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New aryl phosphinite ligands avoiding *ortho*-metallation: Synthesis and molecular structures of *trans*-[$PdCl_2(PPh_2OR)_2$] and *trans*-[$Rh(CO)Cl(PPh_2OR)_2$] (R = 2,4,6-$Me_3C_6H_2$; 2,6-$Ph_2C_6H_3$)

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Abstract

The new aryl phosphinites PPh_2OR (R = 2,4,6-$Me_3C_6H_2$, **1**; R = 2,6-$Ph_2C_6H_3$, **2**) have been prepared from chlorodiphenylphosphine and the corresponding phenols. In these ligands, the *ortho*-positions of the aromatic phosphite function are blocked by methyl and phenyl substituents, which allows coordination to metal centres without *ortho*-metallation. Thus, reaction with [$PdCl_2$(cod)] leads to the complexes *trans*-[$PdCl_2(PPh_2OR)_2$] (R = 2,4,6-$Me_3C_6H_2$, **3**; R = 2,6-$Ph_2C_6H_3$, **4**), while the reaction with [$Rh_2(CO)_4Cl_2$] gives *trans*-[$Rh(CO)Cl(PPh_2OR)_2$] (R = 2,4,6-$Me_3C_6H_2$, **5**; R = 2,6-$Ph_2C_6H_3$, **6**). The single-crystal X-ray structure analyses of **3** and **5** confirm the *trans*-coordination of the new ligands in these square-planar complexes.

Keywords: Palladium; Rhodium; *ortho*-Metallation; Aryl phosphinite ligands

1. Introduction

Because of their remarkable catalytic potential and their large versatility, palladium complexes have become the most popular organometallics used in organic synthesis [1]. In particular, most of carbon–carbon bond forming reactions such as Heck reaction, Stille reaction, Suzuki reaction and other C–C couplings are palladium-catalyzed [2]. One of the intrinsic problems of palladium-catalyzed reactions, the palladium contamination of the products, not acceptable in the production of pharmaceuticals or other fine chemicals, can be overcome by using highly active palladium catalysts, present in very low concentration. Therefore, the development of new highly active palladium catalysts that can be used in low loadings is an ongoing challenge in organometallic chemistry.

Of particular interest in this respect was the use of palladacyclic complexes for carbon–carbon coupling reactions, an area initiated by Beller et al. [3] and the introduction of palladacyclic pincer compounds by Bedford et al. [4–6]. However, these complexes are so reactive that it is generally not possible to detect the catalytic active species or even to recover the palladium catalyst at the end of the reaction.

The most active palladacycles and pincer compounds contain phosphinite ligands and a carbon–palladium bond formed by an aromatic-carbon atom in *ortho*-position (*ortho*-metallation) (Scheme 1). Indeed, since *ortho*-metallation occurs very easily in palladium complexes containing aromatic phosphorous ligands, there are only a very few palladium complexes containing aromatic phosphinite ligands without undergoing *ortho*-metallation. The only complex known so far, to the best of our knowledge, is the fluoro substituted complex [$PdCl_2\{PPh_2(OC_6F_5)\}_2$], synthesized by Ziolkowski and co-workers [7], the molecular structure of which,

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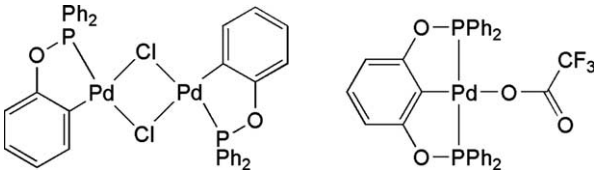


Scheme 1.

however, is not known. *ortho*-Metallation has been shown to occur through the intermediacry of agostic interactions in the case of square-planar carbonyl rhodium complexes by Milstein and co-workers [8], who succeeded to characterize the agostic intermediate $[H\cdots C_6H_3\{CH_2P(t\text{-}Bu)_2\}_2Rh(CO)]^+$ by X-ray crystallography of the triflate salt.

For these reasons we decided to design new phosphinite ligands in which the *ortho*-positions of the aromatic cycle with respect to the oxygen substituent are blocked, so that *ortho*-metallation cannot take place, and to study the coordination of these ligands to dichloropalladium and to chlorocarbonyl rhodium moieties.

