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New Insights into the Palladium-Catalysed Synthesis of δ-Lactones from 1,3-Dienes and Carbon Dioxide

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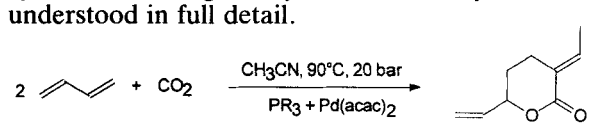
Two-coordinate Pd(0) complexes are shown to be important intermediates in the telomerization of 1,3-dienes and CO_2 using palladium/phosphine catalysts without additives. Only one phosphorus atom is bound to palladium during the C–C bond forming steps, but the second phosphorus atom is crucial in the early stages of the catalytic cycle and for the elimination of the product. A ligand that gave an active palladium catalyst for the coupling of 1,3-butadiene and CO_2 has been designed. Use of a palladium catalyst in the reaction of isoprene with CO_2 allowed for the first time isolation and NMR spectroscopic characterization of the resulting mixture of lactones.

Keywords: palladium catalyst; phosphine; carbon dioxide; carbon–carbon bond formation; telomerization; butadiene; isoprene

INTRODUCTION

There is an ongoing interest in catalytic C–C bond forming reactions of carbon dioxide (CO_2) (for comprehensive review, see Refs 6–8), and one of the few successful examples until now is the palladium-catalysed synthesis of δ-lactone **2** from 1,3-butadiene (**1a**) and CO_2.[1–15] After the pioneering work of Inoue *et al.*[9,10] and Musco,[11] the most detailed study of the telomerization of butadiene and CO_2 has been carried out by Behr using catalysts formed *in situ* from $Pd(acac)_2$ and three equivalents of a suitable phosphine ligand.[13–15] The optimum reaction conditions summarized in Eqn [1] were developed by thorough screening of all relevant reaction parameters. In the following years, a number of somewhat more effective variations of the original palladium/phosphine catalysts have been developed by Behr,[15] Braunstein[12] and others.[6–8] The effects of the various additives remain obscure, however, and even the catalytic cycle of the original system has not yet been understood in full detail.



[1]

Basic trialkyl phosphines are best suited as ligands for the palladium-catalysed telomerization of **1a** and CO_2, and a strong influence of the ligand structure on the performance of the catalyst is observed. The most significant examples reported in the literature[8,15] are included in Table 1 together with results from the present work. As noted earlier,[15,18] the Tolman concept[16] of electronic ($\Sigma\chi^i$) and steric (Θ) parameters is obviously not sufficient to explain the observed ligand effects. The steric parameter E_R recently developed for phosphine ligands on the basis of molecular mechanics[17] also fails to show any correlation with the experimental results. The understanding of these effects, is however, a necessary prerequisite for the development of new and more effective catalysts. We now report results from an investigation that combines classical ligand concepts and a simple molecular modelling approach. Some preliminary results of this study have been reported.[18]

RESULTS AND DISCUSSION

The first question to address in the context of catalyst optimization is the nature of the catalytically active species formed from *in situ* systems. Coordinatively unsaturated palladium(0)–phosphine complexes are known to be important

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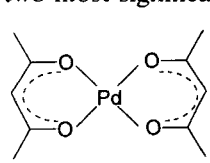
intermediates in many palladium-catalysed C–C coupling reactions, and they are formed from various palladium(II) precursors and phosphine ligands under conditions similar to those used for the preparation of the *in situ* catalysts in the present case.[19–22] The palladium complexes **3** and **4** are known or can be expected to react with phosphines to palladium(0) and exhibit high catalytic activity when used as precursors for *in situ* catalysts with two equivalents of PCy_3 (**11a**). The isolated yields of lactone **2** are 43% with **3** and 37% with **4**, respectively. The cationic palladium(II) complex **6**, however, is practically inactive for the telomerization and only very small amounts of butadiene oligomers are formed. Complex **6** can act efficiently as a catalyst precursor only in the presence of hydroquinone, which may serve as a reducing agent.[12]

