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Phosphine and isonitrile complexes of η^5-tetramethylcyclopentadienylrhodium chlorides; crystal structures of $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_2R)$ (R = Ph or C_6F_5)

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Abstract

The reaction between $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and the phosphines PPh_2R (R = Ph or C_6F_5) or cyclohexylisonitrile yields the complexes $(\eta^5\text{-}C_5Me_4H)RhCl_2L$ (**1**, L = PPh_3; **2**, L = $PPh_2(C_6F_5)$; **3**, L = CNC_6H_{11}). The structures of complexes **1** and **2** have been determined by single-crystal X-ray diffraction. Both exhibit three-legged piano stool geometry about the rhodium atom. Unlike the structures of $(\eta^5\text{-}C_5Me_5)RhCl_2L$ complexes, the rhodium atoms of **1** and **2** do not lie on axes normal to the C_5 centroids, but are displaced towards the CH carbon atoms. Treatment of **1** with cyclohexylisonitrile or **3** with $PPh_2(C_6F_5)$ in the presence of $NaBF_4$ yield the chiral-at-metal salts $[(\eta^5\text{-}C_5Me_4H)RhCl(PPh_2R)(CNC_6H_{11})]^+\cdot BF_4^-$ as racemic mixtures. The bis(isonitrile) complex, $[(\eta^5\text{-}C_5Me_4H)RhCl(CNC_6H_{11})_2]^+\cdot BF_4^-$, is formed similarly from **3**. Treatment of $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ with dppe in the presence of $NaBF_4$ yields $[(\eta^5\text{-}C_5Me_4H)RhCl(dppe)]^+\cdot BF_4^-$. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Phosphine; Rhodium

1. Introduction

Recently we reported that the reaction between the tetramethylcyclopentadienylrhodium complex $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ and the diphosphine $(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ (dfppe) displays remarkable regioselectivity and yields an asymmetric cation originally formulated as $[\{\eta^5\text{-}C_5HMe_2\text{-}2,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\}\text{-}1,3\text{-}RhCl]^+$ [1]. This formulation was based on the regiospecific synthesis of $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$ by the reaction between $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ and dfppe [2]. Subsequently it has been found that the original formulation is wrong and the cation is $[\{\eta^5\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\}\text{-}1,2\text{-}RhCl]^+$ [3] (Fig. 1). In order to understand the differences between the reactions involving the tetramethyl- and pentamethyl-cyclopentadienylrhodium complexes, we wished to compare simple tetramethyl- and pentamethyl-cyclopentadienylrhodium phosphine complexes of the type $(\eta^5C_5Me_4R)RhCl_2(PR'_3)$, $[(\eta^5\text{-}C_5Me_4R)RhCl(PR'_3)L]^+\cdot X^-$ (L = two-electron donor ligand) and $[(\eta^5\text{-}C_5Me_4R)RhCl(R'_2PCH_2CH_2PR'_2)]^+\cdot X^-$ (R = H or Me). Despite numerous examples of pentamethyl-cyclopentadienylrhodium phosphine chloride complexes [4–14], to our knowledge there are no reports of tetramethylcyclopentadienyl analogues. Therefore, it was decided to prepare and investigate these complexes.

2. Results and discussion

2.1. Synthesis and characterization of η^5-tetramethylcyclopentadienylrhodium phosphine and isonitrile complexes

Treatment of $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ [15] with two equivalents of PPh_3 or $PPh_2(C_6F_5)$ in refluxing dichloromethane gave the complexes $(\eta^5\text{-}C_5Me_4H)RhCl_2\{PPh_x(C_6F_5)_{3-x}\}$ (**1** $x = 3$, **2** $x = 2$) in moderate yields (Scheme 1). As for the pentamethyl-cyclopen-

