Phosphane Ligands, 6[◇]

The Remarkable Tridentate Coordination of 4,6-Bis(diphenylphosphanyl)-dibenzofuran in Ruthenium(II) Complexes

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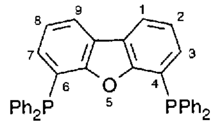
4,6-Bis(diphenylphosphanyl)dibenzofuran (**1**), despite its large P···P distance of 5.74 Å and its bite angle of ca. 131°, was found to be capable of tridentate coordination to ruthenium(II) chloride. Single crystal X-ray structure analyses of the new ruthenium(II) complexes **3**, **4**, and **5** revealed that the ligand **1** coordinates to a single ruthenium atom with both phosphorus centers and the dibenzofuran oxygen atom. The remarkable ligand deformation resulting from the coordination is evident from the decrease of the P···P distance by 1 Å to 4.75 Å and the increase of the bite angle (P–Ru–P) by 25° to 155°–157°. The unprecedented *in-plane* coordination of the dibenzofuran oxygen atom to ruthenium is interesting in view of the hybridisation of the oxygen.

Introduction

Bidentate and polydentate tertiary phosphanes are important ligands in coordination chemistry and catalysis[2]. The importance and application of polydentate ligands is further extented by combining phosphorus centers and nitrogen or oxygen donor atoms in P/N ligands[3] and P/O ligands[4]. In the context of our concept of using polycyclic arenes and heteroarenes as rigid carbon skeletons for the construction of new bidentate phosphane ligands[1,5], we previously reported the synthesis of 4,6-bis(diphenylphosphanyl)dibenzofuran (**1**)[5b]. The framework of 4,6-disubstituted dibenzofuran was chosen on expecting that the rather long distance between the two phosphorus centers together with a unfourable bite angle of their lone pairs do not allow both phosphorus centers to coordinate simultaneously to one metal nucleus. Alternatively, the bidentate ligand **1** was expected to favour the formation and stabilization of dinuclear metal complexes. Such complexes, containing two metal centers to close proximity, possibly introduce interesting properties, especially with respect to the development of catalytic processes. In accordance with our expectance, the P···P distance of **1** was determined to 5.741(1) Å by single crystal X-ray structure analysis and the reaction of **1** with dicobaltoctacarbonyl [$Co_2(CO)_8$] yielded the dinuclear complex 4,6-bis(diphenylphosphanyl)dibenzofurandicobalthexacarbonyl (**2**)[1]. Furthermore, molecular modelling studies on the effect, which the bite angle of diphosphane ligands has on the regioselectivity in the rhodium-catalyzed hydroformylation[6] and nickel-catalyzed hydrocyanation[7], resulted in a calculated natural bite angle of 131° with a flexibility range between 117°–147° (range accessible within less than 3 kcal mol^{-1} excess strain energy) and a P···P distance between 5.760 Å (MM) and 5.965 Å (PM3). It was concluded that **1** does not form chelates, and in accordance with the calculations no increased regioselectivity was observed experimentally when **1** was used as a ligand in the rhodium-catalyzed hydroformylation[6]. In contrast to this, we here want to describe new ruthenium(II) complexes of **1**, which prove that **1** is capable of acting even as a tridentate ligand by coordinating to one metal nucleus with both phosphorus centers and the dibenzofuran oxygen atom.



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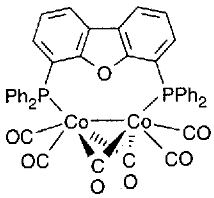

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Results and Discussion

The reaction of the ligand **1**[5b] with ruthenium dichoride, prepared in situ by heating ruthenium trichloride in ethanol under reflux[8], yielded 50% bis[4,6-bis(diphenylphosphanyl)dibenzofuran]ruthenium dichloride (**3**) as a brown solid, m.p. 265°C (dec.). Recrystallisation from dichloromethane/*n*-pentane resulted in brown crystals of **3**. The structure of **3** was indicated by the ^{31}P-NMR spectrum showing three signals, one signal corresponding to one uncoordinated [$\delta = -23.2$ (s, 1 P)] and the two other signals [$\delta = 23.9$ (d, $J_{PP} = 28.4$ Hz, 2 P) and $\delta = 52.5$ (t, $J_{PP} = 28.4$ Hz, 1 P)]

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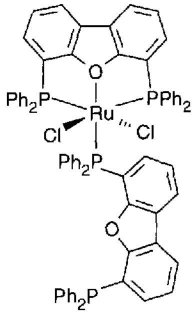
corresponding to three coordinated phosphorus centers. The coupling of the three coordinated phosphorus atoms with a triplet and a doublet split by J_{PP} = 28.4 Hz gives particularly strong evidence for structure **3**.



