

New Diphosphane Ligands Based on Bisphenol A Backbones – Synthesis and Coordination Chemistry

Jarl Ivar van der Vlugt,^[a] Michiel M. P. Grutters,^[a] Allison M. Mills,^[b] Huub Kooijman,^[b] Anthony L. Spek,^[b] and Dieter Vogt^{*[a]}

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A series of easily accessible diphosphane compounds **1–4**, based on bisphenol A derived backbones, has been prepared. A straightforward two-step synthetic route has been employed to obtain these new ligands in good yields from cheap starting materials. Molecular structures for both compound **2** and its oxidized form (**5**·H₂O) have been determined and are discussed in detail. The coordination of ligand **2** to

palladium, platinum, and rhodium precursors has been studied by NMR spectroscopy as well as X-ray crystallography. The molecular structures of the face-to-face dimeric species $[\{\text{PdCl}(\text{CH}_3)(\text{2})\}_2]$ (**6**), $[\{\text{PtCl}_2(\text{2})\}_2]$ (**7**), and $[\{\text{RhCl}(\text{CO})(\text{2})\}_2]$ (**8**) are described in detail.

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Introduction

The coordination chemistry of diphosphane ligands with a variety of transition metals has been widely studied and several types of coordination modes have been established over the years.^[1,2] Numerous families of novel ligands have been synthesized,^[3] with emphasis on *cis*-chelation to form monomeric metal complexes. As well as designing ligands based on desired behaviour towards transition metals and the catalytic activity of the resultant systems, the approach of modular design and availability from cheap resources has gained significant importance.

We have chosen Bisphenol A as a somewhat neglected yet promising starting material for the synthesis of a new ligand class.^[4,5] A wide range of these bisphenols is commercially available at low price since they are used as components in epoxy resins. Generic structures are easily available by simple acid catalyzed condensation of a ketone with two molecules of a phenol.^[6] Based on these versatile compounds we employed a straightforward two-step synthetic route to novel P-containing compounds (Scheme 1).

In the first step, the phenol groups were protected by methylation with iodomethane. Subsequently, selective *ortho*-lithiation of both phenyl rings was followed by reaction with the phosphane source ClPPh₂. Filtration and evaporation of the solvent followed by washing of the crude prod-

uct with methanol afforded the pure compounds in overall yields of 40–50%. Using this method, we obtained compounds **1–3** based on derivatives of the Bisphenol A backbone. Furthermore, the silicon derivative **4** was synthesized in good yield starting from 4-bromoanisole and dichlorodimethylsilane via a modified two-step route. Compounds **1–4** were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy, as well as by elemental analysis. We have previously reported this synthetic route, focussing on the synthesis and catalytic applicability of a ligand derived from 1,2-diphenylbenzene as the backbone.^[5]

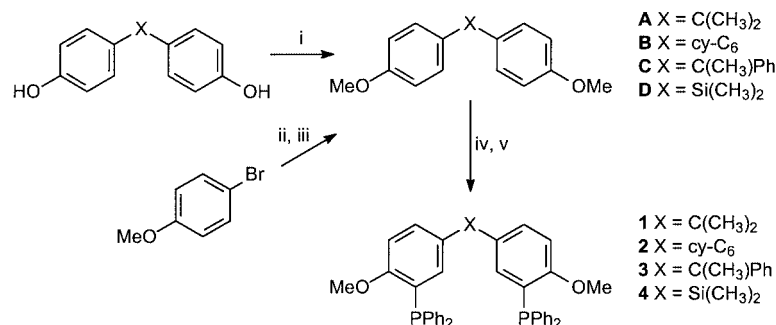
We were able to obtain single crystals, suitable for X-ray analysis, for compounds **1–3**, by recrystallization of the pure solids from hot 1-propanol or hot acetonitrile. Only the molecular structure of compound **2** is depicted in Figure 1, while selected bond lengths and bond angles for all three compounds are summarized in Table 1.

Because of the rotational freedom of the aromatic rings in the backbone, the diphenylphosphane groups are not constrained to any particular mutual orientation. Compound **2** shows approximate C₂ symmetry. The bond distances between the *ipso*-carbons of the backbone with the phosphorus atoms are normal at around 1.84 Å [P¹–C³ 1.840(2) Å and P²–C⁹ 1.845(2) Å]. The central-carbon (C¹⁵) of the backbone is clearly tetrahedrally surrounded. The through-space P¹–O¹ and P²–O² distances are around 2.8–2.9 Å. The intramolecular P–P distance is 9.7664(8) Å.

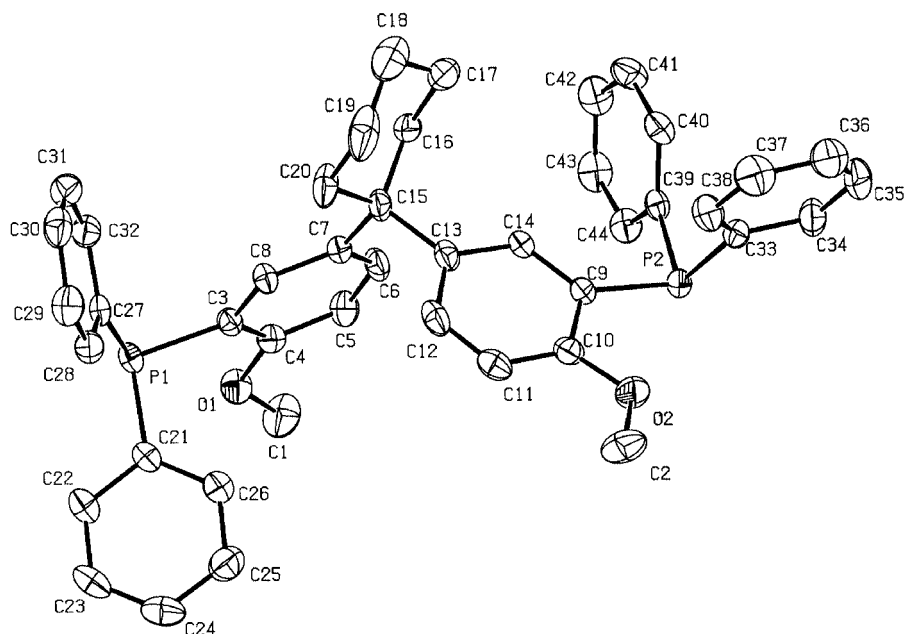
To obtain the corresponding diphosphane oxide, we reacted compound **2** with hydrogen peroxide to yield compound **5**. In the ³¹P NMR spectrum a singlet was observed at δ = 27.7 ppm which is a typical value for a phosphane oxide.^[7] We were able to obtain single crystals, suitable for

^[a] Schuit Institute of Catalysis, Laboratory of Homogeneous Catalysis, Eindhoven University of Technology, P. O. Box 513, 5600 MB Eindhoven, The Netherlands
Fax: (internat.) + 31-40-2455054
E-mail: d.vogt@tue.nl

^[b] Laboratory for Crystal and Structural Chemistry, Department of Chemistry, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands



Scheme 1. Synthetic route to BPphos

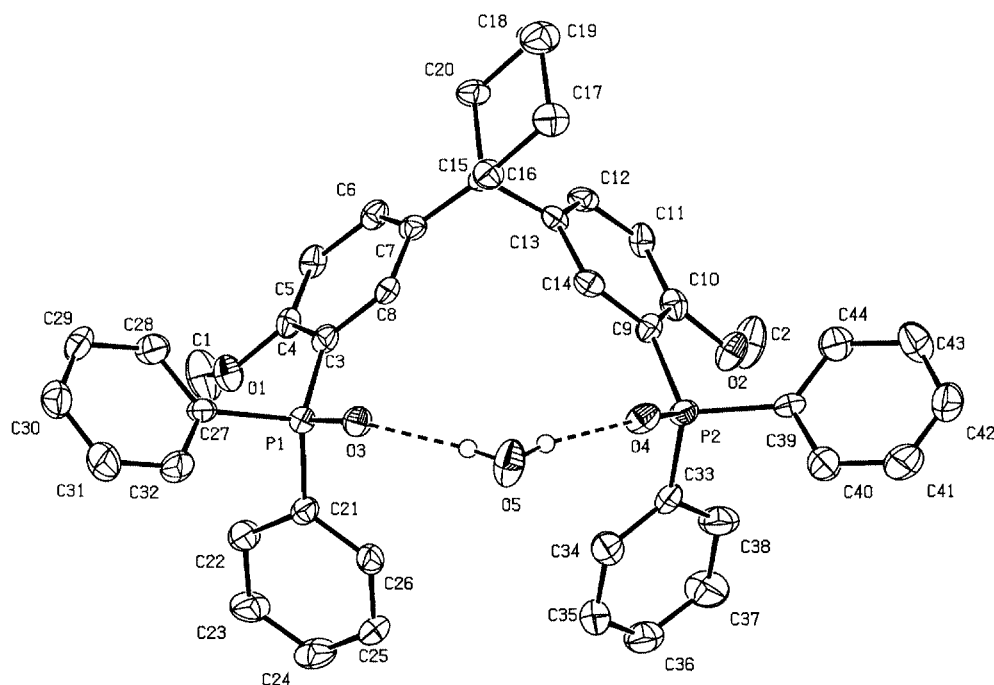
Figure 1. Molecular structure of compound **2**Table 1. Selected bond lengths and angles for compounds **1**–**3**

