# A New Highly Active Diphosphane-Palladium(II) Complex as a Catalyst Precursor for the Heck Reaction

Sven Sjövall,[a] Maria H. Johansson,[a] and Carlaxel Andersson*[a]

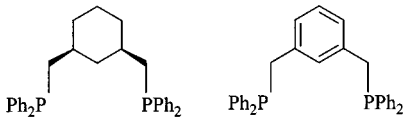
**Keywords:** Palladium / Phosphanes / Catalysis / Heck reaction

The new diphosphane ligand *cis*-1,3-bis[(diphenylphosphanyl)methyl]cyclohexane (**4**) has been prepared and has allowed the synthesis of the palladium complex *cis*-[Pd(**4**)$(CO_2CF_3)_2$] (**6**). To obtain *cis* complexation of the diphosphane in **6** the cyclohexane skeleton adopts a chair conformation with a diaxial orientation of the substituents, a structure that has been verified by an X-ray structure determination. This complex efficiently catalyses the vinylation of iodo- and bromobenzenes in high yields. For the best reaction, with methyl acrylate and iodobenzene, a yield of >98% was obtained with an average turnover frequency of 11 760 $h^{-1}$ and a turnover number of 1 176 000.

## Introduction

Novel or improved homogeneous catalytic reactivities are continuously being achieved with a large variety of organometallic complexes. The main method of controlling and directing the reactivity of a metal in such a compound is by modifying the steric and/or electronic properties of the coordinated ligands.[1] The effect of using different "fine-tuned" ligands in catalysis is perhaps best illustrated by the widely studied Heck reaction,[2] the generation of $sp^2-sp^2$ carbon−carbon bonds by palladium-catalysed arylation of olefins with aryl halides.[3] In order to increase the catalyst efficiency in this potentially industrially important reaction a great deal of efforts have been made recently and this has led to the development of improved palladium catalysts in terms of both stability and activity.[4−10] A variety of different ligands have been investigated for these high-performing catalysts, such as sterically hindered, highly basic phosphanes,[4] carbenes,[5] cyclometallated phosphanes,[6] phosphites,[7] mono- and bis-chelating diphosphanes[8] and imines,[9] as well as more traditional Heck coupling catalysts combined with additives such as $[PPh_4]Cl$ or $PtBu_3$.[10] A key feature of several of these systems is the stabilisation of the active catalyst by either ligand chelation or steric shielding of the transition metal centre. This confers a high thermal stability on the catalyst allowing long reaction times and high reaction temperatures without noticeable catalyst deactivation. Intrigued by the delicate ligand effects in the Heck reaction we have initiated a general program aimed at the development and catalytic investigation of bidentate phosphane ligands that can potentially cyclometallate at an $sp^3$ carbon.

In this paper we report the synthesis of the stereospecific diphosphane *cis*-1,3-$(Ph_2PCH_2)_2C_6H_{10}$ (**4**), which is the fully aliphatic analogue to the well-known tridentate PCP ligand 1,3-$(Ph_2PCH_2)_2C_6H_4$ (**4′**).[11] Thus, by changing the ring carbons from $sp^2$ to $sp^3$, the different electronic properties of ligand **4** relative to **4′** should modify the reactivity of the resulting complex. However, when we first investigated the coordination chemistry of ligand **4** we found a totally different coordination mode, as evidenced by X-ray crystallography, from the analogous aromatic diphosphane. We also describe some preliminary results on the catalytic vinylation of aryl halides by the $Pd^{II}$ complex synthesised herein.




**4** **4′**

## Results and Discussion

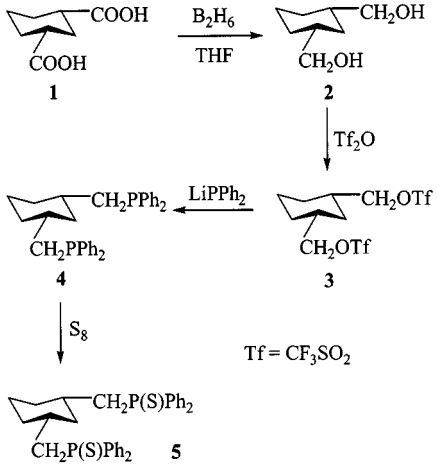
### Ligand Synthesis

Based on the fact that the sterically demanding substituents of *cis*-1,3-cyclohexanedicarboxylic acid (**1**) prefer an equatorial orientation,[12] we have chosen **1** as the starting material for the preparation of *cis*-1,3-bis[(diphenylphosphanyl)methyl]cyclohexane (**4**) following the procedure depicted in Scheme 1. In the initial step, **1** was reduced with an excess of $BH_3$ in THF yielding *cis*-1,3-bis(hydroxymethyl)cyclohexane (**2**). A good leaving group was introduced in **2** by treating it with a stoichiometric amount of trifluoromethanesulfonic anhydride in the presence of a base, giving *cis*-1,3-bis[(trifluoromethylsulfonyloxy)methyl]cyclohexane (**3**). This colourless oil undergoes decomposition within hours, even when it is stored below −18 °C, and was therefore used immediately after isolation. The reaction of **3** with 2 equiv. of $LiPPh_2$ in THF furnished phosphane **4**. An NMR spectroscopic analysis showed the phosphane to be essentially pure and, because of its high air-sensitivity, it was used without further purification. However, sulfuriz-