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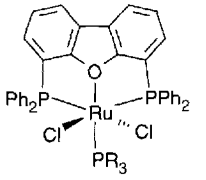
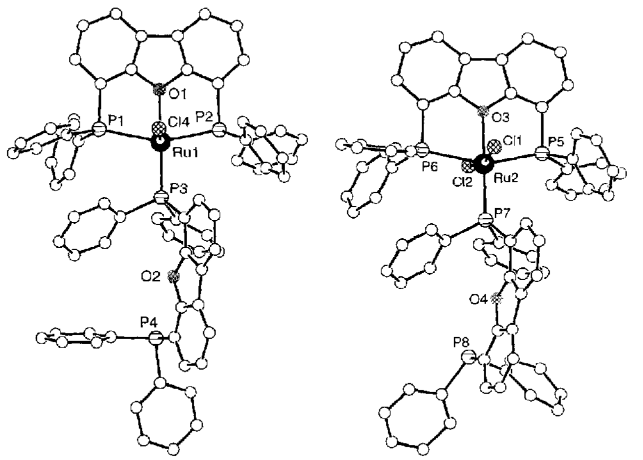


4: R = phenyl
5: R = *p*-tolyl

Figure 1. Molecular structure of bis[4,6-bis(diphenylphosphanyl)-dibenzofuran]ruthenium dichloride (**3**): Top view on the dibenzofuran unit of the tridentate ligand for both independent molecules of the unit cell (solvent molecules dichloromethane and *n*-pentane omitted)



In order to fully characterize **3** and the unexpected coordination of a single metal nucleus to both phosphorus centers of **1**, a single crystal X-ray structure analysis of **3** was performed. The unit cell contains two independent molecules of **3** together with two solvent molecules, one dichloromethane and one *n*-pentane molecule. The two independent molecules of **3** (Figure 1) both contain two ligands **1**, one coordinated tridentately by the two phosphorus centers and the dibenzofuran oxygen atom and one coordinated monodentately by only one phosphorus center to the ruthenium atom. The monodentate ligands **1** have "*in-out*" conformations (one phosphorus lone pair directed towards and the other pointing away from the dibenzofuran oxygen atom) similar to the conformation observed in the crystal structure of **1**[1]. The two independent molecules of **3** mainly differ in the conformation which is taken by the non-coordinated diphenylphosphanyl group of the monodentate ligand **1**. The ruthenium atom is surrounded by three phosphorus atoms, two chlorine atoms, and one oxygen atom in an approximately octahedral coordination. A similar coordination has been observed in a ruthenium dichloride complex with a phosphane containing a polyether chain[9]. In the two molecules of **3** the P···P distances of the tridentately coordinating ligand **1** were found to be $P^1 \cdots P^2$: 4.79 Å and $P^5 \cdots P^6$: 4.78 Å, which is almost 1 Å less than the P···P distances determined in **3** for the monodentately coordinating ligand **1** [$P^3 \cdots P^4$: 5.71 Å; $P^7 \cdots P^8$: 5.58 Å] and for the free ligand **1** [P···P: 5.741(1) Å][1]. Thus considerable strain seems to be imposed on the dibenzofuran skeleton, although its planarity is retained. The strain is evident especially in the deviations which Figure 1 shows for the valence angles at the phosphorus-substituted carbon atoms of the dibenzofuran skeleton. However, insufficient crystal quality and/or the two solvent molecules present in the crystal did not permit to refine the structure to a final stage $R < 0.09$, thus preventing the evaluation of the structure in more detail.