	1	2	3
Bond lengths [Å]			
P ¹ –C ³	1.8484(15)	1.840(2)	1.8354(16)
P ² –C ⁹	1.8428(16)	1.845(2)	1.8385(17)
O ¹ –C ¹	1.429(2)	1.431(3)	1.413(3)
O ¹ –C ⁴	1.374(2)	1.370(2)	1.375(2)
O ² –C ²	1.429(3)	1.425(3)	1.424(2)
O ² –C ¹⁰	1.372(2)	1.372(2)	1.376(2)
P ¹ –P ²	9.8510(6)	9.7664(8)	6.7749(6)
Angles [°]			
C ¹ –O ¹ –C ⁴	117.64(13)	117.52(17)	118.25(14)
C ² –O ² –C ¹⁰	118.26(14)	117.86(16)	117.61(14)
P ¹ –C ³ –C ⁴	118.25(11)	118.01(14)	116.89(12)
P ² –C ⁹ –C ¹⁰	117.17(13)	118.72(15)	116.99(13)
C ⁷ –C ¹⁵ –C ¹³	111.30(13)	106.96(14)	110.23(13)

X-ray analysis, from a THF solution. The molecular structure is depicted in Figure 2, with selected bond lengths and angles listed in Table 2.

The structure of compound **5** represents the diphosphane oxide of **2** but with an additional molecule of water present. There is hydrogen-bonding between the oxo groups of com-

pound **5** and the hydrogen atoms of the water molecule.^[8] The O–H···O(P) contacts are almost equivalent with H[#]–O(P) bond lengths of 1.99(5) Å (H[#]–O³) and 2.01(5) Å (H[#]–O⁴), which are much smaller than the calculated sum of the van der Waals radii of 2.72 Å. The O⁵–O(P) distances are 2.835(7) Å (O³–O⁵) and 2.822(7) Å (O⁴–O⁵) and the O⁵–H[#]–O(P) angles are 166(5)° (P¹) and 168(6)° (P²), respectively. Furthermore, the orientation of the two phosphorus atoms is dramatically altered relative to the structure of the free ligand (vide supra). Due to the template effect of the water molecule, both P-atoms are located on the same side of the molecule with the oxygen atoms pointing towards one another. This leads to a decreased P¹–P² distance of 6.579(2) Å. The bond lengths between the phosphorus and carbon atoms of the ligand backbone (P¹–C³ and P²–C⁹) are slightly shorter than the corresponding distances in compound **2**, due to a decrease of electron density on the phosphorus atoms in the oxidized state. The P–O bond lengths found for both phosphane oxide moieties, 1.491(4) Å (P¹–O³) and 1.492(5) Å (P²–O⁴), are similar to those found in triphenylphosphane oxide hemihydrate^[8] and tris(*p*-tolyl)phosphane oxide^[9] but slightly lower in comparison with the mono oxide of

Figure 2. Crystal structure of compound **5**Table 2. Selected bond lengths and angles for compound **5**·H₂O

Bond lengths [Å]		Angles [°]	
P ¹ –C ³	1.810(7)	C ¹ –O ¹ –C ⁴	117.4(6)
P ² –C ⁹	1.803(9)	C ² –O ² –C ¹⁰	118.9(6)
O ¹ –C ¹	1.427(9)	P ¹ –C ³ –C ⁴	125.4(5)
O ¹ –C ⁴	1.378(8)	P ² –C ⁹ –C ¹⁰	125.6(5)
O ² –C ²	1.416(9)	C ⁷ –C ¹⁵ –C ¹³	105.1(5)
O ² –C ¹⁰	1.383(9)	O ³ –P ¹ –C ³	110.1(3)
P ¹ –O ³	1.491(4)	O ⁴ –P ² –C ⁹	109.9(3)
P ² –O ⁴	1.492(5)		
P ¹ –P ²	6.579(2)		

BINAP.^[10] We are currently investigating the inclusion of other molecules capable of forming hydrogen bonds in order to form three-dimensional networks. The coordination behaviour of the phosphane oxide, which is still a weakly coordinating group,^[11] has also been studied.

We were interested in the coordination of the novel diphosphane compounds to various transition metals and, in particular, whether the chelate ring size of 9 atoms (including the two P-atoms) would have implications for the mode of coordination and if bidentate mononuclear complexes would be formed.

Rauchfuss et al. have already investigated the monophosphane (diphenylphosphanyl)anisole and they concluded that coordination to a metal, such as palladium and platinum, took place only through the phosphorus.^[12] In order to study the coordination chemistry of the new family of BPphos ligands to Pd, Pt, and Rh, we used ligand **2** as a representative example. Marty et al. have reported some experimental evidence for the formation of a monomeric,

trans-coordinated PdCl₂ complex using 3,3'-oxybis[(diphenylphosphanyl)methyl]benzene, which is structurally related to compounds **1**–**4**.^[13]

From the reaction of **2** with [PdClCH₃(cod)] as a starting material, only a singlet at $\delta = 25.0$ ppm was observed in the ³¹P NMR spectrum. In the ¹H NMR spectrum, a broad triplet was present at $\delta = -0.05$ ppm and a singlet at $\delta = 3.8$ ppm was seen in the ¹³C NMR spectrum. These observations are clear indications that a *trans*-coordinated species is present, either monomeric or dimeric. For monomeric *trans*-coordinated [PdClCH₃(Xantphos)] complexes, Zuideveld et al. have reported proton methyl signals at around $\delta = -0.2$ ppm.^[14] Upon slow evaporation of the deuterated solvent, yellow block-shaped single crystals, suitable for X-ray analysis, were obtained for this compound. The crystallographic study undertaken, indicated formation of the dimeric macrocyclic complex **6** which did indeed display a *trans*-coordination for each of the two phosphorus atoms and two bridging palladium atoms. The molecular structure of complex **6** is depicted in Figure 3, while Table 3 contains selected bond lengths and bond angles.

The complex is centrosymmetric and the geometry around the palladium atoms is distorted square planar, as indicated by the corresponding angles listed in Table 2. The P¹–Pd–P² angle is 172.94(3)°, while the C¹–Pd¹–Cl¹ angle is 171.64(13)°. The Pd–P bond lengths of 2.3250(9) Å (Pd–P¹) and 2.3248(9) Å (Pd–P²) are typical for triarylphosphanes^[15,16] as are the lengths of the palladium to chlorine and palladium to methyl bonds.^[17] The P¹–P^{2a} distance was found to be 7.4470(13) Å. Other binuclear palladium complexes with a face-to-face structure that have been described in literature most often have two chlorine ligands coordinated to the metal center instead of one