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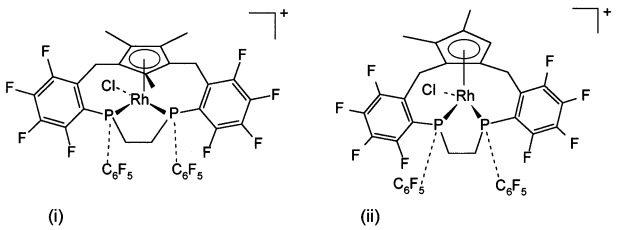
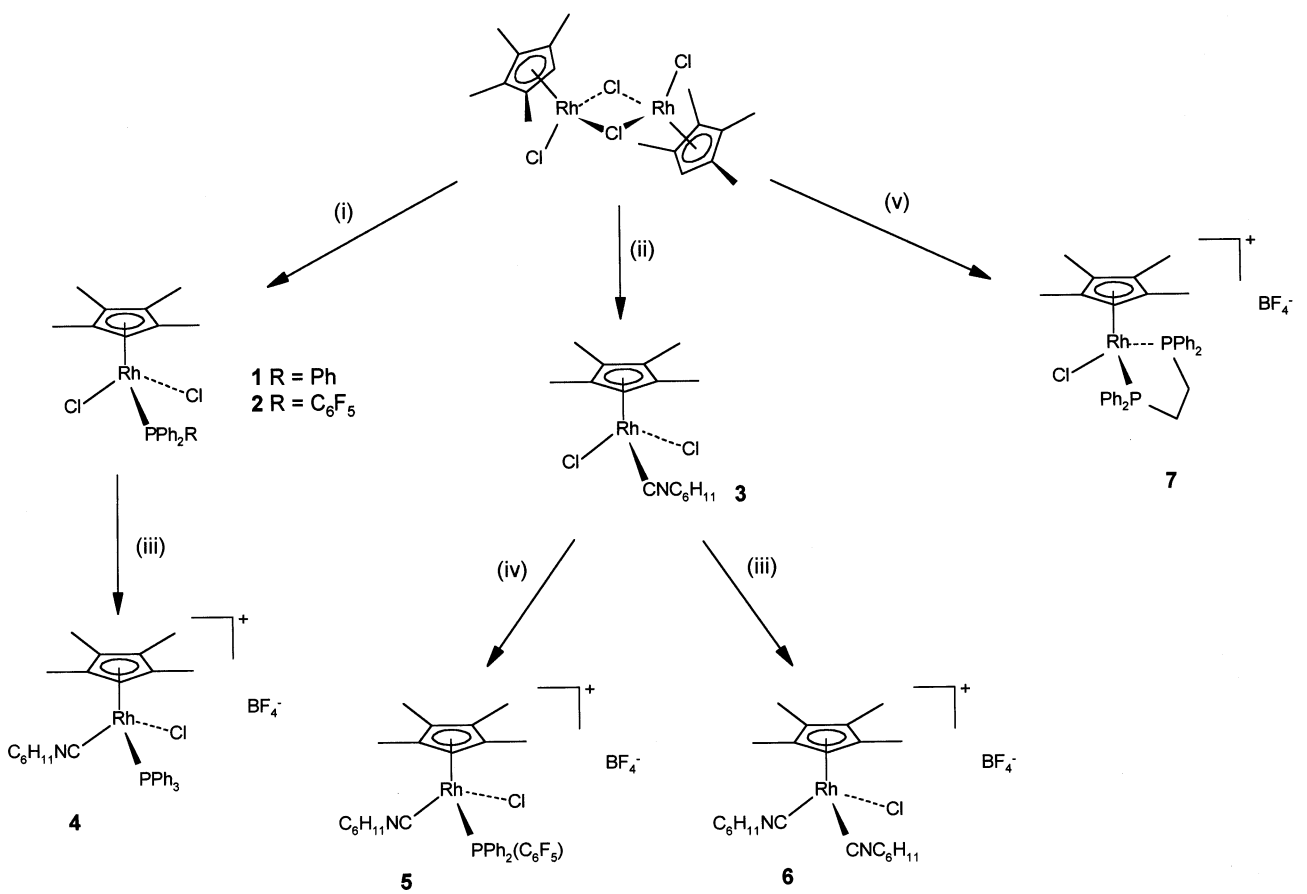


Fig. 1. The cations formed in the reactions between $[(\eta^5\text{-}C_5Me_4R)RhCl(\mu\text{-}Cl)]_2$ and dfppe: (i) R = Me, $[\{\eta^5\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}RhCl]^+$; and (ii) R = H, $[\{\eta^5\text{-}C_5HMe_2\text{-}3,4\text{-}[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,2\}RhCl]^+$.

tadienyl analogue, no reaction was observed with the bulkier phosphine $PPh(C_6F_5)_2$ [12]. Complexes **1** and **2** were characterized by elemental analysis and NMR spectroscopy (Table 1). The ^{31}P-NMR resonances of **1** and **2** appear as doublets at δ 31.4 and 21.4, respectively. These values are at higher frequency than those of $(\eta^5\text{-}C_5Me_5)RhCl_2(PPh_3)$, δ 7.9 [11], and $(\eta^5\text{-}C_5Me_5)RhCl_2\{PPh_2(C_6F_5)\}$, δ 18.8 [12], and in contrast to these complexes the resonance of the triphenylphosphine complex **1** is at higher frequency to that of the pentafluorophenyldiphenylphosphine complex **2**. The ^{1}H-NMR spectra of **1** and **2** show no coupling between the phosphorus and the cyclopentadienyl hydrogen. The methyl resonances of **1** and **2** appear as a pair of doublets at ca. δ 1.7 and 1.2. The higher frequency resonances show a larger coupling to phosphorus of ca. 5 Hz and the lower frequency resonances show a coupling of ca. 1 Hz. In comparison the values of $|^4J_{P-H}|$ for $(\eta^5\text{-}C_5Me_5)RhCl_2(PPh_3)$ and $(\eta^5\text{-}C_5Me_5)RhCl_2\{PPh_2(C_6F_5)\}$ are 4 and 2.2 Hz, respectively [5,12]. Treatment of $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ with two equivalents of cyclohexylisonitrile in dichloromethane at room temperature afforded the complex $(\eta^5\text{-}C_5Me_4H)RhCl_2(CNC_6H_{11})$ (**3**) in high yield (Scheme 1). Compound **3** exhibits ν(CN) at 2214 cm^{-1}, which is similar to that of 2220 cm^{-1} for $(\eta^5\text{-}C_5Me_5)RhCl_2(CNC_6H_{11})$ [6].