When $(\eta^5\text{-}C_5H_5)Pd(\eta^3\text{-}C_3H_5)$ (**5**) is used as a precursor in the presence of **11a**, a bright yellow precipitate separates from the CH_3CN solution but redissolves upon introduction of **1a**. The isolated precipitate was identified as the expected[23,24] complex $(PCy_3)_2Pd$ (**7a**) on the basis of its ^{31}P NMR spectrum (C_6D_6, $\delta = 23$ ppm, s) and a crystallographic determination of the cell parameters carried out on a colourless crystal obtained from slow diffusion of CH_3CN into a benzene solution of **7a**. Crystalline **7a** exhibits similar selectivity and somewhat improved activity compared with the *in situ* systems and **2** could be obtained in 53% isolated yield. In contrast to earlier findings with *in situ* catalysts based on **3**,[15] excess phosphine considerably lowers the activity of $(Cy_3P)_2Pd$. The yield of **2** drops to 29% if **7a** is used in the presence of an additional equivalent of **11a**, i.e. at a P/Pd ratio of 3:1.

These results lead to the conclusion that a maximum of two phosphine ligands is bound to palladium(0) in the active species during the catalytic cycle of the telomerization of 1,3-dienes and CO_2, a simplified picture of which is summarized in Scheme 1. The two most significant simplifications are: (a) most likely the insertion of CO_2 takes place into a Pd–C σ-bond of the η^1-isomer of **9**;[19] (b) the elimination of **2** is reversible[15] (these otherwise important details can be neglected in the present discussion). The key steps in Scheme 1 are either known from other palladium-catalysed reactions or have been demonstrated on model systems[19] and the cycle is closely related to the widely accepted mechanism for the telomerization of **1a** and CO_2.[6–8] However, the number of phosphines bound to palladium and the influence of their structures on the reactivity of key intermediates **7–10** has been neglected in all discussions up to the present date.

Figure 1 shows the X-ray crystal structure[25] of **7a**, together with the numbering scheme used for the modification procedure in the Experimental section. The most significant feature of the solid-state structure of **7a** is the strong deviation from a linear arrangement of the P–Pd–P moiety. This deviation cannot be attributed to repulsion as intermolecular distances in the crystal lattice are too large. In contrast, the ligand **11g**, which has a nearly identical sterical demand to **11a**, forms a complex with a P–Pd–P angle of 177°.[25] The latter observation was confirmed independently by Otsuka *et al.*[23] More recently, a P–Pd–P angle of 180° has been reported for the corresponding complex of **11k**.[26]

Obviously, the P–Pd–P angle in the solid-state structures of complexes R_3P–Pd–PR_3 depends considerably on the ligand structure and we were interested to see whether this ligand–structure relationship correlates in some respect with the observed ligand effects on the catalytic activity. This consideration is supported from the theoretical and experimental work by Hofmann, who has demonstrated the importance of the P–M–P angle for binding of olefins[27] and heterocumulenes[28] to coordinatively unsaturated complexes of the nickel triad metals in the zero oxidation state. A CO_2 complex of palladium(0) with a bent P–Pd–P moiety has been described very recently.[29]



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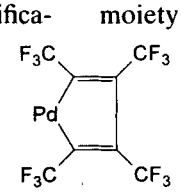

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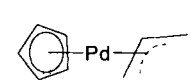


