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Bridging the gap in catalysis *via* multidisciplinary approaches

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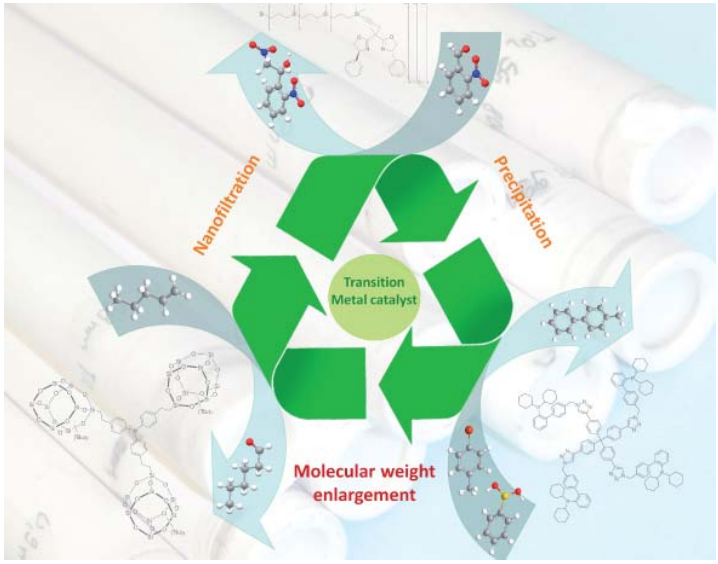

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An approach to bimetallic catalysts by ligand design†

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New diphosphines based on benzofurobenzofuran and dibenzodioxocin backbones, forming exclusively bimetallic complexes were designed and synthesized. Depending on the ligand to metal ratio, face-to-face bimetallic complexes or *syn*-chloride bridged dimeric complexes were formed as main reaction products. The structures of the rhodium complexes of the new ligands **4**, **7**, **10**, **13**, **16** were established in solution by NMR, IR, and MS spectroscopy. The molecular structures of the *syn*-chloride bridged dimeric complexes $[Rh_2(CO)_2(\mu\text{-}Cl)_2(\mathbf{4})]$ (**22**), $[Rh_2(CO)_2(\mu\text{-}Cl)_2(\mathbf{10})]$ (**24**), and the face-to-face bimetallic complexes $[Rh(CO)Cl(\mathbf{4})]_2$ (**17**), $[Rh(CO)Cl(\mathbf{10})]_2$ (**19**), and $[Rh(CO)Cl(\mathbf{13})]_2$ (**20**) were confirmed by X-ray crystallography. Ligands **4**, **7**, **10**, **13**, **16**, and SPANphos were tested in rhodium catalyzed methanol carbonylation at 150 °C and 22 bar of CO gas, showing high activities under catalytic conditions.

Introduction

The study of bimetallic compounds fascinates scientists from very different areas. The construction of synthetic analogues of metallobiomolecules containing bimetallic centres drove its initial development. They have been considered as models to mimic the coordination environment of metals at biologically active sites in an attempt to reproduce their chemical and/or physical properties. Both hetero- and homobimetallic species are known, which may offer new possibilities for activating organic and inorganic molecules.[1–13]

Bimetallic species are interesting entities *per se* due to their peculiarities. When the two metallic centres are in close proximity (often less than 5 Å apart) they exhibit correlated physicochemical properties, responsible for the often claimed cooperative effect between the two metallic centres.[2,14–18] Clearly, homogeneous catalysis could benefit enormously of such systems, as catalysts with improved efficiency and selectivity, able to promote reactions that are not possible using a single metal centre, can be envisaged. Several examples have already been reported in the literature.[19–29]

As concerns applications, the morphological control of the active site is a requisite, which can be achieved through the use of the appropriate binucleating ligand. Often these ligands are tri- and tetradentates. Representative examples are macrocyclic frameworks derived from Schiff bases and polyketonate precursors, cyclic polyethers or polyamines.[1,9]

Homo- and heterobimetallic halogen-bridged dimers are among the most versatile metal precursors for homogeneous catalysis and organometallic synthesis, due to their high intrinsic reactivity. Unfortunately, in the presence of an excess of donor ligands (as phosphines, frequently used in catalysis) the halogen bridge is cleaved to yield the monomeric adduct.[19,30–32] The bimetallic character of those compounds can be maintained by means of ligands able to coordinate to both centres stabilizing the structure and incorporating the donor group intended for catalysis. There are several examples on the use of diphosphines as binucleating ligands for such complexes. When the ligand-to-metal ratio is 1 : 2, dimers containing one diphosphine and two bridging halogen ions were characterized (Fig. 1). These complexes can be described as "edge sharing dimers" as explained elsewhere.[33] One can distinguish four different isomeric forms, taking into account the coordination mode of the ligand and the bending angle defined by the two coordination planes of the metals.

Complexes of this type require binucleating diphosphines with a large P–P distance. There are complexes consisting of mixed-metal assemblies where the diphosphine coordinates in the *syn*-form,[34–36] tetranuclear complexes with two units of halide bridged metal dimers in *syn*-form,[37,38] and dimetallacrown palladium ethers with the diphosphine chelating in both *anti* or *syn*-forms.[39,40] There are few examples of simple diphosphines capable of forming these kind of structures. They were reported for a phosphine derivative of 2-diphenylphosphinobenzoic acid,[41] for SPANphos[42] (giving *anti*-dimeric halide bridged complexes) and more recently for a triptycene based ligand (which forms bent-*syn* dimers).[43] However, these diphosphines are also able to form mononuclear *trans*-chelating complexes in solution.

When two diphosphines are used to stabilize two metals through a double bridge, a different type of structure is obtained. The chemistry of those bimetallic compounds was studied extensively, especially for ligands based on the small diphosphinomethane skeleton,[22,44–52] but also numerous examples containing larger backbones are known.[53–62] One can distinguish basically three structures. When in addition to the two mutually *trans* μ-ligands a metal–metal bond exists the structure is called side-by-side.[46,48,63–68] If there is neither a metal–metal bond nor another bridging ligand apart from the μ-diphosphine the structures are described as face-to-face bimetallic complexes.[22,46–62,69] The last possibility involves structures in which a third ligand bridges the two metals: the so called A-frame compounds (Fig. 2).[46,47,51,70–74]

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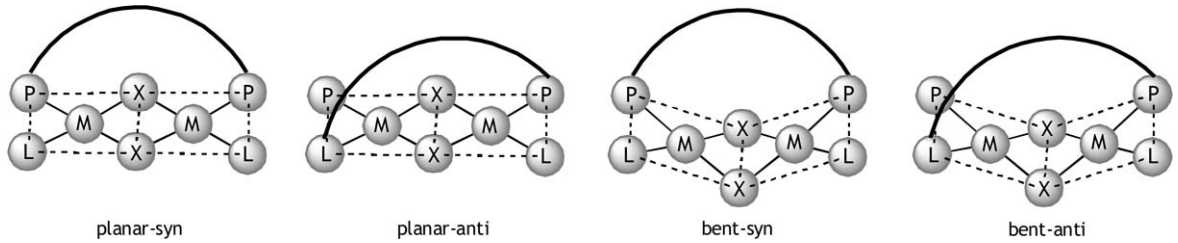


Fig. 1 Dimeric diphosphine-bridged structures containing M_2X_2 core.

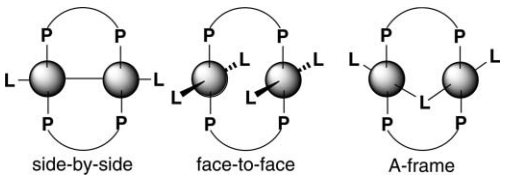


Fig. 2 Bimetallic structures containing mutually *trans*-diphosphines.

In the past, when working with wide bite angle or rigid P–P ligands, we claimed occasionally the possible involvement of bimetallic species as responsible for some of the unusual catalytic events observed.[42,75–77] Unfortunately, the capability of the ligands under study to also form mononuclear species (in which the ligand coordinates either *trans* or in a monodentate manner) did not allow us to attribute the observed activities exclusively to bimetallic intermediates. The design of ligands that form exclusively bimetallic complexes (especially the halogen-bridged ones) is the current challenge. It is not trivial since they should contain large, rigid and properly designed backbones.

Recently, when studying the homogeneous catalytic carbonylation of methanol using SPANphos, we encountered an unprecedented reactivity which we attributed to SPANphos stabilized dinuclear complexes.[42,75] Although the ligand was originally conceived as a *trans*-chelator,[78] it forms unique dimeric species when equimolecular quantities of metal and phosphorus are used. A possible involvement of the oxygen of the backbone, establishing a metal–oxygen bond could not be discarded with certainty.

That catalytic example, which still intrigues us, triggered this research. We thought about a new generation of ligands, in which the backbone design and rigidity ensures that no monomers can form. Looking for backbones with the same P–C–C–O–C–O–C–C–P connectivity created by the bischroman backbone of SPANphos, we decided to explore the potential of benzofurobenzofuran (BFBF) and dibenzodioxocin (DBDOC) skeletons (Fig. 3).

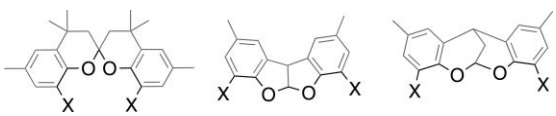


Fig. 3 Bischroman, benzofurobenzofuran and dibenzodioxocin backbones.

Here we report, in addition to ligand design and synthesis, a series of rhodium complexes with two specific types of structures, face-to-face bimetallic and *syn*-dimeric halide bridged complexes. In particular we are interested in $[Rh_2(\mu\text{-}Cl)_2(CO)_2(\text{diphosphine})]$ complexes and their use in rhodium catalyzed methanol carbonylation.

Results and discussion

Ligand design

Before addressing the synthesis of the new ligands we wanted to get structural information on the backbones envisaged. Although it is tempting to consider that CPK models suffice to deduce main trends, a measure of the backbone strain needed to locate the phosphorus atoms not only at the correct distance but also appropriately oriented requires a quantitative methodology.

Looking for objective ligand comparison we considered the use of molecular mechanics. The limitations of these type of calculations for structures involving metals are well known. Accordingly, we limited its use to the evaluation of the energy of the ligand fragment at different conformations as a measure of their tendency to form certain structures (namely bimetallic *vs.* monometallic). The nuclearity of the products obtained at certain ligand-to-metal ratios used depends on the backbone structure and rigidity.

The conformational search was performed introducing metals to take into account approximate distances and orientation of the phosphorus lone pairs, but the energy of **the ligand fragment only** in the final conformations is considered for comparison.

The energy of the free ligand in its most stable conformation was calculated as reference value. As models for compounds having ligand-to-metal ratio 1 : 1, the energy of the ligands on a monometallic chelate (RhL) and a bimetallic (Rh_2L_2) fragment was evaluated. For a lower ligand-to-metal ratio (1 : 2) we restricted the studies to model chloro-bridged dimers, (Rh_2Cl_2L) which were the structures relevant for our investigation.

A schematic representation of the different structures used for the calculations is presented in Fig. 4.

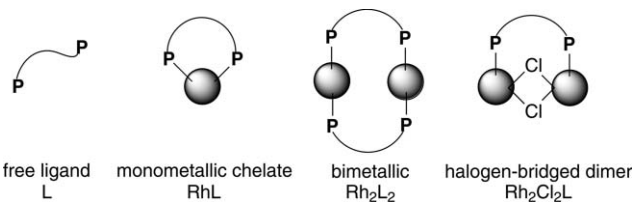


Fig. 4 Structures used for the molecular mechanics calculations.