In our further attempts to obtain single crystals of suitable quality to allow X-ray structure analysis, we considered methods of crystal engineering. Replacing the monodentately coordinated ligand **1** in complex **3** by a simple tertiary phosphane such as triphenylphosphane or tri-*p*-tolylphosphane would result in ruthenium complexes **4** and **5** which have structures much more compact than **3** and which hence can be expected to crystallize more perfectly. Accordingly, 1:1 mixtures of the ligand **1** and triphenylphosphane or of **1** and tri-*p*-tolylphosphane were reacted with ruthenium dichloride in ethanol. Brown solid products were obtained, which consisted of 4,6-bis-(diphenylphosphanyl)dibenzofuran(triphenylphosphane)ruthenium dichloride [**4**, m.p. 300–302°C (dec.), 78%] and of 4,6-bis(diphenylphosphanyl)dibenzofuran(tri-*p*-tolylphosphane)-ruthenium dichloride [**5**, m.p. 293–295°C (dec.), 66%], respectively. Recrystallization of both compounds **4** and **5** from dichloromethane/*n*-pentane gave brown crystals, which still contained solvent molecules of dichloromethane, but no *n*-pentane. However, the quality of both crystals was sufficient to permit single crystal X-ray structure analyses (Figures 2 and 3, Tables 1 and 2).

In both compounds **4** and **5** the ligand **1** is coordinated tridentately to ruthenium (Figure 2a and 3a). As it was already noticed in the structure of **3**, the coordination enforces P···P distances 1 Å shorter than in the free ligand [**4**: $P^1 \cdots P^2$: 4.750(1) Å; **5**: $P^1 \cdots P^2$: 4.754(1) Å; **1**: [1] P···P: 5.741(1) Å]. The P–Ru–P angle is 155.2(3)° in **4** and 156.8(3)° in **5**. This angle exceeds by roughly 25° the bite angle of 131° calculated for the ligand **1**, and still is larger by 10° than the upper limit of the flexibility range which due to the calculations is accessible within less than 3 kcal mol^{-1} excess strain energy[6]. This suggests that in **4** and **5** the tridentate coordination of the ligand **1** imposes a steric strain energy distinctly above 3 kcal mol^{-1}. The strain caused by the shortening of the P···P distance results in strong deformations of the bond angles especially at the phosphorus-substituted dibenzofuran carbon atoms [**4**: $P^1-C^1-C^2$: 131.9(2)°; $P^1-C^1-C^{12}$: 114.2(2)°; $P^2-C^{10}-C^9$: 132.3(2)°; $P^2-C^{10}-C^{11}$: 114.4(2)°. – **5**: $P^1-C^1-C^2$: 130.5(4)°; $P^1-C^1-C^{12}$: 116.1(3)°; $P^2-C^{10}-C^9$: 131.9(4)°; $P^2-C^{10}-C^{11}$: 114.5(4)°]. The short distances between ru-

Figure 2. Molecular structure of 4,6-bis(diphenylphosphanyl)dibenzofuran(triphenylphosphane)ruthenium dichloride (**4**): a) Top view on the dibenzofuran unit of the tridentate ligand (solvent molecules dichloromethane omitted); b) side view on the dibenzofuran unit along the O–Ru bond (the phenyl groups of triphenylphosphane omitted for clearity)

