, 6H,  $\text{OCH}_3$ ), 2.22 (s, 6H,  $\text{CH}_3$  arom.);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  158.0, 153.4, 140.5 (d,  $J(\text{P},\text{C}) = 21.9$  Hz), 139.8 (d,  $J(\text{P},\text{C}) = 32.8$  Hz), 134.8 (d,  $J(\text{P},\text{C}) = 32$  Hz), 133.48 (d,  $J(\text{P},\text{C}) = 1.5$  Hz), 132.3 (d,  $J(\text{P},\text{C}) = 13.5$  Hz), 130.9, 130.7 (d,  $J(\text{P},\text{C}) = 5.8$  Hz), 129.4, 128.7, 127.83, 127.78, 119.67, 119.61, 119.3 (d,  $J(\text{P},\text{C}) = 6.5$  Hz), 117.25, 103.9, 55.7, 20.8;  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$   $-54.50$ . Anal. Calcd for  $\text{C}_{28}\text{H}_{35}\text{O}_3\text{P}$ : C, 74.64; H, 7.83. Found: C, 74.82; H, 7.75.

**Synthesis of 1-(2,8-Dimethylphenoxaphosphino)-2-methylnaphthalene (6).** To a solution of 1-bromo-2-methylnaphthalene (0.72 g, 3.2 mmol) in THF (20 mL) cooled at  $-78^{\circ}\text{C}$  was added dropwise via syringe *n*-BuLi (3.6 mmol, 1.43 mL, 2.5 M in hexane). The resulting mixture was stirred at  $-78^{\circ}\text{C}$  for 0.5 h. Then 10-chloro-2,7-phenoxaphosphine (3.2 mmol, 0.85 g) dissolved in 10 mL of THF was added via syringe. The mixture was allowed to stir at  $-78^{\circ}\text{C}$  for 1 h and then allowed to slowly warm to rt. The solvent was evaporated under vacuum. The resulting solid was dissolved in dichloromethane (20 mL) and filtered off through Celite in order to eliminate the inorganic salts formed during the reaction. Then the solution was concentrated under reduced pressure, and a yellow solid was obtained. Recrystallization from ethanol (20 mL) rendered the phosphine as a white solid (0.58 g, 48%).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  8.85 (m, 1H, *H* arom.), 7.86 (d, 1H,  $J = 8.3$  Hz, *H* arom.), 7.83 (m, 1H, *H* arom.), 7.41 (m, 2H, *H* arom.), 7.32 (dd, 1H,  $J = 2.0$  Hz, 8.3 Hz, *H* arom.), 6.99 (s, 4H, *H* arom.), 6.65 (d,  $J = 9.2$  Hz, 2H, *H* arom.), 2.48 (s, 3H,  $\text{CH}_3$  naph.), 2.08 (s, 6H,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  151.0 (d,  $J(\text{P},\text{C}) = 5.5$  Hz), 145.7 (d,  $J(\text{P},\text{C}) = 12.7$  Hz), 137.6 (d,  $J(\text{P},\text{C}) = 17.3$  Hz), 133.0 (d,  $J(\text{P},\text{C}) = 5.9$  Hz), 132.8 (d,  $J(\text{P},\text{C}) = 4.0$  Hz), 131.49, 131.48 (d,  $J(\text{P},\text{C}) = 20.9$  Hz), 130.3, 130.2 (d,  $J(\text{P},\text{C}) = 3.8$  Hz), 128.6, 127.4, 127.2, 126.66 (d,  $J(\text{P},\text{C}) = 2.1$  Hz), 125.06 (d,  $J(\text{P},\text{C}) = 1.3$  Hz), 119.1 (d,  $J(\text{P},\text{C}) = 8.0$  Hz), 117.1, 23.2 (d,  $J(\text{P},\text{C}) = 17.5$  Hz), 20.6;  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$   $-59.08$ . Anal. Calcd for  $\text{C}_{25}\text{H}_{21}\text{OP}$ : C, 81.50; H, 5.75. Found: C, 81.17; H, 5.84.

**Synthesis of 4-Bromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (12).** 2,7-Di-*tert*-butyl-9,9-dimethylxanthene (3 g, 9.3 mmol) and NBS (14.9 g, 84 mmol) were dissolved in DMF/THF 1/1 in volume (200 mL) and stirred at rt for 3 days. The conversion was monitored by GC/MS. If necessary, more NBS was added. The solvent was evaporated to dryness, and the solid was washed with water and extracted with dichloromethane. The organic layer was separated and dried over  $\text{MgSO}_4$  and evaporated to dryness. The solid obtained was washed with ethanol to give 2.8 g of a white solid (containing a molar mixture of monobromo/dibromo/starting material 90/7/3). The mixture was used without further purification to prepare the phosphine.  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 2.2$  Hz, 1H, *H* arom.), 7.41 (d,  $J = 2.3$  Hz, 1H, *H* arom.), 7.37 (d,  $J = 2.2$  Hz, 1H, *H* arom.), 7.46 (d,  $J = 2.2$  Hz, 1H, *H* arom.), 7.26 (dd,  $J = 2.2$ , 8.5 Hz, 1H, *H* arom.), 7.10 (d,  $J = 8.5$  Hz, 1H, *H* arom.), 1.66 (s, 6H,  $\text{CH}_3$ ), 1.36 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 1.34 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ).