Calculations were performed on CaChe™ using MM2 as Force Field.[79] The results obtained, presented in Table 1, showed that an important increase in conformational energy of the ligand is required to form ML chelating structures (ΔU_{ligand} ~ 15–20 kcal mol^{-1}). The P–P distance needed for the two phosphorus atoms to coordinate to the same metal (around 4.4 Å) is considerably

Table 1 Conformational energy of the ligands and selected structural parameters. Molecular mechanics calculations were performed on free ligands (L), rhodium chelate (RhL), rhodium bimetallic (Rh_2L_2) and halogen-bridged rhodium dimeric compounds (Rh_2Cl_2L). See ESI for details

Ligand	Structure	U/Kcal mol^{-1}	P–P distance/Å	Backbone "folding"/°[b]	P–M–P angle/°
BFBFMe2 **4**	L	−27.9	7.26	111.6	—
	RhL	−8.9	4.36	101.7	140.1
	Rh_2L_2[a]	−26.3	7.54	112.4	178.8
	Rh_2Cl_2L	−15.1	6.64	108.0	—
BFBFH2 **10**	L	−27.7	7.31	112.9	—
	RhL	−8.4	4.28	101.2	135.0
	Rh_2L_2[a]	−26.3	7.43	112.1	176.9
	Rh_2Cl_2L	−14.7	6.63	108.4	—
DBDOC **13**	L	−33.1	6.95	105.6	—
	RhL	−18.4	4.31	98.1	136.9
	Rh_2L_2[a]	−31.4	7.12	105.6	176.7
	Rh_2Cl_2L	−21.4	6.54	103.5	—
TRIPTYCENE[c]	L	−35.8	4.53	120.0	—
	RhL	−35.8	4.08	117.6	123.6
	Rh_2L_2[a]	−32.6	4.74	120.4	170.2
	Rh_2Cl_2L	−27.0	5.39	121.8	—
XANTPHOS	L	−37.4	4.15	136.8	—
	RhL	−35.1	3.80	135.0	110.4
	Rh_2L_2[a]	−28.7	4.94	136.2	167.1
	Rh_2Cl_2L	−24.6	5.03	137.2	—

To achieve meaningful energy comparison, after calculating the most stable conformation of the free ligand (L), the monometallic chelate (RhL), the bimetallic complex (Rh_2L_2), and the chloride-bridged dimer (Rh_2Cl_2L), the energy of only the ligand fragment is evaluated.[a] Averaged values of the parameters measured independently for each ligand in the molecule. [b] Averaged value of dihedral angles of the central atoms of the backbone. An exact definition for each ligand can be found in the supplementary material. [c] 1,8-Bis(diisopropylphosphino)-triptycene.

shorter than the one encountered in the free ligands (7–8 Å). This short P–P distance can only be achieved by a deformation of the ligand. The "folding" of the backbone in such a rigid structure is responsible for the high energy values obtained (Table 1). Bimetallic M_2L_2 type complexes instead, can be formed by a minimal ligand deformation (ΔU_{ligand} ~ 3 kcal mol^{-1}) as they do not impose large changes in P–P distances.

Such complexes were modeled with a backbone conformation close to the one of the free ligand (see distances and backbone "folding" terms in Table 1).

These calculations also showed that all ligands (except **7**) are also suited for the formation of halogen-bridged dimers in a *syn* manner when working at a lower ligand-to-metal ratio. BFBF and DBDOC based ligands suit the structural (P–P distance and phosphorus lone pair orientation) requirements to form such constrained structures.

According to these data, monometallic complexes with the ligand acting as a chelate should not be accessible for BFBF and DBDOC based ligands, but instead they have a marked preference to form bimetallic species. In contrast, other wide bite angle ligands (such as Xantphos[80] and the triptycene derived ligands developed by Gelman) form preferentially monometallic species, which is in agreement with the compounds known.

Ligand synthesis

Scheme 1 summarizes the synthetic pathways to ligands **4**, **7**, **10**, **13** and **16**. Ligands **4**, **10**, **13** and **16** present C_s symmetry. The C_2-symmetric ligand **7**, an isomeric form of ligand **4**, has been included due to its availability (**2** and **5** were reported as thermodynamic and kinetic products of the same reaction[81,82]). It falls outside the original design and for this reason it is treated as an exception along the discussion.

Benzofurobenzofuran-based backbones **2** and **5** were both synthesized by a Claisen rearrangement of diaryloxybutyne **1** using aluminium trichloride as a Lewis acid catalyst in the case of **2**,[83,84] and a Brønsted acid in the presence of N,N-diethylaniline in the case of **5**.[81,85] They were brominated with N-bromosuccinimide (NBS) to obtain dibromo derivatives **3** and **6**, which were reacted at −78 °C first with *n*-BuLi and then with chlorodiphenylphosphine yielding **4** and **7** in 72 and 62% yield respectively.

Interestingly, diphosphine derivative **7** is a C_2-symmetric chiral ligand. Isomeric diphosphines **4** and **7** can be easily distinguished by ^{1}H-NMR spectroscopy. Compound **7** shows a single methyl signal (δ 1.58) for the C(CH_3) group on the fused furan rings whereas compound **4** exhibits two distinct resonances (δ 1.60 and δ 1.41) for the two different C(CH_3) methyl groups. In both molecules the methyl groups on the aromatic rings are equivalent.

Due to the low yields and long reaction times needed for the synthesis of the diaryloxybutyne **1** (common intermediate towards **4** and **7**) we explored an alternative strategy to obtain benzofuro[2,3-b]benzofuran backbones. Acid-catalyzed reaction between *p*-cresol and glyoxal afforded **8** in overall yield of 40% in only one step.[86] Compound **8** is analogous to **2** but it does not contain the methyl groups on the fused furan rings. Dibromo derivative **9** and the desired diphosphine **10** (50% yield) were prepared as reported above for analogous derivatives of **2**.

Dibenzodioxocin-type backbones **11** and **14** were prepared by a Friedel–Crafts reaction and intramolecular acetalization of *p*-cresol or 4-*tert*-butylphenol and tetramethoxypropane in trifluoroacetic acid, which acts as solvent and catalyst.[87] Again, the dibromo derivatives **12** and **15** and the corresponding diphosphines **13** and **16** were prepared following the same procedures described above, with 86% and 66% yield, respectively. Diphosphine **16** was synthesized to increase solubility under catalytic conditions as some problems were encountered for ligand **13**.

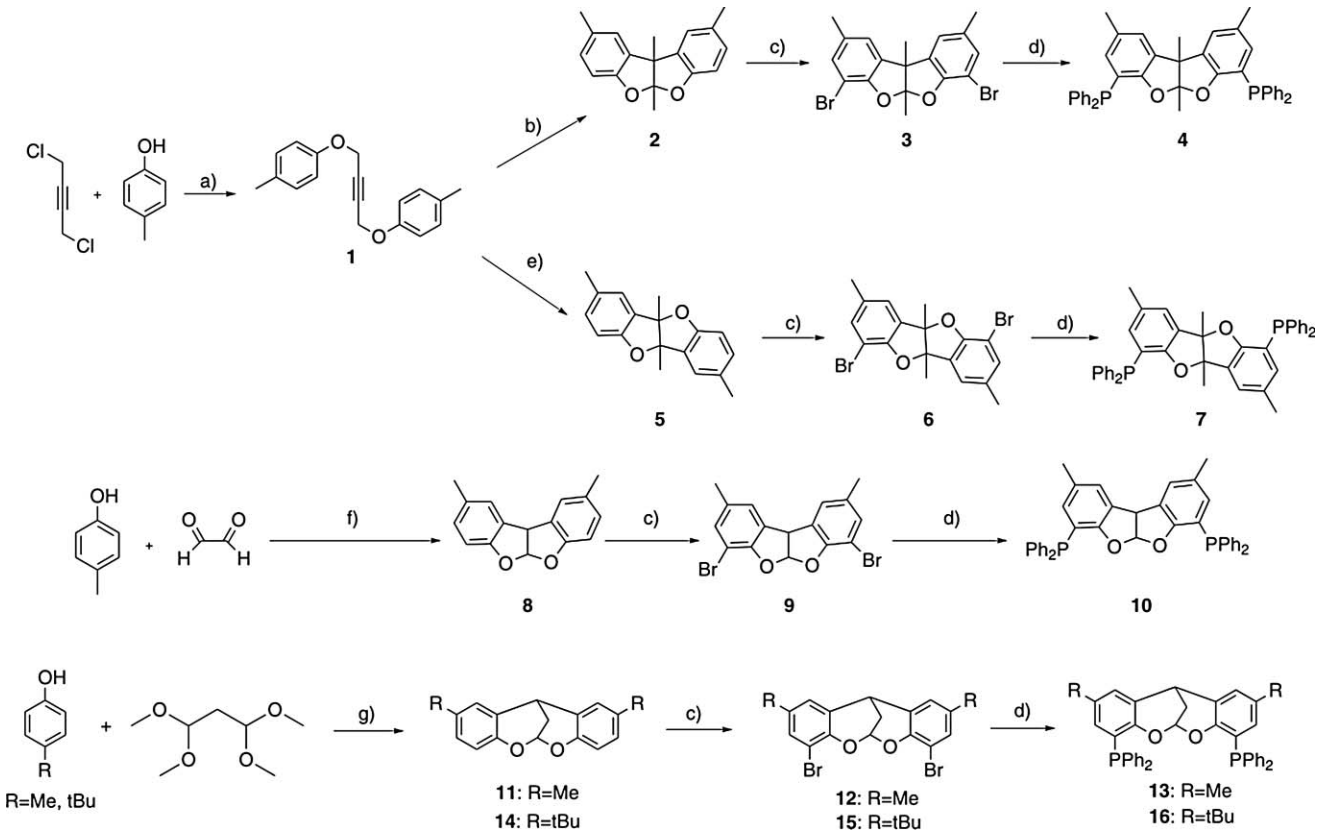
All the compounds and intermediates **1–16** were characterized by NMR spectroscopy, elemental analysis and exact mass spectrometry.

Coordination studies

The coordination ability of the new ligands towards rhodium was studied by *in situ* NMR spectroscopy. Additionally, solid state analysis by X-ray diffraction was performed when crystalline samples were obtained from these solutions.

Ligand-to-metal ratio 1 : 1. Ligands **4**, **7**, **10**, **13** and **16** were reacted with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in 2 : 1 molar ratio (ligand-to-metal ratio of 1 : 1) and the nature of the products obtained was inferred from *in situ* ^{31}P-NMR spectroscopy.

Three different species were observed in the ^{31}P-NMR spectrum of mixtures of ligand **4** with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in a ligand-to-metal ratio of 1 : 1 ($CDCl_3$). Apart from a small doublet due to



Scheme 1 Reaction conditions: (a) K_2CO_3, acetone; (b) $AlCl_3$, DCM; (c) NBS, DMF; (d) *n*-BuLi, $ClPPh_2$, THF; (e) N,N-diethylaniline, APTS, reflux, 3h; (f) H_2SO_4, CH_3COOH, H_2O, 80 °C; (g) CF_3COOH.

a residual quantity of the tetracarbonyl intermediate **27**, (*vide infra*) the main signals present ABX patterns; there is a major one attributed to compound **17a** and a less intense one corresponding to a minor compound **17b** (Table 2). Variable temperature experiments (CD_2Cl_2, in the range 298–193 K) showed that the major signal is independent of the temperature, and the minor one (less intense in this solvent) broadens at lower temperatures. Surprisingly, two CO bands were found in the IR spectrum of **17**, (one at 1970 cm^{-1} and one at 1989 cm^{-1}). The latter, at a rather high frequency is probably due to **22**, originating from the residual quantity of **27** observed in the NMR spectra (as suggested by the referees). Between different attempts the ratio of the two signals varied but we never observed the low-frequency signal only, as expected for **17**. Further analysis on isolated samples are required for a complete characterization of this compound.

The ^{31}P-NMR spectrum of a mixture of ligand **10** with half an equivalent of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in either CD_2Cl_2 or $CDCl_3$ was too broad to be assigned. Variable temperature experiments were performed (CD_2Cl_2). Already at 273 K a sharp signal corresponding to an ABX pattern was distinguished (δ_{PA} 23.9, $^1J_{Rh\text{–}PA}$ = 122 Hz, $^2J_{PB\text{–}PA}$ = 371 Hz; δ_{PB} 20.9, $^1J_{Rh\text{–}PB}$ = 125 Hz, $^2J_{PA\text{–}PB}$ = 371 Hz) on top of several minor signals that could not be identified. When the temperature was lowered to 193 K, the original signal was still present as the main species **19a**, although slightly shifted upfield (δ_{PA} = 23.1 ppm, $^1J_{Rh\text{–}PA}$ = 130 Hz, $^2J_{PB\text{–}PA}$ = 366 Hz, δ_{PB} = 20.6 ppm, $^1J_{Rh\text{–}PB}$ = 125 Hz, $^2J_{PA\text{–}PB}$ = 366 Hz). Additionally, a second set of signals with the same pattern could be distinguished at this temperature and attributed to a closely related compound **19b** (δ_{PA} = 24.4 ppm, $^2J_{Rh\text{–}PA}$ = 132 Hz, $^1J_{PB\text{–}PA}$ = 359 Hz, δ_{PB} = 21.8 ppm, $^2J_{Rh\text{–}PB}$ = 128 Hz, $^1J_{PA\text{–}PB}$ = 359 Hz). The main signals present in the low temperature spectra were simulated assuming two species in 63/37 ratio (Fig. 5). Some minor peaks with similar spectroscopic patterns were also visible at this temperature indicating the presence of more isomers in minor proportions.