Treatment of **1** with cyclohexylisonitrile in the presence of $NaBF_4$ in methanol/dichloromethane afforded the salt $[(\eta^5\text{-}C_5Me_4H)RhCl(PPh_3)(CNC_6H_{11})]^+\cdot BF_4^-$ **4** as a yellow solid. The analogous salt, $[(\eta^5\text{-}C_5Me_4H)RhCl\{(PPh_2(C_6F_5)\}(CNC_6H_{11})]^+\cdot BF_4^-$ **(5)**, was prepared by an alternative route from **3** and $PPh_2(C_6F_5)$. Both **4** and **5** possess chirality at the rhodium, and are formed as racemic mixtures. Treatment of compound **3** with cyclohexylisonitrile and



Scheme 1. (i) PPh_3 or $PPh_2(C_6F_5)$, CH_2Cl_2, reflux; (ii) CNC_6H_{11}, CH_2Cl_2; (iii) CNC_6H_{11}, $NaBF_4$, CH_2Cl_2/MeOH; (iv) $PPh_2(C_6F_5)$, $NaBF_4$, CH_2Cl_2/MeOH; (v) dppe, $NaBF_4$, CH_2Cl_2/MeOH.

Table 1
Analytical and NMR data for compounds **1**–**7**

Compound	Analysis (%)[a]	ν(C≡NR) (cm^{-1})[b]	NMR[c]
1	C, 58.0 (58.2); H, 5.1 (5.1)		^{1}H: 7.88 (m, 6H, C_6H_5), 7.38 (m, 9H, C_6H_5), 4.26 (s, 1H, C_5Me_4H), 1.71 (d, $^4J_{P-H}$ 4.8, 6H, Me), 1.13 (d, $^4J_{P-H}$ 1.2, 6H, Me). ^{31}P{^{1}H}: 31.4 (dm, $^1J_{Rh-P}$ 142)
2	C, 49.5 (50.1); H, 3.2 (3.6)		^{1}H: 7.84 (m, 4H, C_6H_5), 7.32 (m, 6H, C_6H_5), 4.62 (s, 1H, C_5H), 1.69 (d, $^4J_{P-H}$ 5.7, 6H, Me), 1.23 (d, $^4J_{P-H}$ 0.7, 6H, Me). ^{19}F: −120.59 (m, 2F, F_{ortho}), −148.49 (t, $^3J_{F-F}$ 20.5, 1F, F_{para}), −159.53 (m, 2F, F_{meta}). ^{31}P{^{1}H}: 21.4 (dm, $^1J_{Rh-P}$ 147)
3	C, 46.85 (47.55); H, 6.0; N 3.3 (3.5)	2214	^{1}H: 5.00 (1H, s, C_5H), 3.99 (1H, m, CNC*H*), 1.97 (2H, m, C_6H_{11}), 1.84 (6H, s, Me), 1.79 (6H, s, C_6H_{11}), 1.54 (6H, d, $^3J_{Rh-H}$ 1.7, Me), 1.42 (2H, s, C_6H_{11})
4[d]	C, 55.0 (54.6); H, 4.9 (5.3); N 2.1 (1.8)	2216	^{1}H: 7.51 (A_2B_2CM spin system, 15H), 5.31 (s, CH_2Cl_2), 5.09 (1H, s, C_5Me_4H), 3.86 (1H, m, CNC*H*), 1.93 (3H, d, $^4J_{P-H}$ 3.6, Me), 1.87 (3H, d, $^4J_{P-H}$ 5.8, Me), 1.80 (2H, m, C_6H_{11}), 1.55 (3H, d, $^3J_{Rh-H}$ 0.8, Me), 1.49 (4H, m, C_6H_{11}), 1.22 (4H, m, C_6H_{11}), 1.19 (3H, d, $^4J_{P-H}$ 5.9, Me). ^{19}F: −153.19 and −153.25 (2s, 1:4, 4F, BF_4^-)
5[e]	C, 49.2 (49.6); H, 4.5 (4.2); N 1.6 (1.7)	2214	^{1}H: 7.72 (2H, m, PPh_2), 7.58 (8H, m, PPh_2), 5.30 (s, CH_2Cl_2), 5.21 (1H, s, C_5Me_4H), 3.81 (1H, m, CNC*H*), 1.91 (3H, d, $^4J_{P-H}$ 6.1, Me), 1.82 (3H, d, $^4J_{P-H}$ 3.5, Me), 1.78 (2H, m, C_6H_{11}), 1.76 (3H, d, $^4J_{P-H}$ 2.6, Me), 1.45 (4H, m, C_6H_{11}), 1.39 (3H, d, $^3J_{Rh-H}$, 5.0 Me), 1.27 (4H, m, C_6H_{11}). ^{19}F: −123. 59 (2F, d, $^3J_{F-F}$ 19.0, F_{ortho}), −144.78 (1F, m, F_{para}), −153.26 and −153.32 (2s, 1:4, 4F, BF_4^-), −159.54 (2F, m, F_{meta}). ^{31}P{^{1}H}: 24.5 (d, $^1J_{Rh-P}$ 131)
6	C, 49.2 (48.9); H, 6.4 (6.2); N 4.2 (5.0)	2222	^{1}H: 5.78 (1H, s, C_5Me_4H), 4.15 (2H, m, CNC*H*), 2.00 (6H, s, Me), 1.88 (6H, s, Me), 1.78 (8H, m, C_6H_{11}), 1.52 (12H, m, C_6H_{11}). ^{19}F: −153.21 and −153.27 (2s, 1:4, 4F, BF_4)
7[f]	C, 54.7 (54.9); H, 5.1 (4.9)		^{1}H: 7.70 (m, 2H, H_p), 7.45 (m, 14H, C_6H_5), 7.28 (m, 4H, C_6H_5), 5.48 (s, 1H, C_5H), 3.32 (m, 2H, PCH_2), 2.36 (m, 2H, PCH_2), 1.19 (s, 6H, Me), 0.95 (s, 6H, Me).[g] ^{19}F: −152.23 and −152.29 (2s, 1:4, 4F, BF_4).[g] ^{31}P{^{1}H}: 23.7 (dm, $^1J_{Rh-P}$ 138)[g]