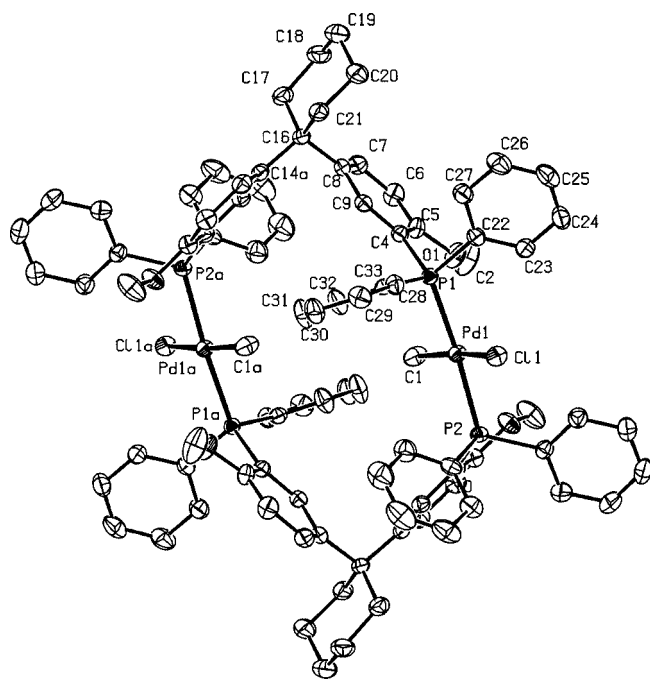


Figure 3. X-ray structure of complex 6

Table 3. Selected bond lengths and angles for complex 6, *trans,trans*-[$\{\text{PdCl}(\text{CH}_3)(\mu\text{-2})\}_2]$

Bond lengths [Å]		Angles [°]	
Pd ¹ –P ¹	2.3250(9)	P ¹ –Pd ¹ –P ²	172.94(3)
Pd ¹ –P ²	2.3248(9)	C ¹ –Pd ¹ –Cl ¹	171.64(13)
Pd ¹ –Cl ¹	2.4330(10)	P ¹ –Pd ¹ –Cl ¹	88.18(3)
Pd ¹ –C ¹	2.075(4)	P ² –Pd ¹ –Cl ¹	88.41(3)
P ¹ –C ⁴	1.836(3)	P ¹ –Pd ¹ –C ¹	92.30(9)
P ² –C ¹⁰	1.830(3)	P ² –Pd ¹ –C ¹	90.17(9)
P ¹ –P ^{2a}	7.4470(13)	C ⁸ –C ¹⁶ –C ^{14a}	105.2(3)
Pd ¹ –Pd ^{1a}	7.4972(4)		

chlorine and one methyl ligand.^[18,19] Davies et al. have described the face-to-face dimer $[\text{Pd}_2\text{Cl}_2(\text{CH}_2\text{NO}_2)(\mu\text{-dmpm})_2]$ ($\text{dmpm} = \text{Me}_2\text{PCH}_2\text{PMe}_2$). The bond lengths between the palladium and the chlorine or the carbon atom of the nitromethyl group turned out to be slightly shorter than in the case of complex 6, due to the electronic withdrawing effect of the nitro unit.^[20] Only very recently the group of James published the synthesis and structural characterization of the Pd_2Cl_4 derivative of dmpm .^[20b] Kemmitt and co-workers quite recently reported various dimeric palladium-diphosphane complexes with a chlorine and a phenyl group attached to the palladium atoms.^[16]

In order to verify if the formation of face-to-face dimeric complexes is always favoured, regardless of the transition metal, we decided to study the complexation of ligand 2 with a platinum precursor. After reaction with $[\text{PtCl}_2(\text{CH}_3\text{CN})_2]$, an off-white solid was obtained. After dissolving this compound in acetone and slow evaporation of the solvent, one product could be isolated as yellow single crystals in good yield. The ^{31}P NMR spectrum of this compound showed a singlet at $\delta = 15.8$ ppm, flanked by

^{195}Pt -satellites, and a coupling constant $J_{\text{Pt-P}}$ of 2705 Hz. This clearly indicates a *trans*-coordination of two phosphorus atoms.^[21] These block-shaped crystals turned out to be suitable for X-ray analysis. The molecular structure for complex 7 is depicted in Figure 4. Selected bond lengths and bond angles are listed in Table 4.

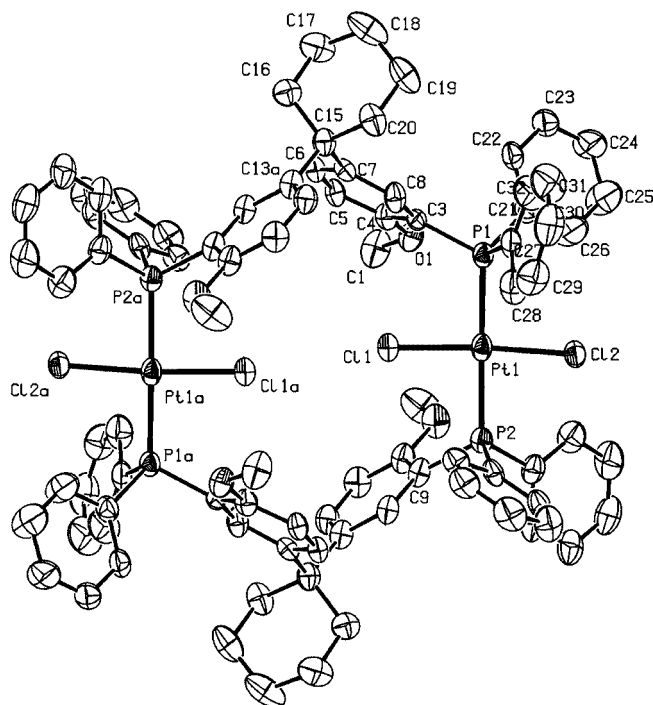


Figure 4. X-ray structure of complex 7

Table 4. Selected bond lengths and angles for complex 7, *trans,trans*-[$\{\text{PtCl}_2(\mu\text{-2})_2\}_2]$

Bond lengths [Å]		Angles [°]	
Pt ¹ –P ¹	2.320(2)	P ¹ –Pt ¹ –P ²	176.78(7)
Pt ¹ –P ²	2.315(2)	P ¹ –Pt ¹ –Cl ¹	92.33(8)
Pt ¹ –Cl ¹	2.294(2)	P ¹ –Pt ¹ –Cl ²	90.09(7)
Pt ¹ –Cl ²	2.3270(18)	Cl ¹ –Pt ¹ –Cl ²	171.77(7)
P ¹ –C ³	1.835(7)	P ² –Pt ¹ –Cl ¹	88.80(7)
P ² –C ⁹	1.827(7)	P ² –Pt ¹ –Cl ²	88.38(7)
P ¹ –P ^{2a}	8.627(3)	C ⁷ –C ¹⁵ –C ^{13a}	108.9(7)
Pt ¹ –Pt ^{1a}	8.6391(5)		

Like the palladium complex 6, the molecular structure of complex 7 also turned out to be dimeric and centrosymmetric. The geometry around the platinum atoms is distorted square planar, with a $\text{P}^1\text{–Pt}^1\text{–P}^2$ angle of $176.78(7)^\circ$ and a $\text{Cl}^1\text{–Pt}^1\text{–Cl}^2$ angle of $171.77(7)^\circ$. The geometry around the central atom C¹⁵ of the ligand backbone is nearly perfectly tetrahedral, as indicated by the angle of $108.9(7)^\circ$ for both phenyl rings. Interestingly, the $\text{P}^1\text{–P}^{2a}$ distance of 8.627(3) Å is larger than in the palladium-dimer 6. The P–Pt and Cl–Pt bond lengths are in their expected ranges, compared with similar structures previously reported.^[22,23] Wood et al. showed that the reaction of 2,6-bis(diphenylphosphanyl)pyridine with PtCl_2 yielded a *cis*-

dimer. When the chlorine-ligands were substituted for iodine-ligands, however, the phosphorus atoms were coordinated in a *trans*-fashion.^[24]

