The Methoxycarbonylation of Vinyl Acetate Catalyzed by Palladium Complexes of [1,2-Phenylenebis(methylene)]bis[di(*tert*-butyl)phosphine]

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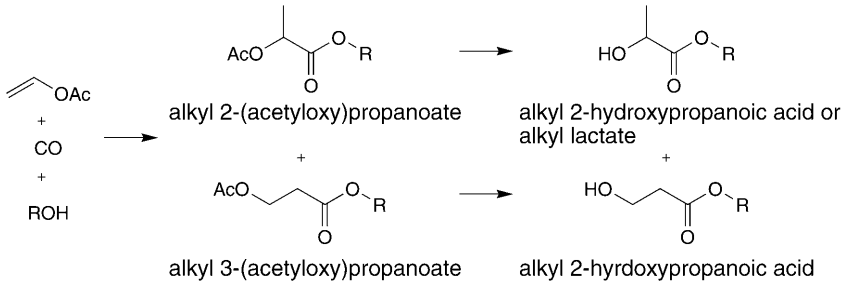
In celebration of the work of *Giambattista Consiglio*, a fine, imaginative scientist

Palladium complexes of [1,2-phenylenebis(methylene)]bis[di(*tert*-butyl)phosphine] (**1**) catalyze the methoxycarbonylation of vinyl acetate (=ethenyl acetate) in the presence of methanesulfonic acid (*Scheme 1*). High selectivities to ester products can be obtained if free phosphine ligand is in excess over the amount of added acid (*Table 1*). Selectivities to methyl 2-acetoxypropanoate, a precursor to lactate esters, can be as high as 3.6 : 1 at low temperature and pressure (*Table 2*). Replacing ^{t}Bu by ^{i}Pr groups leads to less-active catalysts and lower selectivities to the branched product. Replacing the phenylene moiety by a naphthalenediyl moiety also gives lower activity, but with similar selectivity to the phenylene-based analogues. Linear hydrocarbon-chain linkers as the backbone instead of the phenylenebis(methylene) linker leads to poor catalysis, except for a propane-1,3-diyl linker, which gives good rates but poor branched selectivity (*Table 5*). The effect of different reaction conditions on the catalysis is discussed. The syntheses of the new xylene-based diphosphines **2**–**5** with one to four ^{i}Pr groups replacing the ^{t}Bu groups at the P-atoms of **1** and of the ligands **6** and **7** based on 1,2- and 2,3-dimethylnaphthalene are also described (*Schemes 2* and *3*).

Introduction. – In the drive to make chemical processes and products more sustainable, lactate esters have been identified as possible alternative solvents because of their low vapor pressure, good solubilizing properties, and biodegradability. Their (*S*) forms are attractive monomers for the production of biodegradable polymers with properties similar to those of polyethene or polystyrene. Optically pure lactate esters are currently produced from the fermentation of glucose obtained from starch [1], but an alternative route would be the alkoxycarbonylation of vinyl acetate (=ethenyl acetate) to form alkyl esters, which, upon removal of the acetyl group would give the desired hydroxypropanoic acid (lactate for the branched product) esters (*Scheme 1*). An asymmetric version of this reaction could also be envisaged. Although vinyl acetate is derived from ethene and acetic acid, it is a cheap and very readily available feedstock.

Drent [2] has reported the methoxycarbonylation of vinyl acetate using palladium acetate and (propane-1,3-diyl)bis[di(*tert*-butyl)phosphine] as the catalyst system. In MeOH/diglyme (=1,2-dimethoxyethane) at 75° and 40 bar CO, the methyl ester was formed with a branched/linear (b/l) ratio of 2 : 1 at a rate of 200 mol (g Pd h)$^{-1}$. *Kudo et al.* [3] showed that methoxycarbonylation of vinyl acetate can be catalyzed by $PdCl_2/PPh_3$ in the presence of 2,6-lutidine (=2,6-dimethylpyridine) at 120° and 200 bar. A considerable quantity of methyl acetate was formed due to the methanolysis

Scheme 1. *The Alkoxycarbonylation of Vinyl Acetate as a Step in the Production of Alkyl Lactates*



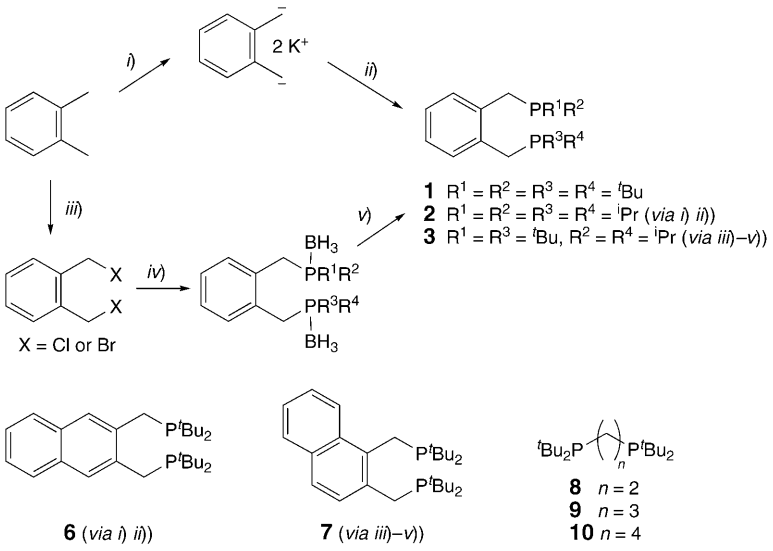
of vinyl acetate. A preliminary account [4] and a patent [5] containing some of the results reported in this paper appeared alongside a paper from *Tanaka* and co-workers [6] in which palladium complexes of [1,2-phenylenebis(methylene)]bis[di(*tert*-butyl)-phosphine] (=bis{(di(*tert*-butyl)phosphino]methyl}benzene=dtbpmb; **1**) and a solid acid catalyst were used to promote the methoxycarbonylation of vinyl acetate at 60 bar and 60° with a b/l ratio of 2.7, but with some loss of vinyl acetate to methanolysis.

Diphosphine **1** has been shown to be an excellent ligand for the Pd-catalyzed methoxycarbonylation of ethene [7], a process which is currently being commercialized. The system Pd/**1** is also highly active for the methoxycarbonylation of long-chain alkenes [8] giving very high linear selectivities, of unsaturated esters and acids giving very high selectivities to α,ω-diesters [9], of styrene giving high branched selectivity [6], or of aromatic chlorides to benzoic acid esters [10]. We now report details of the methoxycarbonylation of vinyl acetate catalyzed by palladium complexes of **1** under mild conditions in the presence of methanesulfonic acid.

Results and Discussion. – *Synthesis of Diphoshines.* A series of diphosphines based on a xylene backbone (see **2**–**5**), a naphthalene backbone (see **6** and **7**), or a chain backbone (**8**–**10**) were synthesized for use in the Pd-catalyzed methoxycarbonylation of vinyl acetate (see *Schemes 2* and *3*). Ligands **2** and **6** were synthesized by reacting 1,2-$C_6H_4(CH_2K)_2$ (for **2**) or the analogue derived from 2,3-dimethylnaphthalene (for **6**) with the appropriate lithium chlorophosphine as previously reported for **1** [11]. The other symmetrically substituted diphosphines, **3** and **7**, were prepared by the reaction of $Li[R^1R^2PBH_3]$ with 1,2-$C_6H_4(CH_2Br)_2$ (for **3**) or the analogue derived from 1,2-dimethylnaphthalene (for **7**) (see *Scheme 2*). The two diastereoisomers of ligand **3**, *rac*-**3** and *meso*-**3**, were separated by fractional recrystallization of the borane adduct prior to removal of the borane by refluxing the adduct in Et_2NH to give the free ligand. The *rac*-isomer of the borane adduct, *rac*-**3**·2 BH_3, was characterized crystallographically, *Fig. 1*.

The unsymmetrical diphosphines were synthesized by using a method adapted from *Leone* and *Consiglio* [12]. They prepared dicyclohexyl{{2-[(diphenylphosphino)methyl]phenyl}methyl}phosphine (=1-[(dicyclohexylphosphino)methyl]-2-[(diphenylphosphino)methyl]benzene) by the reaction of lithium dicyclohexylphosphide with 1,5-dihydro-2,4,3-benzodioxathiepin 3,3-dioxide followed by lithium diphenylphosphide. The synthesis of the more-basic di(*tert*-butyl)phosphine analogues by this method leads to a problem. Once the first phosphine group is added to the backbone

Scheme 2. *Synthesis of Symmetrically Substituted Ligands Used for the Methoxycarbonylation of Vinyl Acetate.*



i) KO^{t}Bu/BuLi. *ii*) R^1R^2PCl. *iii*) *N*-Bromosuccinimide (NBS)/$(PhC(O)O)_2$. *iv*) $Li[R^1R^2PBH_3]$. *v*) Et_2NH.

of the ligand, the strongly nucleophilic P-atom can undergo a nucleophilic attack at the second $CH_2OSO_3^-$ group and form the stable cyclic phosphonium sulfate. This attack can be stopped by using the borane-protected phosphide, as the lone electron pair at the introduced atom is in the P–B dative bond and hence the nucleophilicity of the P-atom is reduced (*Scheme 3*). The second phosphine group can then be introduced, and the borane groups can be removed by refluxing in Et_2NH overnight. This method gave di(*tert*-butyl){{2-[(diisopropylphosphino)methyl]phenyl}methyl}phosphine (**4**) and di(*tert*-butyl){{2-{[(*tert*-butyl)isopropylphosphino]methyl}phenyl}methyl}phosphine (**5**) in 73 and 74% yield, respectively.