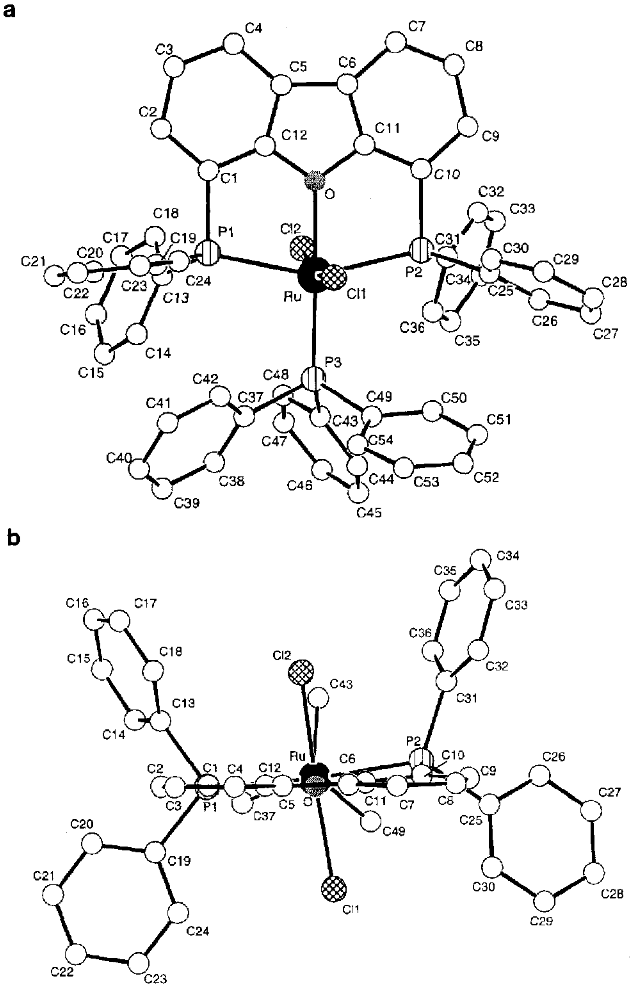


Table 1. Bond lengths [in Å] and bond angles [in °] of **4**

Ru - Cl(1)	2.425(1)	Ru - Cl(2)	2.409(1)
Ru - P(1)	2.425(1)	Ru - P(2)	2.440(1)
Ru - P(3)	2.273(1)	Ru - O	2.101(2)
P(1) - C(1)	1.850(3)	P(2) - C(10)	1.849(3)
C(1) - C(12)	1.370(4)	C(10)- C(11)	1.379(4)
O - C(11)	1.368(3)	O - C(12)	1.366(3)
O - Ru - P(3)	178.1(1)	O - Ru - P(2)	78.1(1)
O - Ru - P(1)	78.2(1)	O - Ru - Cl(2)	80.7(1)
O - Ru - Cl(1)	86.9(1)	P(3) - Ru - P(2)	103.4(1)
P(3) - Ru - P(1)	100.6(1)	P(3) - Ru - Cl(2)	100.7(1)
P(3) - Ru - Cl(1)	91.8(1)	P(2) - Ru - P(1)	155.2(1)
P(2) - Ru - Cl(2)	85.1(1)	P(2) - Ru - Cl(1)	89.7(1)
P(1) - Ru - Cl(2)	84.1(1)	P(1) - Ru - Cl(1)	96.0(1)
Cl(2) - Ru - Cl(1)	167.3(1)	C(1) - P(1) - Ru	101.2(1)
C(10) - P(2) - Ru	100.9(1)	C(12) - O - C(11)	107.4(2)
C(12) - O - Ru	125.4(2)	C(11) - O - Ru	126.2(2)
C(12) - C(1) - C(2)	113.8(2)	C(12) - C(1) - P(1)	114.2(2)
C(2) - C(1) - P(1)	131.9(2)	C(11) - C(10) - C(9)	113.2(2)
C(11) - C(10) - P(2)	114.4(2)	C(9) - C(10) - P(2)	132.3(2)

Figure 3. Molecular structure of 4,6-bis(diphenylphosphanyl)dibenzofuran(tritolylphosphane)ruthenium dichloride (**5**): a) Top view on the dibenzofuran unit of the tridentate ligand (solvent molecules dichloromethane omitted); b) side view on the dibenzofuran unit along the O–Ru bond (the tolyl groups of tritolylphosphane omitted for clearity)