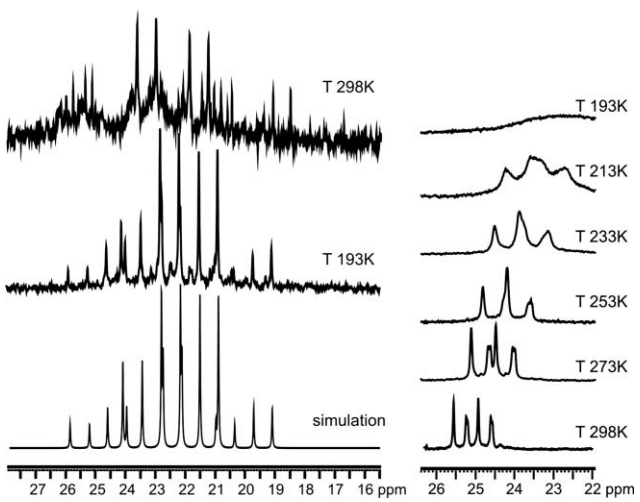


Fig. 5 Variable temperature ^{31}P-NMR spectra. Left: species **19** at 298 K, 193 K and simulation. Right: species **18** at different temperatures.

In the ^{31}P-NMR spectra of complexes **20** and **21**, (in both CD_2Cl_2 and $CDCl_3$) one major species is observed. It appears as

Table 2 Characterization data of rhodium complexes containing ligand-to-metal ratio of 1 ($CDCl_3$, 298 K)

Complex	^{31}P-NMR δ/ppm	$^{1}J_{P-Rh}$/Hz	$^{2}J_{P-P}$/Hz	IR ν(CO)/cm^{-1}
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{4})_2]$ (**17a**)	23.9	131	366	
	16.6	131	366	1970
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{4})_2]$ (**17b**)	24.9	128	368	
	19.7	128	368	
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{7})_2]$ (**18**)	25.4	128	—	1970
	25.0	128	—	
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{10})_2]$ (**19a**)[a]	23.1	130	366	
	20.6	125	366	1973
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{10})_2]$ (**19b**)[a]	24.4	132	359	
	21.8	128	359	
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{13})_2]$ (**20**)	25.7	130	362	1958
	22.6	128	354	
trans,*trans*-$[Rh_2(Cl)_2(CO)_2(\mathbf{16})_2]$ (**21**)	26.8	131	363	1968
	22.5	129	363	

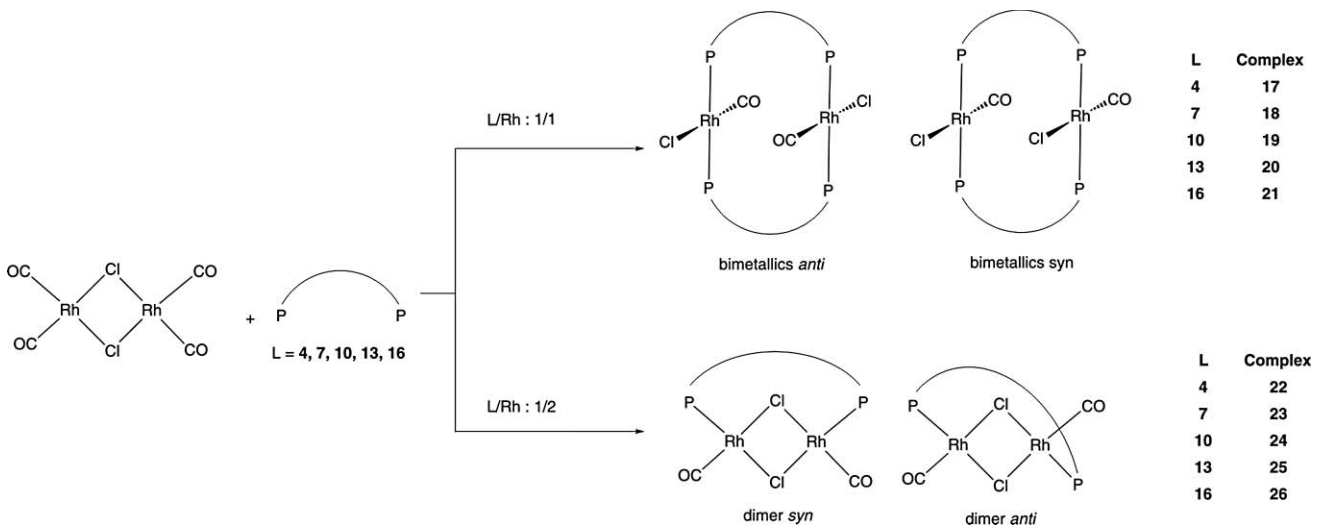
[a] CD_2Cl_2, 193 K.

a sharp ABX pattern with chemical shifts and P–Rh coupling constants similar to those observed for complexes **17** and **19**. Precipitation handicapped low temperature experiments in the case of complex **20**. For the more soluble complex **21**, the spectra did not change with the temperature, which suggests that these ligands form exclusively one complex in solution, or the several isomers are in a fast exchange at the temperature range employed.

Applying this stoichiometry to SPANphos, we obtained exclusively the mononuclear complex *trans*-[Rh(CO)Cl(SPANphos)].[42] Monometallic *trans*-[Rh(CO)Cl(L)] complexes of the ligands described should exhibit C_s symmetry. Thus, in the absence of signals of free phosphine, the existence of inequivalent phosphorus atoms is indicative of a bimetallic structure. The large value of the P–P coupling constant observed in all the cases together with the carbonyl bands observed in the IR spectra at around 1975 cm^{-1} are indicative of a *trans* coordination of two diastereotopic phosphorus atoms at each rhodium centre.[61,88–92]

The situation when using the C_2-symmetric ligand **7** should be analyzed independently. When this ligand was mixed with half an equivalent of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in $CDCl_3$, two doublets (δ 25.4, J = 128 Hz; δ 25.0, J = 128 Hz) were observed in the ^{31}P-NMR spectra around 25 ppm. These signals cannot be attributed to an ABX signal as observed for the other ligands, because variable temperature experiments (in the range 298–193 K) showed that it corresponds to a more complicated pattern (Fig. 5). The doublet at 25.4 ppm which slightly broadens at lower temperatures is probably due to a species in which the two phosphorus nuclei are equivalent. A C_2-symmetric Pd *trans*-P bimetallic derivative of ligand **7** has been observed before by X-ray diffraction.[93] The doublet at higher fields splits into two doublets at 273 K, and broadens at lower temperatures. Most likely it is another isomer of a *trans*-P bimetallic, complex in which the P–P coupling is not observed due to near synchronicity of the phosphorus nuclei.

To better understand the diversity of species observed with some ligands it is worth highlighting several structural facts: for idealized face-to-face (*trans*-P) $[Rh_2(CO)_2Cl_2(L)_2]$ bimetallic complexes (L = diphosphine), two different, *syn* and *anti*, conformers can be envisaged depending on the relative orientation of the CO and Cl in both rhodium centers (Scheme 2). Additionally, even though the two metals show parallel coordination planes, (as has been observed in all the X-ray structures obtained with ligands **4**, **10** and **13**, *vide infra*) there are several conformations that can be obtained by simultaneous rotation of the coordination plane of each metal around their hypothetical P–Rh–P and/or Cl–Rh–CO axes (Fig. 6). Most probably, in solution all these conformations are in a fast exchange, due to the large size of these macrocyclic assemblies, but different rotation angles (γ and ϕ, Fig. 6) can be encountered in solid state structures. Additionally, due to the "folded" structure of the backbones, each ligand can coordinate to the pair of metals exposing its concave or its convex



Scheme 2 Schematic representation of the two types of di-rhodium complexes observed for ligands **4**, **7**, **10**, **13**, and **16**.

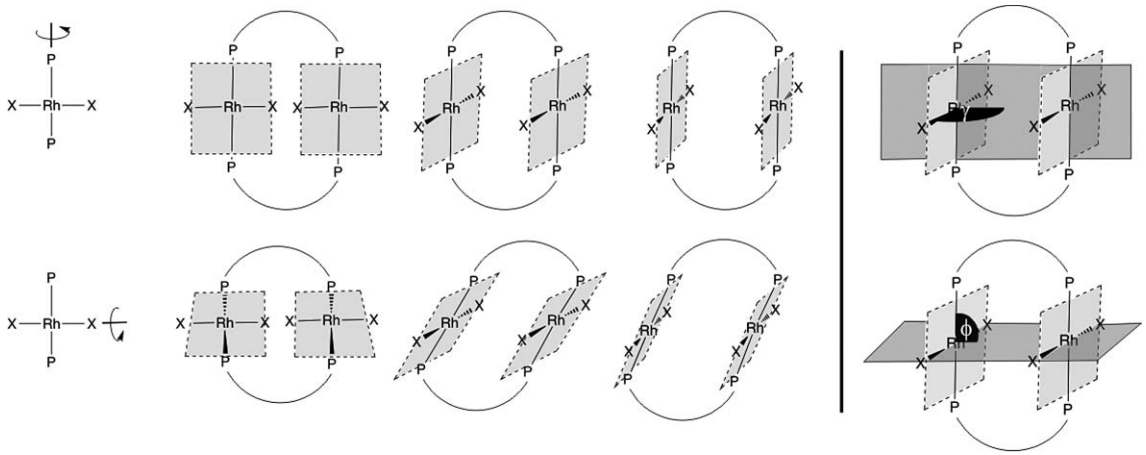


Fig. 6 Different conformations obtained by simultaneous rotation of the two metal coordination planes along their P–Rh–P or X–Rh–X axes.

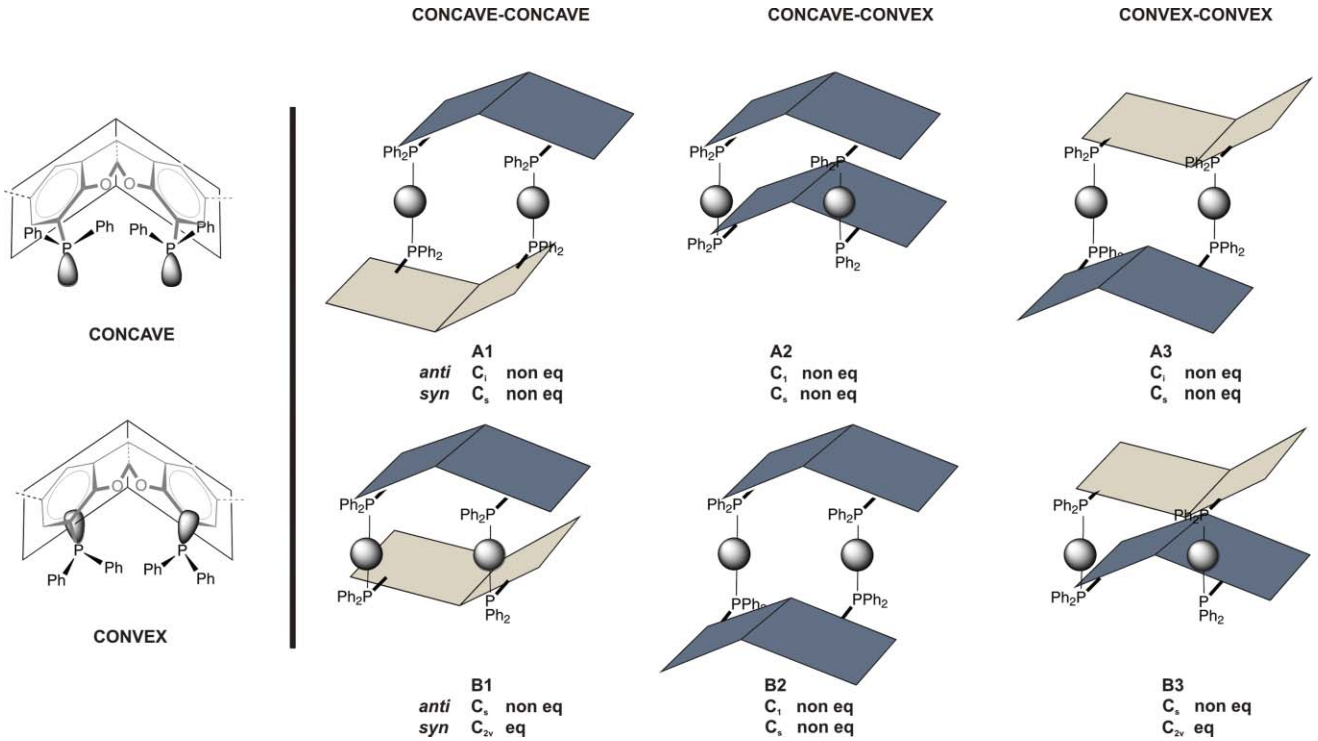


Fig. 7 Isomeric face-to-face (*trans*-P) bimetallic complexes possible with C_s symmetric ligands **4**, **10**, **13** and **16**; three different conformers of each isomer **A** and **B** have been depicted, depending on the side (concave or convex) exposed toward the metal centers. From all these structures, only **B1** and **B3** could eventually display magnetically equivalent phosphorus nuclei in *trans*-$[Rh_2(CO)_2Cl_2L_2]$ face-to-face bimetallic compounds due to their symmetry. Punctual group of symmetry, and the equivalence–non equivalence of the two phosphorus coordinated to the same rhodium on idealized ($\gamma = 90°$, $\varphi = 90°$) *syn* and *anti* derivatives are indicated.

face, not necessarily in a synchronous manner (Fig. 7). With C_s symmetric ligands **4**, **10**, **13** and **16**, two different isomers (**A** and **B** in Fig. 7) can be encountered. The interconversion between them requires the cleavage of the two P–Rh bonds of one of the ligands to permute their positions and thus these isomers should be distinguished in solution. Additionally, several conformers can be envisaged for each isomer (**A** and **B**) which interconvert through concerted rotations around the P–Rh axes (as noticed by the referees). Some representative examples are depicted in Fig. 7.