[a] Inorganic Chemistry, Centre for Chemistry and Chemical Engineering, Lund University,
P.O. Box 124, 221 00 Lund, Sweden

  1434−1948/01/1111−2907 $ 17.50+.50/0 

ation of the phosphane, by treating it with an excess of elementary sulfur, results in the air-stable compound *cis*-1,3-bis[(diphenylphosphane sulfide)methyl]cyclohexane (**5**), which was fully characterised including elemental analysis. Clean removal of the sulfur atoms in **5** with Raney-Nickel or trichlorosilane,[13] was unsuccessful and sulfurization therefore does not provide a simple route to analytically pure **4**.

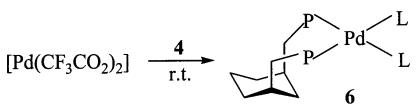



Scheme 1

The $^{13}C\{^1H\}$ NMR spectra of compounds **2**−**5** imply $C_s$ symmetry and thus confirm the *cis* arrangement of the functional groups in the 1,3-positions of the cyclohexane ring. Hence, the respective cyclohexane skeletons give rise to four sets of signals: those of the chemically equivalent methine groups and three chemically different sets of methylene groups. Furthermore, the triflate substituents in **3** cause a significant downfield shift (to δ = 81.2) for the α-methylene group, which is in accordance with its good leaving group capacity.

**Complexation**

Our initial studies revealed that the choice of palladium precursor was of importance, since attempts to synthesise a monomeric palladium complex using a dihalide precursor failed. Hence, when $[PdCl_2(NCPh)_2]$ was stirred overnight with 1 equiv. of **4** in $CH_2Cl_2$ a yellow insoluble material was isolated in high yield. Shaw and co-workers have earlier described similar results, which they explained with the formation of a large-ring polynuclear palladium compound.[14] Instead, the preparation of a monomeric palladium complex was achieved by reacting $[Pd(CO_2CF_3)_2]$ with 1 equiv. of **4** in THF, yielding **6** as air-stable crystals in reasonable yield (Scheme 2).




Phenyls on P omitted for clarity
L = $CF_3CO_2$

Scheme 2

The integral sum in the $^1H$ NMR spectrum of **6** suggests no displacement of hydrogen from ligand **4**. In addition, one of the protons in the cyclohexane ring is substantially shifted downfield to δ = 4.46, implying a through-space interaction with the metal centre. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet, which is consistent with a mirror-plane symmetry of **6**, and the position at δ = 16.5 is in accordance with other Pd *cis*-diphosphane complexes.[15] In the $^{13}C\{^1H\}$ NMR spectrum, the C2 signal occurs as a triplet in the normal aliphatic region (δ = 28.6, $^3J_{PC}$ = 6.6 Hz). Hence, the NMR spectroscopic data is consistent with the structure shown in Scheme 2, i.e. the ligand binds to the metal centre in a *cis*-diphosphane fashion with a diaxial arrangement of the substituents on the cyclohexane ring. This energetically more demanding conformation of the cyclohexane ring, relative to the diequatorial counterpart, was not expected.[12] Moreover, the coordination mode of **4** also deviates substantially from the fully aromatic analogue 1,3-bis[(diphenylphosphanyl)methyl]benzene, which coordinates as a tridentate PCP ligand in a *trans*-configuration.[11] The reason for the reluctance of ligand **4** to activate a C−H bond, even though the spacing between its phosphorous atoms is sufficiently large for *trans*-coordination when diequatorially oriented, must be due to an improper arrangement of its C−H bonds with respect to the palladium metal centre.

An X-ray crystallographic investigation has confirmed the structure of **6**. Yellow blocks were obtained upon crystallisation by layering $Et_2O$ onto a THF solution of **6**. A perspective view of the molecular structure is shown in Figure 1 including selected bond lengths and angles.

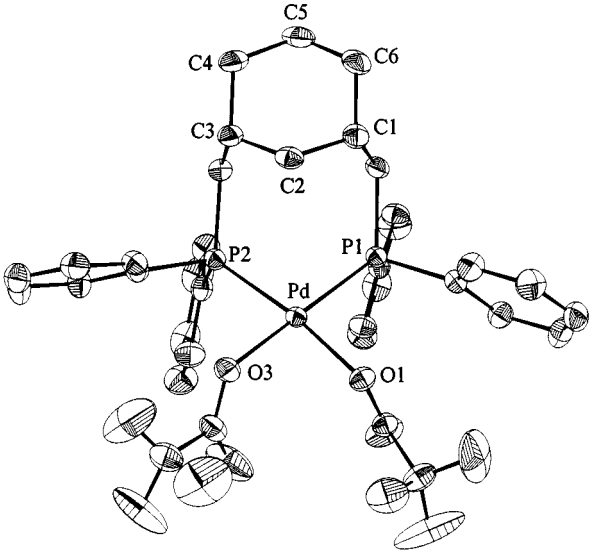



Figure 1. Perspective view (DIAMOND) of **6** (thermal ellipsoids at 30% probability); bond lengths (Å) and angles (deg) with estimated standard deviations: Pd−O1 2.086(2), Pd−O3 2.074(2), Pd−P1 2.261(1), Pd−P2 2.252(1), O1−Pd−O3 83.36(10), P1−Pd−P2 93.81(4), P1−Pd−O1 93.36(8), P1−Pd−O3 173.83(7)

