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Note

Synthesis and characterization of phosphane-substituted hydroxyruthenocenes: crystal structure of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$

Karl Kirchner[a],*, Kurt Mereiter[b],
Klaus Mauthner[a] and Roland Schmid[a]

[a]*Institute of Inorganic Chemistry and* [b]*Institute of Mineralogy, Crystallography and Structural Chemistry, Technical University of Vienna, Getreidemarkt 9, 1060 Vienna (Austria)*

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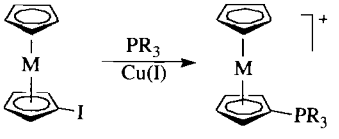
Abstract

Treatment of $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]_2(PF_6)_2$ (**1**) with PR_3 ($PR_3 = PBu^n{}_3$, PCy_3, PMe_3, $PPhMe_2$, PPh_2Me, PPh_3) results in the formation of $[Ru(\eta^5\text{-}C_5H_4PR_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3a–f**) in ≥95% yield. The crystal structure of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3f**) has been determined by X-ray diffraction techniques. **3f** crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.928(2)$, $b = 15.395(3)$, $c = 18.030(3)$ Å, $\beta = 99.07(1)°$, $V = 2721.3(9)$ Å^3, $Z = 4$. The structure was refined to $R = 0.032$ and $R_w = 0.035$. $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]PF_6$ (**2**) reacts with PR_3 ($PR_3 = PBu^n{}_3$, PCy_3, PMe_3, $PPhMe_2$) to give the same products as does **1**, whereas with PPh_2Me, PPh_3, and $P(p\text{-}Ph\text{-}OMe)_3$ a different pathway is observed giving $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PR_3)]PF_6$ (**4a–c**) in ≥95% yield.

Key words: Crystal structures; Ruthenium complexes; Substituted ruthenocene complexes

Introduction

Due to the inertness of coordinated cyclopentadienyl ($C_5H_5^-$) towards nucleophiles it is rather difficult to obtain derivatives via direct nucleophilic substitution, particularly if they are relatively weak nucleophiles such as the phosphanes. Actually, there is only one example of a direct nucleophilic substitution on coordinated $C_5H_5^-$, involving however the powerful nucleophile CH_3^- [1]. Phosphane substituents are typically introduced into coordinated $C_5H_5^-$ by utilizing iodometallocenes and subjecting them to the action of Cu(I) salts in the presence of PR_3 (reaction (1)) [2], or by the treatment of mono-lithiated metallocenes with PR_2Cl [3].



(1)

M = Fe, Ru; R = Alkyl, Aryl

We recently discovered that the $C_5H_5^-$ ligand in $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]_2(PF_6)_2$ (**1**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]PF_6$ (**2**) is unusually electrophilic and reacts with nucleophiles, among them tertiary phosphanes, by directly substituting on the $C_5H_5^-$ ring, and in a few cases also by substituting on the cyclopentadienone ring [4, 5]. These reactions are highly chemoselective and essentially quantitative. Thus, complexes **1** and **2** may serve as useful starting materials for the syntheses of new functionalized ruthenocenes.

In this paper we describe simple high yield syntheses of hydroxyruthenocenes of types $[Ru(\eta^5\text{-}C_5H_4PR_3)(\eta^5\text{-}C_5H_4OH)]^+$ ($PR_3 = PBu^n{}_3$, PCy_3, PMe_3, $PPhMe_2$, PPh_2Me, PPh_3) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PR_3]^+$ ($PR_3 = PPh_2Me$, PPh_3, $P(p\text{-}Ph\text{-}OMe)_3$, and we report the X-ray structure of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$.

Experimental

General

All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures [6]. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. All preparations and reactions were performed under an inert atmosphere of purified nitrogen by using standard Schlenk techniques and/or a glove-box. IR spectra were obtained on a Mattson RS1 FTIR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to $SiMe_4$. Microanalyses were done by the Microanalytical Laboratories, University of Vienna. $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)]_2(PF_6)_2$ (**1**) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CH_3CN)]PF_6$ (**2**) were synthesized according to the literature [4].

