Novel Electron-Rich Hydrophilic Phosphanes with Carboxylated Cyclohexyl Substituents[‡]

David J. Brauer,[a] Konstantin W. Kottsieper,[a] Thomas Nickel,[a] Othmar Stelzer,*[a] and William S. Sheldrick[b]

Dedicated to Professor Dr. M. Schmidt on the occasion of his 75th birthday

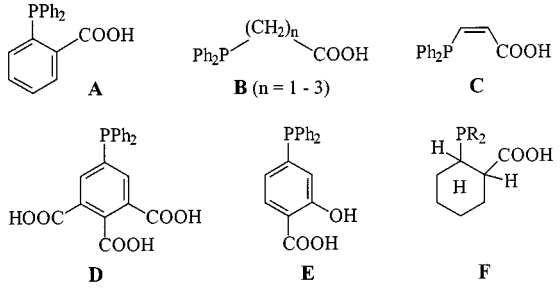
Keywords: Phosphanes / NMR spectroscopy / Carboxylic acids / Chelates / Palladium

Addition of diphenylphosphane or phenylphosphane to methyl 1-cyclohexenecarboxylate (**1**) under base catalysis, yields the novel tertiary or secondary phosphanes **2a**, **3**, or **4a** containing cyclohexyl backbones with the carboxylic groups in the 2-position. The carboxylated derivative of the borane adduct of tricyclohexylphosphane **5a** is accessible by a related reaction using $Cy_2P(BH_3)Li$ instead of Ph_2PH or $PhPH_2$. The complete analysis of the ^1H NMR spectrum of **2a** using 2D NMR spectroscopy (H,H-, C,H-COSY NMR spectra, ^{13}C-INADEQUATE) reveals the bis(equatorial) position of the Ph_2P and COOMe substituents. This is supported by the results of the X-ray structural analysis of **2b** (space group $P2_1/c$). On addition of $Cy_2P(BH_3)Li$ to **1** and subsequent hydrolysis, **5a**, the first functionalized derivative of tricyclohexylphosphane is obtained. In contrast to **2b**, the COOMe substituent in **5a** occupies the axial position, the bulky phosphanyl group being equatorial as indicated by the X-ray structural analysis (space group $P2_1$). Molybdenum(0) and palladium(II) complexes of **2a** and **2b** have been synthesized. The influence of the carboxylated cyclohexyl substituent on the electronic and steric parameters of **2a** and **2b** is discussed.

Introduction

Phosphanylcarboxylic acids play an important role as bifunctional P,O chelating ligands in important catalytic processes like the Shell higher olefin process (SHOP).[2,3] In catalytic and stoichiometric reactions, the weakly coordinated oxygen donor can be replaced reversibly, thus providing a coordination site for an incoming ligand or a substrate molecule. Some of these "hemilabile" ligands,[4] e.g. **A**−**C**, have been known for a long time[5] and efficient synthetic routes have been developed recently.[2c,6] These employ either nucleophilic phosphanylation reactions or Pd-catalyzed P−C coupling reactions between aromatic bromides or iodides and primary or secondary phosphanes.[7] Using the latter synthetic strategy, multiply functionalized aromatic phosphanylcarboxylic acids, e.g. **D** and **E**, have been obtained.

Phosphanylcarboxylic acids containing a cyclohexane backbone (**F**) have not been reported so far, however. In contrast to aromatic phosphanes, e.g. **A**−**E**, with carboxylated phenyl substituents, the coordination chemistry of ligands of type **F** should show novel aspects connected with the cyclohexane backbone. Due to the substitution pattern at the phosphorus atom, these ligands have a bulky and electron-rich P donor group capable of forming P,O chelates with transition metal ions. The mutual *cis* or *trans* position of the R_2P and carboxylic groups will be determined by the bulkiness of the substituents R, thus controlling the tendency of these ligands to form stable P,O chelates with chirogenic bridging carbon atoms C(1) and C(2).



Results

Synthesis of 1-(Diphenylphosphanyl)cyclohexane-2-carboxylic Acid and Derivatives (2a, 2b)

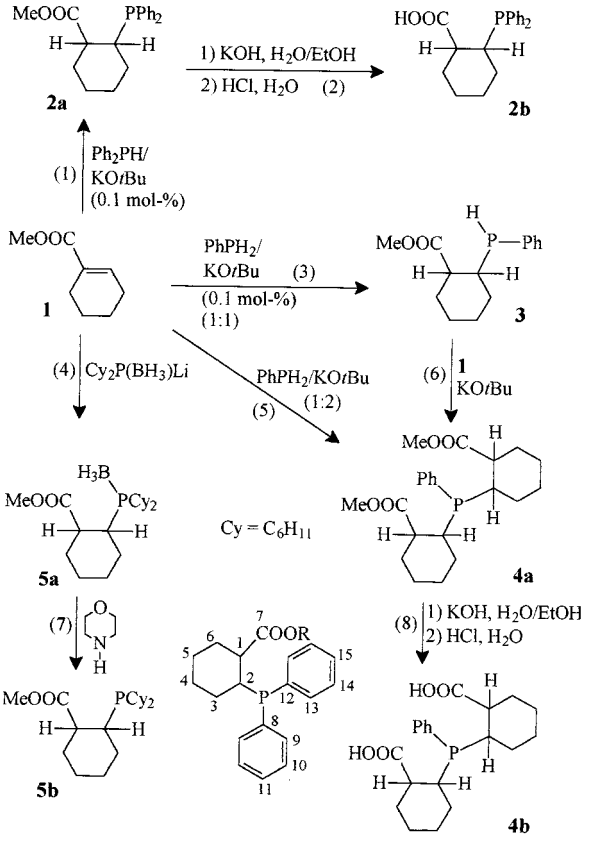
For the syntheses of phosphanylcarboxylic acids and their derivatives containing a 1,2-cyclohexanediyl backbone, methyl 1-cyclohexenecarboxylate (**1**) was used in all cases as a starting material. Base-catalyzed addition of

[‡] Water-Soluble Phosphanes, 16. − Part 15: Ref.[1]

[a] Fachbereich 9, Anorganische Chemie,
Bergische Universität−GH Wuppertal,
Gaußstraße 20, 42097 Wuppertal, Germany
Fax: (internat.) + 49-(0)202/4393053
E-mail: stelzer@uni-wuppertal.de
[b] Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum,
Universitätsstraße 150, 44780 Bochum, Germany
Fax.: (internat.) + 49-(0)234/7094420
E-mail: shel@anachem.ruhr-uni-bochum.de

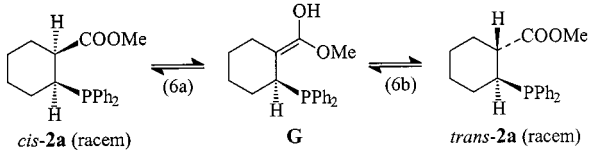
  1434−1948/01/0505−1251 $ 17.50+.50/0

Ph_2PH to **1** using 0.1 mol-% of KO*t*Bu gave **2a** in 71% yield (Scheme 1). Derivative **2a**, with two centers of chirality (α- and β-C), may be formed as a mixture of two pairs of diastereoisomers (*cis*-**2a**, *trans*-**2a**). The regioselectivity of base-catalyzed addition of secondary phosphanes to activated olefins has been discussed elsewhere,[8] the reactions are assumed to take place by Michael addition, the *anti*-Markownikow products being formed exclusively.



Scheme 1

Immediately after completion of the reaction of Ph_2PH with **1** the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows two resonances at $\delta_P = -1.86$ and -9.47 in a 1:2 intensity ratio. On extending the time of reaction the intensity of the signal at $\delta_P = -1.86$ increases at the expense of that at $\delta_P = -9.47$, which after 24 h had disappeared almost completely. The product **2a** obtained after workup of the reaction mixture shows only one signal in the $^{31}P\{^1H\}$ NMR spectrum at $\delta_P = -1.86$. These observations may be explained by an epimerization process by formation of an enol-type intermediate **G**[9] (Scheme 2).