Complex **6** exhibits a *cis* square-planar geometry. The congested conformation of the cyclohexane ring causes the chelate to distort the complex slightly away from an ideal geometry by widening the P1−Pd−P2 angle [93.81(4)°]. Small deviations in the bond lengths, for example for Pd−P1 [2.261(1) Å] and Pd−P2 [2.252(1) Å], illustrate the pseudo-symmetric property of **6**. The diaxial disposition of the substituents on the cyclohexane ring causes the ring to lie well above the plane of the complex (Figure 2). Note the correlation of the position of the equatorial hydrogen on C2 (Figure 2) and its downfield shift in the $^1$H NMR spectrum of **6** (vide supra). The strained cyclohexane ring adopts the chair conformation, where the endocyclic bond angles deviate substantially from free cyclohexane (111.5°).[16]

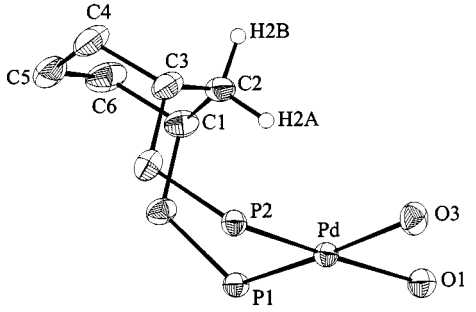
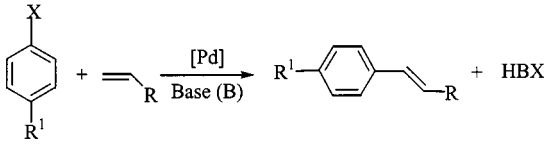



Figure 2. A plot showing the chair conformation of the cyclohexane skeleton in **6** including the hydrogens on C2; bond angles (deg) with estimated standard deviations: C1−C2−C3 115.2 (3), C2−C3−C4 109.0(3), C3−C4−C5 113.3(3), C4−C5−C6 112.2(4), C5−C6−C1 = 112.9(3), C6−C1−C2 108.8 (3)

## Catalysis

As mentioned in the introduction, some chelating diphosphane-palladium(II) complexes are high-performing precatalysts for the vinylation of aryl halides (Scheme 3), as recently communicated by Shaw et al.[8a]




Scheme 3

Until then, the prevailing belief was that diphosphanes were unsuitable ligands in Heck catalysis.[17] Intrigued by this observation we decided to investigate complex **6** as a precatalyst for the same reaction.

As shown in Table 1, complex **6** is indeed very active in the arylation of a variety of olefins with aryl iodides and bromides. The reaction of methyl acrylate with iodobenzene is by far the most active system in the present study where a TON of $1.2 \times 10^6$ was achieved (TOF up to $1.2 \times 10^4$, Table 1, entry 2). This TON is the highest observed so far for a chelating palladium-diphosphane catalyst,[18] and also among the highest reported overall for a phosphane-containing catalyst in a high-yielding Heck reaction.[19] The screening of different bases ($Na_2CO_3$, NaOAc, lutidine, $NBu_3$ and DABCO) revealed that **6** performs best with $NBu_3$ as base. Of the polar solvents tested, *N*-methylpyrrolidone (NMP) was found to be superior in terms of reaction rate (entry 1), relative to *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide, when using the same reaction conditions. The reaction can also be carried out in semi-polar and non-polar solvents, although at lower rates. However, as far as we are aware, the TONs in dioxane (333 000, entry 5) and mesitylene (320 000, entry 6) are unsurpassed.[20] The catalyst system is sensitive and to ensure high catalytic activity the efficient exclusion of air was necessary, as well as the use of pure solvents and starting materials. Complex **6** is thermally stable up to at least 140 °C, presumably due to the stabilising chelate effect, but the reactions were routinely performed at 120 °C for comparative purposes.[8a] To further verify the thermal stability of the complex we intentionally left some reactions for prolonged times: some reaction times could probably be reduced, and in no case was any noticeable formation of palladium metal observed. The catalyst remains highly active after the reaction is completed, and upon addition of more substrates the catalytic reaction resumes at essentially the same rate using the reaction conditions described (Table 1, entry 1).