2. Experimental

All reactions were carried out by using standard Schlenk techniques under argon atmosphere. The solvent *n*-hexane was distilled from sodium benzophenone under N_2 to avoid water and oxygen contaminations. Toluene and methanol were purchased from Merck and were only deoxygenated before use. Methylene chloride was distilled over CaH_2 and saturated with N_2. Chlorodiphenyl phosphine 95% was purchased from Aldrich and distillated under reduced pressure prior to use. Deuterated chloroform was used as received, and all NMR spectra were performed with Varian or Bruker spectrometers (200 and 400 MHz for ^1H, 81 MHz for ^{31}P, and 100 MHz for ^{13}C).

2.1. Synthesis of (2,4,6-trimethylphenyl)-diphenylphosphinite (*1*)

A solution of 408 mg (3 mmol) of 2,4,6-trimethylphenol and 420 μL (3 mmol) of triethylamine in toluene (10 mL) was stirred for 5 min. Then, 540 μL (3 mmol) of chlorodiphenylphosphine were added, which caused immediately a white precipitate of ammonium chloride. The mixture was then heated to 90 °C over a period of 18 h under vigorous stirring. After cooling, the mixture was filtered through a canula equipped with filter-paper. The filtrate was reduced to dryness in vacuo, the resulting oil was dissolved in hexane (5 mL). The cloudy solution was filtrated through filter-paper, and the solvent of the filtrate was evaporated under reduced pressure to give a pale yellow oil (yield 70%). ^1H (200 MHz, $CDCl_3$): δ = 7.99–7.85(m, 4H), 7.61–7.55(m, 6H), 7.01(s, 2H), 2.46(s, 3H), 2.24(s, 6H). ^{13}C ($CDCl_3$, 100 MHz): δ = 152.81(Ar), 142.37(Ar), 133.08(Ar), 131.57(Ar), 130.29(Ar), 129.41(Ar), 128.38(Ar), 127.06 (Ar), 22.18(CH_3), 19.36(CH_3). ^{31}P (81 MHz, $CDCl_3$): δ = 113.98 (s). ESI-MS (*m*/*z*): 455.3, $[2M - (PPh_2)]^+$. *Anal*. Calc.: C, 78.73; H, 6.61. Found: C, 78.53; H, 6.69%.

2.2. Synthesis of (2,6-diphenylphenyl)-diphenylphosphinite (*2*)

A solution of 738 mg (3 mmol) of 2,6-diphenylphenol and 420 μL (3 mmol) of triethylamine in toluene (10 mL) was stirred for 5 min. Then, 540 μL (3 mmol) of chlorodiphenylphosphine were added, which caused immediately a white precipitate of ammonium chloride. The mixture was then heated to 90 °C over a period of 18 h under vigorous stirring. After cooling, the mixture was filtered through a canula equipped with filter-paper. The filtrate was reduced to dryness in vacuo, and the resulting residue was washed with methanol (5 mL). The expected product was extracted with hot hexane (10 mL) and precipitated upon cooling. The white precipitate was isolated by filtration and recrystallized from hexane (65% yield). ^1H (400 MHz, $CDCl_3$): δ = 7.62–7.57(m, 4H), 7.55–7.43(m, 4H), 7.43–7.38(m, 2H), 7.33–7.28(m, 4H), 7.20–7.14(m, 5H), 7.10–7.02(m, 4H). ^{13}C ($CDCl_3$, 100 MHz): δ = 152.19(Ar), 139.41(Ar), 136.26(Ar), 131.05(Ar), 130.81(Ar), 130.44(Ar), 129.29 (Ar), 128.31(Ar), 128.10(Ar), 128.03(Ar), 127.34(Ar), 124.00(Ar). ^{31}P (81 MHz, $CDCl_3$): δ = 120.96 (s) EI-MS (*m*/*z*): 429.0, $[M - H]^+$. *Anal*. Calc.: C, 83.70; H, 5.39. Found: C, 83.46; H, 5.60%.