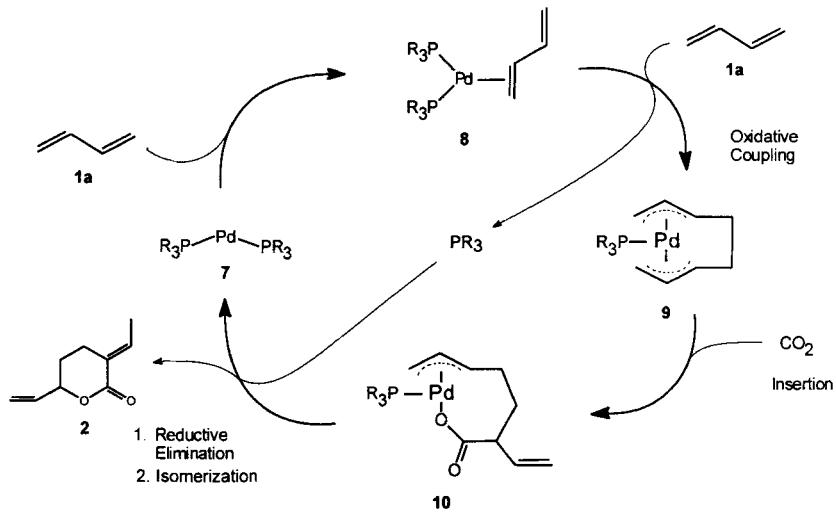
5

$Pd(H_3CCN)_4^{+}\ BF_4^{-}$

6

$Pd(PR_3)_2$

7a-k with PR_3 = **11a-k**



Scheme 1 Key steps of the catalytic cycle for the telomerization of **1a** and CO_2.

Two-coordinated palladium/phosphine complexes are only stable with very bulky ligands, as otherwise the coordination numbers three or four are preferred. Therefore we tried to evaluate whether commercially available and easy-to-use Molecular Modelling packages are capable of providing reasonable estimations for P–Pd–P angles in such complexes without the need for additional parametrization and/or computing work. The PC Model software package was chosen for this purpose as it is based on the MMX force field[31] and has a wide variety of transition metal/donor atom interactions implemented. MMX has been successfully applied in structural studies of transition-metal complexes (Refs 32–36 give recent examples; see references cited in these papers for other force fields). The data from the X-ray crystal analysis of **7a** were used as a fixed starting point for our investigations. A P–Pd–P angle of 160–162° resulted from minimization, when the palladium atom was moved from its place in any direction and the structrure was subsequently minimized under certain constraints (see Experimental section). This value is in reasonably good agreement with the angle of 158° determined by X-ray crystal analysis. The P–Pd–P angles of complexes **7g** and **7k** were also reproduced quite accurately when the Cy groups were modified to Ph and tBu groups using the structure editor of PCModel (Table 1). These results gave us confidence to use the same methodology for the determination of P–Pd–P angles for other complexes of type **7** where no X-ray data are available, due to their tendency to form phosphine adducts with higher coordination numbers in the solid state. The results of the calculations are summarized in Table 1 together with the efficiency of the corresponding *in situ* catalysts.

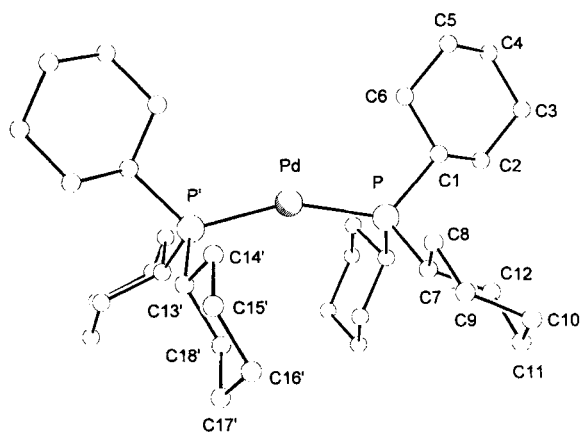


Figure 1 Solid-state structure of $(Cy_3P)_2Pd$ (**7a**); the numbers are used in the modification procedure described in the Experimental section.