Stability of Vinyl Acetate. Initial studies on the catalytic methoxycarbonylation of vinyl acetate (see below) showed significant formation of methyl acetate and 1,1-dimethoxyethane from the methanolysis of vinyl acetate. To restrict the methanolysis, stability tests were carried out. Vinyl acetate was stirred with MeOH in toluene together with combinations of promoters such as **1** and methanesulfonic acid ($MeSO_3H$) (*Table 1*). Vinyl acetate is stable in the presence of **1**, but if $MeSO_3H$ is present, the majority of the vinyl acetate is converted to methyl acetate even at room temperature, confirming that the transesterification of vinyl acetate is catalyzed by acid. However, if both the acid $MeSO_3H$ and the phosphine **1** are present together, there is minimal degradation of the vinyl acetate. As expected, the higher the reaction temperature, the greater the extent of degradation of vinyl acetate, although the side reaction is still inhibited if both acid and base are added together (*i.e.*, the phosphonium salt is present rather than the free acid). *Tanaka* and co-workers have shown that polymeric acids can also reduce the side reactions whilst allowing activity from the same catalytic system [6]. An understanding of the effect of acid on vinyl acetate degradation means that it is possible to

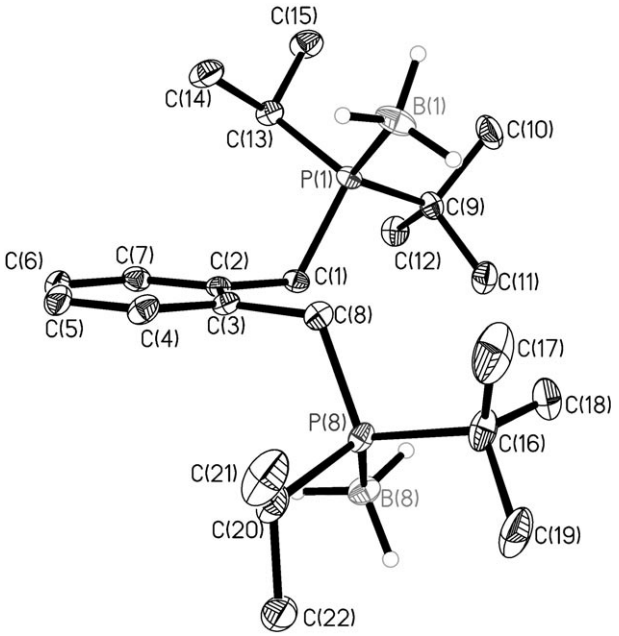
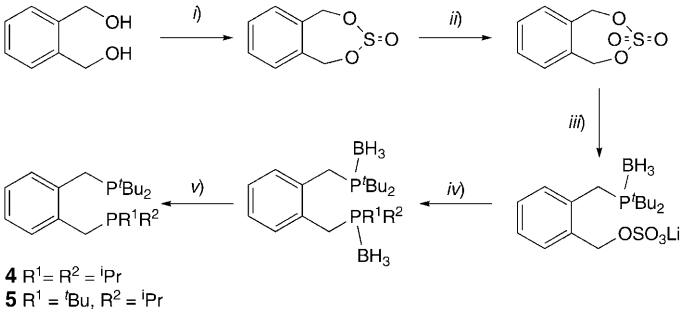


Fig. 1. *Molecular stucture and numbering scheme for* rac-**3**·*2 BH_3*. The (*R,R*) enantiomer is shown, but the crystals contain equal numbers of the (*R,R*) and (*S,S*) isomers. P(1)–C(1) 1.8482(13), P(1)–C(13) 1.8488(14), P(1)–C(9) 1.8717(14), P(1)–B(1) 1.9270(17), P(8)–B(8) 1.8424(14), P(8)–C(20) 1.8510(15), P(8)–C(16) 1.8629(15), and P(8)–B(8) 1.9200(16) Å; C(13)–P(1)–C(1) 105.05(6), C(13)–P(1)–C(9) 109.98(6), C(1)–P(1)–C(9) 102.66(6), C(13)–P(1)–B(1) 111.61(7), C(1)–P(1)–B(1) 114.26(7), C(9)–P(1)–B(1) 112.67(8), C(8)–P(8)–C(20) 104.64(7), C(8)–P(8)–C(16) 104.42(7), C(20)–P(8)–C(16) 112.91(7), C(8)–P(8)–B(8) 113.08(6), C(20)–P(8)–B(8) 109.11(8), and C(16)–P(8)–B(8) 112.42(7) Å.

Scheme 3. *Synthesis of Unsymmetrical Diphosphines*



4 $R^1 = R^2 = {}^i$Pr
5 $R^1 = {}^t$Bu, $R^2 = {}^i$Pr

i) $SOCl_2$, CH_2Cl_2, 0°, 2 h. *ii*) $NaIO_4$, RuO_4, 1,2-$C_2H_4Cl_2$/MeCN/H_2O 1:1:1.5. *iii*) Li[^{t}Bu$_2$PBH$_3$], THF, warmed from −78°. *iv*) Li[R^1R^2 PBH_3], THF, warmed from −78°. *v*) Et_2NH, 40°, 18 h.

tailor the reaction conditions so that no free acid is present in the system and hence that no degradation occurs. Catalytic results show that the phosphonium salt derived from **1** and $MeSO_3H$ is sufficiently acidic to protonate the P-center and initiate the catalytic reaction. As a result of these studies, the majority of catalytic reactions were carried out with an excess of phosphine ligand over $MeSO_3H$.

Table 1. *Stability of Vinyl Acetate in the Presence of MeOH*[a])

$MeSO_3H$ [mmol]	**1** [mmol]	25°		80°	
		VAM [%]	AcOMe [%]	VAM [%]	AcOMe [%]
0	0	100	0	100	0
1	0	50	50	0	100
0	1	100	0	100	0
1	1	100	0	100	0

[a]) Reaction conditions: vinyl acetate (VAM) (2 ml), MeOH (2 ml), toluene (9 ml), reaction time 3 h.

Methoxycarbonylation Catalysis in the Presence of Diphosphine Ligand **1**. For ethene, one of the best methoxycarbonylation catalyst systems known is the [Pd(**1**)] catalyst employed by *Lucite* [7]. Vinyl acetate methoxycarbonylation was initially attempted with similar ratios of Pd/**1**/$MeSO_3H$, but at a higher concentration than used in ethene carbonylation: $[Pd_2(dba)_3]$ (10 mg, 0.01 mmol, 10^{-3} M; dba = 1,5-diphenylpenta-1,4-dien-3-one), **1** (8.7 mg, 0.02 mmol), $MeSO_3H$ (27 µl, 0.4 mmol), MeOH (18 ml), and vinyl acetate (2 ml), 80°, 10 bar. After 3 h, the reaction was stopped, and the conversion of vinyl acetate was found to be 100% with a selectivity to the esters of 9% and a b/l ratio of 15.6 : 1. The remaining products were AcOMe and 1,1-dimethoxyethane, which arise because of the high acid concentration (excess $MeSO_3H$) in the system, which catalyzes the methanolysis of vinyl acetate. Omission of **1** led to 100% conversion of the vinyl acetate but with full selectivity to the degradation products.

To overcome the degradation problem, the ratio of **1** to Pd was varied to find the optimum ratio (*Fig. 2*). During this, the ratio of ligand to acid was kept constant at 1 : 1 thus ensuring that no free acid was present. The result for the reaction where the **1**/Pd ratio is 5 : 1 shows a drop in the b/l ratio. It is believed that the b/l ratio at a **1**/Pd ratio of 2.5 : 1 is artificially inflated because of the low conversion. We have shown in other studies that the b/l ratio drops as the conversion increases. The b/l ratio decreases with temperature (*Fig. 3*) and increases as the pressure of CO is reduced (*Fig. 4*). A possible explanation is that CO displaces the coordinated C=O in a five-membered chelate, thus removing any extra stability of the alkyl intermediate in the branched-chain pathway and rendering the linear and branched pathways of similar activation energy (*Scheme 4*). Five-membered chelates of this kind are observed during the methoxycarbonylation or copolymerization of ethene with CO [13][14].

The maximum b/l ratio of 3.6 : 1 was obtained with the Pd/**1** system when the CO pressure was 3 bar and the reaction was carried out at room temperature (*Table 2*, compound **1**)

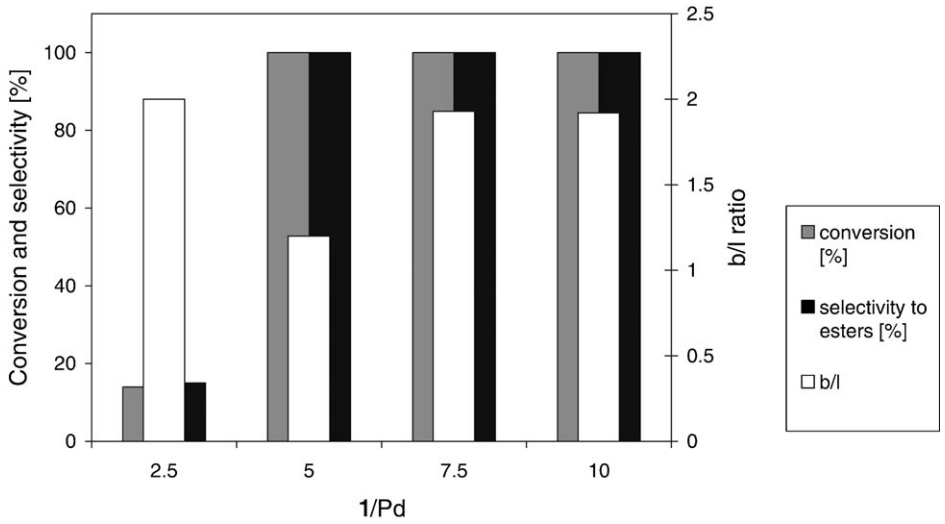


Fig. 2. *Effect of* **1**/*Pd ratio on the products from the methoxycarbonylation of vinyl acetate.* [$Pd_2(dba)_3$] (0.05 mmol), vinyl acetate (2 ml), MeOH (11 ml), $MeSO_3H$ (same mol amount as mol of ligand), 80°, CO (30 bar), 3 h.

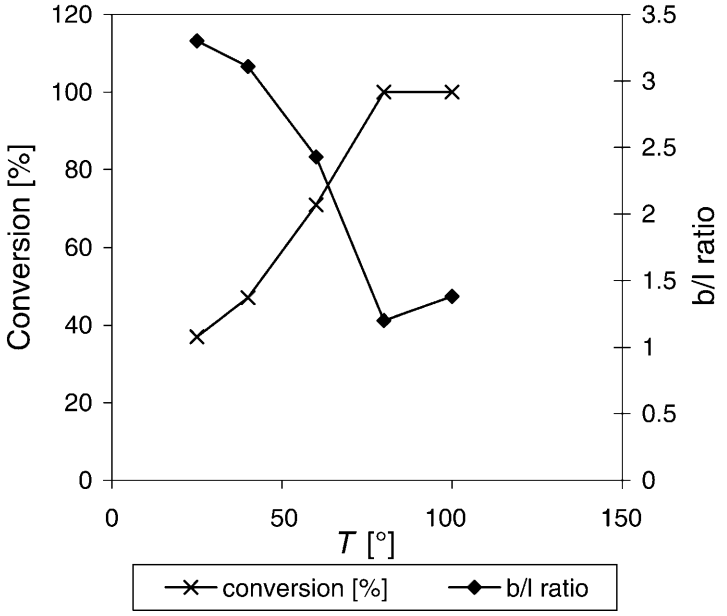


Fig. 3. *Effect of reactor temperature on the methoxycarbonylation of vinyl acetate.* [$Pd_2(dba)_3$] (0.05 mmol), **1** (0.5 mmol), vinyl acetate (2 ml), MeOH (11 ml), $MeSO_3H$ (0.5 mmol), CO (30 bar), 3 h.

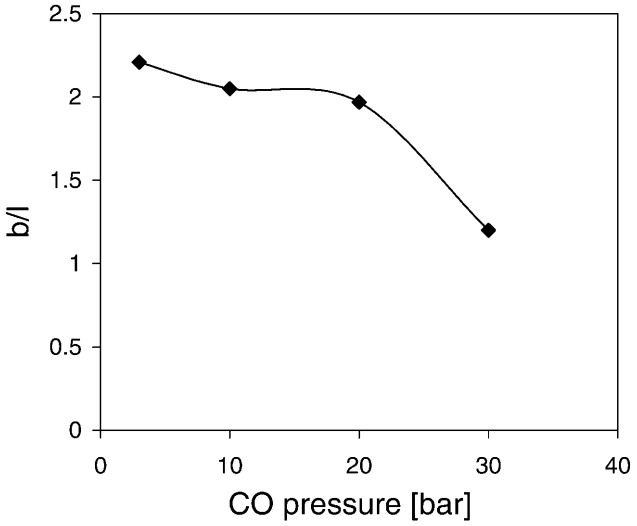


Fig. 4. *Effect of CO pressure on the b/l ratio of the methoxycarbonylation of vinyl acetate.* $[Pd_2(dba)_3]$ (0.05 mmol), **1** (0.5 mmol), vinyl acetate (2 ml), MeOH (11 ml), $MeSO_3H$ (0.5 mmol), 80°, 3 h.