2.3. General method for the synthesis of complexes *3*–*6*

A solution of 1.5 mmol of the corresponding phosphinite ligand and 0.75 mmol of $[PdCl_2(cod)]$ or 0.375 mmol of $[Rh_2Cl_2(CO)_4]$ in methylene chloride (20 mL) was stirred at room temperature for 24 h. After filtration through filter-paper, the solution was reduced in vacuo to half of its volume. Upon dropwise addition of *n*-hexane, a yellow solid precipitated. The yellow precipitate was isolated by filtration, washed with *n*-hexane and dried in vacuo.

2.3.1. *trans*-$[PdCl_2\{PPh_2O(2,4,6\text{-}Me_3C_6H_2)\}_2]$ (*3*)

(85% yield) ^1H (100 MHz, $CDCl_3$): δ = 7.80–7.60(m, 8H), 7.45–7.28(m, 12H), 6.89(s, 4H), 2.39(s, 6H), 2.26(s, 12H). ^{31}P (81 MHz, $CDCl_3$): δ = 105.01 (s). ^{13}C ($CDCl_3$, 100 MHz): δ = 134.95(2C Ar), 133.60(2C Ar), 132.08(8C Ar), 130.66(4C Ar), 130.45(2C Ar), 129.48(4C Ar), 129.07(4C Ar), 127.60(8C Ar), 20.86(2C Me), 19.11(4C Me). ESI-MS (*m*/*z*): 781.0

$[M - Cl]^+$. *Anal.* Calc.: C, 61.67; H, 5.17. Found: C, 61.89; H, 5.26%.

*2.3.2. trans-[$PdCl_2${$PPh_2O(2,6\text{-}Ph_2C_6H_3)$}$_2$] (**4**)*

(80% yield) ^{1}H (400 MHz, $CDCl_3$): δ = 7.62–7.58(m, 8H), 7.53–7.47(m, 8H), 7.45–7.38(m, 4H), 7.37–7.34(m, 4H), 7.31(d, J = 4.4 Hz, 4H), 7.27–7.00(m, 18H). ^{13}C ($CDCl_3$, 100 MHz): δ = 138.96(Ar), 137.98(Ar), 134.12(Ar), 130.75(Ar), 130.37(Ar), 129.76(Ar), 129.26(Ar), 129.15(Ar), 128.59(Ar), 128.07(Ar), 127.43v, 121.11(Ar). ^{31}P (81 MHz, $CDCl_3$): δ = 106.62(s). ESI-MS (*m*/*z*): 571.9, $[M - Cl - PPh_2O\text{-}(C_6H_5)_2(C_6H_3)]^+$. *Anal.* Calc.: C, 69.41; H, 4.47. Found: C, 69.19; H, 4.56%.

*2.3.3. trans-[$Rh(CO)Cl${$PPh_2O(2,4,6\text{-}Me_3C_6H_2)$}$_2$] (**5**)*

(82% yield) ^{1}H (200 MHz, $CDCl_3$): δ = 7.80–7.62(m, 8H Ar), 7.42–7.29(m, 12H Ar), 6.89(s, 4H), 2.38(s, 6H Me), 2.14(s, 12H Me). ^{13}C ($CDCl_3$, 100 MHz): δ = 151.91(CO), 138.32(Ar), 134.01(Ar), 132.35(Ar), 131.36(Ar), 130.83(Ar), 129.97(Ar), 128.12(Ar), 21.32(CH_3), 19.59(2*CH_3). ^{31}P (81 MHz, $CDCl_3$): δ = 122.00(d). ESI-MS (*m*/*z*): 771.17, $[M - Cl]^+$; 743.18, $[M - Cl - CO]^+$. *Anal.* Calc.: C, 63.99; H, 5.25. Found: C, 63.72; H, 5.31%.

*2.3.4. trans-[$Rh(CO)Cl${$PPh_2O(2,6\text{-}Ph_2C_6H_3)$}$_2$] (**6**)*

(79% yield) ^{1}H (200 MHz, $CDCl_3$): δ = 7.37(d, J = 7 Hz, 8H), 7.26–7.16(m, 18H), 7.15–7.09(m, 12H), 7.08–7.02(m, 8H). ^{13}C ($CDCl_3$, 100 MHz): δ = 150.02(CO), 139.66(Ar), 137.34(Ar), 133.21(Ar), 133.13(Ar), 133.06(Ar), 131.26(Ar), 130.02(Ar), 128.26(Ar), 127.52(Ar), 127.45(Ar), 127.40(Ar). ^{31}P (81 MHz, $CDCl_3$): δ = 128.37 (d). ESI-MS (*m*/*z*): 914.9, $[M - (C_6H_5) - Cl + H]^+$. *Anal.* Calc.: C, 71.32; H, 4.51. Found: C, 71.20; H, 4.59%.