According to this description, it is reasonable that in the case of ligands **4** and **10** two different species were observed at 298 and 273 K respectively, with different intensities. They probably correspond to the two isomeric bimetallic compounds (A and B). At lower temperatures the existence of more isomers in equilibrium is evident in both cases. They are probably different rotational conformers of the minor isomer (either *syn–anti* or concave–convex). The fact that the signal of the major isomer (**17a**, **19a** and **21**) remains sharp along the temperature range studied makes us discard the existence of an equilibrium between isomers A and B. We consider that the major isomer exists as a unique conformer, or as a mixture of several of them in a fast exchange on the NMR time scale.

In the case of ligand **7** the situation is different. Due to its C_2 symmetry when a face-to-face bimetallic is formed, decoordination of one of the ligands and permutation of their P–Rh bonds renders the same compound. If the ligand were enantiopure only one isomeric face-to-face bimetallic could be formed (though concave–convex conformations are still possible). In our studies, the ligand is obtained and used as a racemate, so the two enantiomeric compounds and a *meso* bimetallic are possible (Fig. 8).

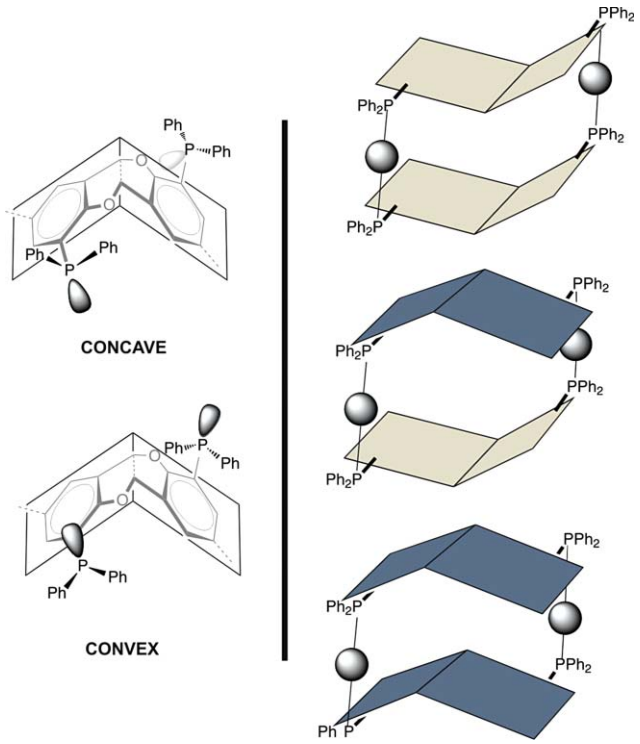


Fig. 8 Diastereoisomeric face-to-face (*trans*-P) bimetallic complexes possible with the C_2 symmetric ligand **7**; top and bottom structures are enantiomers and the middle one is the *meso* form. Only one conformer of each isomer has been depicted.

The bimetallic nature of complexes **17**, **19** and **20** was confirmed by X-ray diffraction (Fig. 9). Selected bond lengths and angles are listed in Table 3. Their molecular structures confirm that they all are face-to-face bimetallic structures. The two metals are in a distorted square planar environment with two approximately linear and antiparallel Cl–Rh–CO moieties (*anti* configuration) bridged by two diphosphines, **4**, **10** and **13** respectively, maintaining a *trans*-P,P-coordination for each rhodium atom. The angles P_1–Rh_1–P_2 and Cl_1–Rh_1–C_1(O) and the P–Rh, Cl–Rh and Rh–C bond lengths lie within the normal range of *trans*-diphosphine complexes.[41,61,94,95] All complexes contain parallel metal coordination planes, but very different torsion angles (see Table 3). It is remarkable that, as observed by the referees, the three structures can be described as isomer A in Fig. 7. In compound **17** the two ligands are coordinated through its concave side (conformer A1, Fig. 7),‡ but convex sides are exposed to the core in molecular structures of **19** and **20** (conformer A3, Fig. 7).

Table 3 Selected bond distances (Å) and angles (°) for **17**, **19** and **20**

	17	**19**	**20**
Rh(1)–P(1)	2.3161(3)	2.3056(9)	2.3244(5)
Rh(1)–P(2)	2.3349(3)	2.3228(8)	2.3305(5)
P(1)–P(2)	4.625(3)	4.577(4)	4.645(3)
P(1)–P(2A)	7.225(3)	7.939(4)	7.405(3)
Rh(1)–Rh(1A)	6.952(2)	8.402(3)	7.469(3)
Rh(1)–Cl(1)	2.3792(3)	2.3764(8)	2.3911(6)
Rh(1)–C(1)	1.8114(11)	1.819(3)	1.810(2)
Rh(1)–O(2)	3.871(3)	3.810(4)	2.991(3)
Rh(1)–O(3)	5.445(3)	6.063(4)	4.737(4)
P(1)–Rh(1)–P(2)	167.857(10)	162.88(3)	172.594(19)
Cl(1)–Rh(1)–C(1)	176.46(3)	177.23(10)	174.90(8)
ϕ^a	47.13(0.01)	72.44(0.03)	74.95(0.02)
γ^a	44.24(0.01)	48.17(0.03)	68.53(0.02)

[a] As described in Fig. 6.

Dimeric chloro-bridged compounds. ^{31}P-NMR spectroscopic analysis of 1 : 1 mixtures of ligands **4**, **7**, **10**, **13** and **16** and [$Rh_2(\mu$-$Cl)_2(CO)_4$] in $CDCl_3$ showed the immediate formation of two rhodium complexes (two doublets), one at around 40–45 ppm ($^1J_{Rh-P}$ ~ 180 Hz) and a second one at higher fields with smaller Rh–P coupling constants (δ ~ 20 ppm, $^1J_{Rh-P}$ ~ 125 Hz). After half an hour reacting or after the sample was submitted to a cycle of vacuum, only the doublet at lower fields was observed.

‡ Diffraction data to determine molecular structure of **17** corresponds to the best out of seven different measured crystals. In all of them a structure type A1 was observed. Structures type A3 have been obtained when other metals were used.

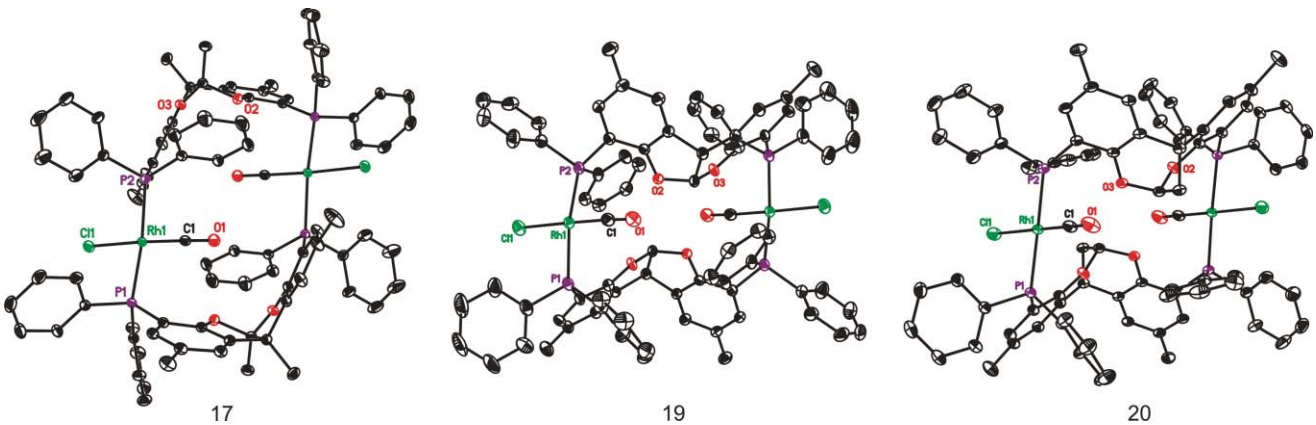
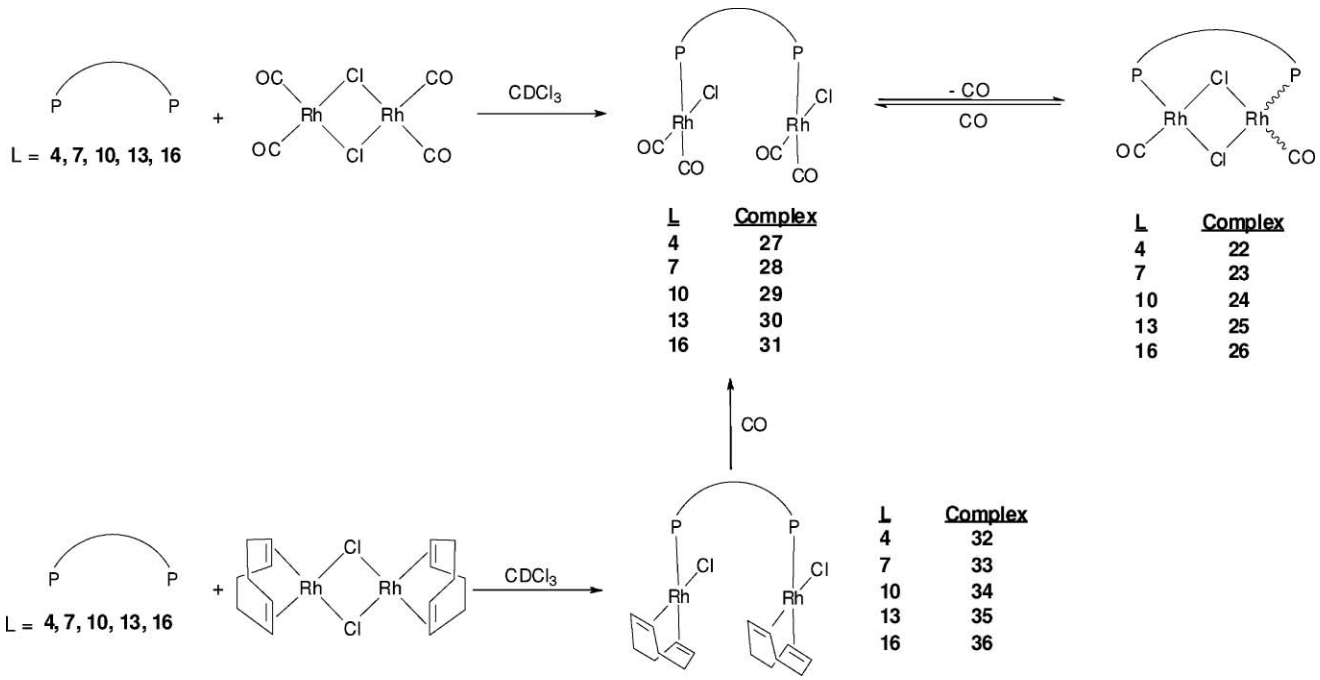


Fig. 9 ORTEP-plots (thermal ellipsoids shown at 50% probability levels) of complexes **17**, **19** and **20**. Non-relevant hydrogen atoms have been omitted for the sake of clarity.



Scheme 3 Schematic representation of the preparation for rhodium chloride bridge diphosphine dimers.