[a] Required values are given in parentheses.
[b] KBr disc
[c] Unless stated otherwise recorded in $CDCl_3$ at 298 K.
[d] Crystallized with 0.5 CH_2Cl_2.
[e] Crystallized with 0.25 CH_2Cl_2.
[f] Crystallized with 0.33 CH_2Cl_2.
[g] Recorded in $(CD_3)_2CO$.

sodium tetrafluoroborate yielded the bis(isocyanide) complex $[(\eta^5\text{-}C_5Me_4H)RhCl(CNC_6H_{11})_2]^+\cdot BF_4^-$ (**6**). The analytical and NMR spectroscopic data of **4**–**6** (Table 1) are entirely consistent with these formulations. The ^{1}H-NMR spectra of **4** and **5** display four methyl resonances due to the chirality at the rhodium atom. All these resonances show coupling to phosphorus. For both salts there are two resonances with $|^4J_{P-H}|$ of ca. 6 Hz, one with a coupling of ca. 3.5, and the other has a coupling of 0.8 for **4** and 2.6 Hz for **5**. The phosphine complexes **4** and **5** exhibit ν(CN) at ca. 2215 and **6** at 2222 cm^{-1}, which are comparable with those of 2210 and 2212 cm^{-1} for $[(\eta^5\text{-}C_5Me_4H)RhCl(PPh_3)(CNC_6H_{11})]^+\cdot BPh_4^-$ and $[(\eta^5\text{-}C_5Me_4H)RhCl(CNC_6H_{11})_2]^+\cdot BPh_4^-$, respectively [6].

Treatment of $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ with $NaBF_4$ in methanol, followed by addition of dppe in dichloromethane gave the salt $[(\eta^5\text{-}C_5Me_4H)RhCl(dppe)]^+\cdot BF_4^-$ **7** in 69% yield (Scheme 1). The salt was characterized by elemental analysis and NMR spectroscopy (Table 1). In contrast to the salts **4** and **5**, coupling between the phosphorus atoms and the hydrogen atoms of the tetramethylcyclopentadienyl group is not observed, and the three resonances appear as singlets at δ 5.48, 1.19 and 0.95. The ^{31}P{^{1}H}-NMR spectrum shows a doublet resonance at δ 23.7 with a

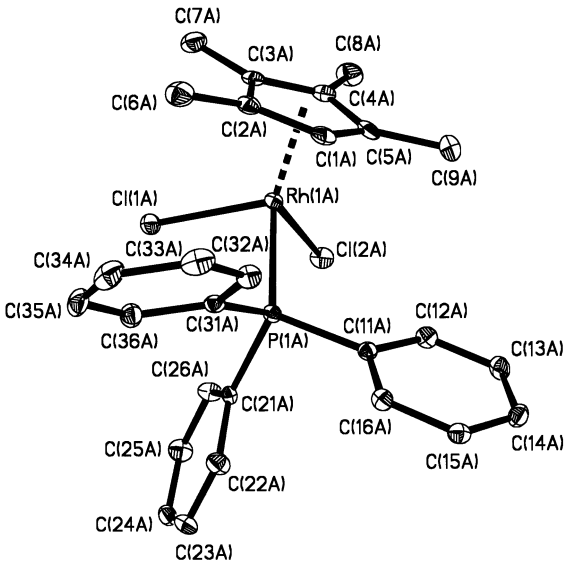


Fig. 2. Molecular structure of one of the independent molecules of $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_3)$ (**1**). Displacement ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

coupling, $|^1J_{Rh-P}|$, of 138 Hz. The value of δ_P is 42.5 ppm to lower frequency of that of the pentamethyl-cyclopentadienyl analogue, but the value of $|^1J_{Rh-P}|$ is only slightly larger [14].

2.2. Crystal structures of $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_2R)$ (**1** $R = Ph$; **2** $R = C_6F_5$)

Complexes **1** and **2** were further characterized by single-crystal X-ray diffraction (Figs. 2 and 3). The crystallographic data are given in Table 2 and selected interatomic distances and angles are given in Table 3. The structures of both complexes contain two independent molecules within the asymmetric unit. For each structure the independent molecules show only minor differences. Both complexes exhibit three-legged piano stool geometry about the rhodium atoms with P–Rh–Cl and Cl–Rh–Cl angles of ca. 90°. The bond distances and angles about the rhodium atoms are comparable with those of $(\eta^5\text{-}C_5Me_5)RhCl_2L$ complexes (L = $PPh_2C_2H_4SiMe_2OH$ [8], $P(OEt)_3$ [10], $PPh_2(OC_6H_3F_2$-2,6) [11], $PPh(OPh)_2$ [11] and $P(C_6H_4C_6F_{13}$-4)$_3$ [13]) and $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2(\mu\text{-dmpe})$ [9]. The Rh–P and Rh–Cl distances of **1** and **2** lie within the ranges of these distances for $(\eta^5\text{-}C_5Me_5)RhCl_2L$: 2.254(3)–2.332(3) and 2.378(3)–2.412(2) Å, respectively, and the C_5Me_4-