2.4. X-ray crystallographic study

Data were collected using a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator (Mo Kα radiation, λ = 0.71073 Å). 200 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 200°$ and with the crystal oscillating through 1° in φ. The resolution was D_{min}–D_{max} 12.45–0.81 Å.

Table 1
Crystallographic data for the structures of complexes **3**·$CHCl_3$ and **5**·$CHCl_3$

	3·$CHCl_3$	**5**·$CHCl_3$
Chemical formula	$C_{43}H_{43}Cl_5O_2P_2Pd$	$C_{44}H_{43}Cl_4O_3P_2Rh$
Formula weight	937.36	926.43
Crystal color and shape	yellow plate	yellow plate
Crystal size	0.50 × 0.50 × 0.10	0.40 × 0.20 × 0.20
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	18.865(2)	17.1373(12)
b (Å)	10.9145(7)	10.6328(5)
c (Å)	21.046(2)	24.4935(18)
β (°)	101.718(13)	97.540(8)
V (Å^3)	4243.1(7)	4424.6(5)
Z	4	4
D_{calc} (g cm^{-3})	1.467	1.391
μ(Mo Kα) (mm^{-1})	0.863	0.737
Temperature (K)	173(2)	173(2)
F(000)	1912	1896
Scan range (°)	$2.28 < \theta < 25.90$	$2.28 < \theta < 25.90$
Cell refinement parameters reflections	8000	8000
Reflections measured	32178	34021
Independent reflections	8115	8569
Reflections observed [$I > 2\sigma(I)$]	4689	6211
R_{int}	0.1048	0.0423
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0472, wR_2[a] = 0.1113	R_1 = 0.0365, wR_2[a] = 0.0893
R indices (all data)	R_1 = 0.0885, wR_2[a] = 0.1221	R_1 = 0.0548, wR_2[a] = 0.0941
Goodness-of-fit	0.882	0.988
Residual density: maximum, minimum $\Delta\rho$ (e Å^{-3})	0.712, −0.986	0.728, −0.664

[a] Structure was refined on F_o^2 : $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, where $w^{-1} = [\sum(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2
Selected bond lengths (Å) and angles (°) in complex **3**·$CHCl_3$

Interatomic distances	
Pd(1)–P(1)	2.3268(12)
Pd(1)–P(2)	2.3098(12)
Pd(1)–Cl(1)	2.3021(13)
Pd(1)–Cl(2)	2.2997(12)
P(1)–O(1)	1.615(3)
P(2)–O(2)	1.616(3)
P(1)–C(1)	1.820(4)
P(1)–C(7)	1.820(5)
P(2)–C(22)	1.814(4)
P(2)–C(28)	1.823(5)
O(1)–C(13)	1.416(5)
O(2)–C(34)	1.419(5)
Bond angles	
P(1)–Pd(1)–P(2)	175.48(5)
Cl(1)–Pd(1)–Cl(2)	179.09(4)
P(1)–Pd(1)–Cl(1)	93.32(4)
P(1)–Pd(1)–Cl(2)	87.59(4)
P(2)–Pd(1)–Cl(1)	91.09(4)
P(2)–Pd(1)–Cl(2)	88.00(4)
C(1)–P(1)–Pd(1)	120.90(16)
C(7)–P(1)–Pd(1)	113.00(16)
C(22)–P(2)–Pd(1)	113.43(16)
C(28)–P(2)–Pd(1)	118.60(14)
O(1)–P(1)–Pd(1)	114.89(11)
O(2)–P(2)–Pd(1)	115.39(11)
C(13)–O(1)–P(1)	125.8(3)
C(34)–O(2)–P(2)	128.6(3)