To further understand the formation of these face-to-face dimers, we chose the rhodium precursor $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$. Complexes prepared from this metal source normally exhibit a *trans*-coordination for the phosphorus atoms. After reaction of this rhodium species with ligand **2**, a doublet was observed in the ^{31}P NMR spectrum at $\delta = 23.7$ ppm, with a coupling constant $J_{\text{Rh-P}}$ of 128.3 Hz. This value is typical of those seen in rhodium diphenylphosphane complexes.^[25] In the carbonyl region of the IR spectrum (ATR-mode) obtained from the solid product, the CO-stretching vibration was present at $\nu_{\text{CO}} = 1976\text{ cm}^{-1}$. This is in good agreement with the value of $\nu_{\text{CO}} = 1974\text{ cm}^{-1}$ reported for $[\text{RhCl}(\text{CO})\{\text{P}(o\text{-An})\text{Ph}_2\}]$ (An = anisole).^[26] Compared with the value of $\nu_{\text{CO}} = 1982\text{ cm}^{-1}$ found for $[\text{RhCl}(\text{CO})\{\text{PPh}_2(\text{C}_6\text{F}_5)\}]$ ^[27] and $\nu_{\text{CO}} = 1980\text{ cm}^{-1}$ for $[\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$ ^[28], the value found for our Rh complex is slightly low. *Note:* Moloy and Petersen have touched upon the discrepancy arising in literature with respect to the CO stretching frequency for $[\text{Rh}(\text{Cl})(\text{CO})(\text{PPh}_3)_2]$. Their own experiments showed a single band at $\nu_{\text{CO}} = 1965\text{ cm}^{-1}$ in CH_2Cl_2 .^[29] The value of 1976 cm^{-1} demonstrates that the ligands from the BPphos family are slightly more basic than the aforementioned two ligand systems. However the value is significantly higher than that found for $\text{Rh}(\text{Cl})(\text{CO})$ complexes with alkyldiarylphosphanes such as those described by Zhang et al.^[30] and by the group of Dilworth ($\nu = 1957\text{ cm}^{-1}$).^[31]

By slow diffusion of acetonitrile into a dichloromethane solution of the compound, single crystals could be grown that were suitable for an X-ray crystallographic study. The molecular structure for centrosymmetric complex **8** is shown in Figure 5. Similar to the Pd and Pt complexes, a face-to-face dimeric structure can be observed. Selected bond lengths and bond angles are listed in Table 5.

The geometry around the rhodium atoms is distorted square planar, with a P-Rh-P angle of $171.01(3)^\circ$ and a Cl-Rh-C(O) angle of $176.99(7)^\circ$. These distances are in the expected range with an average Rh-P bond length of 2.32 \AA . The Rh-Cl and Rh-C(O) bond lengths are $2.3795(5)\text{ \AA}$ and $1.810(2)\text{ \AA}$, respectively. The C-O distance is typical at $1.145(2)\text{ \AA}$.^[30–34] The $\text{P}^1\text{-P}^{2a}$ distance of $8.8150(12)\text{ \AA}$ as well as the corresponding Rh-Rh distance of $9.0005(11)\text{ \AA}$ are in the range found for the palladium and platinum complexes.

Many *trans*- $[\text{RhCl}(\text{CO})]$ complexes with (di)phosphane ligands have been described in the literature, yet most of these systems are solely mononuclear. Relatively few examples are known where a dimeric compound has been formed exclusively and subsequently structurally characterized by X-ray crystallography.^[35–39]

In summary, we have described the easy synthesis of a new class of diphosphane ligands based on commercially available, cheap raw materials derived from Bisphenol A and in good overall yields. In addition to NMR spectroscopy, X-ray crystallography has been used to study the

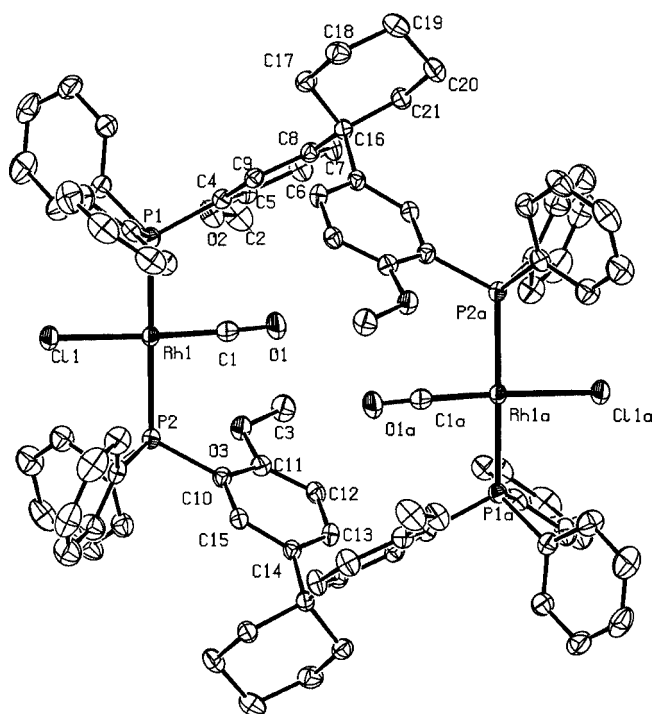


Figure 5. X-ray structure of complex **8**

Table 5. Selected bond lengths and angles for complex **8**, *trans,trans*- $[\{\text{RhCl}(\text{CO})(\mu\text{-2})_2\}_2]$

Bond lengths [\AA]		Angles [$^\circ$]	
$\text{Rh}^1\text{-P}^1$	2.3153(5)	$\text{P}^1\text{-Rh}^1\text{-P}^2$	171.01(3)
$\text{Rh}^1\text{-P}^2$	2.3345(6)	$\text{P}^1\text{-Rh}^1\text{-Cl}^1$	87.85(3)
$\text{Rh}^1\text{-Cl}^1$	2.3795(5)	$\text{P}^2\text{-Rh}^1\text{-Cl}^1$	90.36(3)
$\text{Rh}^1\text{-C}^1$	1.810(2)	$\text{Cl}^1\text{-Rh}^1\text{-C}^1$	176.99(7)
$\text{C}^1\text{-O}^1$	1.145(2)	$\text{P}^1\text{-Rh}^1\text{-C}^1$	89.80(7)
$\text{P}^1\text{-C}^4$	1.8349(17)	$\text{P}^2\text{-Rh}^1\text{-C}^1$	92.24(7)
$\text{P}^2\text{-C}^{10}$	1.8352(18)	$\text{Rh}^1\text{-C}^1\text{-O}^1$	177.33(18)
$\text{P}^1\text{-P}^{2a}$	8.8150(12)	$\text{Rh}^1\text{-P}^1\text{-C}^4$	116.75(6)
$\text{Rh}^1\text{-Rh}^{1a}$	9.0005(11)	$\text{C}^8\text{-C}^{16}\text{-C}^{14a}$	110.19(15)

structural differences between compound **2** and its oxidised form, **5**. In the structure of the latter compound, water acts as a template orientating both phosphorus-atoms to the same side of the molecule in the same direction. Complexation studies undertaken with ligand **2** yielded face-to-face dimeric macrocycles with palladium, platinum and rhodium, as was shown by NMR spectroscopy as well as X-ray crystallography.

We are currently investigating the options available for modifying the ligand backbone to further control and enforce a certain orientation of the phosphane-moieties as well as the modification of these ligands in order to gain access to chelating variants.

Experimental Section

Chemicals were purchased from Aldrich, Acros, and Merck and used as received. All preparations were carried out under an argon

atmosphere using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (THF, diethyl ether, toluene, hexanes, and ethanol) or calcium hydride (CH_2Cl_2 and CDCl_3) prior to use. $[\text{PdCl}_2(\text{cod})]$,^[40] $[\text{PdClMe}(\text{cod})]$ ^[41] and $[\text{PtCl}_2(\text{cod})]$ ^[42] were synthesized according to literature procedures. All glassware was dried by heating under vacuum. The NMR spectra were recorded on a Varian Mercury 400 spectrometer (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$). Chemical shifts are given in ppm referenced to the deuterated solvent (^1H , $^{13}\text{C}\{^1\text{H}\}$) or 85% H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$).

2,2-Bis(4-methoxyphenyl)propane (A): This is a modification of the literature procedure.^[43] To a solution of Bisphenol A [2,2'-bis(4-hydroxyphenyl)propane] (11.48 g, 0.050 mol) in acetone (120 mL) were added K_2CO_3 (27.69 g, 0.20 mol) and CH_3I (21.69 g, 0.15 mol) as well as NBu_4I (0.88 g, 2.38 mmol). The heterogeneous mixture was stirred for 16 h under reflux. The suspension was filtered through celite and poured into a mixture of diethyl ether (100 mL) and a 15 w% aqueous KOH solution (100 mL). The organic phase was further washed with saturated brine (100 mL) and water (50 mL) after which MgSO_4 was added and the organic phase stirred for about 10 h. After filtration through Celite the solvent was removed in vacuo and ethanol (40 mL) was added to the remaining oil. After stirring, the ethanol was removed in vacuo to yield a pure off-white powder (9.44 g, 36.8 mmol) (73%). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 1.65 (s, 6 H, CCH_3), 3.79 (s, 6 H, OCH_3), 6.81 (d, 1J = 8.8 Hz, 4 H, $m\text{-H}^2$), 7.15 (d, 1J = 8.8 Hz, 4 H, $o\text{-H}^1$) (Numbering scheme see Figure 6). ^{13}C NMR (100 MHz, CDCl_3 , 300 K, ppm): δ = 31.1, 41.6, 55.2, 113.2, 127.7, 143.1, 157.4.