Preparation of $[Ru(\eta^5\text{-}C_5H_4PR_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (3) and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_3OH\text{-}2\text{-}PR_3)]PF_6$ (4)

To a solution of **1** (200 mg, 0.25 mmol) in nitromethane (5 ml) 0.30 mmol of PR_3 was added and the reaction mixture was stirred for 2 h at room temperature. During

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*Author to whom correspondence should be addressed.

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that time the red solution turned pale yellow and complexes **3a–f** were formed quantitatively (monitored by ^{1}H NMR spectroscopy in CD_3NO_2). The solution was evaporated to dryness and in order to remove unreacted PR_3 the solid residue was washed three times with anhydrous diethyl ether (10 ml). The crude product was redissolved in nitromethane (3 ml) and undissolved materials were removed by filtration. The solvent was distilled off under reduced pressure and an analytically pure product was obtained. Complexes **4a–c** were prepared in the same manner but with **2** as the starting material. Yield was in all cases $\geqslant$95%.

3a: PBu$^n_3$
Anal. Calc. for $C_{22}H_{36}OP_2F_6Ru$: C, 44.52; H, 6.11; P, 10.44. Found: C, 44.12; H, 6.48; P, 10.02%. ^{1}H NMR ([^{2}H]$_6$-acetone): 5.13 (m, 2H), 4.98 (m, 2H), 4.78 (t, 2H), 4.41 (t, 2H), 2.46 (m, 6H), 1.68 (m, 6H), 1.50 (m, 6H), 0.93 (t, 9H). ^{13}C{^{1}H} NMR ([^{2}H]$_6$-acetone): 128.7 (C–OH), 76.4 (d, *J*(CP) = 9.4 Hz), 75.0 (d, *J*(CP) = 12.6 Hz), 68.5, 64.2, 64.1 (d, *J*(CP) = 92.4 Hz), 25.3 (d, *J*(CP) = 5.2 Hz), 25.1 (d, *J*(CP) = 18.7 Hz), 22.1 (d, *J*(CP) = 51.6 Hz), 14.5 (d, *J*(CP) = 28.1 Hz).

3b: PCy$_3$ (Cy = cyclohexyl)
Anal. Calc. for $C_{28}H_{42}OP_2F_6Ru$: C, 50.07; H, 6.30; P, 9.22. Found: C. 49.96; H, 6.86; P, 9.23%. IR (KBr): 1513 cm^{-1} (s, *ν*(C–O)). ^{1}H NMR (CD_3CN): 4.92 (m, 2H), 4.85 (m, 2H), 4.67 (t, 2H), 4.31 (t, 2H), 2.60–2.40 (m, 3H), 2.20 – 1.20 (m, 30H). ^{13}C{^{1}H} NMR (CD_3CN): 127.5 (C–O), 76.2 (d, *J*(CP) = 8.5 Hz), 75.8 (d, *J*(CP) = 9.8 Hz), 59.7 (d, *J*(CP) = 84.4 Hz), 68.8, 64.2, 31.7 (d, *J*(CP) = 43.8 Hz), 27.7 (d, *J*(CP) = 3.4 Hz), 26.9 (d, *J*(CP) = 12.2 Hz), 26.1.

3c: PMe$_3$
Anal. Calc. for $C_{13}H_{18}OP_2F_6Ru$: C, 33.42; H, 3.88; P, 13.26; F, 22.39. Found: C, 34.10; H, 3.85; P, 12.34; F, 23.82%. ^{1}H NMR ([^{2}H]$_6$-acetone): 5.06 (m, 2H), 5.00 (m, 2H), 4.85 (t, 2H), 4.42 (t, 2H), 3.79 (br, 1H), 2.04 (d, 9H, *J*(HP) = 14.7 Hz). ^{13}C{^{1}H} NMR ([^{2}H]$_6$-acetone): 128.0 (C–OH), 75.8 (d, *J*(CP) = 10.7 Hz), 74.1 (d, *J*(CP) = 14.5 Hz), 67.6, 66.4 (d, *J*(CP) = 99.9 Hz), 63.2, 10.5 (d, *J*(CP) = 59.3 Hz).