Scheme 2

Initially, the *cis* isomer of **2a** (racemate) is formed preferably under kinetic control of the addition reaction, which is rearranged then to the thermodynamically more stable *trans*-**2a** (racemate).

The solution structure of *trans*-**2a** was obtained by analysis of the 400 MHz ^1H and $^1H\{^{31}P\}$ NMR spectrum (Figure 1a, 1b) in the range between $\delta_H = 0.8-2.95$. The ten nonequivalent protons H(1a)−H(6a) (A, B, C, D, E, F, G, H, M, and N) of the 1,2-disubstituted cyclohexane backbone and the ^{31}P nucleus, give rise to a complicated pattern in the ^1H and $^1H\{^{31}P\}$ NMR spectra by H,H and P,H coupling (Figure 1c). The multiplets in the ^1H NMR spectrum of **2a** at $\delta_H = 2.47$ (N) and 2.81 (M) with the appearance of a doublet of doublets of triplets or a doublet of triplets, respectively, may be assigned to the hydrogen atoms at C(1) ($\delta_C = 46.42$) and C(2) ($\delta_C = 36.18$) by analysis of the C,H-COSY NMR spectrum.[10] In a first approximation they may be considered as the MN part of an MNADEFX spin system [M, N = H(1a), H(2a); A = H(3a); D = H(6a); E = H(3e); F = H(6e); X = ^{31}P] with the P−H coupling being very small (0.64 Hz) for H(2a). Comparison of the ^1H NMR and $^1H\{^{31}P\}$ NMR spectrum reveals $^1H-^{31}P$ coupling fine structure of the resonances at $\delta_H = 1.01$, 1.45, 1.82, 1.92, and 2.47. As indicated by the H,H-COSY-45 NMR spectrum the protons with $\delta_H = 2.81$ (M) and 2.47 (N) are coupled to those with $\delta_H = 2.47$, 1.82, and 1.01 or $\delta_H = 2.81$, 1.92, and 1.74, respectively. The carbon atoms connected with the hydrogen atoms ($\delta_H = 1.82$ and 1.01 or $\delta_H = 1.92$ and 1.74) may be assigned to C(3) and C(6). A value of 9.6 Hz was determined for the coupling constant ^3J(HH) between the protons N and M. The resonances of H(N) and H(M) show a large (ca. 10 Hz) and a small (ca. 3.5−4.0 Hz) additional splitting due to vicinal H,H coupling with the hydrogen atoms of the respective neighbouring CH_2 groups. This pattern of ^3J(HH) is consistent with a bis(axial) position of the hydrogen atoms at C(1) and C(2) and a *trans* arrangement of the COOMe and PPh_2 substituents.

In derivatives of cyclohexane, vicinal H,H coupling constants are typically in the range between 7 and 9 Hz for hydrogen atoms in bis(axial) and 2−5 Hz in axial-equatorial or bis(equatorial) positions.[11] Due to overlapping of correlation peaks in the δ_H range between 0.8 and 2.0, a complete analysis of the H,H-COSY-45 NMR spectrum was not possible. In order to obtain an assignment of the $^{13}C\{^1H\}$ NMR signals for all carbon atoms of the cyclohexane backbone of **2a** an INADEQUATE spectrum[12] in the δ_C range between 12 and 50 was obtained. Making use of these results, the H,H-COSY-45 spectrum of **2a** could further be analyzed, thus allowing us to assign the hydrogen atoms in axial and equatorial positions of the cyclohexane backbone. Employing typical values for the geminal and vicinal H,H coupling constants,[11] the $^1H\{^{31}P\}$ NMR spectrum of **2a** was simulated using the program g NMR.[13] The result is shown in Figure 1b, the values obtained for the various coupling constants ^nJ(HH) ($n = 2-4$) and ^nJ(PH) ($n = 2-5$) are collected in Table 1. In agreement with results reported in the literature for 1,2-substituted derivatives of cyclohexane,[14] geminal H,H coupling constants are in a very narrow range between −13.81 and

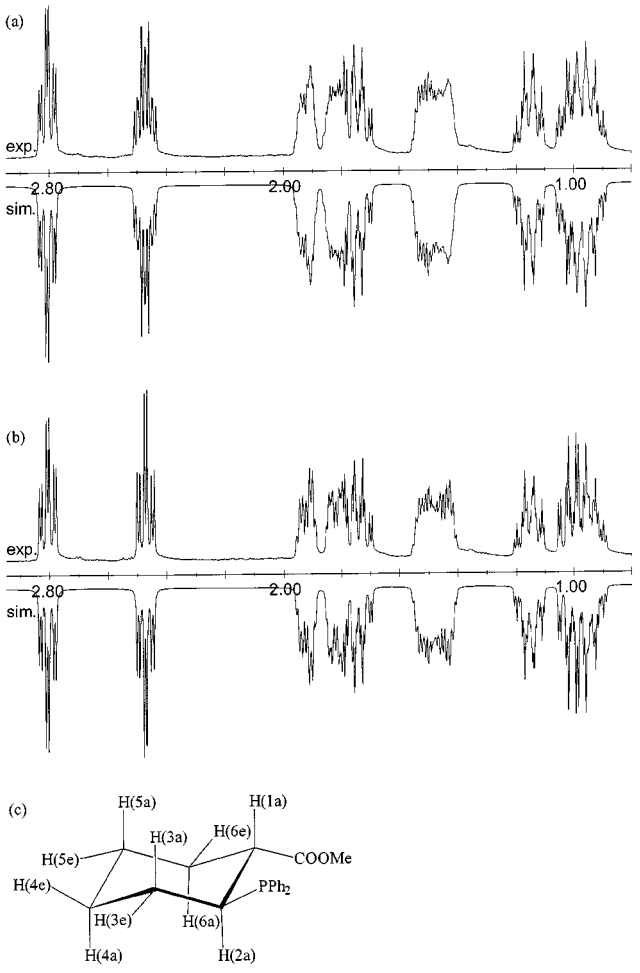


Figure 1. (a) ^{1}H NMR spectrum of **2a** (experimental, simulated); (b) ^{1}H{^{31}P} NMR spectrum of **2a** (experimental, simulated); (c) numbering scheme for the carbon and hydrogen atoms of the cyclohexyl backbones

−13.27 Hz. For axial protons ^3J(HH) is about 10 Hz, with significantly smaller values (ca. 4 or 5 Hz) being observed for protons in axial-equatorial or equatorial-equatorial positions.

The configurational analysis of **2a** was completed by the iterative simulation of the ^{1}H NMR spectrum (Figure 1a). To the best of our knowledge, this is the first complete analysis of a disubstituted derivative of cyclohexane with phosphorus as substituent. Consistent with the results obtained above, the vicinal coupling constants ^3J(PH) (4−7 Hz) obtained are typical for an H−C−C−P arrangement with dihedral angles of about 60°.[15a][15b] The small geminal coupling ^2J(PH) (0.64 Hz) (Table 1) indicates that in the most preferred conformation with respect to the P−C axis the lone pair at the phosphorus atom is in *trans* position to the hydrogen atom.[15c,15d]

Due to the asymmetric substitution at the α- and β-carbon atoms the phenyl groups of the Ph_2P substituent are chemically nonequivalent, as indicated by the doubling of the corresponding resonances in the ^{13}C{^{1}H} NMR spectrum. The assignment of the signals is based on comparison with pertinent data,[16] and ^{13}C{^{1}H}-DEPT NMR spectra.