It is important to note that the calculated P–Pd–P angles given in Table 1 were obtained for the eclipsed conformation of the two PR_3 groups as determined by the X-ray data of **7a**. This does not necessarily correspond to the energy minimum for all other ligands. An eclipsed conformation has been described also for **7g**,[23,25] but **7k**[26] adopts a staggered arrangement. The energy difference between eclipsed and staggered conformation is predicted by PCModel to be zero for complex **7i**, demonstrating that the staggered

Table 1 Influence of ligand parameters and P—Pd—P angle of two-coordinated palladium(0) complexes on the catalytic activity of *in situ* systems ligand/**3** in the formation of **2** from **1a** and CO_2

Ligand	$\Sigma\chi_i$	Θ	E_R	P—Pd—P angle Calc.[a]	P—Pd—P angle X-ray	Yield of **2** (%)[b]
Cy_3P (**11a**)	0.3	170	116	162	158.4	39 43[c] 53[d] 28[e]
iPr_3P (**11b**)	3.0	160	109	165	—	44
Cy_2PEt (**11c**)	2.0	~142[f]	95[g]	161	—	12
$(cyclo\text{-}C_3H_5)_3P$(**11d**)	—	128	—	169[h]	—	15
nBu_3P (**11e**)	4.2	132	64	175	—	3
nPr_3P (**11f**)	—	132	—	176	—	3
tBu_2PPh (**11g**)	4.3	170	124	176	176.6	1[e]
Et_3P (**11h**)	5.4	132	61	178	—	4
Me_3P (**11i**)	7.8	118	39	180	—	3
tBu_3P (**11k**)	0.0	182	154	179	180	0.3
$Cy_2P(CH_2)_2PCy_2$ (**12a**)	—	142	—	124	—	3[c]
$Cy_2P(CH_2)_4PCy_2$ (**12b**)	~2.0[i]	~142[f]	—	146	—	25[c]

[a] Calculated for R_3PPdPR_3; see Experimental section for details.
[b] P/Pd = 3:1, taken from Ref. 15.
[c] P/Pd = 2:1 (this work); see Experimental section for details.
[d] $Pd(PCy_3)_2$ was used (this work).
[e] $[(\eta^3$-2-methylallyl)$Pd(OAc)]_2$ as precursor, P/Pd = 3:1, benzene as solvent, taken from Ref. 8.
[f] Extrapolated from values of **12a**.
[g] Extrapolated from values of $^iPr_2PEt$.
[h] For cyclo-C_2H_4N, as direct calculation was not possible due to limitations of the parameter set; see Experimental section for details.
[i] Extrapolated from values of **11c**.

arrangement in **7k** is due to the extreme steric bulk of the ligand **11k**. Furthermore, we note that the X-ray structure of **7a** seems to correspond to a local rather than to the global minimum on the energy surface of this complex in the MMX force field as indicated by preliminary calculations using the GMMX-software package.[37]

Despite the above-mentioned limitations, the data in Table 1 strongly suggest that only phosphines forming bent two-coordinated palladium(0) complexes show high catalytic activity, while other ligands with P–Pd–P angles close to 180° are almost inactive. Following these considerations it appeared interesting to investigate bulky chelating phosphines $Cy_2P(CH_2)_nPCy_2$ (**12a**, $n=2$; **12b**, $n=4$) as ligands for *in situ* catalysts in the synthesis of δ-lactones from 1,3-dienes and CO_2.