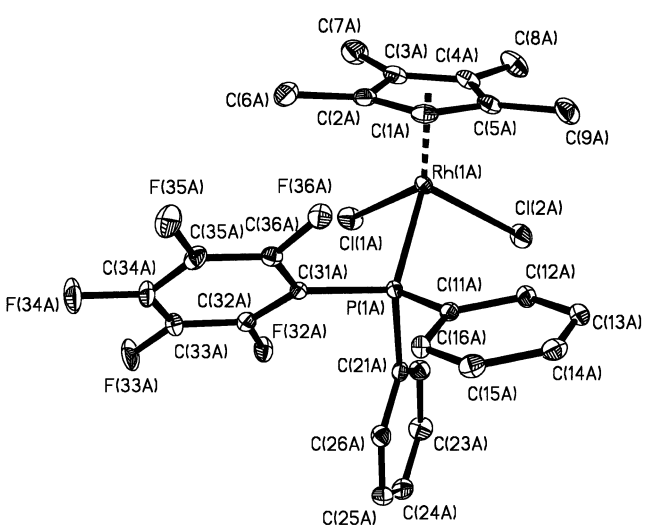


Fig. 3. Molecular structure of one of the independent molecules of $(\eta^5\text{-}C_5Me_4H)RhCl_2\{PPh_2(C_6F_5)\}$ (**2**). Displacement ellipsoids are shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

Table 2
Crystallographic data for $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_3)$ (**1**) and $(\eta^5\text{-}C_5Me_4H)RhCl_2\{PPh_2(C_6F_5)\}$ (**2**)

Formula	$C_{27}HCl_2P_2Rh$	$C_{27}HCl_2F_5P_2Rh$
Formula weight	557.27	647.23
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	10.3720(8)	19.908(2)
b (Å)	14.8314(12)	14.8641(12)
c (Å)	15.7755(14)	17.920(2)
α (°)	86.176(7)	–
β (°)	83.742(7)	102.279(7)
γ (°)	88.483(7)	–
V (Å^3)	2406.5(3)	5181.6(9)
Z	4[a]	8[a]
Crystal size (mm)	$0.58 \times 0.36 \times 0.16$	$0.76 \times 0.52 \times 0.44$
Diffractometer	Siemens P4	Siemens P4
Radiation (λ, Å)	Mo–K_α (0.71073)	Mo–K_α (0.71073)
Monochromator	Graphite	Graphite
μ (Mo–K_α) (mm^{-1})	1.011	0.979
T (K)	153(2)	153(2)
Scan method	ω	ω
h, k, l ranges	0–12, −17–17, −18–18	−23–23, −17–0, −21–0
2θ limits (°)	4.5–50	4.2–50
Total reflections	8995	9459
Unique reflections	8484 [$R_{int} = 0.0197$]	9128 [$R_{int} = 0.0156$]
Observed reflections [$I > 2\sigma(I)$]	6750	7483
Absorption correction method	Semi-empirical based on ψ-scans	Semi-empirical based on ψ-scans
Max/min transmission	0.854, 0.685	0.789, 0.736
Parameters	742	833
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0349$, $wR_2 = 0.0708$	$R_1 = 0.0290$, $wR_2 = 0.0562$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.0784$	$R_1 = 0.0427$, $wR_2 = 0.0610$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 = 0.0357 P^2 = 1.3955P]$[b]	$w = 1/[\sigma^2(F_o)^2 = 0.218 P^2 = 5.1321P]$[b]
$(\Delta/\sigma)_{max}$	0.084	0.067
Max/min $\Delta\rho$ (eÅ^{-3})	0.616, 0.529	0.433, −0.354
Goodness of fit on F^2	1.044	1.053

[a] There are two independent molecules in the unit cell.
[b] $P = [\max(F_o^2, 0) = 2F_c^2]/3$.