Table 3
Selected bond lengths (Å) and angles (°) in complex **5**·$CHCl_3$

Interatomic distances	
Rh(1)–P(1)	2.3103(8)
Rh(1)–P(2)	2.3202(7)
Rh(1)–Cl(1)	2.3411(8)
Rh(1)–C(43)	1.834(4)
C(43)–O(3)	1.105(4)
P(1)–O(1)	1.631(2)
P(2)–O(2)	1.631(2)
P(1)–C(1)	1.808(3)
P(1)–C(7)	1.823(3)
P(2)–C(22)	1.817(3)
P(2)–C(28)	1.821(3)
O(1)–C(13)	1.412(4)
O(2)–C(34)	1.416(3)
Bond angles	
P(1)–Rh(1)–P(2)	177.49(3)
Cl(1)–Rh(1)–C(43)	179.58(11)
O(3)–C(43)–Rh(1)	179.9(4)
P(1)–Rh(1)–Cl(1)	91.27(3)
P(1)–Rh(1)–C(43)	88.92(10)
P(2)–Rh(1)–Cl(1)	90.85(3)
P(2)–Rh(1)–C(43)	88.95(10)
C(1)–P(1)–Rh(1)	119.53(10)
C(7)–P(1)–Rh(1)	115.52(10)
C(22)–P(2)–Rh(1)	113.52(10)
C(28)–P(2)–Rh(1)	120.51(9)
O(1)–P(1)–Rh(1)	115.61(8)
O(2)–P(2)–Rh(1)	115.84(7)
C(13)–O(1)–P(1)	123.43(19)
C(34)–O(2)–P(2)	122.21(17)

The structure was solved by direct methods using the program SHELXS-97 [9] and refined by full matrix least squares on F^2 with SHELXL-97 [10]. The hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied for the complex **3** using DIFABS (PLATON-03 [11], $T_{min} = 0.300$, $T_{max} = 0.740$).

Crystallographic details are given in Table 1, and significant bond lengths and bond angles are listed in Table 2 (**3**) and Table 3 (**5**). The figures were drawn with ORTEP [12].

3. Results and discussion

The new aryl phosphinites PPh_2OR (R = 2,4,6-$Me_3C_6H_2$, **1**; R = 2,6-$Ph_2C_6H_3$, **2**) (Scheme 2) are accessible according to a general method reported by Bedford [4], using chlorodiphenylphosphine and the corresponding phenol (Eq. 1). The nucleophilic substitution reaction with elimination of HCl takes place in toluene at 80 °C, provided that the acid eliminated is trapped by NEt_3 to give the salt $[NEt_3H]Cl$, insoluble in toluene. The synthesis isolation of the products must be carried out with rigorous exclusion of air, in order to avoid oxidation of the phosphinite groups.

$$Ph_2PCl + HOR \rightarrow Ph_2POR + HCl \quad (1)$$

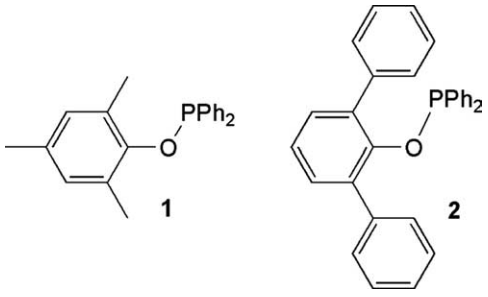
The phosphinite **1** is a very air-sensitive oil of light yellow color, while **2** is a slightly air-sensitive white solid. Both compounds have been characterized by correct NMR (^1H, ^{13}C, ^{31}P) and mass-spectroscopic data as well as by satisfactory elemental analysis data.

The palladium phosphinite complexes are obtained by reacting $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) with the ligands **1** or **2** in methylene chloride at room temperature (Eq. 2). The two complexes $[PdCl_2(\mathbf{1})_2]$ (**3**) and $[PdCl_2(\mathbf{2})_2]$ (**4**) are isolated as yellow powders (Scheme 3).