3d: PPhMe$_2$
Anal. Calc. for $C_{18}H_{20}OP_2F_6Ru$: C, 40.84; H, 3.81. Found: C, 41.57; H, 3.85%. ^{1}H NMR (CD_3NO_2): 7.80–7.60 (m, 5H), 5.10 (m, 4H), 4.87 (t, 2H), 4.47 (t, 2H), 2.35 (d, 6H, *J*(HP) = 14.1 Hz). ^{13}C{^{1}H} NMR (CD_3NO_2): 135.5 (d, *J*(CP) = 3.5 Hz), 132.2 (d, *J*(CP) = 11.0 Hz), 131.0 (d, *J*(CP) = 12.4 Hz), 127.4 (C–OH), 124.2 (d, *J*(CP) = 86.7 Hz), 77.3 (d, *J*(CP) = 10.1 Hz), 74.8 (d, *J*(CP) = 14.4 Hz), 68.9, 65.9 (d, *J*(CP) = 99.1 Hz), 64.3, 10.6 (d, *J*(CP) = 60.6 Hz, Me).

3e: PPh$_2$Me
Anal. Calc. for $C_{23}H_{22}OP_2F_6Ru$: C, 46.71; H, 3.75. Found: C, 47.49; H, 3.47%. ^{1}H NMR (CD_3NO_2): 7.90–7.30 (m, 10H), 5.50 (br, 1H), 5.14 (m, 2H), 4.94 (m, 2H), 4.77 (t, 2H), 4.38 (t, 2H), 2.67 (d, 3H, *J*(HP) = 13.8 Hz). ^{13}C{^{1}H} (CD_3NO_2): 136.0 (d, *J*(CP) = 3.4 Hz), 133.9 (d, *J*(CP) = 10.3 Hz), 131.1 (d, *J*(CP) = 13.3 Hz), 127.5 (C–OH), 122.9 (d, *J*(CP) = 90.3 Hz), 77.7 (d, *J*(CP) = 9.8 Hz), 75.9 (d, *J*(CP) = 13.6 Hz), 69.2, 65.7 (d, *J*(CP) = 103.7 Hz), 64.7, 10.4 (d, *J*(CP) = 64.0 Hz, Me).

3f: PPh$_3$
Anal. Calc. for $C_{28}H_{24}OP_2F_6Ru$: C, 51.46; H, 3.70; P, 9.48; F, 17.44. Found: C, 51.92; H, 3.69; P, 9.55; F, 17.36%. IR (KBr): 1520 cm^{-1} (*ν*(C–O)). ^{1}H NMR (CD_3CN): 7.95–7.77 (m, 15H), 5.89 (s, 1H), 5.09 (m, 2H), 4.83 (m, 2H), 4.51 (t, 2H), 4.19 (t, 2H). ^{13}C{^{1}H} NMR ([^{2}H]$_6$-acetone): 136.6 (d, *J*(CP) = 3.0 Hz), 135.4 (d, *J*(CP) = 10.6 Hz), 131.6 (d, *J*(CP) = 12.8 Hz), 129.0 (C–OH), 122.1 (d, *J*(CP) = 92.0 Hz), 78.2 (d, *J*(CP) = 10.6 Hz), 77.6 (d, *J*(CP) = 13.8 Hz), 69.6, 65.0, 64.7 (d, *J*(CP) = 106.2 Hz).