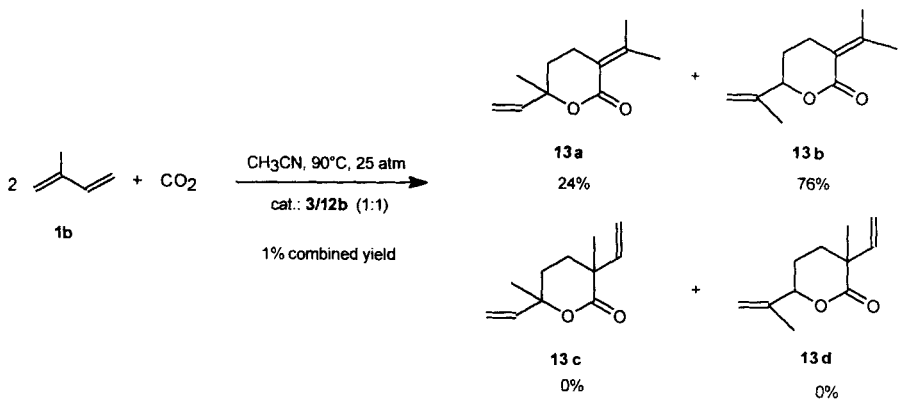
The ligand DCPB **12b** ($n=4$) is predicted to adopt a P–Pd–P angle of 145° and indeed gives a very active *in situ* catalyst for the telomerization of **1a** and CO_2. The isolated yield of 25% lactone **2** is somewhat lower than with **11a**, as the formation of open-chain esters becomes a relevant side reaction. Open-chain esters are almost negligible as side products when **11a** is used,[15] but amount to up to 30% by weight of the crude reaction mixture in the case of **12b**. The formation of esters is the main reaction pathway if bis(diarylphosphino)alkane ligands $Ph_2P(CH_2)_nPPh_2$ are employed.[38] However, the reduced selectivity for **2** in the case of **12b** compared with **11a** can be attributed exclusively to the replacement of one cyclohexyl group by an alkyl chain rather than to a chelate effect, by comparison of the results obtained with **11a** and **11c**. Both ligands induce a similar P–Pd–P angle, but the lactone **2** amounts to up to 80% of the crude reaction mixture in the case of **11a** compared with only 12% for **11c**. Ester contents of up to 50% are observed with ligand **11c**, corresponding to approximately 30% yield based on **1a**.

In contrast to **12b**, the phosphine DCPE (**12a**) with $n=2$ and a P–Pd–P angle of 124° forms a very poor catalyst. This latter observation is readily explained on the basis of the mechanism shown in Scheme 1. The postulated cycle implies that only one coordination site at palladium is occupied by phosphorus during oxidative coupling of two molecules of **1a**. Accordingly, no butadiene dimerization is observed with palladium complexes of **12a** and complexes of type **9** are only accessible via replacement of monodentate phosphines such as **11a**.[19] A strong fixation of two phosphorus atoms to palladium is also detrimental in the subsequent C–C coupling with CO_2. The dissociation of one branch of the chelate to form a 'dangling' ligand[39] is therefore necessary during these steps before reductive elimination of the product is finally induced by the incoming second phosphorus atom. Ligand **12b** is best suited for this 'windscreen wiper' behaviour as it forms a flexible seven-membered chelate ring rather than a tightly fixed five-membered chelate like **12a**. A strong effect of chelate ring size in palladium catalysis was also observed recently by Milstein using the ligands $iPr_2P(CH_2)_nPiPr_2$ ($n=2$–4).[40]

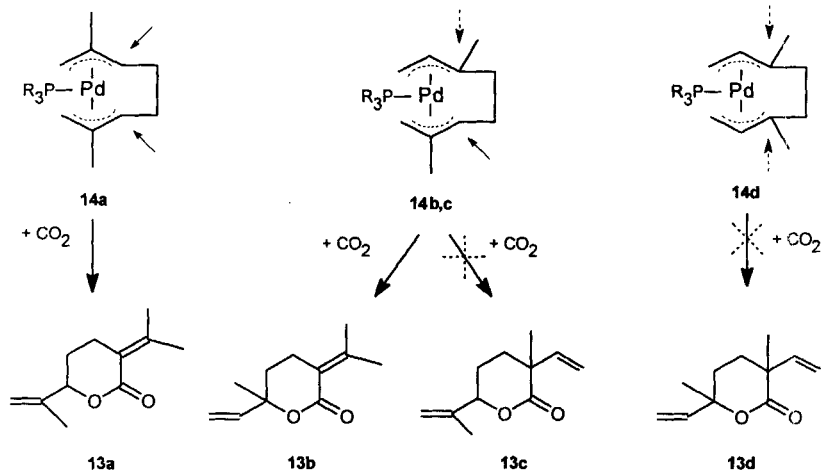
The lactones **13a–13d** can be formed in principle via telomerization of isoprene (**1b**) and CO_2 (Eqn [2]). However, the telomerization of 1,3-dienes to give δ-lactones using the *in situ* catalyst **3/11a** is limited to the use of 1,3-butadiene **1a**, despite a considerble effort towards the optimization of the reaction conditions. Only very small yields of a product from simultaneous co-oligomerization of **1a**, **1b** and CO_2 were described, while **1b** alone could not be converted to isolable amounts of δ-lactones **13a–13d** under conditions similar to those summarized in Eqn [2].[15] Palladium-assisted reactions of **1b** and CO_2 to form five-membered ring lactones[41] and open chain esters[42] have been reported, but with very low turnover numbers.