This signal, consistent with those published for halogen-bridged dimeric complexes,[35,42,43] was attributed to the dimeric species $[Rh_2(\mu\text{-}Cl)_2(CO)_2(L)]$ (L = **4**, **7**, **10**, **13**, **16**). These complexes show a single band in the carbonyl region of the IR spectra at ~1993 cm^{-1}, in agreement with the values reported for similar compounds.[37,38,42] The doublet initially observed was assigned to an intermediate species in which the halide bridges are cleaved, but both rhodium atoms are still coordinated to two carbonyl ligands, a chloride, and a phosphorus atom of a bridging diphosphine, $[Rh_2(Cl)_2(CO)_4(L)]$ (L = **4**, **7**, **10**, **13**, **16**). Indirect evidence on the nature of these species was obtained through their reactivity and alternative synthetic pathway. Complexes **27–31** could be characterized by NMR as unique compounds in solution when CO was bubbled through a $CDCl_3$ solution of the corresponding dimers **22–26** for 10 min. Additionally, **27–31** could also be observed by bubbling CO for 10 min through solutions containing $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (cod = 1,5-cyclooctadiene) and the ligands (*via* intermediates **32–36**) in a ligand-to-metal ratio of 1 : 2 (Scheme 3). Compounds **27–31** are only stable in solutions saturated in CO. Compounds **27–31** were occasionally observed as intermediates towards compounds **17–21**, together with free phosphine. When the CO atmosphere is substituted by argon they evolve to the corresponding halogen-bridged dimers **22–26** mentioned before (Table 4). The presence of a doublet as a unique signal in the ^{31}P-NMR spectra in all the cases except for **23**, suggests a *syn*-arrangement for all the compounds (C_s symmetry). In the latter, the equivalence of the two phosphorus nuclei is indicative of an *anti* form similar to the one described for SPANphos due to the C_2 symmetry of the ligand.[42] (see Scheme 2). ^{31}P-NMR spectra of an equimolar mixture of ligand **7** and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ shows a much broader signal at around 40 ppm than the other derivatives. Perhaps in this case "supramolecular" oligomers are also present due to the large P–P distance of ligand **7**. Additionally, the spectra shows two doublets at 24.9 ($^1J_{Rh\text{-}P}$ = 129.6 Hz), and 25.3 ($^1J_{Rh\text{-}P}$ = 139.3 Hz), probably due to compound **18** formed as by-product.

Table 4 Characterization data of rhodium complexes containing ligand-to-metal ratio of 0.5

Complex	^{31}P-NMR ($CDCl_3$) δ/ppm	$^1J_{P\text{-}Rh}$/Hz	IR ν (CO)/cm^{-1}
syn-$[Rh_2(\mu\text{-}Cl)_2(CO)_2$**(4)**$]$ **(22)**	44.6	180	1992
$[Rh_2(\mu\text{-}Cl)_2(CO)_2$**(7)**$]$ **(23)**	40.4	179	1988
syn-$[Rh_2(\mu\text{-}Cl)_2(CO)_2$**(10)**$]$ **(24)**	44.1	179	1993
syn-$[Rh_2(\mu\text{-}Cl)_2(CO)_2$**(13)**$]$ **(25)**	45.7	182	1991
syn-$[Rh_2(\mu\text{-}Cl)_2(CO)_2$**(16)**$]$ **(26)**	46.6	180	1991
$[Rh_2(Cl)_2(CO)_4$**(4)**$]$ **(27)**[a]	20.5	126	2092, 2010
$[Rh_2(Cl)_2(CO)_4$**(7)**$]$ **(28)**	19.2	127	2092, 2012
$[Rh_2(Cl)_2(CO)_4$**(10)**$]$ **(29)**[a]	21.0	125	2092, 2010
$[Rh_2(Cl)_2(CO)_4$**(13)**$]$ **(30)**	20.1	126	2092, 2010
$[Rh_2(Cl)_2(CO)_4$**(16)**$]$ **(31)**	21.0	127	2092, 2010
$[Rh_2(Cl)_2(cod)_2$**(4)**$]$ **(32)**	25.2	149	—
$[Rh_2(Cl)_2(cod)_2$**(7)**$]$ **(33)**	26.1	151	—
$[Rh_2(Cl)_2(cod)_2$**(10)**$]$ **(34)**	26.7	149	—
$[Rh_2(Cl)_2(cod)_2$**(13)**$]$ **(35)**	24.6	146	—
$[Rh_2(Cl)_2(cod)_2$**(16)**$]$ **(36)**	26.3	145	—

[a] CD_2Cl_2.

The molecular structures of complexes **22** and **24** were determined by X-ray diffraction and they are depicted in Fig. 10. Selected bond lengths and angles are listed in Table 5. Both complexes can be described as bent-*syn* structures, similar to the one published by Gelman for the analogous compound derived from a 1,8-bis(diisopropylphosphino)-triptycene ligand.[43] This is in contrast with complexes observed for SPANphos (presumably responsible for the activities observed in methanol carbonylation), which form the bent-*anti* isomer.[42] A direct consequence of the *syn* structures observed is that the oxygen atoms of the backbone are further away from the metal centres than those in the SPANphos analogues. Whether this structural detail has consequences for the

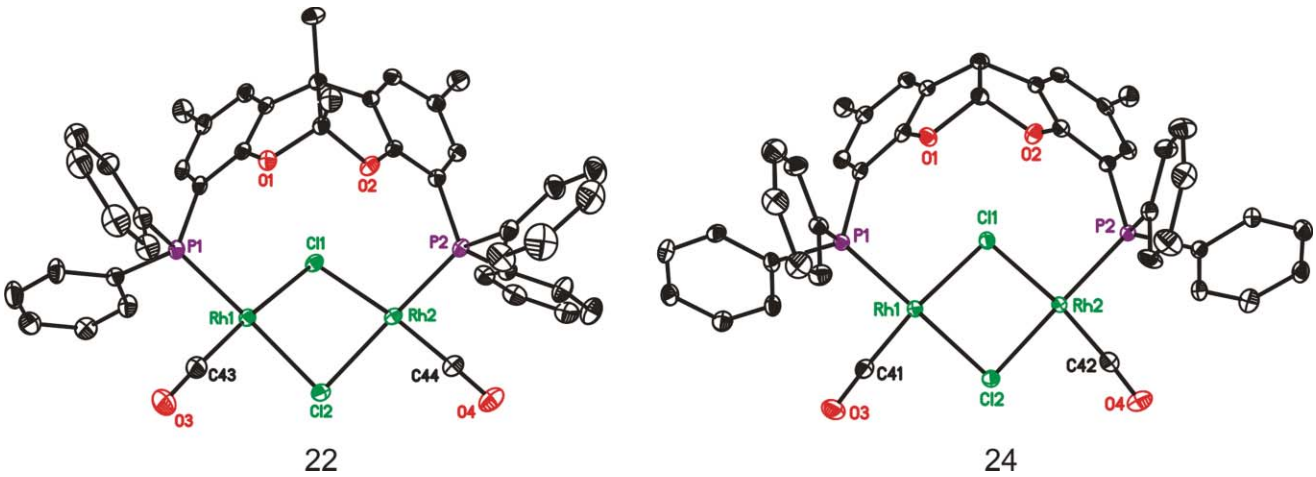


Fig. 10 ORTEP-plots (thermal ellipsoids shown at 50% probability levels) of complexes **22** and **24**. Non-relevant hydrogen atoms have been omitted for the sake of clarity.

Table 5 Selected bond distances (Å) and angles (°) for **22** and **24**

	22	**24**
Rh(1)–P(1)	2.2391(9)	2.2476(9)
Rh(2)–P(2)	2.2402(8)	2.2411(9)
P(1)–P(2)	6.576(3)	6.354(4)
Rh(1)–Rh(2)	3.375(2)	3.245(3)
Rh(1)–Cl(1)	2.3977(8)	2.4037(8)
Rh(1)–Cl(2)	2.4145(9)	2.4154(9)
Rh(2)–Cl(1)	2.3920(8)	2.4017(8)
Rh(2)–Cl(2)	2.4173(8)	2.4024(9)
Rh(1)–C(43/41)[b]	1.805(3)	1.810(3)
Rh(2)–C(44/42)[b]	1.806(3)	1.813(4)
Rh(1)–O(1)	3.675(4)	4.037(5)
Rh(2)–O(2)	3.614(4)	3.998(5)
P(1)–Rh(1)–Cl(2)	174.89(3)	178.20(4)
Cl(1)–Rh(1)–C(43/41)[b]	175.00(12)	173.63(12)
P(2)–Rh(2)–Cl(2)	178.90(2)	174.86(3)
Cl(1)–Rh(2)–C(44/42)[b]	171.68(11)	173.09(11)
Interplanar angle[a]	138.0(2)	127.3(2)

[a] Rh(1)–Cl(1)–Cl(2) and Rh(2)–Cl(1)–Cl(2) interplanar angle. [b] C(43) and C(44) for complex **22**; C(41) and C(42) for complex **24**.

reactivity or not remains a key-question in our research, which hopefully the study of these systems will help to elucidate.

The interplanar angle measured at the Rh_2Cl_2 core was estimated at 138° and 127° for complexes **22** and **24** respectively. The bending is not as large as that reported for triptycene-diphos (Fig. 11),[38,43] possibly due to the larger P–P distance that our ligands exhibit.

This interplanar angle is even larger than the one encountered for analogous SPANphos complexes which accounts for the large Rh–Rh distances observed (3.37 and 3.24 Å for **22** and **24** respectively).[42] Each rhodium atom is in a planar environment. The terminal carbonyl ligands adopt, as expected, a *syn* conformation with Rh–C, Rh–Cl and Rh–P distances within the normal range. As mentioned before, there is no bonding interaction between rhodium and the oxygen atom of the backbone.

Carbonylation of methanol

In situ generated chloro-bridged dimeric complexes derived from ligands **4**, **7**, **10**, **13**, **16** and SPANphos (diphenylphosphine derivative) were tested in the carbonylation of methanol. The reaction

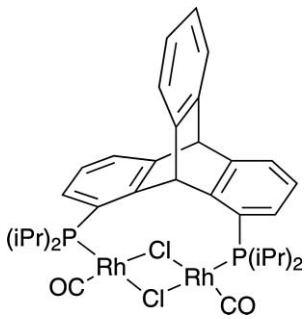


Fig. 11 Triptycene-based *syn*-rhodium chloride bridged dimer.

was carried out at 150 °C under a CO pressure of 22 bar. After 90 min the reaction was stopped and the solution was analyzed by NMR spectroscopy to determine the selectivity. The conversion was calculated from gas consumption of a pressurized reservoir. These highly diluted conditions were chosen, as described in our previous publication with SPANphos[42] to demonstrate that the observed activities could not be attributed to a medium effect caused by phosphine quaternization.

The results obtained (Table 6) showed that the new ligands show similar or better activities to those obtained with SPANphos (diphenyl phosphine derivative).

Table 6 Methanol carbonylation with Rh catalyst and diphosphine ligands[a]

Entry	Ligand	Conv. (%)[b]	TON[c]	TOF[d]
1	4[b]	6.4	679	453
2	7[b]	4.9	527	351
3	10[b]	13.8	1470	980
4	13[b]	13.8	1468	979
5	16[b]	9.6	1030	687
6[e]	SPANphos	8.9	888	592

[a] Conditions: T = 150 °C, P (at 22 °C) = 22 bar of CO, 700 rpm, [Rh(μ-Cl)$(CO)_2]_2$ 57 μmol, 1.5 h, MeOH/MeI/H_2O/Rh = 9670/1000/6820/2. [b] The conversion was calculated from gas consumption of the reservoir autoclave. The solution was analyzed by NMR spectroscopy to determine the selectivity. [c] TON = turnover number (in mol conversion per mol Rh_2). [d] TOF = turnover frequency (in mol conversion per mol Rh_2 per h). [e] SPANphos diphenylphosphine used.

The use of these exclusively binucleating ligands confirms the high activity of dimeric-rhodium complexes as precatalysts in rhodium catalyzed methanol carbonylation. If the actual catalyst is the halo-bridged dimer or the CO-cleaved species (**27–31**), formed under CO pressure is currently under study by means of these binucleating ligands.[96]

Conclusions

A new class of diphosphines able to stabilize dimeric complexes were designed and synthesized. Complexation studies undertaken confirmed the binucleating nature of the ligands. In accordance with molecular mechanics studies, monometallic species with the ligand acting as a chelator were never observed. The outcome of the reaction of these ligands with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ or $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ is determined by the stoichiometry used. When a ligand-to-metal ratio of 1 : 1 was employed, (a ratio suited to form monometallic chelates for most bidentates) bimetallic face-to-face complexes with two ligands acting as a double bridge between the two metals occupying mutually *trans* positions were obtained (as a mixture of different isomers in some cases). When the ligand-to-metal ratio was lowered to 1 : 2, halide-bridged dimers were formed. The molecular structure of these compounds was elucidated by NMR spectroscopy as well as X-ray crystallography.

The new ligands, when tested in rhodium catalyzed methanol carbonylation, showed activities comparable to the ones obtained with SPANphos, which confirms that bimetallic halogen-bridged complexes lead to the most active catalysts for this reaction. The application of these ligands to reactions that may benefit from the cooperative effect of two metal centres in close proximity is currently under study.