H(centroid)–Rh distances of **1** and **2** are consistent with the Cp*–Rh distances of $(\eta^5\text{-}C_5Me_5)RhCl_2L$. Thus, there is no discernible difference in the effects of tetramethyl- and pentamethyl-cyclopentadienyl ligands on these distances. The C_5Me_4H(centroid)–Rh–P angles (ca. 130°) and C_5Me_4H(centroid)–Rh–Cl angles (ca. 120°) are comparable with the Cp*–Rh–P and Cp*–Rh–Cl angles reported for $(\eta^5\text{-}C_5Me_5)RhCl_2L$ ($L = PPh_2(OC_6H_3F_2\text{-}2,6)$ [11], $PPh(OPh)_2$ [11] and $P(C_6H_4C_6F_{13}\text{-}4)_3$ [13]). In both molecules of **1** and **2** the C–H bond is eclipsed with the Rh–P bond, i.e. the H–C–Rh–P torsion angle is ca. 0° and P–Rh–CH is ca. 90°. Presumably this is a consequence of the greater steric requirements of the phosphine compared to the chloride ligands. The Rh–C distances of **1** and **2** lie in the range for those of the $(\eta^5\text{-}C_5Me_5)RhCl_2L$ complexes (2.14(2)–2.25(2) Å). Although it has been commented that for the structure of $(\eta^5\text{-}C_5Me_5)RhCl_2\{P(OEt)_3\}$ [10] the distances of Rh–C approximately *trans* to the phosphorus ligand are longer than the other Rh–C distances, the differences are not significant when the estimated standard deviations are considered. This is also the case for the other $(\eta^5\text{-}C_5Me_5)RhCl_2L$ complexes. In contrast, the Rh–C distances of **1** and **2** do show significant differences. For both molecules of each structure Rh–C(3) and Rh–C(4), which are approximately *trans* to the phosphorus atom (P–Rh–C angles of ca. 150°), lie in the range 2.216(4)–2.247(6) Å. The other Rh–CMe distances (2.155(4)–2.176(4) Å) are at least 0.015 Å shorter and the Rh–CH distances (2.127(4) to 2.146(3) Å) are at least 0.05 Å shorter than Rh–C(3) and Rh–C(4). Thus, compared to the $(\eta^5\text{-}C_5Me_5)RhCl_2L$ complexes the rhodium atoms in **1** and **2** are displaced from the axis normal to the C_5 centroid towards the CH carbon atom of the cyclopentadienyl ring. The C–C ring distances also show considerable variation. The HC–CH_3 distances range from 1.381(6) to 1.429(4) Å and the C(3)–C(4) distances from 1.404(6) to 1.416(4) Å, whereas the other MeC–CMe distances are significantly longer (1.442(4) to 1.460(6) Å), with the exception of C(4)–C(5) for one molecule of **1** (1.427(6) Å). These values may be compared to the mean values of 1.42(2) and 1.431 Å for $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2(\mu\text{-dmpe})$ [9] and $(\eta^5\text{-}C_5Me_5)RhCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}$ [13], respectively. The internal C–C–C ring angles range between 106.4(3) and 110.3(4) with no significant differences between the angles at CMe and those at CH. The C–CH_3 distances lie in the range 1.479(6) to 1.531(6) Å consistent with the mean values of 1.49(3) and 1.498 Å for the phosphine complexes $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2(\mu\text{-dmpe})$ [9] and $(\eta^5\text{-}C_5Me_5)RhCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}$ [13], respectively. There is no significant difference between the C–CH_3 distances of the 1- and 4- positions and those of the 2- and 3-positions.

Table 3
Selected interatomic distances (Å) and angles (°) for $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_3)$ (**1**) and $(\eta^5\text{-}C_5Me_4H)RhCl_2\{PPh_2(C_6F_5)\}$ (**2**)

	1		**2**	
	Molecule A	Molecule B	Molecule A	Molecule B
Bond lengths (Å)				
Rh(1)–P(1)	2.3058(10)	2.3117(10)	2.3101(8)	2.3084(8)
Rh(1)–Cl(1)	2.4088(10)	2.4126(10)	2.3842(8)	2.3947(8)
Rh(1)–Cl(2)	2.4050(10)	2.3847(10)	2.4097(8)	2.3781(8)
Cp†–Rh(1)	1.815	1.823	1.813	1.817
Rh(1)–C(1)	2.127(4)	2.141(4)	2.142(3)	2.146(3)
Rh(1)–C(2)	2.155(4)	2.176(4)	2.163(3)	2.172(3)
Rh(1)–C(3)	2.239(4)	2.230(4)	2.229(3)	2.221(3)
Rh(1)–C(4)	2.247(4)	2.216(4)	2.216(3)	2.225(3)
Rh(1)–C(5)	2.159(4)	2.160(4)	2.164(3)	2.167(3)
C(1)–C(2)	1.424(6)	1.403(6)	1.429(4)	1.420(4)
C(2)–C(3)	1.459(5)	1.460(6)	1.442(4)	1.443(4)
C(3)–C(4)	1.409(5)	1.404(6)	1.411(4)	1.416(4)
C(4)–C(5)	1.450(6)	1.427(6)	1.450(4)	1.442(4)
C(5)–C(1)	1.422(6)	1.381(6)	1.412(4)	1.428(4)
C(2)–C(6)	1.485(6)	1.508(6)	1.492(5)	1.491(4)
C(3)–C(7)	1.488(6)	1.479(6)	1.486(5)	1.489(5)
C(4)–C(8)	1.486(6)	1.503(6)	1.488(5)	1.492(5)
C(5)–C(9)	1.497(6)	1.531(6)	1.490(5)	1.493(5)
P(1)–C(11)	1.834(4)	1.824(4)	1.834(3)	1.830(3)
P(1)–C(21)	1.838(4)	1.824(4)	1.829(3)	1.835(3)
P(1)–C(31)	1.821(4)	1.820(4)	1.848(3)	1.837(3)
Bond angles (°)				
Cp†–Rh(1)–P(1)[a]	127.7	129.3	130.5	130.6
Cp†–Rh(1)–Cl(1)[a]	121.6	119.5	122.3	120.3
Cp†–Rh(1)–Cl(2)[a]	122.7	125.4	120.0	123.1
Cl(1)–Rh(1)–P(1)	92.60(3)	90.10(4)	88.08(3)	91.93(3)
Cl(2)–Rh(1)–P(1)	88.95(3)	90.19(4)	92.26(3)	87.67(3)
Cl(1)–Rh(1)–Cl(2)	93.70(4)	91.69(4)	93.97(3)	93.06(3)
P(1)–Rh(1)–C(1)	93.23(11)	96.08(12)	96.92(9)	96.80(9)
P(1)–Rh(1)–C(2)	109.27(11)	108.54(11)	108.59(9)	118.55(9)
P(1)–Rh(1)–C(3)	147.71(11)	146.04(13)	145.43(9)	156.86(9)
P(1)–Rh(1)–C(4)	151.55(11)	155.32(12)	157.73(8)	146.44(9)
P(1)–Rh(1)–C(5)	113.20(11)	117.35(13)	119.18(9)	109.39(9)
C(1)–C(2)–C(3)	106.6(4)	106.4(4)	106.4(3)	107.3(3)
C(2)–C(3)–C(4)	108.2(3)	107.0(4)	106.4(3)	108.0(3)
C(3)–C(4)–C(5)	108.6(3)	108.6(4)	108.0(3)	108.7(3)
C(4)–C(5)–C(1)	106.9(4)	107.6(4)	107.0(3)	106.6(3)
C(5)–C(1)–C(2)	109.6(4)	110.3(4)	109.7(3)	109.4(3)
Rh(1)–P(1)–C(11)	115.62(12)	116.79(12)	114.02(9)	112.34(10)
Rh(1)–P(1)–C(21)	119.51(12)	118.86(13)	120.94(10)	121.99(10)
Rh(1)–P(1)–C(31)	109.29(11)	108.33(12)	111.75(9)	110.89(10)
C(11)–P(1)–C(21)	102.5(2)	101.9(2)	101.92(13)	100.67(13)
C(11)–P(1)–C(31)	105.2(2)	106.8(2)	104.64(13)	107.51(14)
C(21)–P(1)–C(31)	103.2(2)	102.8(2)	101.66(12)	102.07(13)
H–C(1)–Rh(1)–P(1)	−0.2	−6.2	9.1	−7.9