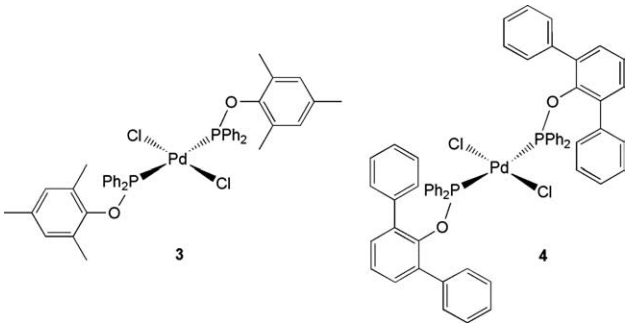
$$PdCl_2(cod) + 2\,ROPPh_2 \rightarrow [PdCl_2\{ROPPh_2\}_2]_2 + cod \quad (2)$$

Both compounds have been characterized by correct NMR (^1H, ^{13}C, ^{31}P) and mass-spectroscopic data as well as by satisfactory elemental analysis data.

Yellow crystals of **3**·$CHCl_3$, suitable for single-crystal X-ray structure analysis were obtained by slow evaporation of a concentrated chloroform solution of the complex during several days at room temperature. This compound crystallized in the monoclinic $P2_1/c$ space group. The molecular formula of this compound is $[PdCl_2\{PPh_2O(2,4,6\text{-}Me_3C_6H_2)\}_2]\cdot CHCl_3$. The molecular structure of **3** is shown in Fig. 1. The Pd metal center is tetracoordinated by the chelating phosphorus



Scheme 2.



Scheme 3.

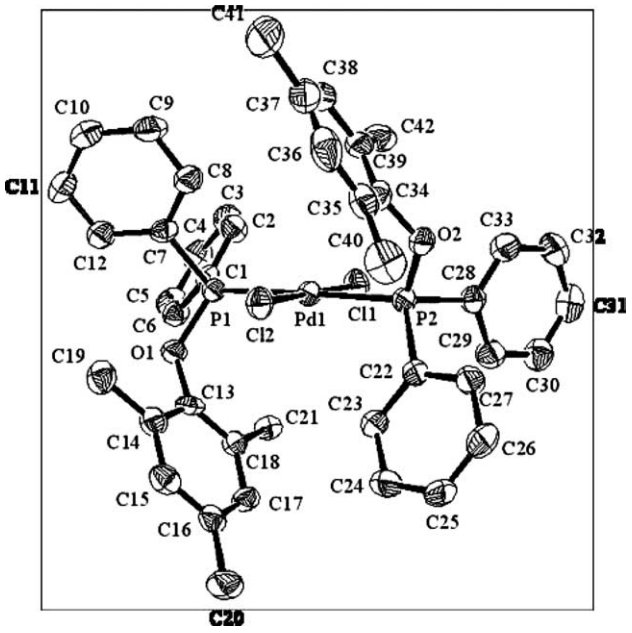


Fig. 1. Molecular structure of **3** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.

ligand and two chloride anions in a typical *trans* square-plane geometry. The Pd is displaced by 0.0111(7) Å out of the square-plane. The two oxo-mesityl arms, situated on the both sides of the P(1)–Pd(1)–P(2) axis, fall back towards the Pd cation. However, we note that the two rings are not parallel (the angle between the two mesityl rings is 17.3(2)°). Significant bond lengths and bond angles are listed in Table 2. The Pd–P and Pd–Cl distances are similar to those of the only example of *trans* Pd complex containing phosphinite ligands [13].

The rhodium phosphinite complexes **5** and **6** (Scheme 4) are accessible from $[Rh_2(CO)_4Cl_2]$ and the ligands **1** and **2**, the reaction taking place in methylene chloride within 24 h (Eq. 3). The two complexes **5** and **6** are obtained as yellow powders. To our knowledge, there are only two other mononuclear chlorocarbonyl rhodium complexes containing aryl-diphenylphosphinite ligands, $[RhCl(CO)\{PPh_2O(C_6H_5)\}_2]$ and $[RhCl(CO)\{2,2'\text{-}(PPh_2O)_2\ C_{12}H_8\}]$, the molecular structures of which, however, are not known [14].

$$1/2\,[Rh_2Cl_2(CO)_4] + 2\,ROPPh_2 \rightarrow [RhCl(CO)(ROPPh_2)_2] + CO \quad (3)$$

Both compounds **5** and **6** have been characterized by correct NMR (^1H, ^{13}C, ^{31}P) and mass-spectroscopic data as well as by satisfactory elemental analysis data.