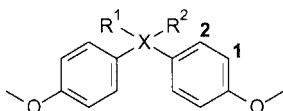


Figure 6. Numbering scheme for protons H^1 and H^2 of compounds **A–D**

1,1-Bis(4-methoxyphenyl)cyclohexane (B): This is a modification of the literature procedure.^[44] Starting from Bisphenol Z [1,1-bis(4-hydroxyphenyl)cyclohexane] (28.8 g, 0.11 mol), compound **B** was obtained as a white crystalline solid, using the same procedure as described for **A**. Yield 83.5% (27.7 g, 93.5 mmol). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 1.55 (m, 6 H, $m\text{-p-CH}_2$, $c\text{-C}^6$), 2.23 (m, 4 H, $o\text{-CH}_2$, $c\text{-C}^6$), 3.77 (s, 6 H, OCH_3), 6.81 (d, 1J = 8.8 Hz, 4 H, $m\text{-H}^2$), 7.18 (d, 1J = 8.8 Hz, 4 H, $o\text{-H}^1$). ^{13}C NMR (100 MHz, CDCl_3 , 300 K, ppm): δ = 22.9, 26.4, 37.4, 45.0, 55.1, 113.4, 128.0, 141.0, 157.1.

2,2-Bis(4-methoxyphenyl)ethylbenzene (C): This is a modification of the literature procedure.^[45] Starting from Bisphenol AP {2,2-bis(4-hydroxyphenyl)ethyl}benzene} (20.0 g, 68.9 mmol), compound **C** was obtained as a pure off-white powder, using the same procedure as described for **A**. Yield 64% (13.92 g, 43.7 mmol). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 2.14 [s, 6 H, $\text{C}(\text{CH}_3)_2$], 3.79 (s, 6 H, OCH_3), 6.79 (d, 1J = 8.8 Hz, 4 H, H^2), 7.00 (d, 1J = 8.8 Hz, 4 H, H^1), 7.09 (m, 2 H, $o\text{-CH}$, Ph), 7.20 (m, 1 H, $p\text{-CH}$, Ph), 7.26 (m, 2 H, $m\text{-CH}$, Ph). ^{13}C NMR (100 MHz, CDCl_3 , 300 K, ppm): δ = 30.7, 55.2, 113.1, 125.8, 127.8, 128.6, 129.7, 141.5, 157.6.

Bis(4-methoxyphenyl)dimethylsilane (D): This is a modification of the literature procedure.^[46] 4-Bromoanisole (5.79 g, 0.031 mmol)

was dissolved in THF (100 mL) and the solution was cooled to -78°C whereupon $n\text{BuLi}$ (2.5 M solution in hexanes) (12.4 mL, 31.0 mmol) was added dropwise by syringe. The reaction mixture was stirred for 1 h followed by addition of $\text{SiCl}_2(\text{CH}_3)_2$ (2.0 g, 31.0 mmol) by syringe. The reaction mixture was allowed to warm up to room temp. and stirring was continued for about 10 h. Solvents were removed in vacuo and the crude product was dissolved in CH_2Cl_2 (30 mL). Washing with distilled water (40 mL) afforded a turbid white organic layer. The organic phase was separated and the solvent removed in vacuo to leave a yellow oil. Upon addition of hexanes (25 mL), a brown precipitate was formed. The solution was isolated and dried with MgSO_4 . After filtration and subsequent removal of solvent, an off-white solid was obtained. Yield 71% (3.00 g, 22.0 mmol). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 0.54 [s, 6 H, $\text{Si}(\text{CH}_3)_2$], 3.83 (s, 6 H, OCH_3), 6.93 (d, 1J = 8.8 Hz, 4 H, H^2), 7.48 (d, 1J = 8.8 Hz, 4 H, H^1). ^{13}C NMR (100 MHz, CDCl_3 , 300 K, ppm): δ = -2.0 , 55.0, 113.5, 129.4, 135.6, 155.0, 160.4.

2,2-Bis[(3-diphenylphosphanyl)-4-methoxy]phenyl]propane (1): TMEDA (12.95 g, 0.11 mol) was added to $n\text{BuLi}$ (2.5 M solution in hexanes) (44.6 mL, 0.11 mol). At -15°C a solution of **A** (13.29 g, 0.052 mol) in diethyl ether (75 mL) was added dropwise over a period of 1.5 h. The mixture was allowed to slowly warm up to room temp. and was stirred for about 10 h to yield a yellow suspension. At 0°C ClPPh_2 (24.6 g, 0.11 mol) in hexanes (30 mL) was added dropwise over a period of 1 h. Solvents were removed in vacuo and CH_2Cl_2 (60 mL) was added together with saturated brine (50 mL). The organic phase was separated and dried with MgSO_4 . After filtration through celite, the solvents were removed in vacuo to yield a pink oil that solidified on standing for about 10 h at room temp. under argon. Ethanol (40 mL) was added to give an orange solution and a white precipitate. The solid was washed with ethanol, filtered, and dried. Yield 54% (17.46 g, 28.1 mmol). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 1.24 (s, 6 H, CCH_3), 3.73 (s, 6 H, OCH_3), 6.40 (dd, 1J = 5.2, 2J = 2.4 Hz, 2 H, H^1), 6.73 (dd, 1J = 8.8, 2J = 4.8 Hz, 2 H, H^2), 7.04 (dd, 1J = 8.8, 2J = 2 Hz, 2 H, H^3), 7.24 (m, 20 H, PPh_2) (Numbering scheme see Figure 7). ^{13}C NMR (100 MHz, CDCl_3 , 300 K, ppm): δ = 30.3 [$\text{C}(\text{CH}_3)_2$], 41.6 [$\text{C}(\text{CH}_3)_2$], 55.7 (OCH_3), 109.5, 124.3, 128.2 (d, J_{PC} = 6.8 Hz), 128.3, 128.4, 132.4, 133.7 (d, J_{PC} = 19.8 Hz), 136.9 (d, J_{PC} = 10.7 Hz), 143.0, 159.0 (d, J_{PC} = 14.5 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 300 K, ppm): δ = -14.8 (s). $\text{C}_{41}\text{H}_{38}\text{O}_2\text{P}_2$: calcd. C 78.83, H 6.13; P, 9.92; found C 78.65, H 6.08; P, 9.98.

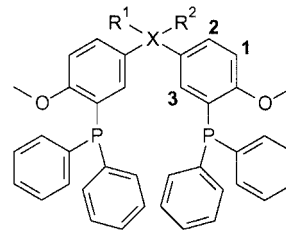


Figure 7. Numbering scheme for protons H^1 , H^2 , and H^3 of compounds **1–8**

1,1-Bis[(3-diphenylphosphanyl)-4-methoxy]phenyl]cyclohexane (2): Starting from **B** (4.99 g, 0.017 mol), compound **2** was obtained as a white powder using the same procedure as described for compound **1**. Yield 56% (6.34 g, 9.4 mmol). ^1H NMR (400 MHz, CDCl_3 , 300 K, ppm): δ = 1.23 (m, 6 H, $m\text{-p-CH}_2$, $c\text{-C}^6$), 1.73 (m,