[a] Cp† denotes the centroid of the tetramethylcyclopentadienyl ring.

The P–C distances of **1** and **2** are identical within experimental error and consistent with the mean value of 1.831 Å for the triarylphosphine complex $(\eta^5\text{-}C_5Me_5)RhCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}$ [13]. Both molecules of **1** possesses Rh–P–C angles of ca. 109, 116 and 119°.

The geometry about the phosphorus atoms of **2** is dissimilar to that of **1**. Both molecules of **2** possess one Rh–P–C_6H_5 angle of ca. 120° and two other Rh–P–C angles of 110.89(10)–114.02(9)°, which are comparable with the values of 118.2(2), 113.0(2) and 113.0(2)° for $(\eta^5\text{-}C_5Me_5)RhCl_2\{P(C_6H_4C_6F_{13}\text{-}4)_3\}$.

3. Conclusions

In conclusion we have prepared η^5-tetramethylcyclopentadienyl rhodium phosphine and isonitrile complexes. The spectroscopic properties of the neutral complexes $(\eta^5\text{-}C_5Me_4H)RhCl_2L$ and the salts $[(\eta^5\text{-}C_5Me_4H)RhClL(CNC_6H_{11})]^+\cdot BF_4^-$ ($L = PPh_3$, $PPh_2(C_6F_5)$ or CNC_6H_{11}) are similar to those of the pentamethyl-cyclopentadienyl analogues. However, δ_P of the salt $[(\eta^5\text{-}C_5Me_4H)RhCl(dppe)]^+\cdot BF_4^-$ is shifted by 42.5 ppm to lower frequency of that of the pentamethyl-cyclopentadienyl analogue. The structures of the phosphine complexes **1** and **2** show that, unlike those of the pentmethylcyclopentadienyl analogues, the cyclopentadienyl ring is displaced so that the Rh–C distances are dissimilar. The Rh–CH bond distance and Rh–CMe bond distances for the 1 and 4 positions are shorter than those of Rh–CMe bonds for the 2 and 3 positions, which are approximately *trans* to the phosphine. This is evidently a consequence of the electronic differences between the carbon atoms of the tetramethylcyclopentadienyl ring.

4. Experimental

4.1. General procedures

The ^{1}H-, ^{19}F- and ^{31}P-NMR spectra were recorded on a Bruker DPX300 spectrometer. ^{1}H-NMR spectra were referenced internally using the residual protio solvent resonance relative to $SiMe_4$ (δ 0), ^{19}F- and ^{31}P-NMR spectra externally to $CFCl_3$ and 85% H_3PO_4, respectively using the high frequency positive convention. All chemical shifts (δ) are quoted in ppm and coupling constants in Hz. Abbreviations used in multiplicities are: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were carried out by A.S.E.P., The School of Chemistry, The Queen's University of Belfast.

4.2. Reagents

The compounds dppe, $NaBF_4$, PPh_3, $PPh_2(C_6F_5)$ and CNC_6H_{11} (Aldrich) were used as supplied. $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ [15] was prepared as described for $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ [16].

4.3. Preparations

4.3.1. Preparation of $(\eta^5\text{-}C_5Me_4H)RhCl_2(PPh_3)$ (1)

A solution of $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ (0.077 g, 0.13 mmol) and PPh_3 (0.076 g, 0.29 mmol) in dichloromethane (50 cm^3) was refluxed under nitrogen for 12 h. Addition of hexane and concentration by rotary evaporation afforded **1** as a red solid, which was washed with hexane and dried by aspirator. Yield 0.086 g (59%).