**General Procedure for the Synthesis of the  $\text{Rh}(\text{CO})_2(\text{phosphine})_2\text{Cl}$ .** Tetracarbonyldi- $\mu$ -chlorodirrhodium complex (10 mg,  $2.57 \times 10^{-5}$  mol) and the desired amount of the phosphine (4

equiv,  $1.03 \times 10^{-4}$  mol) were dissolved in dichloromethane (3 mL). In the case of **10**, the reaction was carried out in THF (because **10** reacts with  $\text{CH}_2\text{Cl}_2$  to give the phosphonium salt).<sup>33</sup> The solution was stirred for 1 h, and then solvent was evaporated to dryness. The yellow solid obtained was analyzed by IR (solid phase) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ ).

**General Procedure for the Synthesis of the Phosphine–Palladium–dvds Complexes.** A suspension of (TMEDA) $\text{Pd}(\text{CH}_3)_2$  (0.1 g, 0.40 mmol) and of the desired phosphine (1 equiv, 0.40 mmol) in degassed and dried tetramethyldivinylsiloxane (dvds, 4 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 diethylether (or pentane) at  $-50^{\circ}\text{C}$  to remove small quantities of unreacted reagents. Because of their low stability at room temperature, the phosphine–palladium–dvds complexes have been characterized only by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy and MS spectrometry and should be stored under inert atmosphere at  $-20^{\circ}\text{C}$ .

**Synthesis of 1a.** Yield of **1a**: 61%, 0.152 g (**1**: 0.40 mmol, 0.136 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.50–7.30 (brm, 14H, *H* arom.), 7.15–6.95 (brm, 5H, *H* arom.), 3.20 (m, 2H, dvds), 2.85 (m, 2H, dvds), 2.66 (m, 2H, dvds), 0.27 (s, 6H, dvds),  $-0.20$  (s, 6H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  27.1. ESI-MS:  $m/z = 630.2$  [ $\text{M}$ ] $^+$ , 653.1 [ $\text{M} + \text{Na}$ ] $^+$  and decomposition peaks.

**Synthesis of 2a.** Yield of **2a**: 59%, 0.162 g (**2**: 0.40 mmol, 0.160 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.53–7.41 (m, 6H, *H* arom.), 7.37–7.28 (m, 7H, *H* arom.), 7.20–7.17 (m, 1H, *H* arom.), 7.11 (t,  $J = 8.4$  Hz, 1H, *H* arom.), 6.30 (d,  $J = 8.4$  Hz, 2H, *H* arom.), 3.45 (s, 6H,  $\text{OCH}_3$ ), 3.29 (dd,  $J = 2.2$ , 11.8 Hz, 1H, dvds), 3.29 (dd,  $J = 2.7$ , 11.4 Hz, 1H, dvds), 2.60–2.41 (m, 4H, dvds), 0.20 (s, 3H, dvds),  $-0.39$  (s, 3H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  24.1. ESI-MS:  $m/z = 713.2$  [ $\text{M} + \text{Na}$ ] $^+$ .

**Synthesis of 3a.** Yield of **3a**: 68%, 0.168 g (**3**: 0.40 mmol, 0.131 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 8.4$  Hz, 1H, *H* arom.), 7.87 (d,  $J = 8.4$  Hz, 1H, *H* arom.), 7.81 (d,  $J = 8$  Hz, 1H, *H* arom.), 7.52 (m, 4H, *H* arom.), 7.36–7.28 (m, 8H, *H* arom.), 7.08 (t,  $J = 8$  Hz, 1H, *H* arom.), 3.35–3.20 (m, 4H, dvds), 2.84 (dd,  $J = 4.8$ , 15.8 Hz, 2H, dvds), 2.30 (s, 3H,  $\text{CH}_3$  arom.), 0.24 (s, 3H, dvds),  $-0.30$  (s, 3H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  26.9. ESI-MS:  $m/z = 641.2$  [ $\text{M} + \text{Na}$ ] $^+$ .