4 H, *o*-CH₂, *c*-C⁶), 3.71 (s, 6 H, OCH₃), 6.47 (dd, ¹*J* = 5.6, ²*J* = 2.4 Hz, 2 H, H¹), 6.72 (dd, ¹*J* = 8.8, ²*J* = 4.8 Hz, 2 H, Ar-H²), 6.99 (dd, ¹*J* = 8.8, ²*J* = 2.4 Hz, 2 H, H³), 7.24 (m, 20 H, PPh₂). ¹³C NMR (100 MHz, CDCl₃, 300 K, ppm): δ = 22.7, 26.2, 37.0, 45.2, 55.6, 109.8, 125.7, 128.2, 128.3 (d, *J*_{PC} = 13.0 Hz), 128.8, 132.9, 133.7 (d, *J*_{PC} = 19.8 Hz), 137.0, 140.9, 159.0 (d, *J*_{PC} = -15.2 (s). C₄₄H₄₂O₂P₂: calcd. C 79.50, H 6.37; P, 9.32; found C 79.39, H 6.39; P, 9.31

2,2-Bis[(3-diphenylphosphanyl-4-methoxy)phenyl]ethylbenzene (3): Starting from **C** (12.4 g, 38.9 mmol), compound **3** was obtained as a white powder using the same procedure as described for compound **1**. Yield 61% (16.5 g, 23.7 mmol). ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = 1.74 (s, 3 H, CCH₃), 3.72 (s, 6 H, OCH₃), 6.33 (dd, ¹*J* = 5.6, ²*J* = 2.4 Hz, 2 H, H¹), 6.67 (dd, ¹*J* = 8.8, ²*J* = 4.8 Hz, 2 H, H²), 6.81 (m, 2 H, *o*-CH, Ph), 6.91 (dd, ¹*J* = 8.8, ²*J* = 2.4 Hz, 2 H, H³), 7.07 (m, 3 H, *m*-*p*-CH, Ph), 7.18 (m, 20 H, PPh₂). ¹³C NMR (100 MHz, CDCl₃, 300 K, ppm): δ = 30.0, 51.2, 55.6, 109.3, 124.2 (d, *J*_{PC} = 13.0 Hz), 125.5, 127.6, 128.2 (d, *J*_{PC} = 6.8 Hz), 128.3 (d, *J*_{PC} = 3.1 Hz), 130.2, 133.6 (d, *J*_{PC} = 19.8 Hz), 134.1, 136.7 (d, *J*_{PC} = 10.7 Hz), 141.3, 149.0, 159.1 (d, *J*_{PC} = 14.5 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = -15.3 (s). C₄₆H₄₀O₂P₂: calcd. C 80.45, H 5.87; P, 9.02; found C 80.52, H 5.76; P, 9.05.

Bis[(3-diphenylphosphanyl-4-methoxy)phenyl]dimethylsilane (4): Starting from **D** (3.00 g, 0.011 mol), compound **4** was obtained as a white powder using the same procedure as described for compound **1**. Yield 65% (4.58 g, 7.20 mmol). ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = 0.09 [s, 6 H, Si(CH₃)₂], 3.75 (s, 6 H, OCH₃), 6.69 (dd, ¹*J* = 8.0, ²*J* = 4.4 Hz, 2 H, H¹), 6.81 (dd, ¹*J* = 8.0, ²*J* = 4.4 Hz, 4 H, H², H³), 7.28 (m, 20 H, PPh₂). ¹³C NMR (100 MHz, CDCl₃, 300 K, ppm): δ = -2.6, 55.5, 109.7, 124.7, 128.2 (d, *J*_{PC} = 6.8 Hz), 128.5, 129.5, 133.8 (d, *J*_{PC} = 19.8 Hz), 136.3, 136.7 (d, *J*_{PC} = 9.9 Hz), 139.5, 161.9 (d, *J*_{PC} = 15.9 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = -16.1 (s). C₄₀H₃₈O₂P₂Si: calcd. C 74.98, H 5.98; P, 9.67; found C 75.06, H 5.93; P, 9.63.

Bis(2,2'-methoxy-5,5'-cyclohexyl)diphenylphosphane Oxide (5): Ligand **2** (0.65 g, 0.98 mmol) was dissolved in CH₂Cl₂ (25 mL) and H₂O₂ (30 wt% aqueous solution) (0.20 mL, 1.96 mmol) in H₂O (20 mL) was added dropwise at 0 °C after which the two-phase system was stirred for about 10 h at room temp. The organic layer was washed with 0.1 M NaOH solution (20 mL) and water (20 mL). After drying with MgSO₄ and subsequent filtration, the solvent was removed in vacuo to leave a white powder. Yield 85% (0.58 g, 0.83 mmol). ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = 1.46 (s, 6 H, *m*,*p*-CH₂, *c*-C⁶), 2.18 (s, 4 H, *o*-CH₂, *c*-C⁶), 3.55 (s, 6 H, OCH₃), 6.81 (dd, ¹*J* = 8.8, ²*J* = 5.6 Hz, 2 H, H¹), 7.32 (dd, ¹*J* = 8.8, ²*J* = 2.4 Hz, 2 H, H²), 7.41 (dt, ¹*J* = 8.0, ²*J* = 2.4 Hz, 8 H, *o*-CH, PPh), 7.51 (dt, ¹*J* = 8.4, ²*J* = 1.2 Hz, 4 H, *p*-CH, PPh), 7.65 (d, ¹*J* = 2.4 Hz, 2 H, H³), 7.69 (q, ¹*J* = 4.8 Hz, 8 H, *m*-CH, PPh). ¹³C NMR (100 MHz, CDCl₃, 300 K, ppm): δ = 22.7, 26.1, 37.0, 45.3, 55.2, 111.3 (d, *J*_{PC} = 7.6 Hz), 128.0 (d, *J*_{PC} = 12.3 Hz), 131.3 (d, *J*_{PC} = 10.8 Hz), 132.8, 133.2, 133.9, 141.0, 158.6 (d, *J*_{PC} = 3.7 Hz). ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = 27.7 (s). C₄₄H₄₂O₄P₂: calcd. C 75.85, H 6.08; found C 76.04, H 6.14.

trans,trans-[PdClCH₃-2]₂, Complex 6: Ligand **2** (40.2 mg, 60.5 μmol) and [PdClCH₃(cod)] (13.9 mg, 52.4 μmol) were dissolved in CDCl₃ (0.5 mL) and the solution was stirred for 2 h before the solution was analyzed by NMR spectroscopy. Single crystals were

obtained by slow evaporation of the solvent from the NMR solution. ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = -0.05 (t, 6 H, PdCH₃), 1.26 (br. s, 12 H, *m*,*p*-CH₂, *c*-C⁶), 1.80 (br. s, 8 H, *o*-CH₂, *c*-C⁶), 3.61 (s, 12 H, OCH₃), 6.71 (d, ¹*J* = 8.0 Hz, 4 H, H³), 7.04 (d, ¹*J* = 8.0 Hz, 8 H, H¹, H²), 7.30 (m, 24 H, PPh₂), 7.71 (br. s, 16 H, PPh₂). ¹³C NMR (100 MHz, CDCl₃, 300 K, ppm): δ = 3.8, 22.8, 26.3, 37.1, 45.1, 55.5, 110.8, 119.0, 119.2, 127.5, 129.2, 130.9, 131.6, 133.3, 135.0, 140.4, 157.9. ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = 25.0 (s). C₉₀H₉₀Cl₂O₄P₄Pd₂: calcd. C 65.78, H 5.52; found C 65.60, H 5.46.

trans,trans-[PtCl₂-2]₂, Complex 7: PtCl₂ (170.3 mg, 640.5 μmol) was heated to reflux in acetonitrile (10 mL) until the solid had completely dissolved. Ligand **2** (425.8 mg, 640.5 μmol) was added and the mixture stirred under reflux for about 10 h. After cooling to room temp., the solvent was evaporated in vacuo to leave a yellow powder. Single crystals were obtained from acetone, by slow evaporation of the solvent. ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = 1.23 (m, 12 H, *m*,*p*-CH₂, *c*-C⁶), 1.71 (br. s, 8 H, *o*-CH₂, *c*-C⁶), 3.63 (s, 12 H, OCH₃), 6.67 (d, ¹*J* = 8.0 Hz, 4 H, H¹), 7.00 (br. s, 4 H, H²), 7.09 (d, ¹*J* = 8.8 Hz, 4 H, H³), 7.37 (br. m, 24 H, PPh₂), 7.73 (q, ¹*J* = 5.6 Hz, 16 H, PPh₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = 15.8 (s, *J*_{Pt-P} = 2705 Hz). C₈₈H₈₄Cl₄O₄P₄Pt₂: calcd. C 56.78, H 4.55; found C 56.65, H 4.45.