4a: PPh$_3$
Anal. Calc. for $C_{28}H_{24}OP_2F_6Ru$: C, 51.46; H, 3.70; P, 9.48. Found: C, 51.67; H, 3.48; P, 9.41%. IR (KBr): 1520 cm^{-1} (*ν*(C–O)). ^{1}H NMR ([^{2}H]$_6$-acetone): 8.00–7.78 (m, 15H), 5.21 (m, 1H), 4.76 (m, 1H), 4.57 (s, 5H), 4.16 (m, 1H). ^{13}C{^{1}H} NMR (CD_3CN): 135.8 (d, *J*(CP) = 3.6 Hz), 135.0 (d, *J*(CP) = 10.9 Hz), 130.8 (d, *J*(CP) = 13.2 Hz), 129.4 (C–OH, d, *J*(CP) = 7.0 Hz), 121.4 (d, *J*(CP) = 93.3 Hz), 74.5 (C_5H_5), 72.3 (d, *J*(CP) = 13.2 Hz), 70.2 (d, *J*(CP) = 10.8 Hz), 65.8 (d, *J*(CP) = 9.0 Hz), 55.3 (d, *J*(CP) = 104.5 Hz).

4b: PPh$_2$Me
Anal. Calc. for $C_{23}H_{22}OP_2F_6Ru$: 46.71; H, 3.75. Found: C, 46.86; H, 3.88%. ^{1}H NMR (CD_3NO_2): 7.90–7.65 (m, 10H), 6.17 (br, 1H), 5.17 (m, 1H), 4.76 (s, 5H), 4.74 (m, 1H), 4.26 (m, 1H), 2.79 (d, 3H, *J*(HP) = 14.1 Hz). ^{13}C{^{1}H} NMR (CD_3NO_2): 136.0 (d, *J*(CP) = 5.3 Hz), 134.0 (d, *J*(CP) = 25.2 Hz), 131.2 (d, *J*(CP) = 12.9 Hz), 127.3 (d, *J*(CP) = 8.8 Hz, C–OH), 122.2 (d, *J*(CP) = 132.6 Hz), 74.9 (C_5H_5), 70.4 (d, *J*(CP) = 13.0 Hz), 66.2 (d, *J*(CP) = 8.0 Hz), 57.3 (d, *J*(CP) = 103.8 Hz), 12.0 (d, *J*(CP) = 63.3 Hz, Me).

4c: P(p-Ph–OMe)$_3$
Anal. Calc. for $C_{31}H_{30}O_4P_2F_6Ru$: C, 50.07; H, 4.07. Found: C. 50.35; H, 3.91%. ^{1}H NMR (CD_3NO_2): 7.80–7.70 (m, 6H), 7.30–7.20 (m, 6H), 5.17 (m, 1H), 4.69 (m, 1H), 4.57 (s, 5H), 4.11 (m, 1H), 3.94 (s, 9H). ^{13}C{^{1}H} NMR (CD_3NO_2): 166.0 (d, *J*(CP) = 2.6 Hz), 137.3 (d, *J*(CP) = 12.4 Hz), 128.9 (d, *J*(CP) = 101.1 Hz),

126.1 (C–OH, d, J(CP) = 8.5 Hz), 116.7 (d, J(CP) = 7.6 Hz), 75.0 (C_5H_5), 73.1 (d, J(CP) = 13.5 Hz), 70.2 (d, J(CP) = 10.7 Hz), 66.4 (d, J(CP) = 8.1 Hz), 58.5 (d, J(CP) = 104.5 Hz), 56.7 (Me).

X-ray crystallography

Crystal data for 3f

$C_{28}H_{24}F_6OP_2Ru$, $M = 653.51$, crystallized by vapor diffusion of diethyl ether into a nitromethane solution at 20 °C as colorless crystals, crystal dimensions 0.42 × 0.44 × 0.55 mm, monoclinic, space group $P2_1/c$, $a = 9.928(2)$, $b = 15.395(3)$, $c = 18.030(3)$ Å, $\beta = 99.07(1)°$, $V = 2721.3(9)$ Å, $Z = 4$, $D_c = 1.595$ g cm^{-3}, $T = 24$ °C.