Yellow crystals of **5**·$CHCl_3$, suitable for single-crystal X-ray structure analysis were obtained by leaving a concentrated chloroform solution of the complex standing several days at room temperature. This compound also crystallized in the monoclinic $P2_1/c$ space group. The molecular formula of this compound is $[RhCl(CO)\{PPh_2O(2,4,6\text{-}Me_3C_6H_2)\}_2]\cdot CHCl_3$. The molecular structure of **5** is shown in Fig. 2. The structure of

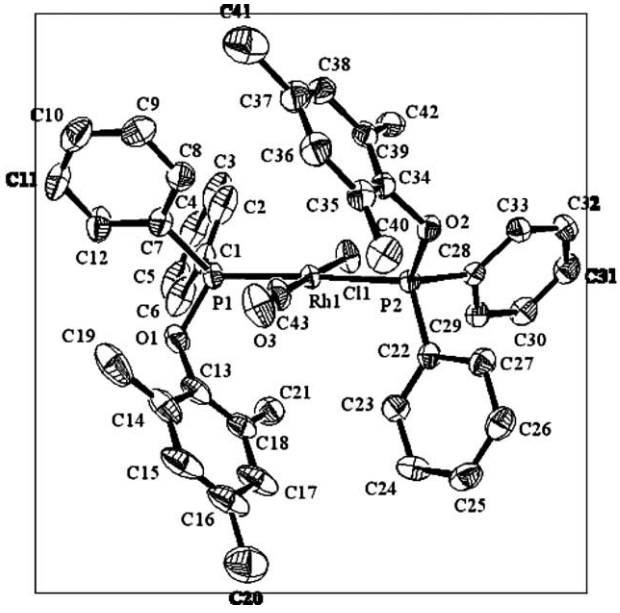
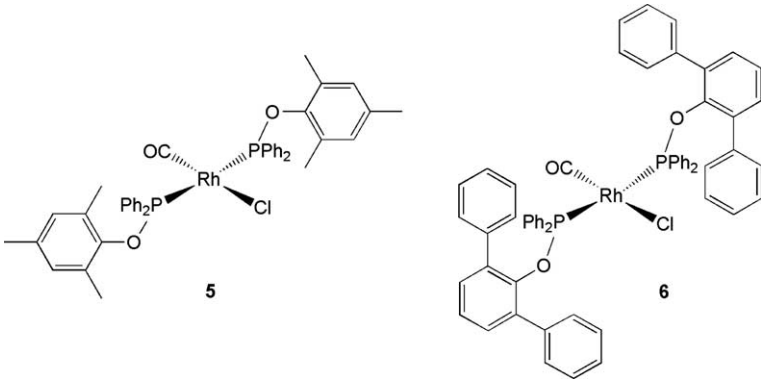


Fig. 2. Molecular structure of **5** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity.



Scheme 4.

5 is similar to that of **3** with a Rh metal center tetracoordinated by the chelating phosphorus ligand, a chloride anion and a carbonyl group in a typical *trans* square-plane geometry. The Rh is displaced by 0.0169(10) Å out of the square-plane. Like in the structure of **3**, the ligand conformation is the same with the two oxomesityl arms, situated on the both sides of the P(1)–Rh(1)–P(2) axis, falling back towards the Rh cation. The two rings are not parallel either, but the angle between the two mesityl rings is smaller (4.77(12)°). Significant bond lengths and bond angles are listed in Table 3. The Rh–CO distance of 1.834(4) Å in **5** is similar to the one in $[Rh(CO)Cl\{PPh_2OR_f\}]_2$[15], the only example of *trans* Rh complex containing phosphinite ligands, while the C–O distance (1.105(4) Å) is slightly shorter by 0.018 Å, consistent with a slightly weaker Rh–CO interaction in **5**. The Rh–P and Rh–Cl distances in **5** are similar to those of this complex.

4. Supplementary material

CCDC-264731 (for $\mathbf{3}\cdot CHCl_3$) and CCDC-264732 (for $\mathbf{5}\cdot CHCl_3$) contain the supplementary crystallographic data for these structures. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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