Scheme 4. *Disruption of Chelate Binding of the Alkyl Intermediates in Methoxycarbonylation of Vinyl Acetate*

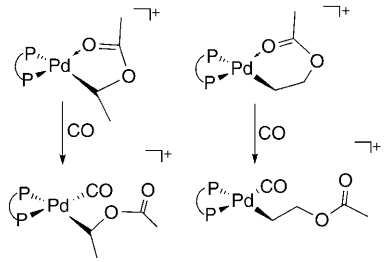


Table 2. *Methoxycarbonylation of Vinyl Acetate with Different Diphosphine Ligands*[a])

Ligand	Conversion [%]	Selectivity to esters [%]	b/l
1	35	100	3.6
2	0	n.a.[b])	n.a.[b])
3	7	100	0.8
rac-**3**	8	100	0.8.
meso-**3**	7	100	0.8
4	47	28	1.4
5	13	85	2.0
6	15	100	3.6
7	18	100	3.6

[a]) $[Pd_2(dba)_3]$ (0.05 mmol), ligand (0.5 mmol), $MeSO_3H$ (0.5 mmol), MeOH (11 ml), vinyl acetate (21 mmol), CO (3 bar), 25°, 3 h. [b]) n.a. = not applicable.

Methoxycarbonylation Catalysis in the Presence of Related Ligands. In an attempt to improve the b/l ratio of the products of the methoxycarbonylation of vinyl acetate over the Pd/**1**/$MeSO_3H$ system, derivatives of **1** were tested in the catalysis (*Table 2*). Retaining the xylene backbone of the ligand but altering the electronic effect slightly by using a naphthalene-1,2-diyl instead of a 1,2-phenylene moiety does not alter the b/l ratio but reduces the reaction rate (compounds **6** and **7**, *Table 2*). We reasoned that better branched selectivity might be obtained if the steric congestion around the Pd-center were slightly reduced. However, it appears to be crucial that the substituents at the P-atoms are ^{t}Bu groups (*Table 2*). When one ^{t}Bu group is replaced by ^{i}Pr (compound **5**), the conversion and branched selectivity are reduced. As further substitution is carried out, the conversion and selectivity drop further. Once all four ^{t}Bu groups have been replaced by ^{i}Pr groups, the ligand is no longer capable of producing an active catalyst.

As ligand **3** has three different substituents at both of the P-atoms, the ligand has four diastereoisomers. Both the *meso* and *rac* forms were tested in the catalysis, and they gave exactly the same result as the racemic mixture.

In the presence of ligand **7** and the optimum ratio **7**/Pd of 5 : 1, the $MeSO_3H$ concentration was varied. As can be seen in *Fig. 5*, the yield of methyl acetoxypropanoates increases up to a $MeSO_3H$/Pd ratio of 10 : 1 ($MeSO_3H$/**7** 2). Assuming that all the catalyst is present as $[Pd(\mathbf{7})HX]^+$ (X = CO, vinyl acetate, or MeOH), the ratio of free $MeSO_3H$/free **7** is 9 : 4 at this point so that excess free acid is present in the system (*Table 3*). After this, the yield of esters drops dramatically as a result of competitive methanolysis of the vinyl acetate catalyzed by the excess acid. The b/l ratio is almost insensitive to [$MeSO_3H$] (see *Fig. 6*).

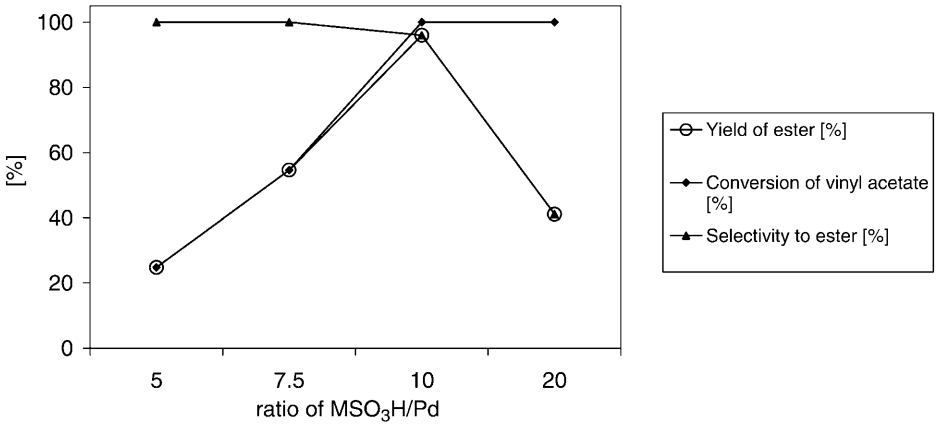


Fig. 5. *Effect of acid concentration on the rate and ester selectivity of the methoxycarbonylation of vinyl acetate.* [$Pd_2(dba)_3$] (0.5 mmol), **7** (0.5 mmol), vinyl acetate (22 mmol), MeOH (11 ml), CO (3 bar), 25°, 3 h.

Steric and Electronic Effects of Ligands. Changing from ^{t}Bu to ^{i}Pr not only reduces the steric bulk at the metal center, but is also expected to reduce the electron-donating power of the ligand. The electron-donating effects of the ligands L were studied by synthesizing [$Mo(CO)_4L$] (L = **1**–**3**, **6**, and **7**) complexes from reactions of [(norborna-2,5-diene)$Mo(CO)_4$] with the relevant ligands. The value of the $\tilde{\nu}_{CO}$ was used to evaluate

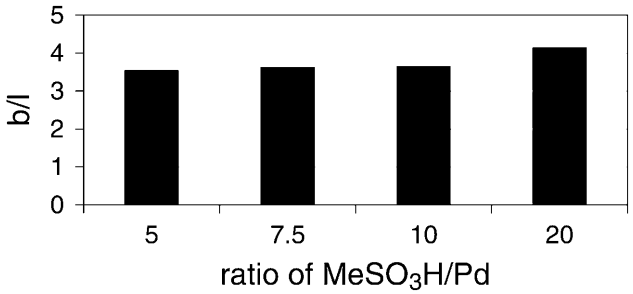


Fig. 6. *Effect of acid concentration on the branched selectivity of the methoxycarbonylation of vinyl acetate.* $[Pd_2(dba)_3]$ (0.5 mmol), **7** (0.5 mmol), vinyl acetate (22 mmol), MeOH (11 ml), 3 bar, 25°, 3 h.

Table 3. *Quantities of Different Species Present in the Reaction Solution and Different Quantities of Acid Added*[a])

Acid added [mmol]	[Pd(phosphine)] complex [mmol]	Quaternized P-atoms [mmol]	Free P-atoms [mmol]	Free acid [mmol]
0.5	0.1	0.5	0.3	0
0.7	0.1	0.7	0.1	0
1.0	0.1	0.8	0	0.1
2.0	0.1	0.8	0	1.1

[a]) Pd (0.1 mmol), **7** (0.5 mmol).

Table 4. *Comparison of the Highest Frequency* $\tilde{\nu}_{CO}$ (in cm^{-1}) *Band for* $[Mo(CO)_4L]$ *Complexes of Bidentate Phosphine Ligands L*[a])

L	$Ph_2PCH_2CH_2PPh_2$	**2**	**3**	$Et_2PCH_2CH_2PEt_2$	**6**	**7**	**1**
$\tilde{\nu}_{CO}$	2021 [17]	2019	2013	2012 [18]	2007	2007	2006

[a]) Spectra recorded in CH_2Cl_2 solution.

the ligand-donor properties. The lower the frequency of $\tilde{\nu}_{CO}$, the greater is the electron-donating power of the ligand. As can be seen from *Table 4*, the ligands with four ^{t}Bu groups at the P-atom, *i.e.*, **1**, **6**, and **7**, are the most electron-donating. They also give the highest rates and selectivities to the branched product in the methoxycarbonylation of vinyl acetate. However, they are the most sterically crowded of the ligands, so it is difficult to disentangle steric from electronic effects in this case. The catalytic mechanism has clearly been shown to proceed *via* a hydride mechanism, at least for the methoxycarbonylation of ethene or linear alkenes such as oct-1-ene [8][15][16]. A greater electron density on the metal center would be expected to lead to more of the Pd-centers being present in the catalytically active form ($[PdH(\mathbf{1})X]^+$, X = CO, MeOH, or vinyl acetate) and hence a higher rate. In addition, the rate-determining step in the carbonylation of ethene or oct-1-ene is known to be late in the cycle – probably methanolysis and this step is accelerated by the presence of bulky ligands, although the exact mechanism of the methanolysis reaction is still the subject of some debate. It, therefore, seems that bulky highly electron donating ligands should give the highest reaction rates, and this is indeed observed.

We originally anticipated that the regioselectivity might be controlled by the steric influences exerted by the ligand, with the bulkiest ligands giving the lowest branched selectivity. However, this is clearly not the case because ligands with all ^{t}Bu substituents give the highest branched selectivities.

Methoxycarbonylation of Vinyl Acetate in the Presence of Other Electron-Rich Diphosphine Ligands. It seems that highly electron-donating phosphine ligands are required for the successful Pd-catalyzed methoxycarbonylation of vinyl acetate. Ligand **1** has a semi-rigid backbone as the central two C-atoms are contained in an aromatic ring. The effect of replacing the backbone by straight alkyl chains was studied by using the ligands (ethane-1,2-diyl)bis[di(*tert*-butyl)phosphine] (**8**), (propane-1,3-diyl)-bis[di(*tert*-butyl)phosphine] (**9**), and (butane-1,4-diyl)bis[di(*tert*-butyl)phosphine] (**10**). The results obtained are shown in *Table 5*. Ligand **8** produced no ester product, and there was 100% degradation of the vinyl acetate. Ligand **10** with a C_4 backbone produced only trace amounts of the ester product. However, a considerable amount of vinyl acetate was degraded to AcOMe. This is surprising as there were enough P-atoms present to bind all of the acid in the solution, and this should have prevented vinyl acetate degradation. Ligand **9**, on the other hand, gave high conversion of the vinyl acetate with 100% selectivity to the esters. Unfortunately the b/l ratio was only 0.79 : 1. Under the same reaction conditions, with **1** as the ligand, the b/l ratio was 1.2 : 1. *Drent* [2] has reported that when **9**/[Pd(OAc)$_2$] was used in the methoxycarbonylation of vinyl acetate, a b/l ratio of 2 : 1 was obtained. *Drent* used a reaction temperature of 75° and a CO pressure of 40 bar, as opposed to 80° and 30 bar used in this study.