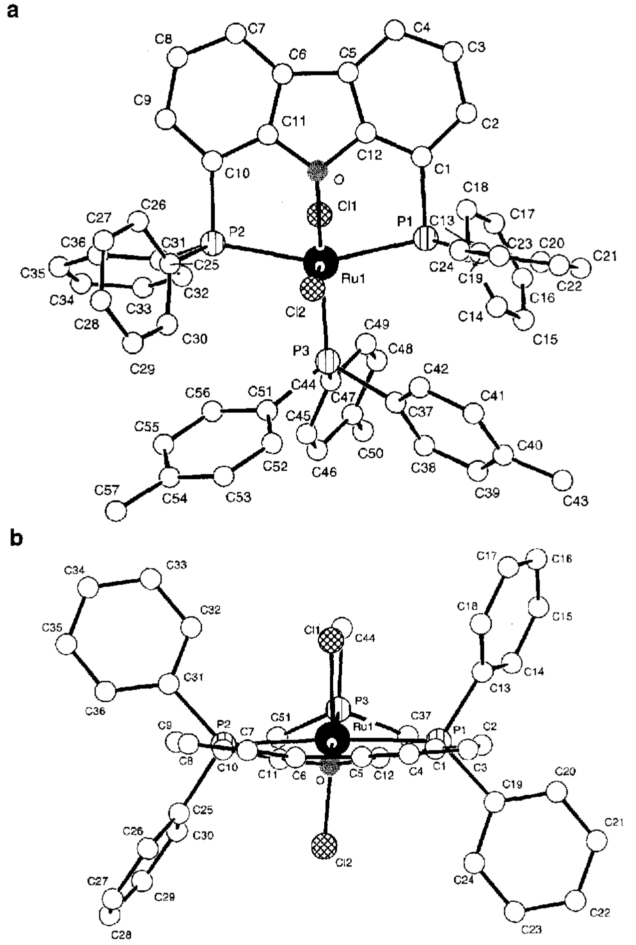


Table 2. Bond lengths [in Å] and bond angles [in °] of **5**

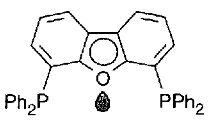
Ru - Cl(1)	2.422(1)	Ru - Cl(2)	2.417(1)
Ru - P(1)	2.406(1)	Ru - P(2)	2.449(1)
Ru - P(3)	2.284(1)	Ru - O	2.139(3)
P(1) - C(1)	1.846(5)	P(2) - C(10)	1.854(5)
C(1) - C(12)	1.372(7)	C(10)- C(11)	1.386(7)
O - C(11)	1.374(6)	O - C(12)	1.384(6)
O - Ru - P(3)	177.8(1)	O - Ru - P(2)	77.4(1)
O - Ru - P(1)	79.4(1)	O - Ru - Cl(2)	88.1(1)
O - Ru - Cl(1)	79.5(1)	P(3) - Ru - P(2)	104.4(1)
P(3) - Ru - P(1)	98.6(1)	P(3) - Ru - Cl(2)	93.2(1)
P(3) - Ru - Cl(1)	99.4(1)	P(2) - Ru - P(1)	156.7(1)
P(2) - Ru - Cl(2)	85.4(1)	P(2) - Ru - Cl(1)	87.3(1)
P(1) - Ru - Cl(2)	96.1(1)	P(1) - Ru - Cl(1)	86.3(1)
Cl(2) - Ru - Cl(1)	166.7(1)	C(1) - P(1) - Ru	100.2(2)
C(10) - P(2) - Ru	100.9(2)	C(12) - O - C(11)	105.6(3)
C(12) - O - Ru	121.7(3)	C(11) - O - Ru	124.1(3)
C(12) - C(1) - C(2)	113.4(4)	C(12) - C(1) - P(1)	116.1(3)
C(2) - C(1) - P(1)	130.5(4)	C(11) - C(10) - C(9)	113.4(4)
C(11) - C(10) - P(2)	114.5(4)	C(9) - C(10) - P(2)	131.9(4)

thenium and the dibenzofuran oxygen atom of 2.101(2) Å for **4** and 2.139(3) Å for **5** has to be interpreted as bonding interaction, and hence **1** serves as a tridentate ligand for ruthenium.

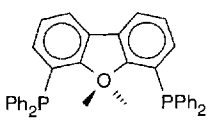
The side views on the dibenzofuran units along the O–Ru bonds (Figures 2b and 3b) show approximate planarity of the dibenzofuran unit, although the complexes **4** and **5** show slight differences in this respect. Whereas the dibenzofuran unit of structure **4** is almost planar [angle between the condensed benzene rings: 176.5(3)°, dihedral angles $C^6-C^{11}-O-C^{12}$: 5.8(3)° and $C^5-C^{12}-O-C^{11}$: 5.0(3)°, angle between the line through O–Ru and the plane $C^{11}-O-C^{12}$: 8.8(3)°], a somewhat bent (or even bowl-shaped) conformation of the ligand **1** is observed in structure **5** [angle between the condensed benzene rings: 165.9(3)°, dihedral angles $C^6-C^{11}-O-C^{12}$: 9.4(3)° and $C^5-C^{12}-O-C^{11}$: 9.7(3)°, angle between the line through O–Ru and the plane $C^{11}-O-C^{12}$: 26.1(3)°]. These differences between **4** and **5** presumably are due to crystal packing of the complexes and the solvent molecules in the crystal.