4.3.2. Preparation of $(\eta^5\text{-}C_5Me_4H)RhCl_2\{PPh_2(C_6F_5)\}$ (2)

$[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ (0.076 g, 0.129 mmol) and $PPh_2(C_6F_5)$ (0.079 g, 0.224 mmol) were treated as in Section 4.3.1. Yield 0.098 g (68%).

4.3.3. Preparation of $(\eta^5\text{-}C_5Me_4H)RhCl_2(CNC_6H_{11})$ (3)

A solution of CNC_6H_{11} (0.040 g, 0.371 mmol) in dichloromethane (10 cm^3) was added drop-wise to $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ (0.110 g, 0.185 mmol) in dichloromethane (40 cm^3) with stirring over 35 min. The solution was concentrated to ca. 15 cm^3 by rotary evaporation and hexane (50 cm^3) was added to afford **3** as an orange solid, which was washed with hexane and dried by aspirator. Yield 0.124 g (83%).

4.3.4. Preparation of $[(\eta^5\text{-}C_5Me_4H)RhCl(PPh_3)(CNC_6H_{11})]^+\cdot BF_4^-$ (4)

Compound **1** (0.060 g, 0.108 mmol) in a mixture of methanol (50cm^3) and dichloromethane (20 cm^3) was treated with CNC_6H_{11} (0.012 g, 0.108 mmol) and $NaBF_4$ (0.100 g, 0.911 mmol). After 45 min the solvent was removed by rotary evaporation and the resulting solid extracted with dichloromethane (15 cm^3). After filtration of the extract, hexane (50 cm^3) was added to yield **4** as a yellow–orange solid, which was washed with hexane and dried by aspirator. Yield 0.056 g (69%).

4.3.5. Preparation of $[(\eta^5\text{-}C_5Me_4H)RhCl\{PPh_2(C_6F_5)\}(CNC_6H_{11})]^+\cdot BF_4^-$ (5)

Compound **3** (0.050 g, 0.124 mmol) was treated with $PPh_2(C_6F_5)$ (0.044 g, 0.124 mmol) and $NaBF_4$ (0.136 g, 1.24 mmol) in a mixture methanol (50 cm^3) and dichloromethane (20 cm^3). After 17 h. the solvent was removed by rotary evaporation and the resulting solid extracted with dichloromethane. (15 cm^3). After filtration of the extract, hexane (50 cm^3) was added to yield **5** as a yellow solid, which was washed with hexane and dried by aspirator. Yield 0.057 g (56%).

4.3.6. Preparation of $[(\eta^5\text{-}C_5Me_4H)RhCl(CNC_6H_{11})_2]^+\cdot BF_4^-$ (6)

Compound **3** (0.062 g, 0.154 mmol), CNC_6H_{11} (0.017 g, 0.154 mmol) and $NaBF_4$ (2.00 g, 1.76 mmol) were treated as in Section 4.3.4. Yield 0.051 g (60%).

4.3.7. Preparation of $[(\eta^5\text{-}C_5Me_4H)RhCl(dppe)]^+ \cdot BF_4^-$ (7)

The salt $NaBF_4$ (ca. 0.3 g, 2.7 mmol) was added to $[(\eta^5\text{-}C_5Me_4H)RhCl(\mu\text{-}Cl)]_2$ (0.060 g, 0.100 mmol) and dppe (0.080 g, 0.200 mmol) in methanol (40 cm^3) and dichloromethane (10 cm^3) with vigorous stirring. After 30 min the solvent was removed by rotary evaporation and the orange solid extracted into dichloromethane (70 cm^3) and filtered. Concentration of the solution by rotary evaporation and addition of hexane yielded yellow crystals of **7**, which were washed with hexane and dried in vacuo. Yield 0.100 g (67%).

4.4. X-ray crystal structure determinations

Crystals of compounds **1** and **2** suitable for X-ray structure determination were grown from acetone-petroleum ether (b.p. 100–120°C) and acetone, respectively. Experimental details and crystal data for **1** and **2** are listed in Table 1. Data were collected at ca. 150 K using omega scans to which Lorentz and polarisation corrections were applied. Empirical absorption corrections were applied using psi scans. The structures were solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atom positions, except for those attached to C(7B), C(8B) and C(9B) of **1**, were located from a difference Fourier and allowed to refine isotropically. For C(7B), C(8B) and C(9B) of **1** the difference map indicated that these methyl groups were disordered and the hydrogens were modelled as having two positions at 50% occupancy and a riding model with fixed thermal parameters, ($U_{ij} = 1.5U_{ij}$(eq)), was used for subsequent refinement. The function minimised for wR_2 was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2|F_o|^2 = (g_1P)^2 = g_2P]$ where $P = [\max|F_o|^2 + 2|F_c|^2]/3$ for all F^2 and the function minimised for R_1 was $\Sigma[w(|F_o| - |F_c|)]$. The XSCANS [17], SHELXTL-PC [18] and SHELXL-97 [19] packages were used for data collection, reduction, structure solution and refinement.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 115092 (compound **1**) and 115093 (compound **2**). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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