As expected, both the electronic properties of the reacting olefin and steric hindrance are decisive factors for the efficiency of the catalyst: methyl acrylate gave a higher average reaction rate than styrene or *n*-butyl acrylate regardless of the aryl halide employed. However, the TONs for the arylation of *n*-butyl acrylate (495 000, entry 3) and styrene (490 000, entry 4) with iodobenzene are again among the highest reported.[6a] Complex **6** was also capable of catalysing the vinylation of relatively unreactive bromobenzenes in excellent yields (entry 7−10). Here it is also evident that an electron-withdrawing group on the aryl ring increases the reaction rate. Unfortunately, **6** is not able to convert the relatively cheaper aryl chlorides to any degree, although the effect of adding expensive promoters like [$NBu_4$][Br] was not tested.[21]

The trend of reactivity for iodo-, bromo- and chlorobenzenes indicates that an oxidative addition of the aryl halide to the catalyst is involved in the rate-determining step for the Heck reaction. Whether this mechanism involves a $Pd^{II}$/$Pd^{IV}$ catalytic cycle, as previously suggested for other palladium-diphosphane catalysts,[8a] or not, is unclear for the moment. However, the greater efficiency of the eight-membered chelate complex **6** in catalysing the Heck reaction, compared to the previously reported four- to seven-membered ones,[8a] suggests that chelate-opening is involved in the catalytic cycle. A similar striking chelate effect on catalytic activity has been reoported by Milstein and coworkers.[4b]

In summary, ligand **4** coordinates as a normal *cis*-diphosphane, which is opposed to its fully aromatic analogue. This is made possible by the diaxial orientation of the substituents in the cyclohexane skeleton. An investigation of the catalytic activity of the resulting diphosphane-palladium

Table 1. Selected results of the Heck reaction with complex **6**; experiments conducted with 1.2 equivalents of $Bu_3N$ in NMP except where noted

| No. | Olefin (mmol)[a] | ArX (mmol)[b] | **6** (mmol) × $10^{-5}$ | time/temp (h)/(°C) | TON[c] | Yield (%)[d] | TOF ($h^{-1}$)[e] |
|---|---|---|---|---|---|---|---|
| 1 | mac (6) | PhI (9) | 6 | 9/120 | 100 000 | 100 | 11 111 |
| 2 | mac (24) | PhI (36) | 2 | 100/120 | 1176 000 | 98 | 11 760 |
| 3 | bac (10) | PhI (15) | 2 | 56/120 | 495 000 | 99 | 8 840 |
| 4 | sty (10) | PhI (15) | 2 | 54/120 | 490 000 | 98[f] | 9 075 |
| 5[g] | mac (10) | PhI (15) | 3 | 36/120 | 333 000 | 99 | 9 250 |
| 6[h] | mac (10) | PhI (15) | 3 | 95/120 | 320 000 | 95 | 3 370 |
| 7 | mac (10) | 4-bba (15) | 3 | 32/120 | 333 000 | 99 | 10 410 |
| 8 | bac (10) | 4-bba (15) | 3 | 41/120 | 333 000 | 99 | 8 125 |
| 9 | mac (10) | PhBr (15) | 4 | 79/140 | 235 000 | 94 | 2 975 |
| 10 | bac (10) | PhBr (15) | 4 | 90/140 | 207 500 | 83 | 2 310 |

[a] mac = methyl acrylate, bac = *n*-butyl acrylate, sty = styrene. – [b] 4-bba = 4-bromobenzaldehyde. – [c] TON = Turnover number (mol product/mol catalyst). – [d] GC yield using 2-methylnaphthalene as internal standard. – [e] TOF = Turnover frequency (mol product/mol catalyst × time). – [f] *trans*-stilbene/*cis*-stilbene = 9. – [g] Dioxane as solvent. – [h] Mesitylene as solvent.

complex **6** has shown it to be by far the most active chelating diphosphane-$Pd^{II}$ catalyst reported for the Heck reaction, and it shows an exceedingly high catalytic activity including reactions of non-activated aryl bromides. Huge TONs are also found in semi-polar or non-polar solvents, and **6** should be placed amongst the most active phosphane-containing catalysts overall for vinylation of aryl halides. We believe that the catalytic cycle is assisted by a labile chelate.

## Experimental Section

All experiments with metal complexes and phosphane ligands were carried out under an atmosphere of argon or nitrogen in a Braun glovebox equipped with an inert gas purifier, or by using standard Schlenk and vacuum-line techniques. All non-deuterated solvents, reagent grade or better, were freshly distilled under a nitrogen atmosphere: $Et_2O$, THF, toluene, *n*-hexane, and *n*-pentane from sodium/benzophenone ketyl; $CH_2Cl_2$ and $CHCl_3$ from $CaH_2$. Deuterated solvents were used as received. Commercially available reagents was purchased from Aldrich and used without purification. The *cis*-1,3-cyclohexanedicarboxylic acid (**1**) was isolated from the commercially available *cis,trans* mixture according to a literature procedure.[22] The lithium phosphide $LiPPh_2$ was prepared by the drop-wise addition of *n*BuLi to an equimolar amount of $PPh_2Cl$ below −60 °C, allowed to age for 2 h at room temperature, and thereafter used in situ for further reaction.