Table 5. *Methoxycarbonylation of Vinyl Acetate Catalyzed by Palladium Complexes of ^{t}Bu$_2$P(CH$_2$)$_n$P^{t}Bu$_2$* **8**–**10** (n = 2–4)[a])

Ligand	Conversion [%]	Selectivity to esters [%]	b/l
8	100	0	n.a.[b])
9	97	100	0.79 : 1
10	70	2	0.87 : 1

[a]) [Pd$_2$(dba)$_3$] (0.05 mmol)], vinyl acetate (VAM) (2 ml), ligand (0.5 mmol), MeSO$_3$H (0.5 mmol), MeOH (11 ml), 80°, 3 h. [b]) n.a. = not applicable.

Mechanistic Considerations. From the mechanistic studies that have been carried out on Pd-complexes of **1** for the methoxycarbonylation of alkenes, it has been shown that the catalytic cycle follows the hydride mechanism [16][19][20]. As palladium hydrides are renowned for their instability, it can be reasoned that the success of systems containing **1** is due to the high degree of electron donation, which stabilizes [PdH(**1**)X]$^+$ (X = CO or vinyl acetate). If this were the only criterion necessary for a successful ligand, it should be possible to carry out the catalysis with other electron-rich ligands. However, as described above, not all electron-rich diphosphines are successful. Ligand **8**, with a C_2H_4 backbone, showed no activity towards the methoxycarbonylation of vinyl acetate, whereas **9**, with a C_3H_6 backbone, showed good activity, and **10**, with a C_4H_8 backbone, showed low activity. This is the same order of reactivity as is observed for ethene, and there is some dispute whether this can be attributed to the different bite angles of the ligands giving different steric constraints [21] at the active

site where the carbonylation takes place, or whether ligands such as **1** and **9** have just the right balance between chelate strength and the ability to become unidentate in the acyl intermediate [13], thus reducing the electron density sufficiently to encourage nucleophilic attack of MeOH.

As indicated above, it appears that the selectivity to branched product is under electronic control, with the most-electron-donating ligands giving the highest branched selectivity. For ethene [16] and oct-1-ene [20] methoxycarbonylation, the rate-determining step is late in the catalytic cycle (probably methanolysis of the Pd–acyl bond). If this were the case for vinyl acetate also, the selectivity should arise from an increased relative rate of methanolysis for the branched acyl complex relative to the linear when using the more-electron-donating ligands. However, the exact mechanism of methanolysis in these systems is the subject of some debate [13][21], so it is very difficult to offer any real mechanistic insight into why the most-elctron-donating ligands give the highest selectivity.

Conclusions. – Pd/**1** Complexes are the most-active catalysts yet discovered for the methoxycarbonylation of vinyl acetate. They also produce the highest selectivity to the branched product, which is a precursor to lactate esters. Attempts to increase the selectivity by reducing the steric bulk of the ligand (replacing ^{t}Bu by ^{i}Pr) were unsuccessful leading to lower rates and lower branched selectivities. Replacing the 1,2-phenylene moiety in the backbone by a naphthalene-1,2-diyl gave catalysts with similar selectivities but lower activity.

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Experimental Part

General. All manipulations of air-sensitive materials were carried out in oven-dried glassware by using standard *Schlenk* line and catheter-tubing techniques under dry, deoxygenated Ar. Ar was dried through a glass column packed with chromium(II)/silica gel. Solid and liquid chemicals were purchased from *Aldrich*, *Acros*, *Avacodo*, and *Strem* and used as received. All gases were purchased from *BOC*. Petroleum ether (40–60°), Et_2O, and THF were distilled over sodium diphenylketyl. CH_2Cl_2 was distilled over CaH_2, and toluene was distilled over Na. Vinyl acetate was distilled over $CaCl_2$ and was stored at 0° in a flask wrapped in tinfoil to exclude light. ^{1}H-, ^{13}C-, and ^{31}P-NMR Spectra: *Varian-300*, *Bruker-300*, or *Varian-500* NMR spectrometers. The ligands **1** [11], **9** [22], and **10**, 1,5-dihydro-2,4,3-benzodioxathiepin 3,3-dioxide [23], and [Mo(CO)$_4$(norborna-2,5-diene)] [24] were prepared by literature methods.

[1,2-Phenylenebis(methylene)]bis[diisopropylphosphine] (**2**). Xylene-α,α'-diyl dipotassium (={μ-[1,2-phenylenebis(methylene)]}dipotassium) [25] (2.86 g, 15.7 mmol) was dissolved in Et_2O (100 ml) and cooled to −20°. Chlorodiisopropylphosphine (=bis(1-methylethyl)phosphinous chloride; 5 g, 32.7 mmol) was added slowly and the soln. allowed to warm to r.t. after which it was stirred overnight. The soln. was removed by filtration and the potassium chloride salt was washed with Et_2O. The Et_2O was evaporated from the combined fractions, and the resulting oil was purified by distillation: 355 mg (6%) of **2**. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*dd*, ^3J(P,H)=12, ^1J(H,H)=7, 12 H, *Me*CHP); 1.08 (*dd*, ^3J(P,H)=12, ^1J(H,H)=7, 12 H, *Me*CHP); 1.57–1.82 (*m*, 3 H, MeC*H*P); 3.05 (*s*, 2 ArCH_2P); 7.00–7.08 (*m*, 2 arom. H); 7.12–7.20 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.4 (*d*, ^2J(P,C)=12, *Me*CHP); 19.7 (*d*, ^2J(P,C)=13, *Me*CHP); 23.3 (*d*, ^1J(P,C)=15, Me*C*HP); 27.9 (*d*, ^1J(P,C)=8, Ar*C*H$_2$P); 28.6 (*d*, ^1J(P,C)=8, Ar*C*H$_2$P); 126.0, 131.1, 131.2 (3*s*, Ar); 137.8 (*s*, *Ar*CH$_2$P). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 5.2 (*s*, ArCH$_2$P^{i}Pr$_2$). HR-ES-MS (pos.): 339.2365 ($C_{20}H_{37}P_2^+$; calc. 339.2371). Anal. calc. for $C_{20}H_{36}P_2$ (338.45): C 71.0, H 10.7; found: C 70.7, H 11.0.

*(*tert-*Butyl)isopropylphosphine–Borane (1/1). tert*-Butyldichlorophosphine (=(1,1-dimethylethyl)-phosphonous dichloride; 9.72 g, 61.1 mmol) was dissolved in Et_2O (50 ml) and cooled to 0°. To this, 2M isopropylmagnesium chloride in hexane (30.5 ml, 61 mmol) was slowly added, and the soln. was allowed to warm to r.t. In the $^{31}P\{^1H\}$-NMR spectrum of the soln., only a signal at δ(P) 139.9 was present, which is consistent with the literature value for ^{t}BuCl^{i}PrP [26]. The soln. was filtered, the residue washed with Et_2O (2×20 ml), and the solvent was evaporated from the combined org. layers leaving a yellow oil. This oil was slowly added to a DMF (20 ml) soln. of $NaBH_4$ (3.02 g, 80 mmol) cooled to 0°. Upon complete addition, the soln. was allowed to warm to r.t. and stirred for 16 h. H_2O (20 ml) was added carefully, and the resultant solution was extracted with Et_2O (3×30 ml). The combined org. phase was washed successively with H_2O (2×20 ml) and brine (2×20 ml) and dried ($MgSO_4$), and the solvent was evaporated: title product (7.22 g, 81%). Clear oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.18 (br. *q*, ^1J(B,H)=50, PH(BH_3)); 1.09 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 3 H, *Me*CHP); 1.15 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 3 H, *Me*CHP); 1.22 (*d*, ^3J(P,H)=14, 18 H, *Me*CP); 2.29 (*dd*, ^3J(H,H)=7, ^2J(P,H)=2, 1 H, MeC*H*P); 3.92 (*dq*, ^1J(P,H)=352, ^2J(B,H)=7, P*H*(BH_3)). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.2 (*s*, *Me*CHP); 20.9 (*s*, Me*C*HP); 25.5 (*d*, *J*=26, Me*C*P); 26.3 (*s*, *Me*CP). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 37.7 (*q*, ^1J(P,B)=50). Anal. calc. for $C_7H_{20}BP$ (146.02): C 57.6, H 13.8; found: C 57.4, H 13.9.

*Diastereoisomer Mixture of [1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]–Borane (1/2).* (*tert*-Butyl)isopropylphosphine–borane (1/1) (3.78 g, 25.9 mmol) was dissolved in THF (30 ml) and cooled to 0°. To this soln., 2.5M BuLi in hexane (10.3 ml, 25.9 mmol) was added slowly, and the soln. was allowed to warm to r.t., before stirring for 30 min. The soln. was cooled to 0°, and a THF (20 ml) soln. of α,α-*o*-dichloroxylene (=1,2-bis(chloromethyl)benzene; 2.23 g, 12.8 mmol) was added dropwise with the soln. temp. not being allowed to rise above 5°. Upon complete addition, the soln. was allowed to warm to r.t. and stirred for 16 h. H_2O (30 ml) was added to the soln., the aq. layer was extracted with Et_2O (2×30 ml), the combined org. phase washed with H_2O (30 ml) and 10% brine (2×30 ml) and dried ($MgSO_4$), the solvent evaporated, and the obtained white solid recrystallized from hexane: 4.36 g (93%) diastereoisomer mixture. Colorless crystals. M.p. 153–154°. ^{1}H-NMR (500 MHz, CD_2Cl_2): 0.29 (*q*, ^1J(P,B)=85, 2 PBH_3); 1.07 (*dd*, ^3J(P,H)=14, ^3J(H,H)=7, 3 H, *Me*CHP); 1.07 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 3 H, *Me*CHP); 1.25 (*d*, ^3J(P,H)=13, 9 H, *Me*CP); 1.26 (*dd*, ^3J(P,H)=14, ^3J(H,H)=7, 3 H, *Me*CHP); 1.28 (*d*, ^3J(P,H)=13, 9 H, *Me*CP); 1.28 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 3 H, *Me*CHP); 1.99 (*dd*, ^2J(P,H)=7, ^3J(H,H)=7, 2 H, MeC*H*P); 2.02 (*dd*, ^2J(P,H)=7, ^3J(H,H)=7, 2 H, MeC*H*P); 3.14 (*dd*, ^2J(H,H)=15, ^2J(P,H)=15, 1 H, ArCH_2P); 3.29 (*dd*, ^2J(H,H)=15, ^2J(P,H)=10, 1 H, ArCH_2P); 3.38 (*dd*, ^2J(H,H)=15, ^2J(P,H)=13, 1 H, ArCH_2P); 3.64 (*dd*, ^2J(H,H)=15, ^2J(P,H)=7, 1 H, ArCH_2P); 7.12–7.20 (*m*, 3 arom. H); 7.28–7.30 (*m*, 1 arom. H). ^{31}P-NMR (202 MHz, CD_2Cl_2, H_3PO_4): 39.2 (*q*, ^1J=50, *rac*-ArCH_2P^{t}Bu$_2$); 40.7 (*q*, ^1J=50, *meso*-ArCH_2P^{t}Bu$_2$). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.3 (*d*, *J*=40, *Me*CHP); 19.5 (*d*, *J*=54, *Me*CHP); 23.9 (*d*, *J*=28, Me*C*HP); 24.2 (*d*, *J*=28, Me*C*HP); 25.2 (*d*, *J*=26, Me*C*P); 25.4 (*d*, *J*=25, Me*C*P); 27.7 (*d*, *J*=6, *Me*CP); 27.8 (*s*, *Me*CP); 31.5 (*d*, *J*=28, Ar*C*H$_2$P^{t}Bu^{i}Pr); 31.6 (*d*, *J*=28, Ar*C*H$_2$P^{t}Bu^{i}Pr); 127.4, 127.4, 132.1, 132.5 (4*s*, arom. CH); 134.5 (*m*, *Ar*CH$_2$P^{t}Bu$_2^i$Pr$_2$); 134.9 (*m*, *Ar*CH$_2$P^{t}Bu$_2^i$Pr$_2$). HR-ES-MS (pos.): 417.3159 ([*M*+Na]$^+$, $C_{22}H_{46}B_2NaP_2^+$; calc. 417.3159). Anal. calc. for $C_{22}H_{46}B_2P_2$ (394.17): C 67.0, H 11.8; found: C 66.9, H 11.9.