trans,trans-RhCl(CO)-2, Complex 8: [RhCl(CO)₂]₂ (170.3 mg, 640.5 μmol) and ligand **2** (425.8 mg, 640.5 μmol) were dissolved in CH₂Cl₂ (10 mL) and the mixture was stirred for 2 h. Evaporation of the solvent in vacuo yielded a yellow solid. Single crystals were obtained by slow diffusion of CH₃CN into a CH₂Cl₂ solution of the solid. ¹H NMR (400 MHz, CDCl₃, 300 K, ppm): δ = 1.20 (br. s, 12 H, *m*,*p*-CH₂, *c*-C⁶), 1.64 (br. s, 8 H, *o*-CH₂, *c*-C⁶), 3.61 (s, 12 H, OCH₃), 6.65 (d, ¹*J* = 8.8 Hz, 4 H), 6.87 (br. s, 4 H), 7.00 (d, ¹*J* = 6.4 Hz, 4 H), 7.38 (t, ¹*J* = 7.2 Hz, 16 H, PPh₂), 7.46 (q, ¹*J* = 7.2 Hz, 8 H, PPh₂), 7.82 (br. s, 16 H, PPh₂). ³¹P{¹H} NMR (162 MHz, CDCl₃, 300 K, ppm): δ = 23.7 (d, *J*_{Rh-P} = 128 Hz). IR (ATR mode, solid, carbonyl region, cm⁻¹): ν̃ = 1976 (RhCO). C₉₀H₈₄Cl₂O₆P₄Rh₂: calcd. C 65.03, H 5.09; found C 64.88, H 4.96.

Molecular Structures of 1–3 and 5–8: The data were collected on a Nonius-Kappa CCD diffractometer with a rotating anode. The structures were solved by direct methods using SHELXS-97 (**2**, **3**)^[47] or DIRDIF99 (**1**, **6–8**)^[48] and refined by least-squares procedures on *F*² using SHELXL-97.^[49] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Compound **3** contained one phenyl ring on one of the phosphanes which is disordered over two positions. Compound **6** contained four molecules of CDCl₃ in the unit cell. Compound **7** contained two acetone molecules which were disordered over two positions. Compound **8** contained disordered dichloromethane molecules. Their contribution was taken into account using the PLATON/SQUEEZE procedure. Structure validation and molecular graphics preparation were performed with the PLATON package.^[50] Crystal data are given in Tables 6 and 7. CCDC-213681 (**1**), -213682 (**2**), -213683 (**3**), -213684 (**5**), -213685 (**6**), -213686 (**7**), and -213687 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Selected crystallographic data for compounds **1–3** and **5**

	1	2	3	5
Formula	C ₄₁ H ₃₈ O ₂ P ₂	C ₄₄ H ₄₂ O ₂ P ₂	C ₄₆ H ₄₀ O ₂ P ₂	C ₄₄ H ₄₂ O ₄ P ₂ ·H ₂ O
FW/M _r	624.65	664.72	686.72	714.73
Crystal size [mm]	0.12 × 0.27 × 0.42	0.12 × 0.15 × 0.45	0.21 × 0.39 × 0.48	0.09 × 0.21 × 0.24
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	C2/c (no. 15)	P2 ₁ /c (no. 14)	P $\bar{1}$ (no. 2)	P2 ₁ /c (no. 14)
<i>a</i> [Å]	28.1693(3)	17.4156(2)	11.1456(1)	12.2410(10)
<i>b</i> [Å]	8.2166(1)	7.8636(1)	12.0144(2)	11.9950(10)
<i>c</i> [Å]	32.3533(4)	28.3503(4)	15.0980(2)	27.398(3)
α [°]			89.1746(9)	
β [°]	115.7420(4)	113.2940(10)	70.6049(9)	114.279(11)
γ [°]			80.4301(5)	
<i>V</i> [Å ³]	6745.21(14)	3566.08(8)	1878.66(4)	3667.1(7)
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.164	0.159	0.153	0.165
<i>Z</i>	8	4	2	4
<i>d</i> _{calcd.} [g cm ⁻³]	1.230	1.238	1.214	1.295
<i>T</i> [K]	150	150	150	150
Reflections collected	26580	28637	27481	4661
Unique reflections (<i>R</i> _{int}) ^[a]	7617 (0.058)	8121 (0.055)	8452 (0.054)	4661 (0.085)
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	5758	5506	6384	3645
<i>wR</i> ₂ of <i>F</i> ² (all data)	0.1025	0.1063	0.1159	0.1921
λ [Å]	0.71073	0.71073	0.71073	0.71073
<i>R</i> _{<i>I</i>}	0.0411	0.0452	0.0431	0.0785
<i>S</i>	1.02	1.03	1.03	1.13
Min., max. residual electron density [e/Å ³]	−0.27, 0.32	−0.28, 0.28	−0.38, 0.35	−0.41, 0.53

^[a] $R_{int} = \Sigma[|F_o^2 - F_o^2(\text{mean})|]/\Sigma[F_o^2]$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

Table 7. Selected crystallographic data for complexes **6–8**

	6	7	8
Formula	C ₉₀ H ₉₀ Cl ₂ O ₄ P ₄ Pd ₂ ·4 CDCl ₃	C ₈₈ H ₈₄ O ₄ P ₄ Pt ₂ ·2 C ₃ H ₆ O	C ₉₀ H ₈₄ O ₆ P ₄ Cl ₂ Rh ₂ ·2 CH ₂ Cl ₂
FW/M _r	2124.68	1977.57	1832.13
Crystal size [mm]	0.06 × 0.12 × 0.18	0.21 × 0.30 × 0.36	0.21 × 0.30 × 0.36
Crystal system	triclinic	monoclinic	monoclinic
Space group	P $\bar{1}$ (no.2)	P2 ₁ /c (no.14)	P2 ₁ /c (no.14)
<i>a</i> [Å]	11.3951(2)	14.4501(2)	14.3323(10)
<i>b</i> [Å]	14.6487(2)	19.5893(3)	19.9531(12)
<i>c</i> [Å]	16.5314(2)	16.5611(2)	16.4423(19)
α [°]	63.8137(6)		
β [°]	77.9245(6)	112.0310(6)	112.66(2)
γ [°]	79.6576(8)		
<i>V</i> (Å ³)	2409.47(6)	4345.60(11)	4339.1(9)
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.877	3.465	0.682
<i>Z</i>	1	2	2
<i>d</i> _{calcd.} [g cm ⁻³]	1.462	1.511	1.272
<i>T</i> [K]	150	150	150
Reflections collected	37005	42286	82640
Unique reflections (<i>R</i> _{int}) ^[a]	10960 (0.061)	8532 (0.072)	9954 (0.0505)
Observed data [<i>I</i> > 2.0 σ (<i>I</i>)]	8417	6829	8179
<i>wR</i> ₂ of <i>F</i> ² (all data)	0.1176	0.1106	0.070
λ [Å]	0.71073	0.71073	0.71073
<i>R</i> _{<i>I</i>}	0.0479	0.0587	0.029
<i>S</i>	1.07	1.36	1.05
Min., max. residual electron density [e/Å ³]	−0.73, 1.17	−0.91, 1.40	−0.49, 0.37

^[a] $R_{int} = \Sigma[|F_o^2 - F_o^2(\text{mean})|]/\Sigma[F_o^2]$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