Experimental

Materials and methods

All reactions were performed using standard vacuum-line and Schlenk techniques under argon atmosphere. Solvents were purchased from Sigma-Aldrich as HPLC grade and dried with an SPS system of ITC-inc. Methyl iodide and deuterated chloroform were purchased from Sigma-Aldrich, distilled over CaH_2 and stored under argon atmosphere. *p*-Cresol, 1,4-dichlorobutyne, glyoxal, *n*-Butyllithium and chlorodiphenylphosphine were purchased from Sigma-Aldrich. 1,1,3,3-Tetramethoxypropane, trifluoroacetic acid, tetracarbonyldi-μ-chlorodirhodium(I) and chloro(1,5-cyclooctadiene)rhodium(I) dimer were purchased from Acros. N-Bromosuccinimide was purchased from Alfa Aesar. 1,4-Bis(*p*-methylphenoxy)-2-butyne (**1**),[83,84] 5a,10b-dihydro-5a,10b-dimethyl-2,9-dimethylbenzofuro[2,3-b]benzofuran (**2**),[83,84] 4b,9b-dihydro-4b,9b-dimethyl-3,8-dimethylbenzofuro[3,2-b]benzofuran (**5**),[81,85] 5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-b]benzofuran (**8**)[86] and 2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-d:1′,2″-g][1,3]dioxocin (**11**),[87] were synthesized according to the published procedures or slight modifications thereof. NMR spectra unless otherwise stated were recorded at the following frequencies: 400.13 MHz (^{1}H), 100.63 MHz (^{13}C), 161.98 MHz (^{31}P). ^{13}C and ^{31}P NMR spectra were recorded using broad band decoupling. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS, used as internal standard. Chemical shifts of ^{31}P NMR spectra are referred to H_3PO_4 as external standard. Signals are quoted as s (singlet), d (doublet), t (triplet), m (multiplet), br (broad)). Mass spectra were run by ESI-TOF on a Waters LCT Premier spectrometer. ATR measurements were carried out in a FT-IR Bruker Tensor 27 with DTGS detector, with a resolution of 4 cm^{-1} and 32 scans, using an ATR Specac Golden Gate accessory with diamond crystal.

Syntheses

4,7-Dibromo-5a,10b-dihydro-5a,10b-dimethyl-2,9-dimethylbenzofuro[2,3-b]benzofuran (3). To a stirred solution of 5a,10b-dihydro-5a,10b-dimethyl-2,9-dimethylbenzofuro[2,3-b]benzofuran **2** (10.08 g, 37.8 mmol) in DMF (400 ml), NBS (40.89 g, 230 mmol) was added. The reaction was monitored by GC chromatography. When there was no signal of starting compound, DMF was removed by evaporation. The residue dissolved in H_2O and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated to obtain **3** as a white solid (11.05 g, 69%). (Found: C, 51.58; H, 3.96. $C_{18}H_{16}Br_2O_2$ requires C, 50.97; H, 3.80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (3H, s, CH_3), 1.81 (3H, s, CH_3), 2.28 (6H, s, CH_3), 6.95 (2H, d, $^4J_{H-H}$ = 0.88 Hz), 7.10 (2H, d, $^4J_{H-H}$ = 0.84 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4 (s), 20.8 (s), 21.2 (s), 58.8 (s), 102.6 (s), 122.3 (s), 125.1 (s), 132.3 (s), 133.2 (s), 133.5 (s), 152.2 (s). *m*/*z* (ESI+): 424 $[M]^+$.

4,7-Bis(diphenylphosphino)-5a,10b-dihydro-5a,10b-dimethyl-2,9-dimethylbenzofuro[2,3-b]benzofuran (4). At –78 °C *n*-butyllithium (7 ml, 2.5 M in hexanes, 17.5 mmol) was added dropwise to a stirred solution of **3** (3.44 g, 8.1 mmol) in dry THF (350 ml). The reaction mixture was stirred for 1 h and then was allowed to warm to –40 °C. At this temperature chlorodiphenylphosphine (3.1 ml, 17.3 mmol) was added and the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo* and the resulting solid was dissolved in dry CH_2Cl_2 and the solution was washed with deoxygenated water. The organic layer was removed *in vacuo* and recrystallized from deoxygenated methanol to afford **4** (3.72 g, 72%) as an air-stable white solid. (Found: C, 78.77; H, 6.25. $C_{42}H_{36}O_2P_2$ requires C, 79.48; H, 5.72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (3H, s, CH_3), 1.60 (3H, s, CH_3), 2.17 (6H, s, CH_3), 6.48 (2H, dd, $^3J_{H-P}$ = 6.0 and $^4J_{H-H}$ = 1.0 Hz, Ar), 7.06 (2H, d, $^4J_{H-H}$ = 1.3 Hz), 7.23–7.34 (20H, m, Ar); ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ –13.7 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8 (s), 21.1 (s), 21.1 (s), 56.4 (s), 118.0 (d, J_{C-P} = 16.1 Hz), 124.4 (s), 125.1 (s), 128.4 (d, J_{C-P} = 6.2 Hz), 128.5 (d, J_{C-P} = 5.4 Hz), 128.7 (s), 131.3 (d, J_{C-P} = 2.2 Hz), 132.5 (d, J_{C-P} = 2.2 Hz), 133.5 (d, J_{C-P} = 6.6 Hz), 133.7 (d, J_{C-P} = 19.7 Hz), 134.1 (d, J_{C-P} = 20.1 Hz), 136.4 (d, J_{C-P} = 3.6 Hz), 136.5 (d, J_{C-P} = 4.1 Hz), 157.4 (d, J_{C-P} = 13.9 Hz). *m*/*z* (ESI+): 635 $[M + H]^+$, 657 $[M + Na]^+$. HR-MS: (ESI+) *m*/*z* calcd for $C_{42}H_{36}O_2NaP_2$ ($[M + Na]^+$) 657.2088, found 657.2092.

1,6-Dibromo-4b,9b-dihydro-4b,9b-dimethyl-3,8-dimethylbenzofuro [3,2-b]benzofuran (6). Compound **6** was prepared using the same procedure described above for compound **3**, but using 4b,9b-dihydro-4b,9b-dimethyl-3,8-dimethylbenzofuro[3,2-b]benzofuran **5** as substrate to brominate. Yield: 99% (Found: C, 50.71; H, 3.49. $C_{18}H_{16}Br_2O_2$ requires C, 50.97; H, 3.80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77 (6H, s, CH_3), 2.30 (6H, s, CH_3), 7.20 (2H, s, Ar), 7.22 (2H, s, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6 (s), 20.7 (s), 97.5 (s), 103.0 (s), 124.4 (s), 129.8 (s), 132.5 (s), 134.4 (s), 153.8 (s). *m/z* (ESI+): 425 [M + H]$^+$, 447 [M + Na]$^+$.

1,6-Bis(diphenylphosphino)-5a,10b-dihydro-5a,10b-dimethyl-3,8-dimethylbenzofuro[3,2-b]benzofuran (7). Ligand **7** was prepared following the same synthetical procedure described above for compound **4**, but using compound **6** as dibrominated precursor. Yield: 62%. (Found: C, 78.00; H, 6.48. $C_{42}H_{36}O_2P_2$ requires C, 79.48; H, 5.72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.58 (6H, s, CH_3), 2.10 (6H, s, CH_3), 6.50 (2H, dd, $^{3}J_{H-P}$ = 6.2 and $^{4}J_{H-H}$ = 1.3 Hz, Ar), 6.80 (2H, d, $^{4}J_{H-H}$ = 1.32 Hz), 7.15–7.33 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ –12.9 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.7 (s), 21.0 (s), 95.9 (d, J_{C-P} = 1.5 Hz), 118.2 (d, J_{C-P} = 13.9 Hz), 126.5 (s), 128.2 (d, J_{C-P} = 6.6 Hz), 128.4 (d, J_{C-P} = 6.6 Hz), 128.5 (s), 128.7 (s), 129.1 (d, J_{C-P} = 2.2 Hz), 130.6 (d, J_{C-P} = 2.2 Hz), 133.6 (d, J_{C-P} = 19.7 Hz), 134.1 (d, J_{C-P} = 20.5 Hz), 135.0 (d, J_{C-P} = 7.3 Hz), 136.2 (d, J_{C-P} = 8.1 Hz), 136.3 (d, J_{C-P} = 7.3 Hz), 158.2 (d, J_{C-P} = 13.2 Hz). *m/z* (ESI+): 635 [M + H]$^+$, 657 [M + Na]$^+$. HR-MS: (ESI+) *m/z* for $C_{42}H_{36}O_2P_2Na$ ([M + Na]$^+$) 657.2088; found 657.2112.

4,7-Dibromo-5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-b]-benzofuran (9). Compound **9** was prepared using the same procedure described above for compound **3**, but using 5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-b]benzofuran **8** as substrate to brominate. Yield: 69%. (Found: C, 48.47; H, 3.09. $C_{16}H_{12}Br_2O_2$ requires C, 48.52; H, 3.05%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.29 (6H, s, CH_3), 5.09 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 6.95 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 7.07 (2H, s, Ar), 7.14 (2H, s, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6 (s), 52.1 (s), 102.6 (s), 112.2 (s), 123.4 (s), 127.8 (s), 132.6 (s), 133.4 (s), 153.3 (s). *m/z* (ESI+): 419 [M + Na]$^+$.

4,7-Bis(diphenylphosphino)-5a,10b-dihydro-2,9-dimethylbenzofuro[2,3-b]benzofuran (10). Ligand **10** was prepared following the same synthetical procedure described above for compound **4**, but using compound **9** as dibrominated precursor. Yield: 50%. (Found: C, 78.58; H, 5.57. $C_{40}H_{32}O_2P_2$ requires C, 79.20; H, 5.32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18 (6H, s, CH_3), 4.91 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 6.52 (2H, d, $^{3}J_{H-P}$ = 5.6 Hz, Ar), 6.74 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 7.17 (2H, s, Ar), 7.26–7.34 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ –14.4 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (s), 50.2 (s), 112.7 (s), 118.3 (d, J_{C-P} = 16.9 Hz), 125.5 (s), 127.0 (d, J_{C-P} = 2.6 Hz), 128.4 (d, J_{C-P} = 4.3 Hz), 128.5 (d, J_{C-P} = 4.4 Hz), 128.7 (d, J_{C-P} = 18.4 Hz), 131.7 (d, J_{C-P} = 1.9 Hz), 133.7 (d, J_{C-P} = 20.1 Hz), 133.8 (s), 134.0 (d, J_{C-P} = 20.5 Hz), 136.2 (d, J_{C-P} = 4.4 Hz), 136.3 (d, J_{C-P} = 4.4 Hz), 158.6 (d, J_{C-P} = 14.9 Hz). *m/z* (ESI+): 607 [M + H]$^+$, 629 [M + Na]$^+$. HR-MS: (ESI+) *m/z* for $C_{40}H_{32}O_2NaP_2$ ([M + Na]$^+$) 629.1775, found 629.1776.

4,8-Dibromo-2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-d:l′,2″-g][l,3]dioxocin (12). Compound **12** was prepared using the same procedure described above for compound **3**, but using 2,10-dimethyl-6,12-methano-12*H*-dibenzo[2,1-d:l′,2″-g][l,3] dioxocin **11** as substrate to brominate. Yield: 87%. (Found: C, 49.91; H, 3.18. $C_{17}H_{14}Br_2O_2$ requires C, 49.79; H, 3.44%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (2H, t, $^{3}J_{H-H}$ = 2.64 Hz, CH_2), 2.24 (6H, s, CH_3), 3.88–3.90 (1H, m, CH), 6.33–6.34 (1H, m, CH), 6.93 (2H, d, $^{4}J_{H-H}$ = 1.72 Hz, Ar), 7.17 (2H, d, $^{4}J_{H-H}$ = 1.52 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4 (s), 25.4 (s), 32.2 (s), 92.9 (s), 110.3 (s), 127.2 (s), 127.3 (s), 132.2 (s), 132.5 (s), 145.8 (s). *m/z* (ESI+): 432.9 [M + Na]$^+$.