rac-*[1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]–Borane (1/2)*. A racemic mixture containing all four diastereoisomers of [1,2-phenylenebis(methylene)]bis[(*tert*-butyl)isopropylphosphine]–borane (1/2) was dissolved in hot MeOH and was left to cool. The colorless crystals produced were collected by filteration and recrystallized three more times from MeOH until the product was diastereoisomerically pure. The configuration of the structure was determined by single-crystal X-ray diffraction (see below). M.p. 167°. ^{1}H-NMR (300 MHz, CD_2Cl_2): 0.29 (*q*, ^1J(P,B)=85, 2 PBH_3); 1.07 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 6 H, *Me*CHP); 1.28 (*d*, ^3J(P,H)=13, 18 H, *Me*CP); 1.28 (*dd*, ^3J(P,H)=13, ^3J(H,H)=7, 6 H, *Me*CHP); 1.99 (*dd*, ^2J(P,H)=7, ^3J(H,H)=7, 2 H, MeC*H*P); 3.14 (*dd*, ^2J(H,H)=15, ^2J(P,H)=15, 2 H, ArCH_2P); 3.64 (*dd*, ^2J(H,H)=15, ^2J(P,H)=7, 2 H, ArCH_2P); 7.26–7.32 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.3 (*d*, *J*=40, *Me*CHP); 23.9 (*d*, *J*=28, Me*C*HP); 25.2 (*d*, *J*=26, Me*C*P); 27.8 (*s*, *Me*CP); 31.6 (*d*, *J*=28, Ar*C*H$_2$P^{t}Bu^{i}Pr); 127.4, 132.1 (2*s*, arom. CH); 134.9 (*m*, *Ar*CH$_2$P^{t}Bu$_2^i$Pr$_2$). ^{31}P-NMR (202 MHz, CD_2Cl_2, H_3PO_4): 39.2 (*q*, ^1J=50, *rac*-ArCH_2P^{t}Bu$_2$). HR-ES-MS (pos.): 417.3165 ([*M*+Na]$^+$, $C_{22}H_{46}B_2NaP_2^+$; calc. 417.3159). Anal. calc. for $C_{22}H_{46}B_2P_2$ (394.17): C 67.0, H 11.8; found: C 67.1, H 11.6.

meso-*[1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]–Borane (1/2)*. The solvent of the soln. left from the first recrystallization of *rac*-[1,2-phenylenebis(methylene)]bis[(*tert*-butyl)isopropylphosphine]–borane (1/2) (see above) was evaporated and the solid was recrystallized from hot MeOH. The colorless crystals produced were collected by filtration and recrystallized three times from MeOH until the product became diastereoisomerically pure. M.p. 140°. ^{1}H-NMR (500 MHz, CD_2Cl_2): 0.29 (*q*, ^1J(P,B) = 85, 2 PBH_3); 1.07 (*dd*, ^3J(P,H) = 13, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.25 (*d*, ^3J(P,H) = 13, 18 H, *Me*CP); 1.26 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 2.02 (*dd*, ^2J(P,H) = 7, ^3J(H,H) = 7, 2 H, MeC*H*P); 3.29 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 10, 2 H, $ArCH_2P$); 3.38 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 13, 2 H, $ArCH_2P$); 7.29 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.5 (*d*, *J* = 54, *Me*CHP); 24.2 (*d*, *J* = 28, Me*C*HP); 25.4 (*d*, *J* = 25, Me*C*P); 27.7 (*d*, *J* = 6, *Me*CP); 31.5 (*d*, *J* = 28, $ArCH_2P^tBu^iPr$); 127.4, 132.5 (2*s*, arom. CH); 134.5 (*m*, $ArCH_2P^tBu_2^iPr_2$). ^{31}P-NMR (202 MHz, CD_2Cl_2, H_3PO_4): 40.7 (*q*, ^1J = 50, *meso*-$ArCH_2P^tBu_2$). HR-ES-MS (pos.): 417.3161 ($[M+Na]^+$, $C_{22}H_{46}B_2NaP_2^+$; calc. 417.3159). Anal. calc. for $C_{22}H_{46}B_2P_2$ (394.17): C 67.0, H 11.8; found: C 67.3, H 11.7.

*Racemic [1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]* (**3**). Racemic [1,2-phenylenebis(methylene)]bis[(*tert*-butyl)isopropylphosphine]–borane (1/2) (450 mg, 1.1 mmol) was dissolved in degassed Et_2NH (20 ml) and heated under reflux for 16 h. The soln. was cooled, and the solvent was evaporated. The white paste was dissolved in toluene (10 ml), and the soln. was passed through a short column of SiO_2 under an inert atmosphere. The column was washed with toluene (20 ml), and the solvent was subsequently evaporated from the combined washings: **3** (346 mg (86%). Clear oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.07 (*dd*, ^3J(P,H) = 13, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.10 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.10 (*d*, ^3J(P,H) = 14, 9 H, *Me*CP); 1.11 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.12. (*dd*, ^3J(P,H) = 13, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.72 (*dd*, ^2J(P,H) = 7, ^3J(H,H) = 7, 2 H, MeC*H*P); 1.73 (*dd*, ^2J(P,H) = 7, ^3J(H,H) = 7, 2 H, MeC*H*P); 2.90 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 15, 1 H, $ArCH_2P$); 2.95 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 10, 1 H, $ArCH_2P$); 2.99 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 13, 1 H, $ArCH_2P$); 2.35 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 7, 1 H, $ArCH_2P$); 7.52–7.60 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.3 (*d*, *J* = 16, *Me*CHP); 19.7 (*d*, *J* = 18, *Me*CHP); 23.4 (*d*, *J* = 12, Me*C*HP); 23.5 (*d*, *J* = 12, Me*C*HP); 26.3 (*d*, *J* = 25, Me*C*P); 26.4 (*d*, *J* = 25, Me*C*P); 29.9 (*d*, *J* = 14, *Me*CP); 30.0 (*d*, *J* = 14, *Me*CP); 30.3 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 30.5 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 126.1, 126.4, 128.3, 128.7 (4*s*, arom. CH); 137.5 (*m*, $ArCH_2P^tBu_2^iPr_2$); 137.7 (*m*, $ArCH_2P^tBu_2^iPr_2$). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 11.4 (*s*, *rac*-$ArCH_2P^tBu_2$); 12.5 (*s*, *meso*-$ArCH_2P^tBu_2$). HR-ES-MS (pos.): 417.3159 ($[M+Na]^+$, $C_{22}H_{46}B_2NaP_2^+$; calc. 417.3178). Anal. calc. for $C_{22}H_{40}P_2$ (366.50): C 72.1, H 11.1; found: C 72.3, H 11.3.

rac-*[1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]* (*rac*-**3**). As described for **3**, with *rac*-[1,2-phenylenebis(methylene)]bis[(*tert*-butyl)isopropylphosphine]–borane (1/2) (322 mg, 0.8 mmol), and Et_2NH (20 ml): *rac*-**3** (215 mg, 72%). Clear oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.06 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.11 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.12 (*dd*, ^3J(P,H) = 13, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.73 (*dd*, ^2J(P,H) = 7, ^3J(H,H) = 7, 2 H, MeC*H*P); 2.90 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 15, 1 H, $ArCH_2P$); 2.35 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 7, 1 H, $ArCH_2P$); 7.52–7.60 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.3 (*d*, *J* = 16, *Me*CHP); 19.7 (*d*, *J* = 18, *Me*CHP); 23.4 (*d*, *J* = 12, Me*C*HP); 23.5 (*d*, *J* = 12, Me*C*HP); 26.3 (*d*, *J* = 25, Me*C*P); 26.4 (*d*, *J* = 25, Me*C*P); 29.9 (*d*, *J* = 14, *Me*CP); 30.0 (*d*, *J* = 14, *Me*CP); 30.3 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 30.5 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 126.1, 128.7 (2*s*, arom. CH); 137.7 (*m*, $ArCH_2P^tBu_2^iPr_2$). ^{31}P-NMR (121 MHz, CD_2Cl_3, H_3PO_4): 11.4 (*s*, *rac*-$ArCH_2P^tBu_2$). HR-ES-MS (pos.): 365.2515 ($[M-H]^+$, $C_{22}H_{39}P_2^+$; calc. 365.2527). Anal calc. for $C_{22}H_{40}P_2$ (366.50): C 72.1, H 11.0; found: C 72.4, H 11.15.

meso-*[1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]* (*meso*-**3**). As described for **3**, with *meso*-[1,2-phenylenebis(methylene)]bis[(*tert*-butyl)isopropylphosphine]–borane (1/2) (450 mg, 1.2 mmol) and Et_2NH (20 ml): *meso*-**3** (334 mg, 83%). Clear oil. ^{1}H-NMR (300, $CDCl_3$): 1.07 (*dd*, ^3J(P,H) = 13, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.10 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.10 (*d*, ^3J(P,H) = 14, 9 H, MeCP); 1.72 (*dd*, ^2J(P,H) = 7, ^3J(H,H) = 7, 2 H, MeC*H*P); 2.95 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 10, 1 H, ArC*H*$_2$P); 2.99 (*dd*, ^2J(H,H) = 15, ^2J(P,H) = 13, 1 H, ArC*H*$_2$P); 7.55–7.61 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.3 (*d*, *J* = 16, *Me*CHP); 19.7 (*d*, *J* = 18, *Me*CHP); 23.4 (*d*, *J* = 12, Me*C*HP); 23.5 (*d*, *J* = 12, Me*C*HP); 26.3 (*d*, *J* = 25, Me*C*P); 26.4 (*d*, *J* = 25, Me*C*P); 29.9 (*d*, *J* = 14, *Me*CP); 30.0 (*d*, *J* = 14, *Me*CP); 30.3 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 30.5 (*d*, *J* = 15, $ArCH_2P^tBu^iPr$); 126.4,

128.7 (2*s*, arom. CH); 137.5 (*m*, *Ar*$CH_2P^tBu_2^iPr_2$). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): (*s*, *meso*-ArCH_2-P^{t}Bu$_2$). HR-ES-MS (pos.): 365.2541 ($[M-H]^+$, $C_{22}H_{39}P_2^+$; calc. 365.2527). Anal. calc. for $C_{22}H_{40}P_2$ (366.50): C 72.1, H 11.0; found: C 72.2, H 11.1).