Ester hydrolysis of **2a** with KOH in an ethanol/water mixture gave the potassium salt of the carboxylic acid **2b**. After concentration of the reaction mixture to dryness, the free acid was precipitated by acidification of the aqueous solution of the residue. The ^{31}P{^{1}H} NMR spectrum of **2b** shows a singlet at $\delta_P = -3.36$. A complete assignment of the 15 signals in the ^{13}C{^{1}H} NMR spectrum of **2b** could be achieved using the ^{13}C{^{1}H}-DEPT NMR spectrum, and by comparison with the results obtained for **2a** (see above). Making use of a C,H-COSY NMR and H,H-COSY-45 NMR spectrum all resonances in the ^{1}H NMR and the ^{1}H{^{31}P} NMR spectrum of **2b** could be assigned to the hydrogen atoms at C(1)−C(6), and their position in axial or equatorial sites of the cyclohexane ring system established. Although the lines are somewhat broadened compared with those of **2a**, the multiplet fine structure of the resonances corresponding to the protons on C(1) and C(2) ($\delta_H = 2.47$ and 2.86) are well resolved. By analysis of this part of the ^{1}H NMR and the ^{1}H{^{31}P} NMR spectrum, the vicinal H,H and H,P coupling constants ^3J(HH) and ^3J(PH) could be obtained. The pattern of the values of these coupling constants compares very well with that in **2a**, indicating a similar stereochemistry in both compounds.

Molecular Structure of 1-(Diphenylphosphanyl)cyclohexane-2-carboxylic Acid (2b)

In order to confirm the stereochemistry of **2b** as derived from the analysis of the NMR spectra, a crystal structure

Table 1. ^{1}H NMR spectroscopic data of **2a**; for the numbering of the hydrogen atoms see Figure 1c

δ_H values [ppm]			
H(1a)	2.47	H(2a)	2.81
H(3a)	1.01	H(3e)	1.82
H(4a)	1.15	H(4e)	1.52
H(5a)	0.94	H(5e)	1.45
H(6a)	1.74	H(6e)	1.92
P−H coupling constants [Hz]			
P−H(1a)	5.70	P−H(2a)	0.64
P−H(3a)	4.25	P−H(3e)	6.39
P−H(5e)	2.39	P−H(6e)	3.03
vicinal $H_{eq}-H_{eq}$ coupling constants [Hz]			
H(3e)−H(4e)	5.47	H(4e)−H(5e)	5.14
H(5e)−H(6e)	5.43		
long-range coupling constants [Hz]			
H(3e)−H(5e)	1.08	H(4e)−H(6e)	1.16
geminal $H_{ax}-H_{eq}$ coupling constants [Hz]			
H(3a)−H(3e)	−13.81	H(4a)−H(4e)	−13.27
H(5a)−H(5e)	−13.49	H(6a)−H(6e)	−13.38
vicinal $H_{ax}-H_{ax}$ coupling constants [Hz]			
H(1a)−H(2a)	9.72	H(2a)−H(3a)	10.19
H(3a)−H(4a)	10.88	H(4a)−H(5a)	10.90
H(5a)−H(6a)	11.09	H(6a)−H(1a)	9.82
vicinal $H_{ax}-H_{eq}$ coupling constants [Hz]			
H(2a)−H(3e)	3.66	H(3a)−H(4e)	3.56
H(5a)−H(4e)	3.76	H(4a)−H(3e)	3.53
H(4a)−H(5e)	3.87	H(1a)−H(6e)	3.92
H(5a)−H(6e)	3.70	H(6a)−H(5e)	3.62

analysis was performed. Recrystallization of **2b** from methanol afforded crystals suitable for X-ray structural analysis. Carboxylic acid **2b** crystallizes in the space group $P2_1/c$ with four molecules in the asymmetric unit showing an (*RS*)

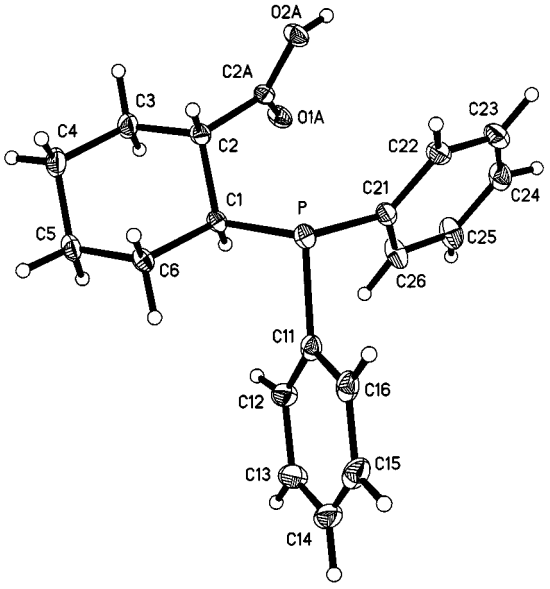


Figure 2. Molecular structure of **2b**; selected bond lengths [Å] and angles [°]: P−C(1) 1.859(3), P−C(11) 1.833(3), P−C(21) 1.832(3), C(1)−C(2) 1.540(3), C(2)−C(3) 1.538(4), C(1)−C(6) 1.533(3), C(5)−C(6) 1.518(4), C(3)−C(4) 1.510(4), C(4)−C(5) 1.504(4), C(2)−C(2A) 1.504(3), C(2A)−O(2A) 1.280(3), C(2A)−O(1A) 1.235(3); C(1)−P−C(11) 101.59(12), C(1)−P−C(21) 103.30(11), C(11)−P−C(21) 99.94(12), P−C(1)−C(2) 111.64(18), C(1)−C(2)−C(2A) 113.45(21), H(1)−C(1)−C(2)−H(2) −178.74, P−C(1)−C(2)−C(2A) 63.96(26)

and (*SR*) configuration. The structure (Figure 2) reveals the bis(equatorial) arrangement of the Ph_2P and COOH substituents with values for the H(1)−C(1)−C(2)−H(2) or P−C(1)−C(2)−C(2A) torsion angles of −178.7 or 63.96(26)°, respectively, in agreement with the solution structure of **2b** obtained by configurational analysis by means of NMR spectroscopy (see above). The carbon−phosphorus distances C(11)−P [1.833(3) Å], C(21)−P [1.832(3) Å], and C(1)−P [1.859(3) Å] (see caption to Figure 2) are in the typical range.[17] Due to the steric effect of the COOH group, the bond angle C(21)−P−C(1) [103.30(11)°] is somewhat enlarged compared with C(11)−P−C(1) [101.59(12)°] and C(21)−P−C(11) [99.94(12)°]. As a result the bond angle C(2A)−C(2)−C(3) [107.56(22)°] is compressed as compared with C(1)−C(2)−C(2A) [113.45(21)°].

Addition of $PhPH_2$ to Methyl 1-Cyclohexenecarboxylate (1)

The base-catalyzed 1:1 addition of $PhPH_2$ to **1** using 0.1 mol-% of KO*t*Bu proceeds stepwise with the secondary phosphane **3** being formed initially. Immediately after the completion of the addition reaction, four signals are observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture δ_P = −30.02, −36.89, −37.95, and −49.67, of which after 24 h only two signals remain (δ_P = −30.02 and −37.95). As a result of the asymmetric substitution at the phosphorus atom, **3** may exist as four pairs of diastereoisomers [*SSS*/*RRR* (*cis*), *SSR*/*RRS* (*cis*), *RSS*/*SRR* (*trans*), *RSR*/*SRS* (*trans*), the sequence of the stereogenic centers being C,C,P], which have been observed initially in the $^{31}P\{^1H\}$ NMR spectrum. Epimerization processes at the β-carbon and phosphorus atoms yield the thermodynamically most stable two *trans* diastereoisomers (see above). The $^{13}C\{^1H\}$ NMR spectrum of **3** shows 24 signals, 16 of them showing doublet fine structure due to C−P coupling. Assignment of all resonances was achieved by comparison with the corresponding data of **2a** and with the aid of a $^{13}C\{^1H\}$-DEPT NMR spectrum. The resonances at δ_C = 175.1 and 175.2 (CO) or 51.07 and 51.09 (OMe), respectively, may be assigned to the COOMe group. The complex ^1H NMR spectrum of the cyclohexane part of **3** could not be analyzed completely as described for **2a** (see above). The signals in the δ_H range 2.0−2.4 correspond to the hydrogen atoms on C(1) and C(2). For the two diastereoisomers of **3** two doublets at δ_H = 3.98 and 4.18 with a large ^1J(PH) splitting (208 and 210 Hz) are observed. Additional fine structure is due to ^3J(HH) coupling between the hydrogen atoms on P and C(2) (ca. 5.6 and 3.6 Hz, respectively).