When a catalyst formed *in situ* from **3** and **12b** was used in the telomerization of **1b** and CO_2, a fraction with a similar retention time to **2** could be isolated from preparative TLC. The IR spectrum confirmed the presence of a carbonyl group ($\nu_{CO}=1736\,cm^{-1}$) and mass spectroscopy suggested the combination of two molecules of **1b** and one molecule of CO_2. Finally, the product was unequivocally identified as the mixture of **13a** and **13b** in a ratio of 24:76 on the basis of ^{1}H-NMR spectroscopic data (see the Experimental section). The combined yield of **13a** and **13b** is still very low (*ca* 1%, corresponding to seven catalytic cycles), as most of **1b** was not converted in this reaction; a small amount of unidentified by-products was also formed.

If the telomerization of **1b** proceeds via a pathway similar to the one shown in Scheme 1, the ratio of complexes **14a–14d** would determine the regioselectivity of product formation. The absence of lactones **13c** and **13d** in the product suggests that CO_2 does not insert into the palladium–allyl moiety, if a quaternary carbon atom has to be the reactive position. This may be due to kinetic reasons or to the fact that the thermodynamically more stable α,β-unsaturated carbonyl moiety cannot be formed in this case. If all possible intermediates **14a–14d** were formed statistically from tail/tail, head/tail and head/head coupling of **1b**, the ratio of **14b**, **14c** to **14a** should be 2:1. The observed 1:3 ratio of lactones **13a** and **13b** suggests that head/tail linkage is somewhat preferred over tail/tail coupling. Head/head linkage to form **14d** is not observed in palladium-assisted dimerization of **1b** at low temperature,[21] but must be considered



[2]



Scheme 2 Possible intermediates and derived products in the palladium-catalysed telomerization of isoprene (**1b**) and CO_2. Solid arrows indicated a reactive position, dashed arrows an unreactive one.

in the rather forcing conditions summarized in Eqn [2].

The reaction sequence represented in Scheme 2 reveals a fundamental problem in the telomerization of substituted 1,3-dienes and CO_2. Intermediate **14d** can only produce homo-oligomers or may even be a dead end for any catalytic reaction, as CO_2 does not seem to attack the intermediates **14** at quaternary carbons. Thus, most of the palladium centres will be trapped in species **14d** after several catalytic cycles, provided its formation can compete with the linking modes leading to **14a–c**. Extremely high selectivity for tail/tail linkage during the oxidative coupling step is therefore a necessary prerequisite for efficient catalysis of the telomerization of substituted 1,3-dienes and CO_2. The design of suitable chelating phosphines forms part of our current efforts to widen the scope of this reaction.