2,10-Dimethyl-4,8-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-d:l′,2″-g][l,3]dioxocin (13). Ligand **13** was prepared following the same synthetical procedure described above for compound **4**, but using compound **12** as dibrominated precursor. Yield: 86%. (Found: C, 79.15; H, 5.57. $C_{41}H_{34}O_2P_2$ requires C, 79.34; H, 5.52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (2H, t, $^{3}J_{H-H}$ = 2.48 Hz, CH_2), 2.11 (6H, s, CH_3), 3.89–3.92 (1H, m, CH), 5.88–5.90 (1H, m, CH), 6.32 (2H, dd, $^{3}J_{H-P}$ = 4.8 and $^{4}J_{H-H}$ = 1.9 Hz, Ar), 7.02 (2H, d, $^{4}J_{H-H}$ = 1.72 Hz, Ar), 7.19–7.35 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ –12.8 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8 (s), 25.7 (s), 32.2 (s), 92.2 (s), 124.6 (d, J_{C-P} = 15.4 Hz), 126.1 (d, J_{C-P} = 2.2 Hz), 128.4 (d, J_{C-P} = 4.9 Hz), 128.5 (d, J_{C-P} = 3.6 Hz), 128.6 (s), 129.0 (s), 130.6 (d, J_{C-P} = 1.5 Hz), 133.0 (d, J_{C-P} = 1.5 Hz), 133.8 (d, J_{C-P} = 19.8 Hz), 134.1 (d, J_{C-P} = 20.5 Hz), 136.8 (d, J_{C-P} = 11.3 Hz), 137.1 (d, J_{C-P} = 11.4 Hz), 150.9 (d, J_{C-P} = 15.0 Hz). *m/z* (ESI+): 621 [M + H]$^+$, 643 [M + Na]$^+$. HR-MS: (ESI+) *m/z* for $C_{41}H_{34}O_2P_2Na$ ([M + Na]$^+$) 643.1932; found 643.1935.

2,10-Di-*tert*-butyl-6,12-methano-12*H*-dibenzo[2,1-d:l′,2″-g]-[l,3]dioxocin (14). To a stirred solution of 4-*tert*-butylphenol (20.48 g, 136.3 mmol) in trifluoroacetic acid (42 ml), was added 1,1,3,3-tetramethoxypropane (11.5 ml, 69.5 mmol) and left stirring overnight at r.t. After addition of acetic acid (80 ml), the crude product was collected by filtration, washed with methanol and finally boiled with water to afford after filtration **14** (8.6 g, 37%) as a white-pink solid. (Found: C, 77.44; H, 8.11. $C_{17}H_{14}Br_2O_2$ requires C, 82.10; H, 8.39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (18H, m, *t*Bu, 2.25 (2H, m, CH_2), 3.90–3.96 (1H, m, CH), 6.10–6.15 (1H, m, CH), 6.82 (2H, d, $^{3}J_{H-H}$ = 8.5 Hz, Ar), 7.11 (2H, d, $^{3}J_{H-H}$ = 8.5 Hz, Ar), 7.20 (2H, s, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9 (s), 31.7 (s), 32.5 (s), 34.3 (s), 92.4 (s), 116.0 (s), 124.3 (s), 125.0 (s), 126.3 (s), 144.2 (s), 148.9 (s). *m/z* (ESI+): 359.2 [M + Na]$^+$.

4,8-Dibromo-2,10-di-*tert*-butyl-6,12-methano-12*H*-dibenzo-[2,1-d:l′,2″-g][l,3]dioxocin (15). Compound **15** was prepared using the same procedure described above for compound **3**, but using compound **14** as substrate to brominate. Yield: 90%. (Found: C, 55.56; H, 5.42. $C_{23}H_{26}Br_2O_2$ requires C, 55.89; H, 5.30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (18H, s, *t*Bu), 2.26 (2H, t, $^{3}J_{H-H}$ = 2.5 Hz, CH_2), 3.95–3.98 (1H, m, CH), 6.33–6.36 (1H, m, CH), 7.12 (2H, d, $^{4}J_{H-H}$ = 2.04 Hz, Ar), 7.35 (2H, d, $^{4}J_{H-H}$ = 2.04 Hz, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4 (s), 31.4 (s), 31.5 (s), 32.8 (s), 34.4 (s), 93.0 (s), 110.2 (s), 123.6 (s), 127.2 (s), 129.2 (s), 145.7 (s), 145.8 (s). *m/z* (ESI+): 517 [M + Na]$^+$.

2,10-Di-*tert*-butyl-4,8-diphenylphosphino-6,12-methano-12*H*-dibenzo[2,1-d:l′,2″-g][l,3]dioxocin (16). Ligand **16** was prepared following the same synthetical procedure described above for compound **4**, but using compound **15** as dibrominated precursor. Yield: 66%. (Found: C, 77.69; H, 6.81. $C_{47}H_{46}O_2P_2$ requires C, 80.09; H, 6.58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (18H, s, *t*Bu), 2.10 (2H, t, $^{3}J_{H-H}$ = 2.46 Hz, CH_2), 3.93–3.97 (1H, m, CH), 5.87–5.90 (1H, m, CH), 6.53 (2H, dd, $^{3}J_{H-P}$ = 5.4 and $^{4}J_{H-H}$ = 2.4 Hz, Ar), 7.19 (2H, d, $^{4}J_{H-H}$ = 2.3 Hz, Ar), 7.26–7.34 (20H, m, Ar);

^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = −11.54 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9 (s), 31.1 (s), 31.4 (s), 31.7 (s), 32.8 (s), 34.3 (s), 92.2 (s), 123.9 (d, J_{C-P} = 15.4 Hz), 125.3 (d, J_{C-P} = 2.9 Hz), 125.7 (d, J_{C-P} = 1.5 Hz), 128.4 (br), 128.5 (br), 128.6 (s), 130.0 (s), 133.9 (br), 134.1 (br), 137.0 (d, J_{C-P} = 11.3 Hz), 137.2 (d, J_{C-P} = 11.7 Hz), 143.8 (s), 150.8 (d, J_{C-P} = 15.4 Hz). *m/z* (ESI+): 705 [M + H]$^+$, 727 [M + Na]$^+$. HR-MS: (ESI+) *m/z* for $C_{47}H_{47}O_2P_2$ ([M]$^+$) calcd. 705.3051, found 705.3074.

[$Rh_2(CO)_2Cl_2(L)_2$] bimetallic complexes 17–21

General synthesis. [$Rh_2(\mu\text{-}Cl)_2(CO)_4$] (8 μmol) and corresponding ligand (16 μmol) were dissolved in 0.8 ml of dry $CDCl_3$ or CD_2Cl_2, and the solution was subjected to one cycle of vacuum and stored under argon.

Alternatively, identical compounds (according to their ^{31}P NMR pattern) can be obtained when [$Rh_2(\mu\text{-}Cl)_2(cod)_2$] (8 μmol) and corresponding ligand (16 μmol) were dissolved in 0.8 ml of dry $CDCl_3$ or CD_2Cl_2. Then CO was bubbled through the solution for 5 min.

[Rh(CO)Cl(4)]$_2$ (17). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21–1.40 (6H, m, CH_3), 2.08–2.15 (6H, m, CH_3), 6.00–6.52 (2H, m, Ar), 7.00–8.2 (22H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 16.6 (dd, $^{1}J_{Rh-P}$ = 131 Hz, $^{2}J_{P-P}$ = 366 Hz), 23.9 (dd, $^{1}J_{Rh-P}$ = 131 Hz, $^{2}J_{P-P}$ = 366 Hz) (major compound); 19.7 (dd, $^{1}J_{Rh-P}$ = 128 Hz, $^{2}J_{P-P}$ = 368 Hz), 24.9 (dd, $^{1}J_{Rh-P}$ = 128 Hz, $^{2}J_{P-P}$ = 368 Hz) (minor compound). IR (ATR mode, solid, carbonyl region, cm^{-1}): ν = 1970, 1989 (**22**).

[Rh(CO)Cl(7)]$_2$ (18). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07–2.14 (6H, br, CH_3), 2.16–2.19 (6H, br, CH_3), 6.66–6.72 (2H, br, Ar), 7.11–7.80 (22H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$, 298 K): δ 25.0 (d, $^{1}J_{Rh-P}$ = 128 Hz), 25.4 (d, $^{1}J_{Rh-P}$ = 128 Hz). IR (ATR mode, solid, carbonyl region, cm^{-1}): ν = 1970.

[Rh(CO)Cl(10)]$_2$ (19). ^{1}H NMR (500 MHz, CD_2Cl_2, 273 K): δ 2.13 (6H, s, CH_3), 2.18 (6H, s, CH_3), 4.48 (1H, m, CH), 4.66 (1H, m, CH), 6.20 (1H, m, CH), 6.29 (1H, m, CH), 6.53–8.76 (48H, m, Ar); ^{31}P {1H} NMR (202 MHz, CD_2Cl_2, 193 K): δ 20.6 (dd, $^{1}J_{Rh-P}$ = 125 Hz, $^{2}J_{P-P}$ = 366 Hz), 23.1 (dd, $^{1}J_{Rh-P}$ = 130 Hz, $^{2}J_{P-P}$ = 366 Hz) (major compound); 21.8 (dd, $^{1}J_{Rh-P}$ = 128 Hz, $^{2}J_{P-P}$ = 359 Hz), 24.4 (dd, $^{1}J_{Rh-P}$ = 132 Hz, $^{2}J_{P-P}$ = 359 Hz) (minor compound). IR (ATR mode, solid, carbonyl region, cm^{-1}): ν = 1973

[Rh(CO)Cl(13)]$_2$ (20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03–2.07 (12H, br, CH_3), 2.11–2.15 (4H, br, CH_2), 3.67–3.97 (2H, br, CH), 6.31–6.37 (4H, br, Ar), 6.40–6.50 (2H, br, CH), 6.55–6.61 (2H, br, Ar), 6.74–7.91 (42H, br, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 22.6 (dd, $^{1}J_{Rh-P}$ = 128 Hz and $^{2}J_{P-P}$ = 354 Hz), 25.7 (dd, $^{1}J_{Rh-P}$ = 130 Hz and $^{2}J_{P-P}$ = 362 Hz). IR (ATR mode, solid, carbonyl region, cm^{-1}): ν = 1958.

[Rh(CO)Cl(16)]$_2$ (21). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98–1.05 (18H, s, *t*Bu), 1.05–1.12 (18H, s, *t*Bu), 1.16–1.32 (2H, m, CH_2), 1.40–1.48 (2H, m, CH_2), 3.71–3.76 (2H, m, CH), 6.33–6.51 (2H, m, CH), 6.74–6.85 (4H, m, Ar), 7.20–7.28 (4H, m, Ar), 7.30–7.94 (40H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 22.5 (dd, $^{1}J_{Rh-P}$ = 129 Hz, $^{2}J_{P-P}$ = 363 Hz), 26.8 (dd, $^{1}J_{Rh-P}$ = 131 Hz, $^{2}J_{P-P}$ = 363 Hz). IR (ATR mode, solid, carbonyl region, cm^{-1}): ν = 1968.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2(L)$] dimeric complexes 22–26

General synthesis. [$Rh_2(\mu\text{-}Cl)_2(CO)_4$] (8 μmol) and corresponding ligand (8 μmol) were dissolved in 1–2 ml of CH_2Cl_2. After 5 min the solvent was removed by vacuum and the residue dissolved in 0.8 ml of $CDCl_3$ or CD_2Cl_2.

Alternatively, identical compounds (according to their ^{31}P NMR pattern) can be obtained when [$Rh_2(\mu\text{-}Cl)_2(cod)_2$] (8 μmol) and corresponding ligand (8 μmol) were dissolved in 1–2 ml of CH_2Cl_2. Then CO was bubbled through the solution for 5 min, the solvent was removed by vacuum and the residue dissolved in 0.8 ml of $CDCl_3$ or CD_2Cl_2.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2$(4)] (22). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26 (3H, s, CH_3), 1.69 (3H, s, CH_3), 2.08 (6H, s, CH_3), 6.10 (2H, d, $^{3}J_{H-P}$ = 10.8 Hz, Ar), 6.96 (2H, s, Ar), 7.37–7.48 (12H, m, Ar), 7.76–7.84 (8H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 44.6 (d, $^{1}J_{Rh-P}$ = 180.3 Hz). MALDI+ve: *m/z*: 931 [M − Cl]$^+$. IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 1992.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2$(7)] (23). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26–1.64 (6H, br, CH_3), 2.09–2.34 (6H,br, CH_3), 6.61–7.86 (24H, br, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 40.4 (d, $^{1}J_{Rh-P}$ = 179.5 Hz), 24.9 (**18** as *by-product*, d, $^{1}J_{Rh-P}$ = 129.6 Hz), 25.3 (**18** as *by-product*, d, $^{1}J_{Rh-P}$ = 139.3 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 1988.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2$(10)] (24). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.08 (6H, s, CH_3), 4.96 (1H, d, $^{3}J_{H-H}$ = 6.2 Hz, Ar), 6.14 (2H, d, $^{3}J_{H-P}$ = 10.8, Ar), 6.64 (1H, d, $^{3}J_{H-H}$ = 6.2 Hz, CH), 7.08 (2H, s, Ar), 7.37–7.48 (12H, m, Ar), 7.74–7.82 (8H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 44.1 (d, $^{1}J_{Rh-P}$ = 179 Hz); IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 1993.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2$(13)] (25). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.99–2.02 (2H, m, CH_2), 2.05 (6H, s, CH_3), 3.79–3.83 (1H, m, CH), 5.54–5.58 (1H, m, CH), 6.14 (2H, d, $^{3}J_{H-P}$ = 11.2, Ar), 6.92 (2H, s, Ar), 7.35–7.80 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 45.7 (d, $^{1}J_{Rh-P}$ = 182 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 1991.