If $PhPH_2$ is added to **1** in a 1:2 molar ratio using 0.1 mol-% of KO*t*Bu as catalyst, the tertiary phosphane **4a** is formed in high yield. The four diastereoisomers (*cis* and *trans* isomers) of the secondary phosphane **3** are formed initially. During this time, rearrangement of the *cis*/*trans* isomeric mixture of the intermediate **3** occurred to yield the *trans* isomer only. For a completion of the addition reaction with formation of the tertiary phosphane **4a** the reaction mixture had to be heated under reflux for 8 h.

The tertiary phosphane **4a** has a maximum of five stereogenic centers (four carbon atoms and one phosphorus atom), thus forming six pairs of enantiomers and four *meso* compounds. In all *meso* isomers the phosphorus atom (P) is pseudo-asymmetric,[18] while the molecule as a whole is achiral. The phosphorus atom in two of the racemic pairs [e.g. $S_CS_C(P)S_CS_C$] is achiral. In agreement with these considerations the $^{31}P\{^1H\}$ NMR spectrum of **4a** shows ten signals in a δ_P range typical for tertiary phosphanes,[19] five of them [δ_P = −2.23 (28%), −2.96 (11%), −5.17 (46%), −7.26 (8%), and −10.32 (5%)] having intensities higher than ca. 5%. Due to overlapping of the $^{13}C\{^1H\}$ and ^1H NMR resonances of the numerous diastereoisomers, signal assignments for **4a** were only possible for some groups.

Addition of Cy_2PH to Methyl 1-Cyclohexenecarboxylate (1)

Addition of Cy_2PH to methyl 1-cyclohexenecarboxylate (**1**) under the conditions employed for the synthesis of **2a**, **3**, and **4a** did not succeed due to its lower acidity compared with Ph_2PH and $PhPH_2$.[20] If the lithium phosphanide Cy_2PLi,[21] obtained by metallation of Cy_2PH with methyllithium, was employed in this addition reaction, a mixture of compounds was obtained. The BH_3 adduct of the tertiary phosphane **5a** was formed, however, in high yields if the borane complex $Cy_2P(BH_3)Li$ was used instead of the free phosphide. Phosphane−borane complexes[22] have recently

been used as valuable intermediates in the syntheses of phosphane derivatives not accessible by other methods.[23]

Due to the coupling of the phosphorus with the boron nucleus, the $^{31}P\{^1H\}$ NMR spectrum of **5a** shows a broadened signal at $\delta_P = 32.73$. In the ^{11}B NMR spectrum a doublet [^1J(BP) = 47 Hz] with additional fine structure is observed. In the $^{13}C\{^1H\}$ NMR spectrum of **5a**, 16 of the 20 resonances show $^{31}P-^{13}C$ coupling fine structure. The signal at $\delta_C = 41.0$ corresponds to C(1), while the resonances at 34.9 [^1J(PC) = 28 Hz], 32.09 [^1J(PC) = 9 Hz], and 31.6 [^1J(PC) = 11 Hz] may be assigned to the *ipso*-carbon atoms C(2), C(8), and C(9) using $^{13}C\{^1H\}$-DEPT NMR spectra. The assignments for C(2) and C(6) were proven to be correct by the combination of the results of the C,H-COSY- and H,H-COSY-45 NMR spectra. The ^1H NMR spectrum of **5a** could not be analyzed due to extensive signal overlapping.

Deprotection of **5a** with a large excess of morpholine gave the borane-free tertiary phosphane **5b** in high yield as indicated by $^{31}P\{^1H\}$ NMR spectrum ($\delta_P = 8.52$). This deprotection procedure has been used extensively by Imamoto and others.[24] After evaporation of morpholine and the morpholine−borane complex in vacuo, the free phosphane **5b** was obtained as a colorless oil. The $^{31}P\{^1H\}$ NMR spectrum of **5b** shows a singlet at $\delta_P = 8.52$. In the 100.6 MHz $^{13}C\{^1H\}$ NMR spectra of **5b** eleven of the 20 resonances show a $^{31}P-^{13}C$ coupling fine structure. Due to signal overlapping four resonances in the range of $\delta_C = 28.03-28.19$ could not be assigned. The signal at $\delta_C = 44.02$ [^2J(PC) = 20.3 Hz] corresponds to C(1), while the resonances at 33.35 [^1J(PC) = 22.4 Hz], 33.10 [^1J(PC) = 19.3 Hz], and 32.11 [^1J(PC) = 20.3 Hz] may be assigned to the *ipso*-carbon atoms C(2), C(8), and C(9) as indicated by the $^{13}C\{^1H\}$-DEPT NMR spectrum.

Molecular Structure of 5a

In order to elucidate the structure of **5a**, an X-ray crystallographic study was undertaken. The crystals used in the investigation were grown from a solution in methanol. A view of the molecular structure is given in Figure 3. It shows that the phosphorus atom occupies an equatorial position of each cyclohexyl ring while the COOMe substituent is in an axial position. Since the latter is directed towards the perimeter of the molecule, steric interactions involving this substituent are minimal. In fact, the smallest C−P−B bond angle [108(5)°] involves the cyclohexyl group bearing the ester, the others being on the average 4(1)° larger. The P−B and average P−C bond lengths of 1.920(6) and 1.841(9) Å, respectively, are normal.

The atoms P, B, and C(15) define a pseudo-mirror plane for the molecule which is violated mainly by the methoxycarbonyl group. Since this pseudo-asymmetry element lies perpendicular to the monoclinic axis of the noncentrosymmetric space group $P2_1$, a considerable proportion of the structure is distributed centrosymmetrically in the crystal. This coincidence, along with the large atomic displacements of the cyclohexyl groups are probably responsible for the large variation of the C−C bond lengths, 1.32(1)−1.61(1) Å, which should not be taken seriously.

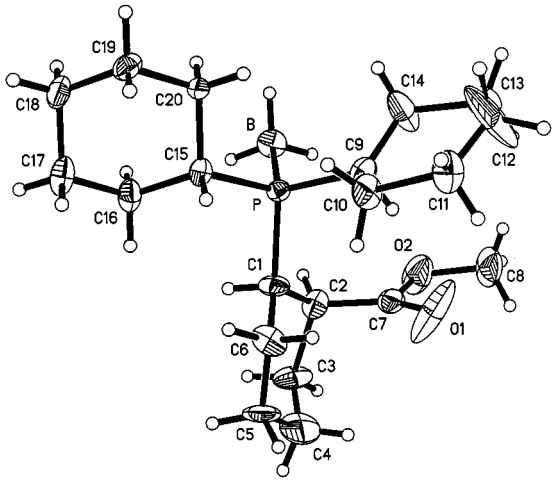
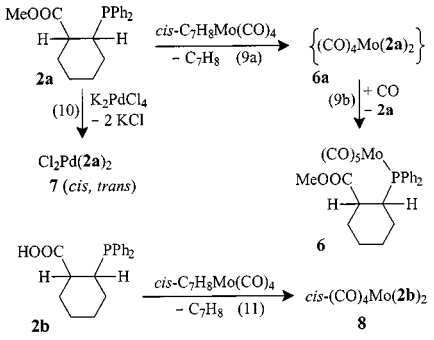