In conclusion, we have shown that two-coordinate palladium(0) complexes are most likely to be important intermediates in the telomerization of 1,3-dienes and CO_2 using palladium/phosphine catalysts without additives. Only one phosphorus atom is bound to palladium during the C–C bond forming steps, but the second phosphorus atom is crucial in the early stages of the catalytic cycle and for the elimination of the product. We were able to demonstrate that molecular mechanics using the MMX force field allows estimation of P–Pd–P angles for complexes $(PR_3)_2Pd$ with ligands **11** and **12**. The information thus obtained was used to design ligand **12b** which gave an active palladium catalyst for the coupling of 1,3-butadiene (**1a**) and CO_2. However, replacement of one cyclohexyl group of **11a** by an alkyl chain was found to lead to a reduced selectivity for the formation of δ-lactone **2**. The use of a palladium catalyst based on **12b** in the reaction of isoprene (**1b**) with CO_2 allowed for the first time isolation and NMR spectroscopic characterization of the mixture of lactones **13a** and **13b**. The selectivity for isomers **13a** and **13b** and the extremely low catalytic efficiency in this reaction could be rationalized on the basis of the proposed mechanism.

EXPERIMENTAL

General remarks

All experiments involving palladium–phosphine compounds were carried out under an argon atmosphere. Solvents were dried according to standard procedures and distilled under argon prior to use. 1,3-Butadiene was liquefied by condensation in a cold trap at −40 °C and used without further purification. Palladium complexes **3**, **4** and **6** were commercial products and used as received; **5** was synthesized according to Ref. 43. Phosphine **11a** was purchased from Fluka and used after crystallization from ethanol. $ClPCy_2$ and **11c** were synthesized using the method reported by Issleib and Seidel,[44] and $HPCy_2$ was obtained by reduction of $ClPCy_2$ with $LiAlH_4$ according to Ref. 45. The following analytical equipment was used: IR, Perkin–Elmer 16PC; GC MS, Chrompack CP 9000 equipped with a

25 m CP SIL5 column; NMR, Bruker AC 200F. Chemical shifts are reported relative to the solvent resonance for ^1H and relative to external H_3PO_4 for ^{31}P.

Synthesis of 1,ω-bis(dicyclohexyl)-phosphinoalkanes 12a and 12b

A 12.4 ml portion of a 1.6 M solution of *n*-butyllithium in hexane was added to a solution of 4.0 ml (19.8 mmol) dicyclohexylphosphane in 40 ml THF at −78 °C. The yellow solution was allowed to warm to −20 °C and 0.5 equiv. of the corresponding dibromide $Br(CH)_nBr$ in 20 ml THF were added dropwise. The almost colourless mixture was warmed to room temperature and stirred for approximately 1 h. After hydrolysis with aqueous NH_4Cl, the products were extracted with diethyl ether. Removal of the solvent yielded white, slightly oily residues from which white crystalline solids were obtained by crystallization from ethanol in 80% yield. Analytical data: ^{31}P NMR ($CDCl_3$); **12a**, δ 3.2(s) [lit.: δ 1.5(s)[46]]; **12b**, δ −3.2; m.p.: **12a**, 94–96 °C; **12b**, 97–99 °C (lit.: 96–97 °C[46] and 98–100 °C,[47] respectively).

Catalytic experiments using 1,3-butadiene (1a)

In a typical procedure, 53.1 mg (0.17 mmol) of **3** together with 2 equiv. of **11a** or 1 equiv. of **12a** or **12b** were dissolved in 30 ml CH_3CN and stirred for 20 min. The yellow solution was transferred under an argon atmosphere to a 100 ml stainless steel autoclave equipped with a PTFE insert and a magnetic stirring bar. The autoclave was cooled to 0 °C and 13.5 g (0.25 mol) of **1a** was added as a liquid. The pressure vessel was closed and allowed to equilibrate at room temperature before it was pressurized with a total amount of 30 g of CO_2. The total pressure at room temperature was about 15 bar and rose to 25–30 bar when the autoclave was heated to the reaction temperature of 90 °C. The reaction temperature was maintained constant for 20 h during which the pressure dropped slowly to about 15 bar. The autoclave was then cooled to room temperature, vented to a fume hood and opened. The volatiles were removed from the yellow-to-orange reaction mixture and the yield of lactone **2** was determined by preparative TLC (hexane/ethyl acetate = 95:5) of a small fraction of the crude product. The purity of the product was checked by NMR analysis and comparison with reported data.[13]

Catalytic experiments using isoprene (1b)

The experiments were carried out following the above procedure using the catalyst formed from **3** and **12b**. Only one fraction containing δ-lactones was isolated after preparative TLC, and it could not be further separated by this method. The ratio of lactones **13a** and **13b** was obtained from the ^1H NMR spectra by integration of the signals of the methine proton of **13a** at δ 4.53 and the olefinic proton of **13b** at δ 5.81.