**Synthesis of 4a.** Yield of **4a**: 71%, 0.226 g (**4**: 0.40 mmol, 0.203 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.55 (m, 4H, *H* arom.), 7.45 (d,  $J = 2.1$  Hz, 1H, *H* arom.), 7.34 (m, 7H, *H* arom.), 6.97 (dd, d,  $J = 2.1$ , 8.5 Hz, 1H, *H* arom.), 6.86 (dd, d,  $J = 2.0$ , 10.6 Hz, 1H, *H* arom.), 6.06 (d,  $J = 8.5$  Hz, 1H, *H* arom.), 3.35 (d,  $J = 5.8$  Hz, 1H, dvds), 3.32 (d,  $J = 5.2$  Hz, 1H, dvds), 3.13 (m, 4H, dvds), 1.64 (s, 6H,  $\text{CH}_3$ ), 1.29 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 1.18 (s, 9H,  $\text{C}(\text{CH}_3)_3$ ), 0.25 (s, 3H, dvds),  $-0.25$  (s, 3H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  15.3. ESI-MS:  $m/z = 821.4$  [ $\text{M} + \text{Na}$ ] $^+$ .

**Synthesis of 5a.** Yield of **5a**: 57%, 0.166 g (**5**: 0.40 mmol, 0.1762 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.45–7.35 (m, 2H, *H* arom.), 7.28 (m, 1H, *H* arom.), 7.13 (t,  $J = 8.3$  Hz, 1H, *H* arom.), 7.04 (brm, 5H, *H* arom.), 6.94 (m, 2H, *H* arom.), 6.29 (d,  $J = 8.3$  Hz, 2H, *H* arom.), 3.47 (s, 6H,  $\text{O}(\text{CH}_3)_2$ ), 3.33 (d,  $J = 5.8$  Hz, 1H, dvds), 3.29 (d,  $J = 5.6$  Hz, 1H, dvds), 2.91 (m, 2H, dvds), 2.70 (d,  $J = 6.0$  Hz, 1H, dvds), 2.66 (d,  $J = 6.2$  Hz, 1H, dvds), 2.25 (s, 6H,  $\text{CH}_3(\text{POP})$ ), 0.22 (s, 6H, dvds),  $-0.33$  (s, 6H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$   $-10.1$ . ESI-MS:  $m/z = 755.2$  [ $\text{M} + \text{Na}$ ] $^+$ .

**Synthesis of 6a.** Yield of **6a**: 85%, 0.234 g (**6**: 0.40 mmol, 0.148 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  9.08 (brs, 1H, *H* arom.), 7.95 (d,  $J = 7.9$  Hz, 1H, *H* arom.), 7.86 (d,  $J = 7.3$  Hz, 1H, *H* arom.), 7.43–7.25 (m, 3H, *H* arom.), 7.02 (brs, 4H, *H* arom.), 6.81 (d,  $J = 10.5$  Hz, 2H, *H* arom.), 3.27 (brs, 4H, dvds), 2.85 (brm, 2H, dvds), 2.35 (s, 3H,  $\text{CH}_3(\text{naph})$ ), 2.13 (s, 6H,  $\text{CH}_3(\text{POP})$ ), 0.21 (s, 6H, dvds),  $-0.39$  (s, 6H, dvds).  $^{31}\text{P}\{^1\text{H}\}$  (160 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$   $-27.8$ . ESI-MS:  $m/z = 683.2$  [ $\text{M} + \text{Na}$ ] $^+$ .

**Synthesis of 7a.** Yield of **7a**: 30%, 0.145 g (**7**: 0.40 mmol, 0.621 g).  $^1\text{H}$  NMR (400 MHz,  $25^{\circ}\text{C}$ ,  $\text{CDCl}_3$ )  $\delta$  7.27 (dd,  $J = 1.4$ , 9.9



Hz, 6H, *H* arom.), 7.14–7.10 (m, 6H, *H* arom.), 7.04 (brs, 8H, *H* arom.), 7.03 (brs, 4H, *H* arom.), 6.94 (m, 3H, *H* arom.), 3.31–3.15 (m, 6H, dvds), 1.88 (s, 36H, *CH*<sub>3</sub> arom.), 0.21 (s, 3H, dvds), –0.47 (s, 3H, dvds). <sup>31</sup>P{<sup>1</sup>H} (160 MHz, 25 °C, CDCl<sub>3</sub>) δ 29.8. ESI-MS: *m/z* = 1201.6 [M + Na]<sup>+</sup> and intense decomposition peaks.