Figure 3. Molecular structure of **5a**; selected bond lengths [Å] and angles [°]: P−C(1) 1.835(6), P−C(9) 1.851(8), P−C(15) 1.837(4), P−B 1.920(6), C(2)−C(7) 1.505(11), C(7)−O(1) 1.267(11), C(7)−O(2) 1.378(9); C(1)−P−C(9) 107.9(3), C(1)−P−C(15) 104.9(4), C(9)−P−C(15) 107.8(3), C(1)−P−B 108.9(5), C(9)−P−B 114.4(5), C(15)−P−B 112.4(3), H(1)−C(1)−C(2)−H(2) 55.3(2)

Transition Metal Complexes of 2a and 2b

In order to obtain some information about the influence of the bulky cyclohexyl substituent on the ligand properties of the phosphanes **2a** and **2b**, molybdenum(0) and palladium(II) complexes were synthesized. Phosphane **2b** reacted with *cis*-$C_7H_8Mo(CO)_4$ in a straightforward manner to give the disubstituted complex **8** (Scheme 3), which is insoluble in most solvents. The corresponding reaction of **2a** proceeded very slowly. Initially, the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed in addition to the signal of **2a** two resonances at $\delta_P = 46.81, 46.24$, which may be assigned to the disubstituted complex **6a** formed as a mixture of diastereoisomers. If the reaction was run for a further couple of hours in order to complete the consumption of **2a** a third resonance at $\delta_P = 47.05$ appeared in the $^{31}P\{^1H\}$ NMR spectrum. This signal increased at the expense of those at $\delta_P = 46.81$ and 46.24 that disappear completely after ca 90 h. The resonance at $\delta_P = 47.05$ could be assigned to the monosubstituted complex **6** being formed by decomposition of **6a** with liberation of **2a**. Compound **6** was isolated from the reaction mixture by thin layer chromatography. Obviously, **2a** is too bulky to form a stable *cis*-disubstituted $Mo(CO)_4$ complex. Decomposition of **8** is not observed since it is precipitated from the reaction mixture during its formation.

The electronic parameter χ_i^{Ni} derived from the $\nu(CO)(A_1)$ stretching frequencies of the complexes $(CO)_3Ni(PR^1R^2R^3)$ may be taken as a measure for the electronic donor−acceptor properties of the phosphane ligands $PR^1R^2R^3$ as proposed by Tolman.[25a] As shown by us and others,[25b,25c] the analogous values χ_i^{Mo} obtained from the *cis*-$(CO)_4Mo(PR^1R^2R^3)_2$ complexes may be used instead of those obtained from the nickel complexes (χ_i^{Ni}). By compar-



Scheme 3

ison of the χ_i^{Mo} values obtained for **2b** (2020 cm^{-1}) with those of Ph_2PH (2028 cm^{-1}), Ph_3P (2023 cm^{-1}), Me_3P (2016 cm^{-1}), and Cy_3P (2010 cm^{-1}), phosphane **2b** may be placed in between Ph_3P and Me_3P.

On reaction of **2a** with K_2PdCl_4 the palladium(II) complexes of type **7** are formed. The ^{31}P NMR spectrum of the reaction mixture shows two intense signals at $\delta_P = 29.02$ and 28.84, and two weak resonances at $\delta_P = 28.05$ and 27.85. The low-field signals at $\delta_P \approx 29$ may be assigned to the *meso* (*SR*, *RS*) and *rac* forms (*SR*, *SR*) of the *trans* isomer, while the resonances at $\delta_P \approx 28$ correspond to the *cis* isomer. Since the difference in δ_P of the *cis* and *trans* isomers of **7** is much smaller than the typical range (10−15)[26] observed for $Cl_2Pd(PR_3)_2$ complexes it is of no diagnostic value. The assignment of the intense signals at $\delta_P = 29.02$ and 28.84 to the *trans* structure of **7** is based upon the triplet fine structure of some of the resonances in the $^{13}C\{^1H\}$ NMR spectrum of **7** (see Exp. Sect.). The carbon atoms in **7** represent the X part of an ABX spin system (A, B = ^{31}P, X = ^{13}C),[27a] which for a large value of $^2J(PP)$ as in *trans*-$Cl_2Pd(PR_3)_2$ complexes appears as a triplet.[27b][27c]

It has been shown that the ^{31}P NMR chemical shift of *trans*-$(PR_3)_2PdCl_2$ complexes correlates well with the steric parameters θ_{Tol} [28] or θ[29] of the ligands PR_3, derived from X-ray data. For the ligand **2a** a value of ca. 150° may be derived for θ_{Tol}.

Experimental Section

General: For experimental details, see Part 15 of this series.[1] − Phenylphosphane, diphenylphosphane,[30a,30b] dicyclohexylphosphane,[30c] and $C_7H_8Mo(CO)_4$ [31] were synthesized by known methods. Methyl 1-cyclohexenecarboxylate (**1**) was purchased from Aldrich GmbH. ^1H-, ^{31}P-, ^{13}C-, and ^{11}B NMR spectra were recorded with a Bruker AC 400 or AM 250 and a JEOL FX90 Q Fourier transform spectrometer. Mass spectra were obtained with a Varian MAT 311 A.

Synthesis of 2a: Diphenylphosphane (5.21 g, 28 mmol) and KO*t*Bu (0.34 g, 3 mmol) were dissolved in 50 mL of toluene. To this solution methyl 1-cyclohexenecarboxylate (4.21 g, 30 mmol) was added. After stirring for 12 h, 10 mL of water was added and the reaction mixture was neutralized with 6 mL of 0.5 M hydrochloric acid. The organic phase was separated and dried with Na_2SO_4. The product (8.44 g, 92%) obtained after evaporation of the solvent was recrystallized from methanol. Yield 6.49 g (71%). − **2a:** $C_{20}H_{23}O_2P$ (326.4): calcd. C 73.60, H 7.10; found C 73.69, H 6.95. − MS; *m/z:* 326 [M^+]. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 46.42 (C1, *J* = 19.3 Hz), 36.18 (C2, *J* = 16.3 Hz), 27.28 (C3, *J* = 4.1 Hz), 25.59 (C4, *J* = 4.1 Hz), 24.94 (C5), 30.05 (C6, *J* = 9.2 Hz), 175.13 (C7, *J* = 3.0 Hz), 137.28, 136.42 (C8, C12, *J* = 14.2, 17.3 Hz), 135.21, 133.03 (C9, C13, *J* = 21.0, 17.2 Hz), 128.60, 128.46 (C10, C14, *J* = 5.7, 7.6 Hz), 129.21, 128.19 (C11, C15), 51.04 (Me, *J* = 2.0 Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −1.86.

Synthesis of 3: The synthesis was performed as reported for **2a** using 3.08 g (28 mmol) of $PhPH_2$, 4.21 g (30 mmol) of methyl 1-cyclohexenecarboxylate, and 0.34 g (3 mmol) of KO*t*Bu as the catalyst. The product obtained was purified by distillation in vacuo (113−120 °C, < 0.01 mbar). Yield 4.64 g (66%). − **3:** $C_{14}H_{19}O_2P$ (250.3): calcd. C 67.19, H 7.65; found C 67.05, H 7.51. − MS; *m/z*: 250 [M^+]. − ^1H NMR (C_6D_6): δ = 2.32, 2.37 (H1, m), 2.12, 2.28 (H2, m), 0.78−1.90 (H3, m, H6, m), 1.03, 1.43 (H4, m), 0.94, 1.46 (H5, m), 3.39, 3.40 (Me, s), 7.00−7.60 (arom. H), 3.98, 4.18 [PH, *J*(PH) = 208, *J*(HH) = 5.6, *J*(PH) = 210, *J*(HH) = 3.6 Hz]. − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 48.4, 47.6 (C1, *J* = 12.2, 12.2 Hz), 36.1, 35.9 (C2, *J* = 14.2, 11.1 Hz), 31.5, 30.8, 30.6, 30.4 (C3, C6, *J* = 2.0, 8.1, 11.2, 8.1 Hz), 26.4, 25.9 (C4, *J* = 6.1, 7.1 Hz), 24.9, 24.8 (C5), 175.2, 175.1 (C7), 134.1, 133.6 (C8, *J* = 13.2, 13.2 Hz), 135.8, 135.0 (C9, *J* = 16.3, 15.3 Hz), 128.53, 128.51 (C10, *J* = 6.1, 5.6 Hz), 128.7, 128.4 (C11), 51.09, 51.07 (Me). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −30.02, −37.95 (*J* = 208, 210 Hz).