[$Rh_2(CO)_2(\mu\text{-}Cl)_2$(16)] (26). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.0 (18H, s, tBu), 2.07–2.11 (2H, m, CH_2), 3.90 (1H, m, CH), 5.64(1H, m, CH), 6.27 (2H, d, $^{3}J_{H-P}$ = 12.1 and $^{4}J_{H-H}$ = 2.1 Hz, Ar), 7.09 (2H, d, $^{4}J_{H-H}$ = 2.1 Hz, Ar), 7.3–7.8 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 46.6 (d, $^{1}J_{Rh-P}$ = 180 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 1991.

[$Rh_2(CO)_4Cl_2(L)$] bimetallic complexes 27–31

General method. [$Rh_2Cl_2(CO)_4$] (8 μmol) and corresponding ligand (8 μmol) were dissolved in 0.8 ml of dry $CDCl_3$. Then CO was bubbled through the solution for 10 min.

[$Rh_2(CO)_4(Cl)_2$(4)] (27). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.30 (3H, s, CH_3), 1.50 (3H, s, CH_3), 2.21 (6H, s, CH_3), 6.76 (2H, d, $^{3}J_{H-P}$ = 11.7 Hz, Ar), 7.24–7.76 (22H, m, Ar); ^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ = 20.5 (d, J_{Rh-P} = 125.7 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 2092, 2010.

[$Rh_2(CO)_4(Cl)_2$(7)] (28). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (6H, s, CH_3), 2.2 (6H, s, CH_3), 6.7 (2H, d, $^{3}J_{H,P}$ = 11.6 Hz,

Ar), 6.9 (2H, s, Ar), 7.33–7.50 (10H, m, Ar), 7.56–7.67 (10H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ 19.2 (d, J_{Rh-P} = 127.0 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 2092, 2012.

[Rh$_2$(CO)$_4$(Cl)$_2$(10)] (29). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.24 (6H, s, CH_3), 4.89 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 6.72–6.76 (2H, m, Ar), 6.77–6.82 (1H, m, CH), 7.28–7.82 (22H, m, Ar); ^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ 21.0 (d, J_{Rh-P} = 125.5 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 2092, 2010.

[Rh$_2$(CO)$_4$(Cl)$_2$(13)] (30). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (2H, m, CH_2), 2.18 (6H, s, CH_3), 3.97 (1H, m, CH), 6.13 (1H, m, CH), 6.60 (2H, d, $^{3}J_{H-P}$ 11.1 Hz, Ar), 7.24–7.77 (22H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 20.1 (d, J_{Rh-P} = 126.1 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 2092, 2010.

[Rh$_2$(CO)$_4$(Cl)$_2$(16)] (31). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (18H, s, *t*Bu), 2.06 (2H, m, CH_2), 4.0 (1H, m, CH), 6.06 (1H, m, CH), 6.84 (2H, d, $^{3}J_{H-P}$ 11.8 Hz, Ar), 7.27–7.75 (22H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 21.0 (d, J_{Rh-P} = 126.8 Hz). IR (ATR mode, liquid, carbonyl region, cm^{-1}): ν = 2092, 2010.

[Rh$_2$(cod)$_2$Cl$_2$(L)] bimetallic complexes 32–36.

General method. [Rh$_2$Cl$_2$(cod)$_2$] (8 μmol) and corresponding ligand (8 μmol) were dissolved in 0.8 ml of dry $CDCl_3$.

[Rh$_2$(cod)$_2$(Cl)$_2$(4)] (32). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 (3H, s, CH_3), 1.68 (3H, s, CH_3), 2.23 (6H, s, CH_3),1.60–2.50 (16H, m, CH_2 (cod)), 3.14 (2H, m, CH (cod)), 3.36 (2H, m, CH (cod)), 5.36 (2H, m, CH (cod)), 5.57 (2H, m, CH (cod)), 6.06–6.50 (20H, m, Ar), 8.10–8.15 (4H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 25.2 (d, J_{Rh-P} = 149 Hz).

[Rh$_2$(cod)$_2$(Cl)$_2$(7)] (33). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (6H, s, CH_3), 1.50–2.06 (8H, m, CH_2 (cod)), 2.21 (6H, s, CH_3), 2.30 (8H, m, CH_2 (cod)), 3.02 (2H, m, CH (cod)), 3.23 (2H, m, CH (cod)), 5.47 (4H, m, CH (cod)), 6.95–6.98 (4H, m, Ar), 7.27–7.89 (20H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 26.06 (d, J_{Rh-P} = 150.6 Hz).

[Rh$_2$(cod)$_2$(Cl)$_2$(10)] (34). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.64–2.52 (16H, m, CH_2 (cod)), 2.26 (6H, s, CH_3), 3.17 (2H, m, CH (cod)), 3.40 (2H, m, CH (cod)), 4.97 (1H, d, $^{3}J_{H-H}$ = 6.8 Hz, CH), 5.37–5.55 (4H, m, CH (cod)), 6.93 (1H, d, $^{3}J_{H-H}$ = 6.7 Hz, CH), 7.09–7.44 (20H, m, Ar), 7.04–8.12 (4H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 26.75 (d, J_{Rh-P} = 148.6 Hz).

[Rh$_2$(cod)$_2$(Cl)$_2$(13)] (35). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62–2.51 (16H, m, CH_2 (cod)), 2.11 (2H, m, CH_2), 2.19 (6H, s, CH_3), 3.21 (2H, m, CH (cod)), 3.54 (2H, m, CH (cod)), 3.96 (1H, m, CH), 5.20 (2H, m, CH (cod)), 5.50 (2H, m, CH (cod)), 6.47 (1H, m, CH), 7.02 (2H, d, $^{3}J_{H-P}$ = 10.8 Hz, Ar), 7.09–7.47 (18H, m, Ar), 8.08–8.17 (4H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 24.58 (d, J_{Rh-P} = 146.5 Hz).

[Rh$_2$(cod)$_2$(Cl)$_2$(16)] complex 36. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19–1.24 (18H, br, *t*Bu), 1.60–1.95 (8H, m, CH_2 (cod)), 2.02 (2H, m, CH_2), 2.09–2.52 (8H, m, CH_2 (cod)), 3.20 (2H, m, CH (cod)), 3.40 (2H, m, CH (cod)), 3.98 (1H, m, CH), 5.20 (2H, m, CH (cod)), 5.47 (2H, m, CH (cod)), 6.19 (1H, m, CH), 7.19–8.16 (24H, m, Ar); ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ = 26.32 (d, J_{Rh-P} = 145 Hz).

Catalysis. In a typical experiment 29.4 mL of a mixture MeOH–H_2O was placed in a 100 mL Hastelloy autoclave. The autoclave was then pressurized to 10 bar of carbon monoxide and heated to 150 °C with vigorous stirring (700 rpm). When the reaction temperature was reached and had stabilized, a solution of [Rh$_2$(μ-Cl)$_2$(CO)$_4$] and the appropriate quantity of the corresponding ligand in 3.55 mL of MeI were added through a liquid injection port and the autoclave was pressurized to the desired reaction pressure. Pressure was maintained constant during the reaction by feeding gas from a 300 mL autoclave pressurized with over 60 bar of carbon monoxide. After the required reaction time, the autoclave was cooled to room temperature. The solution was analyzed by NMR spectroscopy to determine the selectivity. The conversion was calculated from gas consumption of the reservoir autoclave.

X-Ray structure determinations†

Crystals of complexes **17**, **19**, and **22** were obtained by slow diffusion of Et_2O into a $CDCl_3$ solution. Crystals of complex **20** and **24** were obtained by slow diffusion of Et_2O into CD_2Cl_2 solution. Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation.

Data collection. Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo-Kα radiation, Montel mirrors as monochromator and a Kryoflex low temperature device (T = –173 °C). Full-sphere data collection was used with ω and φ scans. Programs used: Data collection Apex2 V. 1.0-22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction SADABS V. 2.10 (2003).

Structure solution and refinement. SHELXTL Version 6.14 (Sheldrick, 2008) was used.[97]

Comments to the structures. See Table 7 for full details. Compounds **17**, **19** and **20** crystallize with a half molecule in the asymmetric unit showing a similar C_i-symmetry. Compound **19**: several crystals were attempted for the structure determination. The measured sample was a twin with domains ratio 64 : 36. Structure determination was possible after integration of two crystals. The absorption correction was done with the program TWINABS.[98,99] The asymmetric unit contains fourteen disordered positions of water molecules which correspond to a total of six water molecules for each half molecule of complex. Water occupancies were freely refined. The best data completeness obtained reached 90.2% since overlapping reflections of the two different crystals were omitted. Compound **20**: the asymmetric unit contains half molecule of the complex and two molecules of dichloromethane, disordered in two positions with occupation ratio 61 : 39. Compound **22**: due to the formation of ice no better data completeness could be obtained (91%). Compound **24**: the asymmetric unit contains 0.25 molecules of dichloromethane disordered in two orientations and centered on an inversion axis (–4). The measured data correspond to a racemic twin with a ratio of 51 : 49.

Table 7 Crystal data for compounds **17**, **19**, **20**, **22** and **24**

Compound	**17**	**19**	**20**	**22**	**24**
Formula	$C_{90}H_{76}Cl_{14}O_6P_4Rh_2$	$C_{82}H_{88}Cl_2O_{18}P_4Rh_2$	$C_{88}H_{76}Cl_{10}O_6P_4Rh_2$	$C_{45}H_{37}Cl_5O_4P_2Rh_2$	$C_{42.25}H_{33.5}Cl_{2.5}O_4P_2Rh_2$
Solvent in asymmetric unit	4 Chloroform	3 H_2O	2 Dichloromethane	1 Chloroform	1/4 Dichloromethane
Formula weight	2079.51	1654.03	1913.69	1086.76	961.58
Crystal size/mm	$0.10 \times 0.10 \times 0.05$	$0.2 \times 0.2 \times 0.3$	$0.20 \times 0.10 \times 0.05$	$0.4 \times 0.3 \times 0.3$	$0.02 \times 0.03 \times 0.3$
T/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$I\bar{4}$
A/Å	16.6357 (4)	18.1626(9)	12.7468(5)	11.2602(16)	28.7585(6)
B/Å	18.7449(5)	17.4391(9)	18.3066(7)	14.114(4)	28.7585(6)
C/Å	14.8117(4)	13.3646(6)	19.1337(8)	14.469(2)	9.2270(2)
α/°	90	90	90	87.046(10)	90
β/°	100.5780(10)	108.713(2)	105.1580(10)	76.892(8)	90
γ/°	90	90	90	79.328(9)	90
V/Å^3	4540.3(2)	4009.3(3)	4309.5(3)	2200.8(8)	7631.2(3)
Z	2	2	2	2	8
ρ/Mg m^{-3}	1.521	1.370	1.475	1.640	1.674
μ/mm^{-1}	0.898	0.616	0.819	1.169	1.167
Completeness to θ (%)	96.0 ($\theta = 39.65°$)	90.2 ($\theta = 36.54°$)	95.7 ($\theta = 37.50°$)	91.0 ($\theta = 32.50°$)	94.0 ($\theta = 33.17°$)
Number of all reflections	90 973	49 393	65 761	30 226	41 695
Unique reflections	26 435 [$R_{int} = 0.0223$]	17 840 [$R_{int} = 0.0674$]	21 725 [$R_{int} = 0.0224$]	14 497 [$R_{int} = 0.0274$]	12 617 [$R_{int} = 0.0597$]
F(000)	2104	1816	1944	1088	3852
Absorption correction	Empirical (SADABS)	Empirical (TWINABS)	Empirical (SADABS)	Empirical (SADABS)	Empirical (SADABS)
Max., min transmission	0.96 and 0.92	0.98 and 0.81	0.96 and 0.85	1.00 and 0.82	0.99 and 0.89
Data/restraints/parameters	26 435/0/527	17 840/124/546	21 725/57/538	14 497/0/527	12 617/7/491
R_1, wR_2 [$I > 2\sigma(I)$]	0.0349/0.0955	0.0728/0.1971	0.0456/0.1284	0.0499/0.1327	0.0411/0.921
R_1, wR_2 [all data]	0.0435/0.1021	0.0999/0.2213	0.0558/0.1385	0.0609/0.1473	0.0539/0.0989
Goodness-of-fit (F^2)	1.029	1.074	1.075	1.049	1.033
Peak/hole (e/Å^3)	2.153/−1.885	3.597/−1.773	1.854/−2.204	2.896/−2.848	2.473/−0.644

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