**Synthesis of 9a.** Yield of **9a**: 60%, 0.155 g (**9**: 0.40 mmol, 0.141 g). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>) δ 7.43–7.31 (m, 6H, *H* arom.), 6.91 (brt, *J* = 7.5 Hz, 3H, *H* arom.), 6.82 (dd, *J* = 3.9, 8.1 Hz, 3H, *H* arom.), 3.40 (s, 9H, OCH<sub>3</sub>), 3.06–2.87 (m, 6H, dvds), 0.24 (s, 3H, dvds), –0.21 (s, 3H, dvds). <sup>31</sup>P{<sup>1</sup>H} (160 MHz, 25 °C, CDCl<sub>3</sub>) δ –17.7. ESI-MS: *m/z* = 667.2 [M + Na]<sup>+</sup>.

**Synthesis of 10a.** The complex is obtained after evaporation of dvds without washing. Yield of **10a**: quant, 0.325 g (**10**: 0.40 mmol, 0.213 g). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>) δ 5.98 (d, *J* = 2.9 Hz, 6H, *H* arom.), 3.80 (s, 9H, *p*-OCH<sub>3</sub>), 3.46 (s, 18H, *o*-OCH<sub>3</sub>), 3.22 (dd, *J* = 6.6, 13.4 Hz, 2H, dvds), 2.79 (m, 2H, dvds), 2.64 (m, 2H, dvds), 0.21 (s, 3H, dvds), –0.21 (s, 3H, dvds). <sup>31</sup>P{<sup>1</sup>H} (160 MHz, 25 °C, CDCl<sub>3</sub>) δ –21.6.

**Synthesis of 11a.** Yield of **11a**: 65%, 0.191 g (**11**: 0.40 mmol, 0.164 g). <sup>1</sup>H NMR (400 MHz, 25 °C, CDCl<sub>3</sub>) δ 7.59 (m, 1H, *H* arom.), 7.39–7.31 (m, 2H, *H* arom.), 7.21 (t, <sup>3</sup>*J* = 8.3 Hz, 1H, *H* arom.), 6.99 (m, 1H, *H* arom.), 6.43 (d, *J* = 8.3 Hz, 2H, *H* arom.), 3.64 (s, 6H, OCH<sub>3</sub>), 3.15 (dd, *J* = 5.5, 13.4 Hz, 2H, dvds), 2.92 (dd, *J* = 4.7, 15.7 Hz, 2H, dvds), 2.42 (m, 2H, dvds), 2.15–2.05 (m, 2H, P-Cy), 1.82–1.60 (m, 10H, P-Cy), 1.35–1.10 (m, 10H, P-Cy), 0.26 (s, 3H, dvds), –0.23 (s, 3H, dvds). <sup>31</sup>P{<sup>1</sup>H} (160 MHz, 25 °C, CDCl<sub>3</sub>) δ 35.8. ESI-MS: *m/z* = 725.2 [M + Na]<sup>+</sup>.

**Catalysis.** Catalytic reaction carried out at 60 °C with phosphine–palladium–dvds complexes (cf. Table 4). In a glovebox, the desired amounts of NaOMe (1 mol %, 0.07 g), MeOH (0.266 mol, 8.52 g, 10.8 mL), and palladium complex (0.005 mol %) were mixed in a stainless steel autoclave equipped with a Teflon inset (25 mL). At the bench, the desired amount of 1,3-butadiene (0.133 mol, 7.2 g) was condensed from the gas bottle into a cooled (N<sub>2</sub> liquid/acetone bath) metallic cylinder (Swagelok, 30 mL). Then, the 1,3-butadiene was condensed from the cylinder into the cooled autoclave, and the vessel was heated to the reaction temperature for the desired time. After 16 h, the autoclave was cooled down with an ice bath, and the remaining butadiene was recondensed in a cylinder. Then, the autoclave was opened, and decane (0.5 mL, 0.365 g) was added to the reaction mixture. The conversion and yield of the telomerization product were determined by GC-FID analysis.

**Scale-Up Catalytic Reaction (cf. Table 5).** The reaction was carried out in a 1 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). The autoclave was closed, purged twice with low pressure nitrogen (6 bar or 600 kPa) to substantially remove oxygen contained in the autoclave. A stainless steel sample cylinder was filled with a crude C4 stream that contained 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 (60, 75, 90, or 100 °C, as shown in Table 5). The catalyst was prepared with palladium acetyl acetonate (Pd(acac)<sub>2</sub>) plus 2 molar 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. 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 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.

**Palladium Precipitation.** In the reactor, precipitation is determined by measuring palladium concentration in the liquid phase after the reaction and comparing that to a theoretical number based on total amount of palladium added and 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 is measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). Tests for conversion, selectivity to MOD-1, and palladium precipitation were made at methanol to butadiene ratios of 2, 2.6, and 5, respectively.

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**Supporting Information Available:** Representative experimental procedures, kinetics, data for the catalytic experiments and X-ray crystallography data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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