The "*in-plane*" coordination of the dibenzofuran oxygen atom to ruthenium, observed in the complexes **3**, **4**, and **5**, is remarkable and raises the interesting question which hybridisation is appropriate for describing the valence electrons of the dibenzofuran oxygen atom. The hybridisation can be assumed to be either sp^2 (**1a**) or sp^3 (**1b**). Based on aromaticity arguments one tends to give the preference to the sp^3-hybridisation (**1b**), which does not disturb the conjugation of the two annelated benzene rings. A similar argumentation is used to explain the very different acidities of cyclopentadiene ($pK_a = 16$) and of fluorene (dibenzocyclopentadiene, $pK_a = 23$)[10]. To our knowledge no single crystal X-ray structure analysis describing the coordination of the dibenzofuran oxygen atom to a transition metal has yet been reported[11]. However, several X-ray structures were reported on the coordination of dibenzothiophene, the sulfur analogon of dibenzofuran, to transition metals which in all cases show the "*out-of-plane*" coordination of the dibenzothiophene sulfur atom to the metal[12]. For instance, in the X-ray structure of an iron dibenzothiophene complex the plane of the dibenzothiophene and the Fe–S bond form an angle of 119.4[12c], which clearly indicates that sp^2-hybridisation is not an appropriate model to describe the valence electrons of the dibenzothiophene sulfur atom. If the analogy between sulfur and oxygen is permitted, the structural data of the dibenzothiophene coordination also support our argumentation in favor of the sp^3-hybridisation model (**1b**). On the other hand, the rigid skeleton of the ligand **1** and the tight geometry within the complexes **3**, **4** and **5** gives the dibenzofuran oxygen atom no other choice but the "*in-plane*" coordination to ruthenium. However, the structural data of **4** and **5**, e.g. the C–C bond distances determined for the dibenzofuran units, give no hint that the *in-plane*" coordination of the oxygen atom enforces the rehybridisation from sp^3 to sp^2, which possibly could be expected to have an effect on the bond distances due to a partial π-bond localisation as indicated by **1a**.

In conclusion, our syntheses and structural characterisation of the new ruthenium dichloride complexes **3**, **4**, and **5** have demonstrated, that 4,6-bis(diphenylphosphanyl)dibenzofuran (**1**), despite its long P···P distance of 5.74 Å and the unfavorable bite angle around 131°, is capable of acting as a tridentate ligand, which coordinates to a single transition metal nucleus with both phosphorus centers and the dibenzofuran oxygen atom. The complexation causes strong deformations of the ligand **1** by decreasing the P···P distance by 1 Å to 4.75 Å and increasing the bite angle (P–Ru–P) by 25° to 156°. Ligands such as **1**, which contain aromatic skeletons and hence are considered to be more or less rigid, seem to have still more flexibility than it was expected or it was predicted by calculations using molecular mechanics. Experiments to explore the potential of the new complexes in catalysis are currently under way.



1a: oxygen sp^2



1b: oxygen sp^3

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Experimental Section

General: All experiments were carried out under an atmosphere of argon using a vacuum line and Schlenk flasks. Solvents were dried, distilled and saturated with argon. Standard analytical and spectroscopic equipment was used throughout. Melting points: Büchi B-510. – Before use, $RuCl_3$ was dissolved in conc. HCl. After removing the liquid by heating the black slurry, an activated black powder of $RuCl_3 \cdot H_2O$ was obtained. – NMR: Bruker AC200, Bruker AC300; for ^1H NMR TMS as internal standard and for ^{31}P-NMR a 85% H_3PO_4 aqueous solution were used as external standard, respectively. – Elementary analyses: Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr.

Bis[4,6-bis(diphenylphosphanyl)dibenzofuran]ruthenium Dichloride (**3**): To 100 mg (0.86 mmol) of 4,6-bis(diphenylphosphanyl)dibenzofuran (**1**)[5b] in 10 ml of ethanol was added a solution of 50 mg (0.186 mmol) of ruthenium(III) chloride in 10 ml of ethanol. The mixture was heated under reflux for 40 h. The brown solid formed was separated by filtration, washed with ethanol and dried in vacuo to yield 60 mg (50%) of **3**, m.p. 265°C (dec.). Recrystallisation from CH_2Cl_2/*n*-pentane, by dissolving crude **3** in CH_2Cl_2, addition of *n*-pentane and slow diffusion of the *n*-pentane into the CH_2Cl_2 layer, yielded brown crystals, suitable for single crystal X-ray diffraction. – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} (CH), 1607 (C=C), 1572, 1482, 1467, 1433, 1409, 1401, 1389, 1214, 1173, 1091, 1027, 742, 693, 569, 742, 693, 569, 528, 503. – IR (PE): $\tilde{\nu}$ = 327 cm^{-1} (RuCl). – ^1H NMR ([D$_8$]THF, 200 MHz): δ = 8.24 (dd, J = 13.8 Hz, 1H), 8.09 (d, J = 7.1 Hz, 2H), 7.82 (m, 2H), 7.54–6.97 (m, 40H), 6.75 (m, 3H), 6.52 (m, 4H) 3.28 (q, 2H, ethanol) 1.00 (t, 3H, ethanol) – ^{31}P NMR ([D$_8$]THF, 81 MHz): δ = 52.5 (t, $^2J_{PP}$ = 28.4 Hz, 1 P), 23.9 (d, $^2J_{PP}$ = 28.4 Hz, 2 P), −23.2 (s, 1 P). – $C_{72}H_{52}Cl_2O_2P_4Ru \cdot CH_3CH_2OH$ (1291.15): calcd. C 68.84, H 4.53, P 9.60, Cl 5.49, Ru 7.83; found C 68.47, H 4.30, P 9.72, Cl 5.65, Ru 7.74.