NMR spectra were recorded either on a Varian Unity 300 MHz instrument ($^1H$, $^{31}P$, $^{19}F$) or a Bruker ARX 500 MHz spectrometer ($^{13}C$). A $^{13}C$ DEPT NMR spectrum was routinely recorded for each compound. The NMR spectroscopic measurements were performed in $CDCl_3$ unless stated otherwise. $^1H$ and $^{13}C$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane but were measured relative to the residual $^1H$ in the deuterated solvent. $^{31}P$ NMR chemical shifts are reported in ppm downfield from an external 85% solution of phosphoric acid. $^{19}F$ NMR chemical shifts are reported in ppm downfield from an external sample of $CClF_3$ in $CDCl_3$ v = virtual. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. Fast Atom Bombardment (FAB) mass spectroscopic data were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Gas chromatographic analyses were performed on a Varian 3300 instrument equipped with a 12-m BP-10 fused silica capillary column (0.22 ID). Elemental analyses were performed by MikroKemi AB, Uppsala, Sweden.

Except for the workup of reaction mixtures, all Heck reactions were carried out under argon. Stock solutions of catalyst were used due to low concentrations. These were freshly prepared under anaerobic conditions for each reaction and used only once. The solvents, aryl halides and bases were distilled when possible and used immediately. The olefin substrates were carefully deoxygenated by at least three freeze-pump-thaw cycles.

**General Procedure for the Heck Reactions:** The solvent (10 mL), aryl halide, base, olefin, 2-methylnaphthalene (internal standard) and a magnet were placed in a Schlenk tube with a screw cap. Three freeze-pump-thaw cycles were performed before the addition of an appropriate volume of the catalyst stock solution. The Schlenk tube was sealed and placed in a pre-heated, temperature-controlled oil-bath. The mixture was stirred vigorously for the desired time. Workup was achieved by pouring the cooled reaction mixture into an excess of 5% HCl (aq) and extracting with $CH_2Cl_2$ or $Et_2O$. The combined organic phases were neutralised with 10% $NaHCO_3$ (aq) and dried with $MgSO_4$. After removal of the solvent the products were analysed by $^1H$ NMR spectroscopy and MS; the yields were determined by GC. All of the products are known compounds.[23]

**Preparation of *cis*-1,3-Bis(hydroxymethyl)cyclohexane (2):** Over a period of 1.5 h, $BH_3$ (100 mL, 2.2 equiv. as a 1.0 M THF solution) was slowly added to an ice-cooled, stirred solution of **1** (7.75 g, 45.0 mmol) in 20 mL of THF. After the addition was completed the suspension was stirred at room temperature for an additional 2 h, and the excess hydride was thereafter carefully decomposed by the addition of 20 mL of 2 M HCl (aq). The water phase was neutralised with NaOH and about 8−10 g of $K_2CO_3$ was added in order to transfer the water-soluble diol to the organic phase. The organic phase was isolated and the water phase was further extracted with 2 × 10 mL of $CHCl_3$; the combined organic phases were then dried over silica. Filtration and removal of the organic solvent resulted in a highly viscous, colourless oil which solidified upon standing. Yield: 5.71 g (88%). – $^1H$ NMR ($D_2O$): δ = 0.45 (q, $^2J_{HH}$, $^3J_{HH}$ = 12.0 Hz, 1 H, $CH_eH_a$), 0.71 (m, 2 H, $CH_2$), 1.15 (m, 1 H, $CH_eH_a$), 1.39 (m, 2 H, CH), 1.62 (m, 4 H, $CH_2$), 3.41 (d, $^3J_{HH}$ = 6.3 Hz, 4 H, $CH_2OH$). – $^{13}C\{^1H\}$ NMR ($D_2O$): δ = 25.1

(s, $CH_2CH_2CH_2$), 29.3 (s, $CHCH_2CH_2$), 32.3 (s, $CHCH_2CH$), 39.4 [s, $(CH)_2CHCH_2$], 67.9 (s, $CH_2OH$). − MS ($FAB^+$): *m*/*z* = 142 [$C_8H_{14}O_2^+$]. − $C_8H_{16}O_2$ (144.21): calcd. C 66.6, H 11.2; found C 66.5, H 11.4.