X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation, and the θ–2θ scan technique. The intensities of 5299 reflections were measured in the range $\theta = 2$ to 25°, $h = -11$ to 11, $k = 0$ to 18, and $l = 0$ to 21. The data were corrected for Lorentz and polarization factors and for absorption by the Gaussian integration method ($\mu = 7.40$ cm^{-1}, minimum and maximum transmission coefficients 0.72 and 0.78). They were then merged to 4797 unique non-extinct reflections ($R_{merge} = 0.016$ on F). The structure was solved by direct methods using the XTAL3.1 suite of programs [7]. The oxygen of the C_5H_4OH moiety was found to be disordered and to be distributed over two different sites in an approximate ratio of 2 to 1. Structure refinement was carried out with the program SHELX76 [8] using anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors for hydrogen atoms in idealized positions fixed relative to the atom to which they were bonded (C–H = 0.96 Å), 3757 reflections with $F_o > 6\sigma(F_o)$, weights $w = 1/(\sigma^2(F_o) + 0.0001F_o^2)$, and 354 varied parameters. Final residuals were $R = 0.032$ and $R_w = 0.035$. The parameter for extinction correction was 0.00052(5). A final difference electron density synthesis showed minimum and maximum values of −0.34 and +0.61 e Å^{-3}. Atomic coordinates of non-hydrogen atoms are given in Table 1. Selected bond lengths are shown in Table 2.

Results and discussion

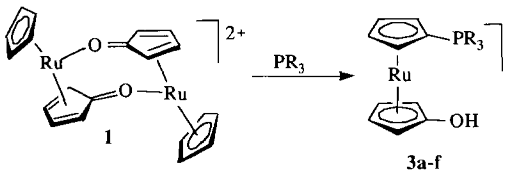
Synthesis and spectroscopic data

The tertiary phosphanes PBu^n_3, PCy_3, PMe_3, $PPhMe_2$, PPh_2Me, and PPh_3 react with **1** to give the 1,1′-disubstituted ruthenocenes **3a–f** in ⩾95% isolated yield (reaction (2)). The identity of the products has been established by ^1H, $^{13}C\{^1H\}$ NMR and IR spectroscopy and by elemental analyses.

TABLE 1. Atomic coordinates and equivalent isotropic temperature factors for $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3f**)