13a: ^1H NMR ($CDCl_3$): δ 5.01 [m, 1H, $H_2C{=}C(CH_3)$—*cis*], 4.91 [m, 1H, $H_2C{=}C(CH_3)$—*trans*], 4.53 [dm, 1H, $=C(CH_3)$—$CH(OR)CH_2$—, $^3J \approx 10$ Hz], 2.60–2.40 [m, 2H, —H_2C—CH_2—C(COOR′)=], 2.18 [t, 3H, —C(COOR″)=$C(CH_3)_2$ *cis*, $^5J = 1.9$ Hz], 2.00–1.70 [2H, m, —H_2C—CH_2—C(COOR′)=], 1.82 [s, 3H, —C(COOR″)=$C(CH_3)_2$ *trans*], 1.76 [m, 3H, $H_2C{=}C(CH_3)$—].

13b: ^1H NMR ($CDCl_3$): δ 5.81 (dd, 1H, $H_2C{=}CH$—, $^3J = 17.3$ Hz and $^3J = 10.9$ Hz), 5.16 (dd, 1H, $H_2C{=}CH$—*trans*, $^2J = 0.9$ Hz, $^3J = 17.3$ Hz), 5.08 (dd, 1H, $H_2C{=}CH$—*cis*, $^2J = 0.9$ Hz, $^3J = 10.9$ Hz), 2.60–2.40 [m, 2H, —H_2C—CH_2—C(COOR′)=], 2.20 [t, 3H, —C(COOR″)=$C(CH_3)_2$ *cis*, $^5J = 1.9$ Hz], 2.00–1.70 [2H, m, —H_2C—CH_2—C(COOR′)=], 1.79 [s, 3H, —C(COOR″)=$C(CH_3)_2$ *trans*], 1.39 [s, 3H, =CH—$C(CH_3)(OR)CH_2$—].

Molecular modelling studies

The data from X-ray crystal structure analysis of **7a** were converted into the PCModel X-ray format. The cyclohexyl groups were modified using the structural editor following a standard procedure: hydrogen atoms were removed and the carbon atoms were deleted in numerical order (Fig. 1). New C–C bonds were closed and subsequently hydrogen atoms were added again and replaced by carbon if necessary. The phenyl group was generated by changing the atom type of $C(sp^3)$ to C(aromatic) after removal of H. If only one ring had to be changed, the two nearly parallel rings containing C1 and C1′ were used. The Pd–P distance was fixed at 2.28 Å with a force constant of 0.5 μN $Å^{-1}$. This resulted in a final Pd–P distance of 2.28–2.29 Å for all ligands. The Pd–P distances in **7a**, **7g** and **7k** are 2.26 Å[25], 2.28 Å[23] and 2.29 Å,[26] respectively. No further constraints were implied and minimization was

carried out using the MMX-M command. This procedure only failed with ligand **11d**, as the bond between a cyclopropyl carbon and phosphorus(III) is not parametrized in PCModel. Therefore, cyclopropane was generated independently and fixed in the geometry obtained from minimization without additional substituents. One carbon was then changed to nitrogen and the cyclohexyl groups of **11a** were replaced with these dummy groups. The N–P distance was fixed at 1.87 Å (taken from the P–C distance in **7a**) with a force constant $k = 0.5\ \mu N\ Å^{-1}$ and the resulting aminophosphine (N–P distance of 1.83 Å) was used as a model for (cyclo-C_3H_5)$_3$P.

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