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- [1] C. A. Bessel, P. Aggarwal, A. C. Marschilok, K. J. Takeuchi, *Chem. Rev.* **2001**, *101*, 1031–1066.
- [2] [2a] C. A. McAuliffe, *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; New York, **1973**. [2b] C. A. McAuliffe, W. Levason, *Phosphane, Arsane and Stibine Complexes of the Transition Elements*; Elsevier Science: New York, **1978**. [2c] D. M. A. Minahan, W. E. Hill, C. A. McAuliffe, *Coord. Chem. Rev.* **1984**, *55*, 31.
- [3] W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029–3069.
- [4] W. Ahlers, R. Paciello, D. Vogt, J. I. van der Vlugt (to BASF AG), US Patent Appl. 20020111517 [*Chem. Abstract.* **2002**, 169060].
- [5] J. I. van der Vlugt, J. M. Bonet, A. M. Mills, A. L. Spek, D. Vogt, *Tetrahedron Lett.* **2003**, *44*, 4389–4392.
- [6] Ullmann's Encyclopedia of Industrial Chemistry, 6th electronic edition, Wiley-VCH, Weinheim, **2002**.
- [7] ³¹P NMR spectroscopy in stereochemical analysis (Ed.: J. G. Verkade, L. D. Quin); VCH, Weinheim, **1987**.
- [8] [8a] P. W. Baures, J. V. Silverton, *Acta Crystallogr., Sect. C* **1990**, *46*, 715–717. [8b] P. W. Baures, *Acta Crystallogr., Sect. C* **1991**, *47*, 2715–2716. [8c] C. Lariucci, R. Helena de Almeida Santos, J. R. Lechat, *Acta Crystallogr., Sect. C* **1986**, *42*, 1825–1828.
- [9] M. R. Churchill, R. F. See, S. L. Randall, J. D. Atwood, *Acta Crystallogr., Sect. C* **1993**, *49*, 345–347.
- [10] S. Gladiali, S. Pulacchini, D. Fabbri, M. Manassero, M. Sansoni, *Tetrahedron: Asymmetry* **1998**, *9*, 391–395.
- [11] [11a] W. J. Marshall, V. V. Grushin, *Organometallics* **2003**, *22*, 555–562. [11b] S. Priya, M. S. Balakrishna, J. T. Mague, S. M. Mobin, *Inorg. Chem.* **2003**, *42*, 1272–1281. [11c] T.-W. Teo, S. Selvaratnam, J. J. Vittal, P.-H. Leung, *Inorg. Chim. Acta* **2003**, *352*, 213–219.
- [12] T. B. Rauchfuss, F. T. Patino, D. M. Roundhill, *Inorg. Chem.* **1975**, *14*, 652–656.
- [13] W. Marty, P. N. Kapoor, H. B. Bürgi, E. Fischer, *Helv. Chim. Acta* **1987**, *70*, 158–170.
- [14] M. A. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.* **2002**, 2308–2317.
- [15] K. Takenaka, Y. Obora, L. H. Jiang, Y. Tsuji, *Organometallics* **2002**, *21*, 1158–1166.
- [16] A. Montes, R. D. W. Kemmitt, J. Fawcett, D. R. Russeli, *Polyhedron* **1999**, *18*, 1141–1145.
- [17] S. J. Young, B. Kellenberger, J. H. Reibenspies, S. E. Himmel, M. Manning, O. P. Anderson, J. K. Stille, *J. Am. Chem. Soc.* **1988**, *110*, 5744–5753.
- [18] A. Pryde, B. L. Shaw, B. Weeks, *J. Chem. Soc., Dalton Trans.* **1976**, 322–327.
- [19] C. E. Housecroft, B. A. M. Shaykh, A. L. Rheingold, B. S. Haggerty, *Inorg. Chem.* **1991**, *30*, 125–130.
- [20] [20a] J. A. Davies, S. Dutremez, A. A. Pinkerton, M. Vilmer, *Organometallics* **1991**, *10*, 2956–2958. [20b] C. B. Pamplin, S. J. Rettig, B. O. Patrick, B. R. James, *Inorg. Chem.* **2003**, *42*, 4117–4126.
- [21] C. J. Cobley, P. G. Pringle, *Inorg. Chim. Acta* **1997**, *265*, 107–115.
- [22] N. W. Alcock, L. Judd, P. G. Pringle, *Inorg. Chim. Acta* **1986**, *113*, L13–L15.
- [23] F. C. March, R. Mason, K. M. Thomas, B. L. Shaw, *J. Chem. Soc., Chem. Commun.* **1975**, 584–585.
- [24] F. E. Wood, J. Hvosllef, H. Hope, A. L. Balch, *Inorg. Chem.* **1984**, *23*, 4309–4315.
- [25] B. E. Mann, C. Masters, B. L. Shaw, *J. Chem. Soc.* **1971**, 1104–1106.
- [26] P. Suomalainen, S. Jääskeläinen, M. Haukka, R. H. Laitinen, J. Pursiainen, T. A. Pakkanen, *Eur. J. Inorg. Chem.* **2000**, 2607–2613.
- [27] M. J. Atherton, K. S. Coleman, J. Fawcett, J. H. Holloway, E. G. Hope, A. Karaçar, L. A. Peck, G. C. Saunders, *J. Chem. Soc., Dalton Trans.* **1995**, 4029–4038.
- [28] L. Vaska, J. Peone Jr., *J. Chem. Soc., Chem. Commun.* **1971**, 418–419.
- [29] K. G. Moloy, J. L. Petersen, *J. Am. Chem. Soc.* **1995**, *117*, 7696–7710.
- [30] F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Z.-Z. Zhang, *Organometallics* **2002**, *21*, 4894–4896.
- [31] J. R. Dilworth, Y. Zheng, D. V. Griffiths, *J. Chem. Soc., Dalton Trans.* **1999**, 1877–1882.
- [32] C. M. Thomas, R. Mafua, B. Therrien, E. Rusanov, H. Stöckli-Evans, G. Süss-Fink, *Chem. Eur. J.* **2002**, *8*, 3343–3352.
- [33] T. W. Graham, A. Llamazares, R. McDonald, M. Cowie, *Organometallics* **1999**, *18*, 3502–3510.
- [34] N. W. Alcock, J. M. Brown, J. C. Jeffery, *J. Chem. Soc., Dalton Trans.* **1977**, 888–893.
- [35] M. Cowie, S. K. Dwight, *Inorg. Chem.* **1980**, *19*, 2500–2507.
- [36] A. L. Balch, L. A. Fossett, M. M. Olmstead, D. E. Oram, P. E. Reedy Jr., *J. Am. Chem. Soc.* **1985**, *107*, 5272–5274.
- [37] X. Liu, A. H. Eisenberg, C. L. Stern, C. A. Mirkin, *Inorg. Chem.* **2001**, *40*, 2940–2941.
- [38] M. F. M. Al-Dulaymmi, D. L. Hughes, R. L. Richards, *J. Organomet. Chem.* **1992**, *424*, 79–86.
- [39] M. Cowie, S. K. Dwight, A. R. Sanger, *Inorg. Chim. Acta* **1978**, *31*, L407–L409.
- [40] D. R. Drew, J. R. Doyle, *Inorg. Synth.* **1990**, *28*, 346–349.
- [41] F. T. Ladipo, G. K. Anderson, *Organometallics* **1994**, *13*, 303–306.
- [42] H. C. Clark, L. E. Manzer, *J. Organomet. Chem.* **1973**, *59*, 411–428.
- [43] [43a] N. Yonezawa, T. Hino, Y. Tokita, K. Matsuda, T. Ikeda, *Tetrahedron* **1997**, *53*, 14287–14296. [43b] S. H. Dai, C. Y. Lin, D. V. Rao, F. A. Stuber, P. S. Carleton, H. Ulrich, *J. Org. Chem.* **1985**, *50*, 1722–1725.
- [44] B. Gerharz, G. Meier, E. W. Fischer, *J. Chem. Phys.* **1990**, *92*, 7110–7122.
- [45] I. E. Marko, J. M. Southern, M. L. Kantam, *Synlett* **1991**, *4*, 235–237. [45a] I. E. Marko, M. L. Kantam, *Tetrahedron Lett.* **1991**, *32*, 2255–2258.
- [46] [46a] A. Studer, M. Bossart, T. Vasella, *Org. Lett.* **2000**, *2*, 985–988. [46b] C. A. van Walree, X. Y. Lauteslager, A. M. A. van Wageningen, J. W. Zwikker, L. W. Jenneskens, *J. Organomet. Chem.* **1995**, *496*, 117–125.
- [47] G. M. Sheldrick, *SHELXS-97*. University of Göttingen, Germany, **1997**.
- [48] P. T. Beurskens, G. Beurskens, R. de Gelder, S. García-Granda, R. O. Gould, R. Israel, J. M. M. Smits, *The DIRDIF99 Program System*, University of Nijmegen, The Netherlands, **1999**.
- [49] G. M. Sheldrick, *SHELXL-97*. University of Göttingen, Germany, **1997**.
- [50] A. L. Spek, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, **2002**.

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