*Di(*tert*-butyl)phosphine–Borane (1/1)*. $NaBH_4$ (1.30 g, 34 mmol) was dissolved in dry and degassed DMF (30 ml). The soln. was cooled to 0° and di(*tert*-butyl)chlorophosphine (= bis(1,1-dimethylethyl)-phosphinous chloride; 6.00 g, 33.2 mmol) was added dropwise. Upon complete addition, the soln. was allowed to warm to r.t. and stirred for 16 h. H_2O (30 ml) was slowly added to the soln. followed by Et_2O (30 ml). The aq. layer was extracted with Et_2O (2×20 ml), the combined org. phase washed with H_2O (30 ml) and brine (2×30 ml) and dried ($MgSO_4$), the solvent evaporated, and the obtained white solid recrystallized from hexane: title compound (4.88 g, 92%). Colorless crystals. M.p. 41°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.34 (*d*, ^3J(P,H) *J* = 13, 18 H, *Me*CP); 4.12 (*dq*, ^1J(P,H) = 351, ^2J(H,B) = 7). ^{13}C-NMR (75 MHz, $CDCl_3$): 29.3 (*d*, ^2J(P,C) = 2, *Me*$_3$CP); 30.2 (*d*, ^1J(P,C) = 28, Me$_3$*C*P). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 49.0 (*q*, ^1J(P,B) = 49, $ArCH_2P(BH_3)(^tBu)_2$). HR-ES-MS (pos.): 183.1456 ($[M+Na]^+$, $C_{22}H_{39}$-NaP_2^+; calc. 183.1450). Anal. calc. for $C_8H_{22}BP$ (160.05): C 60.0, H 13.9; found: C 60.1, H 13.9.

*Di(*tert*-butyl){{2-[(diisopropylphosphino)methyl]phenyl}methyl}phosphine–Borane (1/2)*. Di(*tert*-butyl)phosphine–borane (1/1) (574 mg, 3.6 mmol) was dissolved in THF (20 ml) and cooled to 0°. To this, 2.5M BuLi in hexane (1.45 ml, 3.6 mmol) was slowly added, and the soln. was allowed to warm to r.t. This soln. was slowly added to a THF (30 ml) soln. of 1,5-dihydro-2,4,3-benzodioxathiepin 3,3-dioxide (581 mg, 3.6 mmol) cooled to −78°. After complete addition, the soln. was warmed to r.t. and stirred for 30 min. A ^{31}P{^{1}H}-NMR spectrum of the soln. showed one peak at δ(P) 50.3 indicating full deprotonation of the phosphine. The soln. was recooled to −78°, and a THF (20 ml) soln. of $LiP^iPr_2(BH_3)$ (prepared from diisopropylphosphine–borane (1/1) (476 mg, 3.6 mmol) and 2.5M BuLi in hexane (1.45 ml, 3.6 mmol)) was added slowly. After the addition, the soln. was allowed to warm to r.t. and stirred for 3 h. After this time, H_2O (20 ml) was carefully added, and the soln. was extracted with Et_2O (3×20 ml). The combined org. phase was washed successively with H_2O (20 ml) and brine (2×20 ml) and dried ($MgSO_4$), the solvent evaporated, and the crude solid recrystallized from hexane: title product (1.12 g, 79%). Colorless crystals. M.p. 114–115°. ^{1}H-NMR (300 MHz, $CDCl_3$): −0.45 to +0.92 (br. *m*, 2 PBH_3); 0.93 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.02 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.09 (*d*, ^3J(P,H) = 12, 18 H, *Me*CP); 1.82 (*dsept.*, ^2J(P,H) = 10, ^3J(H,H) = 7, 2 H, MeC*H*P); 3.13 (*d*, ^2J(P,H) = 12, 2 H, ArCH_2P); 3.25 (*d*, ^2J(P,H) = 12, 2 H, ArCH_2P); 7.10–7.22 (*m*, 3 arom. H); 7.55–7.62 (*m*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.8 (*d*, *J* = 8, *Me*CHP); 22.0 (*d*, *J* = 32, Me*C*HP); 24.4 (*d*, *J* = 24, Me*C*P); 26.7 (*d*, *J* = 26, Ar$CH_2P^iPr_2$); 29.0 (*d*, *J* = 14, *Me*CP); 33.3 (*d*, *J* = 24, Ar$CH_2P^tBu_2$); 127.0, 127.1, 131.6, 132.9 (4*s*, arom. CH); 131.1 (*s*, *Ar*CH_2); 135.0 (*s*, *Ar*CH_2). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 35.2 (*m*, $ArCH_2P(BH_3)^iPr_2$); 50.0 (*m*, $ArCH_2P(BH_3)^tBu_2$). ES-MS (pos.): 417.27 (100, $[M+Na]^+$, based on ^{11}B). Anal. calc. for $C_{22}H_{46}B_2P_2$ (294.17): C 67.0, H 11.8; found: C 66.8, H 11.6.

*Di(*tert*-butyl){{2-[(diisopropylphosphino)methyl]phenyl}methyl}phosphine* (**4**). Di(*tert*-butyl){{2-[(diisopropylphosphino)methyl]phenyl}methyl}phosphine–borane (1/2) (0.96 g, 2.4 mmol) was dissolved in Et_2NH (10 ml) and refluxed under N_2 for 16 h. The soln. was cooled, and the Et_2NH was evaporated leaving a white paste which was dissolved in toluene (10 ml) and passed through a plug of SiO_2. Toluene (10 ml) was used to wash the column, and the solvent was evaporated from the combined org. fractions leaving a crude white solid. Recrystallizing from MeOH gave **4**. (0.82 g, 93%). White powder. M.p. 43–44°. ^{1}H-NMR (300, $CDCl_3$): 0.93 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.02 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.09 (*d*, ^3J(P,H) = 12, 18 H, *Me*CP); 1.82 (*dsept.*, ^2J(P,H) = 10, ^3J(H,H) = 7, 2 H, MeC*H*P); 3.13 (*d*, ^2J(P,H) = 12, 2 H, ArCH_2P); 3.25 (*d*, ^2J(P,H) = 12, 2 H, ArCH_2P); 7.10–7.22 (*m*, 3 arom. H); 7.55–7.62 (*m*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.6 (*d*, *J* = 8, *Me*CHP); 22.2 (*d*, *J* = 32, Me*C*HP); 24.4 (*d*, *J* = 24, Ar*C*$H_2P^iPr_2$); 26.8 (*d*, *J* = 26, Me*C*P); 30.1 (*d*, *J* = 24, MeCP); 33.5 (*d*, *J* = 24, Ar*C*$H_2P^tBu_2$); 127.0, 127.1, 131.6, 132.9 (4*s*, arom. CH); 131.1 (*s*, *Ar*CH_2); 135.0 (*s*, *Ar*CH_2). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 5.3 (*s*, Ar$CH_2P^iPr_2$); 28.5 (*s*, ArCH_2-P^{t}Bu$_2$). HR-ES-MS (pos.): 367.2691 ($C_{22}H_{41}P_2^+$; calc. 367.2684). Anal. calc. for $C_{22}H_{40}P_2$ (366.50): C 72.1, H 11.0; found: C 72.3, H 11.3.

*Di(*tert*-butyl){{2-{[(*tert*-butyl)isopropylphosphino]methyl}phenyl}methyl}phosphine–Borane (1/2)*. Di(*tert*-butyl)phosphine–borane (511 mg, 3.2 mmol) was dissolved in THF (20 ml) and cooled to 0°. To

this, 2.5M BuLi in hexane (1.3 ml, 3.2 mmol) was slowly added and the soln. allowed to warm to r.t. This soln. was slowly added to a THF (30 ml) soln. of 1,5-dihydro-2,4,3-benzodioxathiepin 3,3-dioxide (516 mg, 3.2 mmol) cooled to −78°. After complete addition, the soln. was warmed to r.t. and stirred for 30 min. A $^{31}P\{^1H\}$-NMR spectrum of the soln. showed one peak at δ 50.3 indicating full deprotonation of the phosphine. The soln. was recooled to −78°, and a THF (20 ml) soln. of LiP^{t}Bu^{i}Pr(BH_3) (prepared from (*tert*-butyl)isopropylphosphine–borane (1/1) (467 mg, 3.2 mmol) in THF cooled to 0° and 2.5M BuLi in hexane (1.3 ml, 3.2 mmol)) was added slowly. After the addition, the soln. was allowed to warm to r.t. and stirred for 3 h. After this time, H_2O (20 ml) was carefully added, and the soln. was extracted with Et_2O (3×20 ml). The combined org. phase was washed successively with H_2O (20 ml) and brine (2×20 ml) and dried ($MgSO_4$), the solvent evaporated, and the crude solid recrystallized from hexane: title product (1.20 g, 87%). Colorless crystals. M.p. 151°. ^{1}H-NMR (300, $CDCl_3$): −0.11 to +1.02 (*m*, 2 PBH_3); 1.12 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, MeC*H*P); 1.28 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 3 H, *Me*CHP); 1.25 (*d*, ^3J(P,H) = 12, 9 H, *Me*CP); 1.29 (*d*, ^3J(P,H) = 12, 9 H, *Me*CP); 1.30 (*d*, ^3J(P,H) = 12, 9 H, *Me*CP); 2.03 (*dsept.*, ^2J(P,H) = 11, ^3J(H,H) = 7, 1 H, MeC*H*P); 3.18–3.68 (*m*, 4 H, ArCH_2P); 7.10–7.21 (*m*, 3 arom. H); 7.53–7.63 (*m*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.2 (*d*, *J* = 11, *Me*CHP); 23.7 (*d*, *J* = 28, MeCHP); 24.8 (*d*, *J* = 24, ArCH$_2$P^{i}Pr^{t}Bu); 25.5 (*d*, *J* = 26, Me*C*P); 29.0 (*d*, *J* = 7, *Me*CP); 33.3 (*d*, *J* = 7, ArCH$_2$P^{t}Bu$_2$); 127.0, 131.7, 132.9 (3*s*, arom. CH); 133.6 (*Ar*CH$_2$P); 135.0 (*A*rCH$_2$P). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 41.8 (*q*, ^1J(P,B) = 72, P^{t}Bu^{i}Pr(BH_3)); 50.1 (*q*, ^1J(P,B) = 74, P^{t}Bu$_2$(BH_3)). ES-MS (pos.): 431.30 (100; based on ^{11}B). Anal. calc. for $C_{23}H_{48}B_2P_2$ (408.20): C 67.7, H 11.9; found: C 67.7, H 12.1.