Synthesis of 4a: The synthesis of **4a** was performed as reported for **3** using 2.20 g (20 mmol) of $PhPH_2$, 7.01 g (50 mmol) of methyl 1-cyclohexenecarboxylate, and 0.22 g (2 mmol) of KO*t*Bu. The oily residue obtained after evaporation of the solvent could not, however, be purified by recrystallization from different solvents. Yield 6.95 g (89%). − **4a:** $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −0.6, −2.23, −2.96, −3.0, −3.12, −4.38, −5.17, −7.26, −7.31, −10.32.

Hydrolysis of 2a and 4a: Compounds **2a** (1.96 g, 6 mmol) or **4a** (6.95 g, 18 mmol) were added to a solution of 0.69 g (11 mmol) or 4.91 g (74 mmol) of KOH (85%) in a water/ethanol mixture (15:50 or 10:30 mL) with gentle warming. The reaction mixtures were heated under reflux for 4 h. Thereafter the solvents were distilled off in vacuo, and the residues were dissolved in 40 mL of water. Insoluble material was removed by filtration and the clear filtrate was acidified with hydrochloric acid (0.5 or 3 M). Colorless precipitates were formed, which were collected by filtration, washed with two aliquots of water (5 mL) and dried in vacuo. Yields 1.51 g (81%) for **2b**, 5.62 g (87%) for **4b**. − **2b**: $C_{19}H_{21}O_2P$ (312.3): calcd. C 73.06, H 6.78; found C 73.18, H 6.97. − ^1H NMR (C_6D_6): δ = 2.47 (H1a, m), 2.86 (H2a, m), 1.02 (H3a, m) 1.80 (H3e, m), 1.14 (H4a, m), 1.55 (H4e, m), 0.98 (H5a, m), 1.44 (H5e, m), 1.72 (H6a, m), 1.95 (H6e, m), 7.00−7.65 (arom. H), 11.9 (COOH, br.). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 45.7 (C1, *J* = 19.3 Hz), 35.5 (C2, *J* = 15.3 Hz), 26.7 (C3, *J* = 5.1 Hz), 25.0 (C4, *J* = 4.1 Hz), 24.6 (C5), 29.2 (C6, *J* = 9.2 Hz), 182.4 (C7, *J* = 5.1 Hz), 137.1, 136.3 (C8, C12, *J* = 14.2, 17.3 Hz), 135.2, 133.1 (C9, C13, *J* = 21.4, 18.3 Hz), 128.7, 128.5 (C10, C14, *J* = 6.1, 7.1 Hz), 129.2, 128.4 (C11, C15). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −3.36. − **4b:** $C_{20}H_{27}O_4P{\cdot}0.5\ H_2O$ (371.4): calcd. C 64.68, H 7.60; found C 64.05, H 7.19. − MS; *m/z*: 362 [M^+]. − ^1H NMR (C_6D_6): δ = 0.80−3.00 (H1−H6, m), 7.00−7.90 (arom. H), 12.0 (COOH, br.). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 45.8−48.6 (C1), 32.2−33.7 (C2), 24.6−30.8 (C3−C6), 133.9, 134.3 (C8, *J* = 21, 16 Hz), 134.8, 135.3, 136.0, 136.4 (C9, *J* = 20, 15, 16, 21 Hz), 127−131 (C10, C11), 181−182 (COOH). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 3.10, 2.02, −1.25, −4.45, −6.26.

Synthesis of 5a: To a solution of $Cy_2PH{\cdot}BH_3$ (5.74 g, 27 mmol) in 90 mL of THF was added *n*BuLi (15% in *n*-hexane) (11.79 g, 28 mmol) at −78 °C within a period of 30 min. The reaction mixture was stirred for 10 min at −76 °C and then allowed to warm up to ambient temperature. Thereafter the solution was again cooled down to −45 °C and 3.68 g (26 mmol) of methyl 1-cyclohexenecarboxylate was added. The reaction mixture was warmed to ambient temperature and stirred for 1 h. Water (35 mL) was added, and the reaction mixture was neutralized with 1 M hydrochloric acid. The organic phase was separated and dried with Na_2SO_4. The colorless residue left after removal of the solvent in vacuo was recrystallized from methanol. Yield 6.09 g (66%). − **5a:** $C_{20}H_{38}BO_2P$ (352.3): calcd. C 68.19, H 10.87; found C 67.56, H 10.87. − MS; *m*/*z*: 351 [M^+ − H]. − ^{1}H NMR (C_6D_6): δ = 3.30 (H1, m), 1.86 (H2, m), 1.33, 1.94 (H6, m), 2.19 (H8, m), 1.84 (H9, m), 3.41 (Me, s), 0.6−2.8 (overlapping multiplets). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 41.03 (C1), 34.91 (C2, *J* = 27.9 Hz), 32.02 (C6, *J* = 9.4 Hz), 175.35 (C7, *J* = 1.3 Hz), 32.09 (C8, *J* = 9.0 Hz), 31.62 (C9, *J* = 11.2 Hz), 51.94 (Me), 29.94, 29.17 (*J* = 3.9 Hz), 28.80, 28.62 (*J* = 12.2 Hz), 28.23 (*J* = 9.2 Hz), 28.19 (*J* = 8.0 Hz), 27.86 (*J* = 9.8 Hz), 27.77 (*J* = 8.6 Hz), 27.70 (*J* = 4.4 Hz), 27.15 (*J* = 1.3 Hz), 26.98 (*J* = 1.2 Hz), 24.02 (*J* = 4.0 Hz), 22.50 (*J* = 1.1 Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 32.73 [$^1J(^{11}B-^{31}P)$ = 47 Hz].

Deprotection of 5a: Compound **5a** (0.27 g, 0.8 mmol) was dissolved in 15 mL of morpholine. The solution was stirred for 2 h at 90 °C. Thereafter the solvent and the morpholine−borane complex were removed in vacuo (100 °C, < 0.01 mbar). The crude **5b** was obtained as a colorless oil. Purification was achieved by recrystallization from methanol. Yield 0.25 g (98%). − **5b:** $C_{20}H_{35}O_2P$ (338.5): calcd. C 70.97, H 10.42; found C 70.14, H 10.35. − MS; *m*/*z*: 338 [M^+ − H]. − ^{1}H NMR (C_6D_6): δ = 2.85 (m, H1), 3.48 (s, Me), 1.00−2.35 (aliph. H). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 44.02 (C1, *J* = 20.3 Hz), 33.35 (C2, *J* = 22.4 Hz), 33.10 (C8, *J* = 10.3 Hz), 32.11 (C9, *J* = 20.3 Hz), 50.60 (Me), 174.52 (C7), 32.51 (*J* = 17.3 Hz), 31.75 (*J* = 14.2 Hz), 31.02 (*J* = 9.2 Hz), 30.23 (*J* = 10.2 Hz), 30.22 (*J* = 8.1 Hz), 28.19−28.03 (4 C atoms), 27.43 (*J* = 5.1 Hz), 26.97−26.94 (2 C atoms), 25.16 (*J* = 6.1 Hz), 21.95. − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 8.52.