Crystal-Structure Determination for Compound **3**: Empirical formula: $C_{72}H_{52}Cl_2O_2P_4Ru \cdot 0.5\ CH_2Cl_2$, molecular mass: 1287.4 g · mol^{-1}, crystal size 0.20 × 0.12 × 0.02 mm^3, a = 16.456(1), b = 21.346(1), c = 21.409(1) Å, α = 107.20(1)°, β = 105.51(1)°, γ =

109.9(1)°, V = 6205.5(6) Å^3, triclinic, $P\bar{1}$ (No. 2), Z = 4, $D_{\text{calcd.}}$ = 1.378 Mg · m^{-3}, μ = 0.532 mm^{-1}, λ = 0.71073 Å, Siemens SMART diffractometer, T = 173 K, 27317 measured reflections [$\pm h$, $\pm k$, $\pm l$], $[(\sin\Theta)/\lambda]_{\max}$ = 0.65 Å^{-1}, 19980 independent reflections, 13486 observed reflections [$I > 2\sigma(I)$], hydrogen atoms calculated, 1476 refined parameters, $R(F)$ = 0.099, $wR(F^2)$ = 0.241, $w = 1/[\sigma^2(F_o^2) + (0.1284P)^2 + 112.8238P]$ with $P = (F_o^2 + 2\,F_c^2)/3$. The structure was solved with Patterson methods using SHELXL86[13], structure refinement was carried out using SHELXL93[14]. Because of insufficient refinement the crystallographic data of **3** have not been deposited.

4,6-Bis(diphenylphosphanyl)dibenzofuran(triphenylphospane)-ruthenium Dichloride (**4**): A suspension of 200 mg (0.744 mmol) of ruthenium(III) chloride in 10 ml of ethanol was heated under reflux for 40 h. Then 200 mg (0.372 mmol) of 4,6-bis(diphenylphosphanyl)dibenzofuran (**1**)[5b] and 98 mg (0.372 mmol) of triphenylphosphane in 10 ml of ethanol were added and the mixture was heated under reflux for 10 h. The brown solid formed was separated by filtration, washed with ethanol and dried in vacuo to yield 270 mg (78%) of **4**, m.p. 300–302°C (dec.). Recrystallisation from CH_2Cl_2/*n*-pentane yielded brown crystals, suitable for single crystal X-ray diffraction. For elemental analysis the crystals of **4** were dried in high vacuo. – IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1} (CH), 1480, 1433, 1417, 1088, 733, 692, 528, 501. – ^{1}H NMR (CD_2Cl_2; 300 MHz): δ = 8.09 (d, ^3J = 7.6 Hz, 2H, 1-, 9-H), 7.49 (dd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, 2H, 2-, 8-H) 7.44–7.23 (m, 20H, aromatic H), 7.16 (m, 11H, aromatic H), 6.87 (m, 6H, aromatic H). – ^{31}P NMR (CD_2Cl_2; 121.5 MHz): δ = 55.2 (t, $^2J_{PP}$ = 28.0 Hz, 1 P, PPh_3), 24.4 (d, $^2J_{PP}$ = 28.0 Hz, 2 P, PPh_2). – $C_{54}H_{41}Cl_2OP_3Ru$ (970.82): calcd. C 66.81, H 4.26, P 9.57, Cl 7.30, Ru 10.41; found C 66.45, H 4.24, P 9.81, Cl 7.47, Ru 10.28.