*Di(*tert*-butyl){{2-{[(*tert*-butyl)isopropylphosphino]methyl}phenyl}methyl}phosphine* (**5**). As described for **4**, with di(*tert*-butyl){{2-{[(*tert*-butyl)isopropylphosphino]methyl}phenyl}methyl}phosphine–borane (0.85 g, 2.1 mmol) and Et_2NH (10 ml): **5** (0.67 g, 85%). M.p. 68–69°. ^{1}H-NMR (300, $CDCl_3$): 1.02 (*dd*, ^3J(P,H) = 10, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.05 (*d*, ^3J(P,H) = 11, 9 H, *Me*CP); 1.06 (*d*, ^3J(P,H) = 11, 9 H, *Me*CP); 1.07 (*d*, ^3J(P,H) = 11, 9 H, *Me*CP); 2.92–3.00 (*m*, 4 H, ArCH_2P); 6.96–7.01 (*m*, 2 arom. H); 7.20–7.24 (*m*, 1 arom. H); 7.50–7.54 (*m*, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 20.9 (*d*, *J* = 9, *Me*CHP); 22.7 (*d*, *J* = 18, Me*C*H); 24.1 (*d*, *J* = 20, *Me*CP); 26.4 (*d*, *J* = 24, Me*C*P); 27.1 (*d*, *J* = 24, ArCH_2-P^{t}Bu^{i}Pr); 29.1 (*d*, *J* = 13, *Me*CP); 30.3 (*d*, *J* = 13, *Me*CP); 32.3 (*d*, *J* = 23, ArCH_2P^{t}Bu$_2$); 125.7 (*d*, *J* = 20), 131.0 (*d*, *J* = 10), 131.3 (*d*, *J* = 14), 131.4 (*d*, *J* = 17, arom. CH); 138.2 (*d*, *J* = 7, *Ar*CH$_2$P); 139.1 (*d*, *J* = 11, *Ar*CH$_2$P). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 16.7 (*s*, ArCH$_2$P^{t}Bu^{i}Pr); 28.6 (*s*, ArCH$_2$P^{t}Bu$_2$). HR-ES-MS (pos.): 381.2845 ($C_{23}H_{43}P_2^+$; calc. 381.2840). Anal calc. for $C_{23}H_{42}P_2$ (380.53): C 72.6, H 11.1; found: C 72.3, H 11.3.

1,2-Bis(chloromethyl)naphthalene. A mixture of 1-(chloromethyl)-2-methylnaphthalene (5.16 g, 27.1 mmol) in 1,2-dichloroethane (30 ml) and dibenzoyl peroxide (150 mg) was stirred until all solids were dissolved. Then, *N*-chlorosuccinimide (3.73 g, 28 mmol) was added. The soln. was heated under reflux and stirred for 40 h. The soln. was cooled and the solid removed by filtration and washed with cold 1,2-dichloroethane (10 ml). The soln. was washed with H_2O (3×30 ml), the org. layer dried ($MgSO_4$), the solvent evaporated, and the crude yellow solid dissolved in hot benzene/hexane 1:1, and filtered hot to remove any remaining succinimide compounds. The soln. was cooled and the title compound recrystallized: 4.61 g (76%). White solid. M.p. 131°. ^{1}H-NMR (300 MHz, (D_6)acetone): 4.95 (*s*, ArCH_2Cl); 5.26 (*s*, 2 H, ArCH_2Cl); 7.51 (*m*, 2 arom. H); 7.57 (*m*, 2 arom. H); 7.86 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, (D_6)acetone): 40.2 (*s*, Ar*C*H$_2$Cl); 45.2 (*s*, Ar*C*H$_2$Cl); 125.9, 128.5, 129.1, 129.6, 130.5, 131.8, 133.4, 134.0, 135.7, 136.5 (10*s*, arom. C). EI-MS: 226.0 (M^+ (^{37}Cl)), 224.0 (M^+ (^{35}Cl)). Anal. calc. for $C_{12}H_{10}Cl_2$ (225.11): C 64.0, H 4.5; found: C 64.5, H 3.7.

*[Naphthalene-2,3-diylbis(methylene)]bis[(di(*tert*-butyl)phosphine]* (**6**). To an Et_2O (10 ml) soln. of 2,3-dimethylnaphthalene (2.56 g, 16.4 mmol) and KO^{t}Bu (4.03 g, 36 mmol) cooled to −78°, 2.5M BuLi in hexane (14.4 ml, 36 mmol) was added slowly. The soln. was allowed to warm to r.t. and then heated under reflux for 2 h. The soln. was cooled to 0° and di(*tert*-butyl)chlorophosphine (6.84 ml, 6.50 g, 36 mmol) was added over 20 min. The soln. was warmed to r.t. and stirred for 16 h, during which time a salt formed. After filtration, H_2O (10 ml) was slowly added. Then, the aq. layer was extracted with Et_2O (2×20 ml), the combined org. phase washed successively with H_2O (20 ml) and brine (2×20 ml) and dried ($MgSO_4$), the solvent evaporated, and the obtained white solid recrystallized from hot MeOH: **6** (4.92 g, 68%). M.p. 148°. ^{1}H-NMR (300, $CDCl_3$): 1.16 (*d*, ^3J(P,H) = 11, 36 H, *Me*CHP); 3.22 (*d*,

^2J(P,H) = 4, 4 H, ArCH_2P); 7.30–7.40 (*m*, 2 arom. H); 7.70–7.77 (*m*, 2 arom. H); 8.02–8.08 (*m*, arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 27.3 (*d*, ^1J(P,C) = 24, Me*C*P); 32.5 (*d*, ^2J(P,C) = 13, *Me*CP); 33.3 (*d*, ^1J(P,C) = 23, Ar*C*H_2P); 125.4, 127.3, 129.4, 132.2 (4*s*, arom. C); 138.4 (*dd*, ^2J(P,C) = 10, ^3J(P,C) = 2, *Ar*CH_2P). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 26.3 (*s*, $ArCH_2P^tBu_2$). HR-ES-MS (pos.): 445.3138 ($C_{28}H_{47}P_2^+$; calc. 445.3153). Anal. calc. for $C_{28}H_{46}P_2$ (444.31): C 75.6, H 10.4; found: C 75.4, H 10.7.

*[Naphthalene-1,2-diylbis(methylene)]bis[di(*tert*-butyl)phosphine]–Borane (1/2)*. Di(*tert*-butyl)phosphine–borane (2.04 g, 12.8 mmol) was dissolved in Et_2O (30 ml) and cooled to −30°. To this soln., 2.5M BuLi in hexane (5.2 ml, 6.4 mmol) was added slowly. The resulting soln. was allowed to warm to r.t. and stirred for 3 h. The soln. was cooled to 0°, and a Et_2O (20 ml) soln. of 1,2-(dichloromethyl)naphthalene (1.20 g, 5.3 mmol) was added dropwise, not allowing the temp. to rise above 5°. Upon complete addition, the soln. was allowed to warm to r.t. and stirred for 16 h. H_2O (30 ml) was added, the aq. layer extracted with Et_2O (2×30 ml), the combined org. layer washed with H_2O (30 ml) and brine (2×30 ml) and dried ($MgSO_4$), and the solvent evaporated: off-white oil. To this, hexane was added and the title compound crystallized: 1.08 g (43%). Pure white solid. M.p. 173–174°. ^{1}H-NMR (300 MHz, $CDCl_3$): −0.02 to +2.11 (br., 42 H, BH_3 and MeC); 3.18–4.40 (br., 4 H); 7.45 (*t*, *J* = 7.0, 1 arom. H); 7.53 (*t*, *J* = 7.0, 1 arom. H); 7.68 (*d*, *J* = 8.5, 1 arom. H); 7.80 (*d*, *J* = 8.5, 1 arom. H); 7.92 (*d*, *J* = 8.5, 1 arom. H); 8.15 (*d*, *J* = 8.5, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 22.4 (*d*, ^1J(P,C) = 22, Me_3*C*P); 26.7 (*d*, ^1J(P,C) = 23, Me_3*C*P); 29.0 (*d*, ^2J(P,C) = 14, *Me*$_3$CP); 33.6 (*d*, ^1J(P,C) = 25, Ar*C*H_2P); 34.6 (*d*, ^1J(P,C) = 25, Ar*C*H_2P); 125.0, 125.7, 126.2, 127.0, 128.7, 129.3, 130.8, 133.2, 133.4 (9*s*, arom. CH); 134.3 (*s*). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 53.1 (br. *t*, ^1J(P,B) = 94, $ArCH_2P^tBu_2(BH_3)$). ES-MS (pos.): 495 ($[M+Na]^+$). Anal. calc. for $C_{28}H_{50}B_2P_2$ (470.27): C 71.5, H 10.7; found: C 71.6, H 10.7.

*[Naphthalene-1,2-diylbis(methylene)]bis[di(*tert*-butyl)phosphine]* (**7**). [Naphthalene-1,2-diylbis(methylene)]bis[di(*tert*-butyl)phosphine]–borane (1/2) (1.08 g, 2.3 mmol) was dissolved in degassed Et_2NH (20 ml) and heated under reflux. The soln. was cooled and the solvent evaporated. The white solid was dissolved in toluene (10 ml), and the soln. was passed through a short column of SiO_2 under an inert atmosphere. The column was washed with toluene (30 ml), the solvent subsequently evaporated, and the obtained off-white solid recrystallized from MeOH: **7** (854 mg, 84%). M.p. 145°. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*d*, ^3J(P,H) = 11, 18 H, *Me*CP); 1.15 (*d*, ^3J(P,H) = 10, 18 H, *Me*CP); 3.25 (*d*, ^2J(P,H) = 3, 2 H, ArCH_2P); 3.52 (br. *s*, 2 H, ArCH_2P); 7.32–7.42 (*m*, 1 arom. H); 7.45–7.53 (*m*, 1 arom. H); 7.58 (*d*, ^3J(H,H) = 8, 1 arom. H); 7.68–7.76 (*m*, 2 arom. H); 8.40 (*d*, ^3J(H,H) = 8, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 27.7 (*d*, *J* = 23, Me*C*P); 29.8 (*d*, *J* = 13, *Me*CP); 29.9 (*d*, *J* = 13, *Me*CP); 32.1 (*d*, *J* = 22, Ar*C*$H_2P^tBu_2$); 32.4 (*d*, *J* = 25, Ar*C*$H_2P^tBu_2$); 124.5, 125.0, 125.7, 125.8, 128.4, 129.3, 129.6, 131.2 (8*s*, arom. CH); 132.5 (*d*, *J* = 11, *Ar*CH_2P); 133.1 (*d*, *J* = 5, *Ar*CH_2P). ^{31}P-NMR (121 MHz, $CDCl_3$, H_3PO_4): 34.4 (*s*, $ArCH_2P^tBu_2$); 35.4 (*s*, $ArCH_2P^tBu_2$). HR-ES-MS (pos.): 444.3149 ($C_{28}H_{47}P_2^+$; calc. 445.3153). Anal. calc. for $C_{28}H_{46}P_2$ (444.61): C 75.6, H 10.4; found: C 75.4, H 10.6.

*Tetracarbonyl{[1,2-phenylenebis(methylene)]bis[di(*tert*-butyl)phosphine-κP]}molybdenum* ([$Mo(CO)_4$(**1**)]). [$Mo(CO)_4$(norborna-2,5-diene)] (150 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (10 ml), and **1** (200 mg, 0.5 mmol) was added. The soln. was heated under reflux for 2 h and then cooled. MeOH (10 ml) was added, and the CH_2Cl_2 was evaporated precipitating a yellow solid. The soln. was filtered, and the solid was washed with MeOH: [$Mo(CO)_4$(**1**)] (173 mg, 57%). M.p. 190° (dec.). IR (CH_2Cl_2; selected data): 2006 (Mo–CO), 1894 (Mo–CO), 1878 (Mo–CO), 1859 (Mo–CO). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.40 (*d*, ^3J(P,H) = 11, 36 H, *Me*CP); 3.42 (*d*, ^2J(P,H) = 5, 4 H, ArC$H_2P^tBu_2$); 7.10–7.12 (*m*, 2 arom. H); 7.32–7.35 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 30.1 (*s*, *Me*CP); 31.6 (*d*, *J* = 14, Me*C*P); 37.2 (*d*, *J* = 4, Ar*C*$H_2P^tBu_2$); 126.3, 132.4 (2*s*, arom. CH); 135.5 (*s*, Ar); 207.4 (*d*, ^2J(P,C) = 8, P–Mo–CO); 213.3 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.8 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.3 (*d*, ^2J(P,C) = 8, P–Mo–CO). ^{31}P-NMR (121 MHz, $CDCl_3$): 57.9. Anal. calc. for $C_{28}H_{44}MoO_4P_2$ (602.53): C 55.8, H 7.4; found: C 56.0, H 7.4.