**Preparation of *cis*-1,3-Bis[(trifluoromethylsulfonyloxy)methyl]cyclohexane (3):** A stirred suspension of **2** (1.00 g, 6.93 mmol) and pyridine (1.15 mL, 14.2 mmol) in 15 mL of $CH_2Cl_2$ was cooled in an ice-bath. Dropwise addition of trifluoromethanesulfonic anhydride (2.40 mL, 14.2 mmol), diluted with 10 mL of $CH_2Cl_2$, resulted in a yellow-tinted solution. After 30 min., the ice-bath was removed and the solution was allowed to age for an additional hour. The suspension was then filtered through a short plug of silica on a G3 glass frit and the plug was rinsed with additional $CH_2Cl_2$. Removal of the organic solvent on a rotary evaporator resulted in a colourless oil. The compound is too unstable for microanalysis. Yield 2.29 g (82%). − $^1$H NMR: δ = 0.89 (q, $^2J_{HH}$, $^3J_{HH}$ = 12.0 Hz, 1 H, $CH_eH_a$), 1.03 (m, 2 H, $CH_2$), 1.37 (m, 1 H, $CH_eH_a$), 1.97−1.83 (m region, 6 H, CH and $CH_2$), 4.36 (d, $^3J_{HH}$ = 6.0 Hz, 4 H, $CH_2OTf$). − $^{13}$C{$^1$H} NMR: δ = 24.6 (s, $CH_2CH_2CH_2$), 28.4 (s, $CHCH_2CH_2$), 31.1 (s, $CHCH_2CH$), 37.2 [s, $(CH)_2CHCH_2$], 81.2 (s, $CH_2OTf$), 119.0 (q, $^1J_{FC}$ = 320 Hz, $CF_3$). − $^{19}$F NMR: δ = 51.5 (s, $CF_3$).

**Preparation of *cis*-1,3-Bis[(diphenylphosphanyl)methyl]cyclohexane (4):** A solution of **3** (2.33 g, 5.71 mmol) in 15 mL of THF was carefully added to a cooled (−60 °C) and stirred deep-red solution of $LiPPh_2$ (2.14 g, 11.4 mmol) in 15 mL of THF. The solution was allowed to reach room temperature over a period of 1 h, and stirred for an additional 18 h. The orange solution was then quenched with 5 mL of degassed water and the colourless organic phase was isolated. The water phase was further extracted with 2 × 10 mL of $Et_2O$ and the combined organic phases were dried over silica. Filtration and removal of the solvent resulted in a viscous, almost colourless oil which partly solidified upon standing. NMR spectroscopic analysis showed the product to be essentially pure. The air-sensitivity precluded further purification and the phosphane was therefore not subjected to microanalysis. Yield: 2.52 g (92%). − $^1$H NMR: δ = 1.41−0.84 (m region, 6 H, $CH_2$), 1.72 (m, 1 H, $CH_2$), 1.93 (m, 2 H, CH), 2.02 (d, $^3J_{HH}$ = 6.9 Hz, 4 H, $CH_2P$), 2.24 (m, 1 H, $CH_2$), 7.33 (m, 12 H, Ar), 7.43 (m, 8 H, Ar). − $^{13}$C{$^1$H} NMR: δ = 26.0 (s, $CH_2CH_2CH_2$), 34.5 (d, $^3J_{PC}$ = 9.7 Hz, $CHCH_2CH_2$), 35.3 [d, $^2J_{PC}$ = 13.6 Hz, $(CH)_2CHCH_2$], 36.7 (d, $^1J_{PC}$ = 13.1 Hz, $CH_2P$), 43.5 (t, $^3J_{PC}$ = 9.6 Hz, $CHCH_2CH$), 128.3 (br. s, CH), 132.8 (m, CH), 133.9 (m, CH), 134.1 (m, CH), 139.4 (m, CH). − $^{31}$P{$^1$H} NMR: δ = −21.3 (s).

**Preparation of *cis*-1,3-Bis[(diphenylphosphane sulfide)methyl]cyclohexane (5).** Sulfur (1.76 g, 6.86 mmol) was added to a solution of **4** (827 mg, 1.72 mmol) in 15 mL of toluene and the mixture was stirred for 16 h. The solution was decanted and removal of the toluene resulted in a pale yellow solid. The crude compound was loaded on a column of silica of 10 cm height. Eluting with *n*-hexane removed the remaining elementary sulfur and the white solid **5** was recovered by washing the column with $CH_2Cl_2$ and removing the solvent under vacuum. Yield: 759 mg (81%). − $^1$H NMR: δ = 0.74 (m, 2 H, $CH_2$), 0.87 (q, $^2J_{HH}$, $^3J_{HH}$ = 11.6 Hz, 1 H, $CH_eH_a$), 1.12 (m, 1 H, $CH_eH_a$), 2.01−1.42 (m region, 6 H, CH and $CH_2$), 2.32 (m, 4 H, $CH_2P$), 7.43 (m, 12 H, Ar), 7.82 (m, 8 H, Ar). − $^{13}$C{$^1$H} NMR: δ = 25.6 (s, $CH_2CH_2CH_2$), 33.0 (br. s, $CHCH_2CH_2$), 34.0 [d, $^2J_{PC}$ = 6.9 Hz, $(CH)_2CHCH_2$], 39.2 (d, $^1J_{PC}$ = 55.1 Hz, $CH_2P$), 43.5 (t, $^3J_{PC}$ = 10.2 Hz, $CHCH_2CH$), 128.5 (m, CH), 130.9 (m, CH), 131.3 (br. s, CH), 133.2 (d, $J_{PC}$ = 28.2 Hz, CH), 134.2 (d, $J_{PC}$ = 28.9 Hz, CH). − $^{31}$P{$^1$H} NMR: δ = 37.1 (s). − MS ($FAB^+$): *m*/*z* = 544 [$C_{32}H_{34}P_2S_2^+$]. − $C_{32}H_{34}P_2S_2$ (544.69): calcd. C 70.6, H 6.3, S 11.8; found C 70.4, H 6.1, S 11.6.