Synthesis of 6: $C_7H_8Mo(CO)_4$ (0.15 g, 0.5 mmol) and **2a** (0.33 g, 1 mmol) were dissolved in 10 mL of dichloromethane. The reaction mixture was stirred at ambient temperature for 96 h. Thereafter the solvent was removed in vacuo (20 °C, 0.01 mbar) and the remaining solid was purified by thin layer chromatography (SiO_2 PSC plates, Merck). The yellow zone containing **6** was extracted with CH_2Cl_2 and the solvent removed in vacuo. Yield: 0.11 g (38%). − **6:** $C_{25}H_{23}MoO_7P$ (562.4): calcd. C 53.34, H 4.12; found C 53.25, H 4.40. − MS; *m*/*z*: 533 [M^+ (^{95}Mo) − CO − 4 H]. − ^{1}H NMR (C_6D_6): δ = 2.80 (m, H1), 3.08 (m, H2), 0.8−1.8, 2.2 (m, H3−H6), 2.88 (s, Me), 6.95−7.93 (arom. H). − $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 45.2 (C1), 38.5 (C2, *J* = 14 Hz), 26.0 (C3, *J* = 12 Hz), 28.6 (C4, *J* = 8 Hz), 24.7 (C5), 31.0 (C6, *J* = 6 Hz), 174.8 (C7, *J* = 3 Hz), 137.3, 133.3 (C8, C12, *J* = 32, 30 Hz), 135.4, 132.8 (C9, C13, *J* = 12, 11 Hz), 129.3, 129.1 (C10, C14, *J* = 8, 10 Hz), 131.2, 130.3 (C11, C15, *J* = 2, 2 Hz), 51.5 (Me), 207.2 (CO_{eq}, *J* = 9 Hz), 211.1 (CO_{ax}, *J* = 23 Hz). − $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 47.05. − IR (KBr disc, cm^{-1}): $\tilde{\nu}$ = 2072, 1961, 1930, 1915.

Synthesis of 7: Dichloromethane (30 mL) and methanol (10 mL) were added to a mixture of **2a** (0.65 g, 2 mmol) and potassium tetrachloropalladate (K_2PdCl_4) (0.33 g, 1 mmol). The mixture was stirred at ambient temperature for 5 d and the solid material was removed by filtration through a suction funnel. After removal of all volatiles from the filtrate in vacuo (20 °C, < 0.01 mbar) **7** was obtained as a yellow solid. Yield 0.77 g (93%). − **7:** $C_{40}H_{36}Cl_2O_4P_2Pd$ (830.1): calcd. C 57.88, H 5.59; found C 57.52, H 5.6. − ^{1}H NMR (CD_2Cl_2): δ = 2.40 (m, H1), 3.45 (m, H2), 0.97, 1.62 (m, H5), 3.03, 3.08 (s, Me), 7.96 (m, H9), 7.71 (m, H13), 1.72, 1.59, 2.42, 0.86, 1.64, 1.43 (aliph. H), 7.25−7.65 (arom. H). −

Table 2. Crystal data of **2b** and **5a**

	2b	**5a**
Empirical formula	$C_{19}H_{21}O_2P$	$C_{20}H_{38}BO_2P$
Molecular mass	312.3	352.3
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$
a [Å]	8.090(2)	6.859(1)
b [Å]	8.590(2)	11.429(2)
c [Å]	23.910(5)	13.913(2)
β [°]	90.52(3)	100.15(1)
V [Å^3]	1661.5(6)	1073.6(3)
Z	4	2
D(calcd.) [g cm^{-3}]	1.249	1.090
Radiation	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71073	0.71073
Temperature [K]	243	293
Diffractometer	Siemens P4	Siemens P3
Crystal size [mm]	0.30 × 0.36 × 0.60	0.15 × 0.24 × 0.44
μ [mm^{-1}]	0.17	0.14
Transmission	0.642−0.448	0.804−0.923
2 theta (max.) [°]	49.98	50.09
Limiting indices	$0 \le h \le 9$, $0 \le k \le 10$, $-28 \le l \le 28$	$-8 \le h \le 8$, $-13 \le k \le 13$, $-16 \le l \le 16$
Reflections	3123	6018
Unique	2903	3797
R(int)	0.0382	0.0177
Observed ($F > 4\sigma$)	1918	2792
*R*1 (observed)	0.0504	0.1018
*wR*2 (all data)	0.1285	0.2719
Goodness-of-fit	0.881	1.770
Parameters	281	221
Δ*E* [e Å^{-3}]	0.42/−0.34	0.86/−0.74

$^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 44.49, 44.37 (C1), 33.93, 33.94 (C2, *N* = 24.0, 22.4 Hz), 24.80, 24.72 (C5), 31.28, 31.22, 28.62, 28.49, 26.00, 25.93 (C3, C4, C6, *N* = 7.6, 7.6, 5.0, 5.0, 14.8, 15.2 Hz), 174.49, 174.39 (C7), 51.28, 51.24 (Me), 128.87, 128.85, 125.45, 125.35 (C8, C12, *N* = 39.2, 39.2, 45.8, 46.2 Hz), 136.74, 136.70 133.69, 133.64 (C9, C13, *N* = 12.8, 12.8, 11.6, 11.2 Hz), 127.98, 127.96, 127.91, 127.88 (C10, C14, *N* = 9.6, 10.2, 10.6, 10.6 Hz), 131.06, 131.06, 130.18, 130.10 (C11, C15). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 28.84, 29.01.

Synthesis of 8: To a solution of $C_7H_8Mo(CO)_4$ (0.15 g, 0.5 mmol) in 10 mL of dichloromethane was added **2b** (0.31 g, 1 mmol), and the reaction mixture was stirred at ambient temperature for 12 h. The crystals precipitated were collected by filtration using a suction funnel, washed with three aliquots of 2 mL of dichloromethane and dried in vacuo (20 °C, 0.01 mbar). Yield 0.33 g (78%). – **8:** $C_{42}H_{42}MoO_8P_2$ (832.7): calcd. C 60.58, H 5.08; found C 59.80, H 4.96. – HPLC ESI(–) MS; *m/z*: 749 [M^- – 3 CO – H]. – IR (KBr disc): $\tilde{\nu}$ = 2020, 1915, 1901, 1859 cm^{-1}.

X-ray Structure of 2b: A crystal (0.30 × 0.36 × 0.60 mm) was sealed in a glass capillary. X-ray data were measured with a Siemens P4 diffractometer equipped with a graphite monochromator and employing Mo-K_α radiation. The structure was solved by direct methods using the SHELXTL program package. Selected crystallographic details are listed in the caption to Figure 2. Experimental data are collected in Table 2.

X-ray Structure of 5a: A crystal (0.15 × 0.24 × 0.44 mm) was glued to a glass fiber. X-ray data were collected with a Siemens P3 diffractometer equipped with a graphite monochromator and employing Mo-K_α radiation. A complete set of intensities including Friedel opposites were measured, and they were corrected empirically for absorption. Systematic absences suggested that the space group was either $P2_1$ or $P2_1/m$ and since the latter would impose mirror symmetry on **5a**, the chirality of **5a** suggested that the former would be correct. Direct methods assuming $P2_1$ yield the positions of the P, B, and cyclohexyl-C atoms, but the arrangement of these atoms obeyed the mirror symmetry required by $P2_1/m$. A subsequent difference Fourier synthesis contained a mirror-related pair of COOC fragments, and the pseudo-mirror plane was broken by incorporating only the entity bonded to the C(2) atom. The structure was refined anisotropically with isotropic hydrogen atoms added in idealized positions by various riding models, and the discussion is based on this model. Unfortunately, the Flack absolute structure parameter, 0.4(2), has been determined imprecisely, so the crystal under investigation may have contained molecules exhibiting the (*R*,*R*) configuration shown in Figure 3, the mirror-related (*S*,*S*) configuration or a mixture of both. Because of the poor convergence encountered in the refinement of the structure in the noncentrosymmetric space group, an attempt was made to develop the structure in $P2_1/m$. This effort led to satisfactory coordinates for the cyclohexyl group divided by the mirror plane and the P and B atoms, but other atoms were poorly defined, the C(8) atom residing on the mirror plane, therefore this model was discarded. Experimental data are collected in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147247 (**2b**) and -146877 (**5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by Ministerium für Bildung, Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie. Celanese GmbH and Clariant GmbH are thanked for financial support. We thank Prof. Dr. R. Eujen for his assistance running the INADEQUATE NMR spectra.