Tetracarbonyl{[1,2-phenylenebis(methylene)]bis[diisopropylphosphine-κP]}molybdenum ([$Mo(CO)_4$(**2**)]). As described for [$Mo(CO)_4$(**1**)], with [$Mo(CO)_4$(norborna-2,5-diene)] (100 mg, 0.3 mmol), CH_2Cl_2 (10 ml), and **2** (101 mg, 0.3 mmol): [$Mo(CO)_4$(**2**)] (97 mg, 59%). M.p. 186° (dec.). IR (CH_2Cl_2; selected data): 2019 (Mo–CO); 1924 (Mo–CO); 1908 (Mo–CO); 1869 (Mo–CO). ^{1}H-NMR (300, $CDCl_3$): 1.24 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 12 H, *Me*CHP); 1.28 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 12 H, *Me*CHP); 2.12 (*sept.*, ^3J(H,H) = 7, 4 H, Me*C*HP); 3.03 (*d*, ^2J(P,H) = 7, 4 H, ArC$H_2P^iPr_2$);

7.01–7.04 (*m*, 2 arom.H); 7.12–7.15 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$) 19.0 (*s*, *Me*CHP); 19.9 (*s*, *Me*CHP); 27.6 (*d*, ^1J(P,C) = 9, Me*C*HP); 31.4 (*s*, ArCH_2P); 126.9 (*s*, Ar); 131.7 (*s*, arom. CH); 135.9 (*s*, *Ar*CH_2P); 207.4 (*d*, ^2J(P,C) = 8, P–Mo–CO); 213.1 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.2 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.0 (*d*, ^2J(P,C) = 8, P–Mo–CO). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 35.5 (*s*, $ArCH_2(^iPr)_2Mo$). Anal. calc. for $C_{24}H_{36}MoO_4P_2$ (546.43): C 52.75, H 6.6; found: C 52.5, H 6.7.

*Tetracarbonyl{[1,2-phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine-κ*P*]}molybdenum* ([Mo(CO)$_4$(**3**)]). As described for [Mo(CO)$_4$(**1**)], with [Mo(CO)$_4$(norborna-2,5-diene)] (100 mg, 0.3 mmol), CH_2Cl_2 (10 ml), and **3** (110 mg, 0.3 mmol): [Mo(CO)$_4$(**3**)] (109 mg, 63%). M.p. 189° (dec.). IR (CH_2Cl_2; selected data): 2013 (Mo–CO), 1909 (Mo–CO), 1893 (Mo–CO), 1864 (Mo–CO). ^{1}H-NMR (300, $CDCl_3$): 1.25 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.27 (*dd*, ^3J(P,H) = 14, ^3J(H,H) = 7, 6 H, *Me*CHP); 1.40 (*d*, ^3J(P,H) = 11, 18 H, *Me*CP); 2.10 (*sept.*, ^3J(H,H) = 7, 2 H, MeC*H*P); 3.38 (*d*, ^2J(P,H) = 7, 4 H, ArCH_2P^{t}Bu^{i}Pr); 7.04–7.07 (*m*, 2 arom H); 7.12–7.14 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.1 (*s*, *Me*CHP); 19.9 (*s*, *Me*CHP); 25.3 (*s*, *Me*CP); 27.4 (*d*, ^1J(P,C) = 9, Me*C*HP); 30.2 (*s*, Me*C*P); 31.4 (*s*, Ar*C*H_2P); 126.5 (*s*, Ar); 131.7 (*s*, arom CH); 136.1 (*s*, *Ar*CH_2P); 207.3 (*d*, ^2J(P,C) = 8, P–Mo–CO); 213.1 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.3 (*t*, ^2J(P,C) = 8, P–Mo–CO); 214.9 (*d*, ^2J(P,C) = 8, P–Mo–CO). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 42.1 (*s*, $ArCH_2P(^tBu^iPr)Mo$). Anal. calc. for $C_{26}H_{46}MoO_4P_2$ (580.53): 53.8, H 8.0; found: C 53.7, H 8.1.

*Tetracarbonyl{[naphthalene-2,3-diylbis(methylene)]bis[(di(*tert-*butyl)phosphine-κ*P*]}molybdenum* ([Mo(CO)$_4$(**6**)]). As described for [Mo(CO)$_4$(**1**)], with [Mo(CO)$_4$(norborna-2,5-diene)] (100 mg, 0.3 mmol), CH_2Cl_2 (10 ml), and **6** (182 mg, 0.3 mmol): [Mo(CO)$_4$(**6**) (118 mg, 52%). M.p. 189° (dec.). IR (CH_2Cl_2; selected data): 2007 (Mo–CO), 1900 (Mo–CO), 1881 (Mo–CO), 1861 (Mo–CO). ^{1}H-NMR (300, $CDCl_3$): 1.38 (*d*, ^3J(P,H) = 11, 36 H, *Me*CP); 3.40 (*d*, ^2J(P,H) = 4, 4 H, ArCH_2P^{t}Bu$_2$); 7.29–7.38 (*m*, 2 arom. H); 7.58–7.64 (*m*, 2 arom. H); 7.71 (*s*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 30.4 (s); 31.7 (*d*, *J* = 14); 38.2 (s); 126.6, 127.2, 132.1, 132.2 (4*s*, arom CH); 135.5 (*s*, Ar); 207.4 (*d*, ^2J(P,C) = 8, P–Mo–CO); 213.4 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.2 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.3 (*d*, ^2J(P,C) = 8, P–Mo–CO). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 60.9 (*s*, $ArCH_2P(^tBu)_2Mo$). HR-ES-MS (pos.): 649.1880 ([*M* – CO + Na]$^+$, $C_{31}H_{46}{}^{98}MoNaO_3P_2$; calc. 649.1879). Anal. calc. for $C_{32}H_{46}MoO_4P_2$ (653.60): C 58.9, H 7.1; found: C 58.6, H 7.3.

*Tetracarbonyl{[naphthalene-1,2-diylbis(methylene)]bis[di(*tert-*butyl)phosphine-κ*P*]}molybdenum* ([Mo(CO)$_4$(**7**)]). As described for [Mo(CO)$_4$(**1**)], with [Mo(CO)$_4$(norborna-2,5-diene)] (100 mg, 0.3 mmol), CH_2Cl_2 (10 ml), and **7** (182 mg, 0.3 mmol): [Mo(CO)$_4$(**7**)] (141 mg, 62%). M.p. 187° (dec.). IR (CH_2Cl_2; selected data): 2007 (Mo–CO), 1896 (Mo–CO), 1880 (Mo–CO), 1860 (Mo–CO). ^{1}H-NMR (300, $CDCl_3$): 1.48–1.62 (*m*, 36 H, *Me*CP); 3.56 (*d*, ^2J(P,H) = 12, 2 H, ArCH_2P^{t}Bu$_2$); 3.91 (*d*, ^2J(P,H) = 8, 2 H, ArCH_2P^{t}Bu$_2$); 7.38–7.62 (*m*, 4 arom. H); 7.78 (*d*, ^3J(H,H) = 6, 1 arom. H); 8.21 (*d*, ^3J(H,H) = 6, 1 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 25.2 (*s*, *Me*CP); 31.6 (*d*, *J* = 14, Me*C*P); 38.1 (*d*, *J* = 6, Ar*C*H_2P^{t}Bu$_2$); 38.7 (*d*, *J* = 4, Ar*C*H_2P^{t}Bu$_2$); 124.9, 125.7, 126.3, 127.0, 129.3 (5*s*, arom CH); 131.6, 132.2, 133.3, 133.7, 135.4 (5*s*, Ar); 207.3 (*d*, ^2J(P,C) = 8, P–Mo–CO); 213.4 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.4 (*t*, ^2J(P,C) = 8, P–Mo–CO); 215.8 (*d*, ^2J(P,C) = 8, P–Mo–CO). ^{31}P-NMR (121 MHz, CD_2Cl_2, H_3PO_4): 58.0 (*d*, ^5J(P,P) = 24, $ArCH_2P(^tBu)_2Mo$); 61.1 (*d*, ^5J(P,P) = 24, $ArCH_2P(^tBu)_2Mo$). HR-ES-MS (pos.): 649.1880 ([*M* – CO + Na$^+$], $C_{31}H_{46}{}^{98}MoNaO_3P_2$; calc. 649.1874). Anal. calc. for $C_{32}H_{46}MoO_4P_2$ (652.60): C 58.9, H 7.1; found: C 58.6, H 7.3.

Example of Ligand Testing in Methoxycarbonylation of Vinyl Acetate. [Pd_2(dba)$_3$] (23 mg, 0.05 mmol Pd) and **1** (197 mg, 0.5 mmol) were weighed into a *Schlenk* flask under N_2, to which MeOH (11 ml) was added. After all of the solid had dissolved, $MeSO_3H$ (48 mg, 0.5 mmol) was added, followed by vinyl acetate (1.8 g, 21 mmol). This soln. was added to a *Fischer-Porter* bottle that had been evacuated and back filled with N_2 three times. CO was added to a pressure of 3 bar, and the soln. was kept at 25° with an oil bath. After 3 h, the soln. was cooled and the CO slowly vented. A portion of the soln. was hydrolzed with $NaHCO_3$ and then analyzed by GC.

X-Ray Crystallography for rac-*[1,2-Phenylenebis(methylene)]bis[(*tert-*butyl)isopropylphosphine]-Borane (1/2).* $C_{22}H_{46}B_2P_2$, *M* 394.15; colorless prism grown from MeOH, crystal size 0.2 × 0.08 × 0.08 mm, monoclinic, *P*2(1)/*c*, *a* = 12.630(2), *b* = 18.239(2), *c* = 11.595(2) Å, β = 110.869(4)°; *V* = 2495.6(7) Å^3, *Z* = 4, D_{calc} = 1.049 mg m^{-3}; Mo*Kα* radiation (confocal optic, λ 0.71073 Å), μ = 0.179 mm^{-1}, *T* = 93(2) K. The 15220 data (4467 (*R*(int) = 0.0224), 2.06 < θ < 25.34) were collected on a *Rigaku-*

MM007/Mercury CCD diffractometer and were corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values of all data [27] to give $wR = \{\Sigma[w(F_o^2 F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0905$, conventional $R = 0.0352$ for F values of reflections with $F_o^2 > 2\sigma(F_o^2)$ [4170 observed reflections], $S = 0.993$ for 242 parameters. Residual electron density extremes were 0.357 and -0.253 e Å^{-3}. CCDC-294580 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif. from the *Cambridge Crystallograhic Data Centre.*

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