	x/a	y/b	z/c	U_{eq}[a] (Å^2)
Ru	0.27895(3)	0.10428(2)	0.04031(1)	0.0475(1)
P(1)	0.32853(8)	0.32248(5)	−0.00684(4)	0.0431(2)
C(1)	0.2428(3)	0.2219(2)	−0.0244(2)	0.044(1)
C(2)	0.1167(3)	0.1965(2)	−0.0007(2)	0.052(1)
C(3)	0.0819(4)	0.1140(2)	−0.0326(2)	0.063(1)
C(4)	0.1801(4)	0.0889(2)	−0.0762(2)	0.068(1)
C(5)	0.2792(4)	0.1545(2)	−0.0723(2)	0.055(1)
C(6)	0.4366(3)	0.1125(3)	0.1395(2)	0.066(1)
C(7)	0.3112(4)	0.0911(3)	0.1626(2)	0.068(1)
C(8)	0.2657(4)	0.0119(3)	0.1297(2)	0.075(2)
C(9)	0.3641(5)	−0.0168(3)	0.0859(2)	0.078(2)
C(10)	0.4690(4)	0.0450(3)	0.0920(2)	0.073(2)
O(1)[b]	0.2541(4)	0.1304(3)	0.2148(2)	0.091(2)
O(2)[b]	0.1643(10)	−0.0211(7)	0.1504(6)	0.101(5)
C(11)	0.2178(3)	0.4075(2)	−0.0470(2)	0.050(1)
C(12)	0.2294(4)	0.4910(2)	−0.0170(2)	0.065(1)
C(13)	0.1494(4)	0.5568(2)	−0.0512(2)	0.082(2)
C(14)	0.0576(4)	0.5407(3)	−0.1144(3)	0.088(2)
C(15)	0.0413(4)	0.4585(3)	−0 1429(2)	0.088(2)
C(16)	0.1205(4)	0.3918(2)	−0.1097(2)	0.072(1)
C(17)	0.4759(3)	0.3180(2)	−0.0529(2)	0.049(1)
C(18)	0.4803(4)	0.3651(3)	−0.1179(2)	0.065(1)
C(19)	0.5928(5)	0.3568(3)	−0.1545(2)	0.087(2)
C(20)	0.6977(4)	0.3019(3)	−0.1268(2)	0.079(2)
C(21)	0.6934(3)	0 2568(3)	−0.0620(2)	0.069(1)
C(22)	0.5846(3)	0.2634(2)	−0.0245(2)	0.057(1)
C(23)	0.3781(3)	0.3460(2)	0.0910(2)	0.048(1)
C(24)	0.5035(4)	0.3814(2)	0.1178(2)	0.066(1)
C(25)	0.5372(5)	0.4024(3)	0.1933(2)	0.088(2)
C(26)	0.4448(5)	0.3903(3)	0.2407(2)	0.094(2)
C(27)	0.3211(5)	0.3541(3)	0.2147(2)	0.105(2)
C(28)	0.2874(4)	0.3316(3)	0.1404(2)	0.078(2)
P(2)	−0.1387(1)	0.17542(7)	0.16769(5)	0.0648(3)
F(1)	−0.0194(3)	0.1098(2)	0.1632(2)	0.122(1)
F(2)	−0.2610(3)	0.2382(2)	0.1701(2)	0 134(1)
F(3)	−0.2119(3)	0.1022(2)	0.2076(2)	0.110(1)
F(4)	−0.0644(3)	0.2466(2)	0.1272(2)	0.130(1)
F(5)	−0.2109(3)	0.1395(2)	0.0894(1)	0.131(1)
F(6)	−0.0698(3)	0.2084(2)	0.2470(2)	0.123(1)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \mathbf{a}_j)$. [b] Alternately occupied sites, refined occupation factor 0.67(1) for O(1) and 0.29(1) for O(2).



(2)

The α and β protons of η^5-C_5H_4OH give rise to two apparent triplets, and the α and β protons of η^5-$C_5H_4PR_3$ exhibit two apparent multiplets. The signals of the OH protons are detected only in complexes **3c** and **3f**. The $^{13}C\{^1H\}$ NMR spectra reveal a characteristic singlet assigned to the resonances of the 'hydroxy' carbon at 128.7, 127.0, 128.0, 127.4, 127.5, and 129.0 ppm in

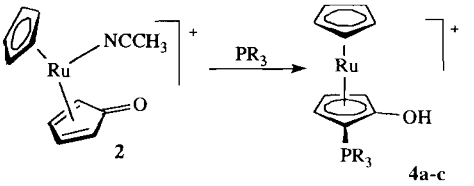
TABLE 2. Selected bond distances (Å) for $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3f**)

Ru–C(1)	2.154(3)	P(1)–C(23)	1 792(3)
Ru–C(2)	2.186(3)	C(1)–C(2)	1.440(4)
Ru–C(3)	2.183(3)	C(1)–C(5)	1.432(4)
Ru–C(4)	2.187(3)	C(2)–C(3)	1.414(5)
Ru–C(5)	2.172(3)	C(3)–C(4)	1.400(6)
Ru–C(6)	2.186(3)	C(4)–C(5)	1.404(5)
Ru–C(7)	2 188(3)	C(6)–C(7)	1.414(5)
Ru–C(8)	2.169(4)	C(6)–C(10)	1.415(6)
Ru–C(9)	2 156(4)	C(7)–C(8)	1.399(6)
Ru–C(10)	2.169(4)	C(8)–C(9)	1.420(6)
P(1)–C(1)	1.771(3)	C(9)–C(10)	1.403(6)
P(1)–C(11)	1.787(3)	C(7)–O(1)[a]	1 319(6)
P(1)–C(17)	1.794(3)	C(8)–O(2)[a]	1.236(11)

[a] O(1) and O(2) are alternately occupied sites, see text.