**Reaction of 4 with $[Pd(CO_2CF_3)_2]$. Formation of $[Pd(4)(CO_2CF_3)_2]$ (6):** Phosphane **4** (25.1 mg, 52.2 μmol) and $[Pd(CO_2CF_3)_2]$ (17.4 mg, 52.2 μmol) were dissolved in 3 mL of THF. After stirring for 3 h, 12 mL of $Et_2O$ was layered on top of the red THF solution. After 3 days yellow air-stable crystals were harvested. Yield: 20.5 mg (48%). − $^1$H NMR ($CD_2Cl_2$): δ = 1.89−1.54 (m region, 7 H, $CH_2$), 2.25 (m, 4 H, $CH_2P$), 2.81 (m, 2 H, CH), 4.46 (br. d, $^2J_{HH}$ = 15.3 Hz, 1 H, $CH_eH_a$), 7.39 (m, 16 H, Ar), 7.82 (m, 4 H, Ar). − $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): δ = 28.3 (s, $CH_2CH_2CH_2$), 28.6 (t, $^3J_{PC}$ = 6.6 Hz, $CHCH_2CH$), 33.5−33.0 (m region, CH and $CH_2$), 116.4 (q, $^1J_{FC}$ = 291 Hz, $CF_3$), 129.0 (vt, $J_{PC}$ = 11.1 Hz, CH), 129.7 (vt, $J_{PC}$ = 11.1 Hz, CH), 131.9 (s, CH), 132.5 (s, CH), 132.9 (vt, $J_{PC}$ = 10.0 Hz, CH), 133.8 (vt, $J_{PC}$ = 11.1 Hz, CH), 160.8 (q, $^2J_{FC}$ = 36.2 Hz, C=O). − $^{31}$P{$^1$H} NMR ($CD_2Cl_2$): δ = 16.5 (s). − $^{19}$F NMR ($CD_2Cl_2$): δ = 52.8 (s). − MS ($FAB^+$): *m*/*z* = 812 [$C_{36}H_{34}F_6O_4P_2Pd^+$] (correct isotope pattern). − $C_{36}H_{34}F_6O_4P_2Pd$ (813.00): calcd. C 53.2, H 4.2; found C 53.2, H 4.2.

**X-ray Crystal Structure Determination of Complex 6:**[24] Crystal data and details of the data collection and refinement are given in Table 2. The intensity data were collected at 293 K with a Bruker Smart CCD system using ω scans and a rotating anode with Mo-$K_\alpha$ radiation (λ = 0.710 73 Å).[25] The intensities were corrected for Lorentz, polarisation and absorption effects with SADABS.[26]

Table 2. Crystallographic data

| | Complex **6** |
|---|---|
| Formula | $C_{36}H_{34}F_6O_4P_2Pd$ |
| Crystal description | Yellow prism |
| Crystal size (mm) | 0.19 × 0.11 × 0.10 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| *a* (Å) | 10.950(2) |
| *b* (Å) | 12.174(2) |
| *c* (Å) | 15.014(3) |
| α (°) | 91.83(3) |
| β (°) | 104.93(3) |
| γ (°) | 114.76(3) |
| *V* (Å$^3$) | 1733.7(6) |
| *Z* | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.557 |
| No. of refl. used for cell parameters | 7080 |
| μ (mm$^{-1}$) | 0.698 |
| *F*(000) | 824 |
| $T_{min}/T_{max}$ | 0.745/0.920 |
| θ- range | 1.4−31.7 |
| No. of collected refl | 19208 |
| No. of unique refl. | 10293 |
| No. of observed refl., *m* [$I > 2\sigma(I)$] | 7589 |
| Parameters, *n* | 442 |
| *hkl* range | $-15 < h < 16$<br>$-17 < k < 17$<br>$-21 < l < 21$ |
| *R*[a] | 0.0486 |
| w*R*[b] | 0.1264 |
| *S*[c] | 1.035 |
| (Δ/σ) max | 0.002 |
| ρ max/min (e$^-$/Å$^3$) | 1.482/−0.958 |

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. − [b] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$. − [c] $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

The first 50 frames were collected again at the end to check for decay. No decay was observed. All reflections were merged and integrated with SAINT.[27] The structure was solved by direct methods and refined by a full-matrix least-squares calculation on $F^2$.[28] Non-H atoms were refined with anisotropic displacement parameters. The hydrogen atoms were constrained to their parent sites using a riding model.

## Acknowledgments

We thank Mr David Dominguez-Guiteéres for helpful assistance in the laboratory. Financial support by the TFR (The Swedish Research Council for Engineering Sciences) and the NFR (The Swedish Natural Science Research Council) is gratefully acknowledged.

[1] [1a] J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Book, CA, **1987**. – [1b] *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**.