Crystal-Structure Determination of Compound **4**[15]: Empirical formula: $C_{54}H_{41}Cl_2OP_3Ru \cdot 2\,CH_2Cl_2$; molecular mass: 1140.60 g· mol^{-1}; crystal size 0.42 × 0.53 × 0.70 mm^3, a = 12.839(1) Å, b = 23.652(1) Å, c = 16.907(1) Å, β = 102.83(1)°, V = 5006.1(2) Å^3, monoclinic, $P2_1/c$ (No. 14), Z = 4, $D_{\text{calcd.}}$ = 1.513 Mg · m^{-3}, μ = 0.770 mm^{-1}, λ = 0.71073 Å, Siemens SMART diffractometer, T = 100 K, 57008 measured reflections [$\pm h$, $\pm k$, $\pm l$], $[(\sin\Theta)/\lambda]_{\max}$ = 0.65 Å^{-1}, 18235 independent reflections, 13869 observed reflections [$I > 2\sigma(I)$], hydrogen atoms were found and refined with fixed ADP's, 739 refined parameters, $R(F)$ = 0.057, $wR(F^2)$ = 0.158, $w = 1/[\sigma^2(F_o^2) + (0.10\,P)^2]$ with $P = (F_o^2 + 2\,F_c^2)/3$. The structure was solved with Patterson methods using SHELXL86[13], structure refinement was carried out using SHELXL93[14].

4,6-Bis(diphenylphosphanyl)dibenzofuran(tri-p-tolylphosphane)-ruthenium Dichloride (**5**): A suspension of 200 mg (0.744 mmol) of ruthenium(III) chloride in 10 ml of ethanol was heated under reflux for 40 h. Then 200 mg (0.372 mmol) of 4,6-bis(diphenylphosphanyl)dibenzofuran (**1**)[5b] and 113 mg (0.372 mmol) of tri-*p*-tolylphosphane in 10 ml of ethanol were added and the mixture was heated under reflux for 10 h. The brown solid formed was separated by filtration, washed with ethanol and dried in vacuo to yield 250 mg (66%) of **5**, m.p. 293–295°C (dec.). Recrystallization from CH_2Cl_2/*n*-pentane yielded brown crystals, suitable for single crystal X-ray diffraction. For elemental analysis the crystals of **5** were dried in high vacuo. – IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (CH_{arom}), 2920 (CH_{aliph}), 1431, 1417, 1398, 1204, 1088, 736, 639, 527, 502. – ^{1}H NMR (CD_2Cl_2; 300 MHz): δ = 8.09 (d, ^3J = 7.8 Hz, 2H, 1-, 9-H), 7.49 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 2H, 2-, 8-H), 7.44–7.28 (m, 14H, aromatic H), 7.22–7.11 (m, 14H, aromatic H), 6.67 (m, 6H, aromatic H), 2.22 (s, 9H, CH_3). – ^{31}P NMR (CD_2Cl_2; 121.5 MHz): δ = 52.3 [t, $^2J_{PP}$ = 27.8 Hz, 1 P, $P(tol)_3$], 24.9 (d, $^2J_{PP}$ = 27.8 Hz, 2 P, PPh_2). – $C_{57}H_{47}Cl_2OP_3Ru$ (1012.90): calcd. C 67.59, H 4.68, P 9.17, Cl 7.00, Ru 9.98; found C 67.71, H 4.69, P 9.16, Cl 7.11, Ru 10.11.

Crystal-Structure Determination of Compound **5**[15]: Empirical formula: $C_{57}H_{47}Cl_2OP_3Ru \cdot 2\,CH_2Cl_2$; molecular mass: 1111.78 g · mol^{-1}; crystal size 0.32 × 0.53 × 0.63 mm^3, a = 12.232(1) Å, b = 12.941(1) Å, c = 19.412(1) Å, α = 70.43(1), β = 78.44(1), γ = 66.15(1)°, V = 2640.9(3) Å^3, triclinic, $P\bar{1}$ (No. 2), Z = 2, $D_{\text{calcd.}}$ = 1.398 Mg · m^{-3}, μ = 0.630 mm^{-1}, λ = 0.71073 Å, Siemens SMART diffractometer, T = 100 K, 10576 measured reflections [$\pm h$, $\pm k$, $\pm l$], $[(\sin\Theta)/\lambda]_{\max}$ = 0.65 Å^{-1}, 7483 independent reflections, 6719 observed reflections [$I > 2\sigma(I)$], hydrogen atoms were found and refined with fixed ADP's, 784 refined parameters, $R(F)$ = 0.056, $wR(F^2)$ =0.157, $w = 1/[\sigma^2(F_o^2) + (0.10\,P)^2]$ with $P = (F_o^2 + 2\,F_c^2)/3$. The structure was solved with Patterson methods using SHELXL86[13], structure refinement was carried out using SHELXL93[14].

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[15] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100306. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

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