3a–f, respectively. The other ^{13}C resonances do not bear unusual features and will not be discussed further. The IR spectra show a strong absorption in the range of 1520 to 1513 cm^{-1} assigned to the C–O stretching frequency. In the parent hydroxyruthenocene complex the C–O stretching frequency is observed at 1498 cm^{-1} [9].

With **2** as starting material only in the case of the more basic phosphanes PBu^n_3, PCy_3, PMe_3 and $PPhMe_2$ were the same products as obtained for **1**. The basicity of the phosphanes employed decreases in the sequence: $PBu^n_3 > PCy_3 > PMe_3 > PPhMe_2 > PPh_2Me > P(p\text{-}Ph\text{-}OMe)_3 > PPh_3$ (based on pK_a and heat of protonation values [10, 11]). As established by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (reaction (3)), PPh_3, $PPhMe_2$ and $P(p\text{-}Ph\text{-}OMe)_3$ react with **2** by solely substituting on the cyclopentadienone ligand to afford complexes **4a–c**.



(3)

These compounds have been characterized by a combination of ^1H, $^{13}C\{^1H\}$ NMR, and IR spectroscopy and elemental analyses. The ^1H NMR spectra show three multiplets (1H) which are assigned to the protons of the 1,2-disubstituted C_5 ring, one singlet (5H) which is assigned to the protons of the $C_5H_5^-$ ligand, and the corresponding resonances of the phosphine moiety. Due to the coupling with ^{31}P of the phosphine substituent, the ^{13}C resonances of the disubstituted ring are split into doublets, including the 'hydroxy' carbons observed at 129.4 (d, $J(CP) = 7.0$ Hz), 127.3 (d, $J(CP) = 8.8$ Hz) and 126.1 (d, $J(CP) = 8.5$ Hz) ppm in **4a–c**, respectively. The signals at 74.5, 74.9 and 75.0 ppm are assigned to the unsubstituted $C_5H_5^-$ ring in **4a–c**, respectively. The IR spectrum of **4a** displays the expected peak for the C–O stretching frequency at 1520 cm^{-1}.

It is interesting to note that a similar α-electrophilic behavior of an η^4-cyclopentadienone has been reported recently [12]. The cationic complex $[Mo(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CO)_2]^+$ reacts with certain carbanions to give 5-substituted η^3-cyclopentenoyl complexes.

Crystal structure of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (3f)

A view of the $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]^+$ cation and one PF_6^- anion is shown in Fig. 1 and a packing diagram is presented in Fig. 2. The five-membered rings are nearly parallel to one another, the angle between the two planes being 2.8(2)°. The rings adopt an eclipsed conformation. The C_5H_4OH ring exhibits a disorder of the OH group which occurs in two alternately occupied positions with refined site occupancies of 67(1)% of the C(7)-bonded O(1) and 29(1)% for the C(8)-bonded O(2). In both orientations the hydroxy group is hydrogen bonded to F(1) of the PF_6^- anion as depicted in Fig. 1 (O(2) has been omitted for clarity). The O···F(1) bond distances are 2.747(6) Å for O(1) and 2.752(11) Å for O(2) which can be compared to O···F bond distances of intermediate strength in simple fluoride hydrates [13]. Both OH and PPh_3 groups deviate from the cyclopentadienyl planes, in that O(1), O(2) and P(1) are located 0.182(8), 0.144(12) and 0.118(5) Å, respectively, out of the C_5 ring planes bent away from the metal. The Ru–C distances are all similar averaging to 2.176(6) Å and can be compared to other cyclopentadienyl Ru(II) complexes [5, 14]. Within the C_5 ring of the $C_5H_4PPh_3$ moiety an inductive effect of the formally positively charged tetravalent phosphorus P(1) can be seen. The P(1)-bonded C(1) exhibits C–C bonds (mean value 1.436