[2] For excellent reviews see: [2a] I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009−3066. – [2b] A. de Meijere, F. E. Meyer, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379−2411. – [2c] V. V. Grushin, H. Alper, *Chem. Rev.* **1994**, *94*, 1047−1062.

[3] [3a] R. F. Heck, J. P. Nolley, *J. Org. Chem.* **1972**, *37*, 2320−2322. – [3b] T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581.

[4] [4a] M. Portnoy, Y. Ben-David, D. Milstein, *Organometallics* **1993**, *12*, 4734−4735. – [4b] Y. Ben-David, M. Portnoy, M Gozin, D. Milstein, *Organometallics* **1992**, *11*, 1995−1996.

[5] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371−2374.

[6] [6a] B. L. Shaw, S. D. Perera, E. A. Staley, *Chem. Commun.* **1998**, 1361−1362. – [6b] W. A. Herrmann, C. Brossmer, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357−1364. – [6c] W. A. Herrmann, C. Brossmer, K. Öfele, C. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844−1849.

[7] [7a] D. Morales-Morales, R. Redon, C. Yung, C. M. Jensen, *Chem. Commun.* **2000**, 1619−1620. – [7b] D. Morales-Morales, C. Grause, K. Kasaoka, R. Redon, R. E. Cramer, C. M. Jensen, *Inorg. Chim. Acta* **2000**, *300*, 958−963. – [7c] M. Beller, A. Zapf, *Synlett.* **1998**, 792−793. – [7d] D. A. Albisson, R. B. Bedford, P. N. Scully, *Tetrahedron Lett.* **1998**, *39*, 9793−9796.

[8] [8a] B. L. Shaw, S. D. Perera, *Chem. Commun.* **1998**, 1863−1864. – [8b] M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688.

[9] M. Ohff, A. Ohff, D. Milstein, *Chem. Commun.* **1999**, 357−358.

[10] [10a] A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10−11. – [10b] M T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem. Int. Ed.* **1998**, *37*, 481−483.

[11] [11a] P. R. Ashton, P. Calcagno, N. Spencer K. D. Harris, D. Philip, *Org. Lett.* **2000**, *2*, 1365−1368. – [11b] F. Gorla, L. M. Venanzi, M. Luigi, A. Albinati, *Organometallics* **1994**, *13*, 43−54. – [11c] H. Rimml, L. M. Venanzi, *J. Organomet. Chem.* **1983**, *259*, C6−C7.

[12] T. L. Westman, R. Paredes, S. B. Wallace, *J. Org. Chem.* **1963**, *28*, 3512−3518.

[13] [13a] S. R. Gilbertson, C.-W. T. Chang, *J. Org. Chem.* **1998**, *23*, 8424−8430. – [13b] M. B. Goli, S. O. Grim, *Tetrahedron Lett.* **1991**, *32*, 3631−3634.

[14] N. A. Al-Salem, W. S. McDonald, R. Markham, M. C. Norton, B. L. Shaw, *J. Chem. Soc., Dalton Trans.* **1980**, 59−63.

[15] L. E. Overman, D. J. Poon, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 518−521.

[16] G. Mann, *Z. Chem.* **1990**, *30*, 1−9.

[17] [17a] R. F. Heck, *Vinyl Substitution with Organometallic Intermediates*, in *Comprehensive Organic Synthesis* (Eds. B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, *4*, p. 833. – [17b] W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2−7.

[18] A TON of 139 000 was reported for the reaction of iodobenzene with methyl acrylate after 9 days at 95 °C with a yield of 92%. See ref.[8a]

[19] [19a] A. S. Gruber, D. Zim, G. Ebeling, A. L. Monteiro, J. Dupont, *Org. Lett.* **2000**, *2*, 1287−1290. – [19b] See ref.[9]

[20] A TON of 130 300 was reported for the reaction of iodobenzene with methyl acrylate in mesitylene after 16 h at 140 °C with a yield of 93%. See ref.[9]

[21] [21a] T Jeffery, *Tetrahedron Lett.* **1985**, *26*, 2667−2669. – [21b] T. Jeffery, *J. Chem. Soc., Chem. Commun.* **1984**, 1287−1289.

[22] A. Skita, R. Rossler, *Ber. Dtsch. Chem. Ges.* **1939**, *72B*, 265−269.

[23] T. Yoshino, Y. Nagata, E. Itoh, M. Hashimoto, T. Katoh, S. Terashima, *Tetrahedron Lett.* **1996**, *37*, 3475−3478.

[24] Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-158133. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1233/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[25] BrukerAXS, *SMART*, Area Detector Control Software, Bruker Analytical X-ray System, Madison, Wisconsic, USA, **1995**.

[26] G. M. Sheldrick, *SADABS*: Program for Absorption Correction, University of Göttingen, Göttingen, Germany, **1996**.

[27] BrukerAXS, *SAINT*, Integration Software, Bruker Analytical X-ray System, Madison, Wisconsin, USA, **1995**.

[28] G. M. Sheldrick, *SHELXTL5.1*, Program for Structure Solution and Least Square Refinement, University of Göttingen, Göttingen, Germany, **1998**.

Received April 18, 2001
[I01138]