[1] D. J. Brauer, M. Hingst, C. Liek, K. W. Kottsieper, M. Tepper, S. Schenk, O. Stelzer, W. S. Sheldrick, *J. Mol. Catal. A: Chemical*, submitted for publication.
[2] [2a] M. Peuckert, W. Keim, *Organometallics* **1982**, *2*, 594. – [2b] S. Mecking, W. Keim, *Organometallics* **1996**, *15*, 2650. – [2c] W. Keim, R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21.
[3] J. Bank, P. Steinert, B. Windmüller, W. Wolfsberger, H. Werner, *J. Chem. Soc., Dalton. Trans.* **1996**, 1153.
[4] A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27; C. S. Slone, D. A. Weinberger, C. A. Mirkin, *Progr. Inorg. Chem.* **1999**, *48*, 233.
[5] [5a] K. Issleib, H. Zimmermann, *Z. Anorg. Allg. Chem.* **1967**, *353*, 197. – [5b] J. A. van Doorn, N. Meijboom, *Phosphorus, Sulfur, Silicon* **1989**, *42*, 211.
[6] [6a] M. Hingst, M. Tepper, O. Stelzer, *Eur. J. Inorg. Chem.* **1998**, 73. – [6b] C. Liek, P. Machnitzki, T. Nickel, S. Schenk, M. Tepper, O. Stelzer, *Z. Naturforsch.* **1999**, *54b*, 1532.
[7] [7a] O. Herd, A. Heßler, M. Hingst, M. Tepper, O. Stelzer, *J. Organomet. Chem.* **1996**, *522*, 69. – [7b] O. Herd, A. Heßler, M. Hingst, P. Machnitzki, M. Tepper, O. Stelzer, *Catal. Today* **1998**, *42*, 413.
[8] H. R. Hudson, in *The Chemistry of Organophosphorus Compounds*, vol.1 (Ed.: F. R. Hartley) John Wiley & Sons, Chichester, **1990**, p. 385.
[9] P. Braunstein, S. Coco Cea, A. DeCian, J. Fischer, *Inorg. Chem.* **1992**, *31*, 4203; W. Wolfsberger, J. Bank, H. Werner, *Z. Naturforsch.* **1995**, *50b*, 1319.
[10] P. Bigler, *NMR Spectroscopy: Processing Strategies*, VCH Publishers, Weinheim, **1997**.
[11] [11a] H. Friebolin, *Ein- und zweidimensionale NMR-Spektroskopie*, p. 90, VCH Publishers, Weinheim, **1992**. – [11b] J. W. Emsley, J. Feeney, L. H. Suttcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy*, vol. 1, Pergamon Press, Oxford, London, New York, Toronto, Sydney, Paris, Braunschweig, **1966**.
[12] [12a] J. Buddrus, H. Bauer, *Angew. Chem.* **1987**, *99*, 642; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 625. – [12b] H. Kessler, M. Gehrke, C. Griesinger, *Angew. Chem.* **1988**, *100*, 507; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 490.
[13] g NMR program, Ivory Soft, **1995**, P. H. M. Budezelaar, Cherwell Scientific Publishing, Ltd., **1995**.
[14] [14a] H. Günther, *NMR-Spektroskopie*, Georg Thieme Verlag, Stuttgart, **1973**. – [14b] H. Booth, *Progress in Nuclear Magnetic Resonance Spectroscopy*, vol. 5 (Eds.: J. W. Emsley, J. Feeney, L. H. Sutliffe), Pergamon Press, Oxford, **1969**, p. 149.
[15] [15a] W. G. Bentrude, W. N. Setzer, L. D. Quin, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, vol. 8, VCH Publishers, Deerfield Beach, **1987**, p. 366. – [15b] C. Benzra, *J. Am. Chem. Soc.* **1973**, *95*, 6890. – [15c] J. P. Albrand, D. Gagnaire, J. B. Robert, *J. Chem. Soc., Chem. Commun.* **1968**, 1469; *Bull. Soc. Chim. Fr.* **1969**, 40. – [15d] T. A. Albright, *Org. Magnet. Res.* **1976**, *8*, 489; G. Mavel, *Ann. Report NMR Spectroscopy* **1973**, *5b*, 1.
[16] H. O. Kalinowski, S. Berger, S. Braun, *^{13}C NMR Spektroskopie, Georg Thieme Verlag, Stuttgart,* **1984***, p. 237; J. Schraml, M. Capka, V. Blechta, Magn. Reson. Chem.* **1992**, *30*, 544.
[17] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
[18] E. L. Eliel, S. H. Wilen, *Organische Stereochemie*, Wiley-VCH, Weinheim, **1998**.
[19] S. Berger, S. Braun, H. O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, vol. 3 ("^{31}P NMR Spektroskopie"), Georg Thieme Verlag, Stuttgart, **1993**.
[20] K. Issleib, R. Kümmel, *J. Organomet. Chem.* **1965**, *3*, 84.
[21] K. Issleib, A. Tzschach, H. U. Block, *Chem. Ber.* **1968**, *100*, 2931.

[22] H. Schmidbaur, *J. Organomet. Chem.* **1980**, *200*, 287.
[23] [23a] B. Mohr, D. M. Lynn, R. H. Grubbs, *Organometallics* **1996**, *15*, 4317. – [23b] T. Imamoto, T. Oshiki, T. Onozawa, M. Matsuo, T. Hikosaka, M. Yanagawa, *Heteroatom Chem.* **1992**, *3*, 563. – [23c] T. Oshiki, T. Imamoto, *J. Am. Chem. Soc.* **1992**, *114*, 3975.
[24] T. Imamoto, *Pure Appl. Chem.* **1993**, *65*, 655; S. Juge, M. Stephan, J. A. Laffitte, J. P. Genet, *Tetrahedron Lett.* **1990**, *31*, 6357.
[25] [25a] C. A. Tolman, *Chem. Rev* **1977**, *77*, 313. – [25b] T. Bartik, T. Himmler, H. G. Schulte, K. Seevogel, *J. Organomet. Chem.* **1984**, *272*, 29. M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, E. Unger, *J. Chem. Soc., Dalton Trans.* **1975**, 1207. – [25c] C. L. Hyde, D. J. Darensbourg, *Inorg. Chem.* **1973**, *12*, 1286.
[26] S. O. Grim, R. L. Keiter, *Inorg. Chim. Acta* **1970**, *4*, 56; D. A. Redfield, J. H. Nelson, *Inorg. Chem.* **1973**, *12*, 15.
[27] [27a] R. J. Abraham, H. J. Bernstein, *Can. J. Chem.* **1961**, *39*, 216. – [27b] F. B. Ogilvie, J. M. Jenkins, J. G. Verkade, *J. Am. Chem. Soc.* **1970**, *92*, 1916. – [27c] G. Balimann, H. Motschi, P. S. Pregosin, *Inorg. Chim. Acta* **1977**, *23*, 191.
[28] T. Bartik, T. Himmler, *J. Organomet. Chem.* **1985**, *293*, 343; T. Bartik, B. Bartik, B. E. Hanson, I. Guo, I. Toth, *Organometallics* **1993**, *12*, 164.
[29] A. Immirzi, A. Musco, *Inorg. Chim. Acta* **1977**, *25*, L41.
[30] [30a] F. Pass, H. Schindlbaur, *Monatsh. Chem.* **1959**, *90*, 148. – [30b] W. Gee, R. A. Shaw, B. C. Smith, *Inorg. Synth.* **1967**, *9*, 19. – [30c] K. Issleib, A. Tzschach, *Chem. Ber.* **1959**, *92*, 704.
[31] R. B. King, in *Organometallic Synthesis*, vol. 1 ("Transition Metal Compounds") (Eds.: J. Eisch, R. B. King), Academic Press, New York, **1965**, p. 124.

Received July 19, 2000
[I00286]