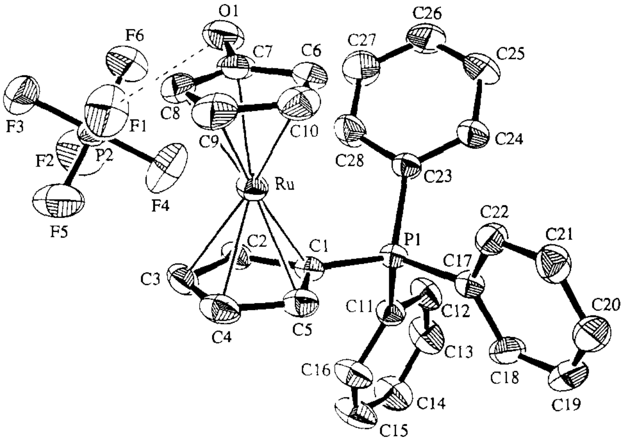


Fig. 1. ORTEP plot (30% ellipsoids) of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3f**). The dotted line indicates a hydrogen bond

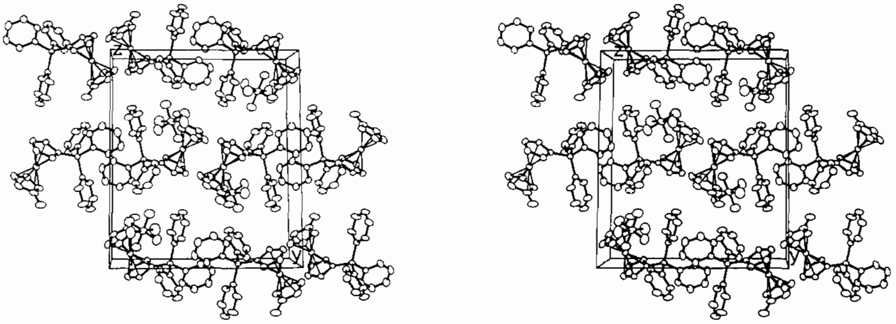


Fig. 2 Packing diagram and stereoview of $[Ru(\eta^5\text{-}C_5H_4PPh_3)(\eta^5\text{-}C_5H_4OH)]PF_6$ (**3f**). The x axis is normal to the page.

Å) that are longer than the remaining three C–C bonds (mean value 1.406 Å) by 0.030 Å. This effect is also observed for the phenyl groups, however, it is not as pronounced as for the C_5 ring (the mean C–C bond length for the P-bonded carbon atoms is 1.386 Å, for the other C–C bonds the mean C–C distance is 1.371 Å). The C–C bond lengths of the C_5H_4OH ring do not show a comparable inductive effect of the OH group. The C(7)–O(1) bond distance is 1.319(6) Å. It has to be noted that the C(8)–O(2) bond distance is 1.24(1) Å and appears to be unrealistically short.

The P(1)–C(1) distance is 1.771(3) Å whereas in the free $C_5H_4PPh_3$ ligand the P–C(C_5) bond distance is 1.718(2) Å. The significant shortening of this bond has been attributed to an approximately 20% ylene contribution to the ground state of the free ligand [15]. As inferred from the much longer P(1)–C(1) bond distance, the coordinated $C_5H_4PPh_3$ ligand in **3f** apparently exhibits no ylene character.

Conformation and geometry aspects of **3f** are very similar to that of the analogous tricyclohexyl compound **3b** which has been reported previously [5]. The C_5H_4OH ring of **3b** also exhibits a disorder of the OH group, however, a different orientation with respect to the hydroxy groups is adopted (the OH groups are bonded to C(6) and C(10), respectively). In both orientations the hydroxy groups of **3b** are also hydrogen bonded (O–H···F) to the PF_6^- anion.

Supplementary material

Listings of anisotropic temperature factors, hydrogen atom parameters, complete bond distances and angles can be obtained from the authors on request.

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