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Synthesis, properties and crystal structures of pentamethylcyclopentadienyl– and cyclopentadienyl–ruthenium(II) diphenylphosphine complexes

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Abstract

The synthesis, characterization and single-crystal structure determination of chiral compounds (η^5-C_5R_5)Ru($PHPh_2$)(PPh_3)Cl (R = H **3**, R = Me **4**) and prochiral Cp*Ru($PHPh_2$)$_2$Cl (**6**) are described. Compound **6** has been available from reaction of $PHPh_2$ and several starting materials. The X-ray structure comparison between **3**, **4** and **6** allowed us to compare the influence of the phosphine, Cp and Cp* ligands in these half-sandwich compounds. In addition, a structural investigation was carried out on Cp*Ru(NBD)Cl (**7**).

Keywords: Ruthenium; Cyclopentadienyls; Phosphines

1. Introduction

We have been investigating the chemistry of the secondary phosphine $PHPh_2$ with pentadienyl manganese [1] and ruthenium [2] compounds. Our interest arises from the fact that $PHPh_2$ offers the possibility of further functionalization once it is coordinated. Despite the vast literature describing tertiary phosphine coordination to half-sandwich cyclopentadienyl (Cp) [3–5] and pentamethylcyclopentadienyl (Cp*) [5,6] ruthenium(II) compounds, reactions of secondary phosphines with these compounds are scarce in the literature [7–9]. Compounds CpRu($PHPh_2$)(PPh_3)X (X = H, Cl) have barely been mentioned in the literature [7], and neither preparative details nor characterization have to date been reported. Synthesis of the disubstituted CpRu($PHPh_2$)$_2$Cl has been described by Singleton and coworkers [8] and [(*p*-cymene)Ru(acac)($PHPh_2$)]BF_4 by Oro and coworkers [9].

As the first part of our studies we wish to report on the synthesis, properties, characterization and single-crystal structure determination of chiral (η^5-C_5R_5)Ru($PHPh_2$)(PPh_3)Cl (R = H **3**, R = Me **4**) and prochiral Cp*Ru($PHPh_2$)$_2$Cl (**6**). In addition, a structural investigation was carried out on Cp*Ru(NBD)Cl (**7**). The synthesis of this η^4-diene complex has previously been reported almost simultaneously by Moro-Oka and coworkers [10] and Bercaw and coworkers [11]. An improved synthetic method for **7** has been reported in 86% and 94% by Conroy-Lewis and Simpson [12] and Fagan et al. [13] using Cp*Ru(PPh_3)$_2$Cl and [Cp*RuCl]$_4$ as starting materials, respectively.

2. Results and discussion

2.1. Syntheses

Replacement of one triphenylphosphine in (η^5-C_5R_5)Ru(PPh_3)$_2$Cl (R = H **1**, R = Me **2**) occurred under $PHPh_2$ addition, in stoichiometric 1:2 and 1:1.2 ratios respectively, to give the chiral compounds (η^5-C_5R_5)Ru($PHPh_2$)(PPh_3)Cl (R = H **3**, R = Me **4**) (Scheme 1).

The half-sandwich compounds **3** and **4** were obtained as orange-red crystalline solids in 81% and 56% yield respectively. Compound **4** was obtained in low yield, owing to the formation of the disubstituted compound **6** (vide infra), even when the synthesis was carried out with less than two equivalents of $PHPh_2$. **4** cannot be easily separated from **6** (see Section 3.3). Structures **3**

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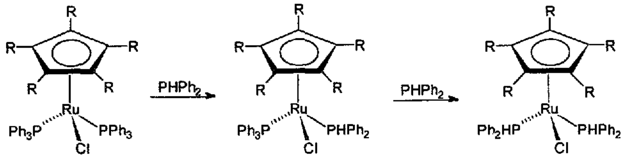


R= H 1 3 5

R= Me 2 4 6

Scheme 1.

and **4** have been established by ^{1}H, ^{31}P NMR (Table 1), ^{13}C NMR (Table 2), mass spectrometry and single-crystal X-ray diffraction studies (Figs. 1 and 2) (Section 2.2).

The prochiral yellow species **5** was isolated by Singleton and coworkers [8] from a reaction between CpRu(COD)Cl and $PHPh_2$ in acetone at room temperature for 60 min in 74% yield. In this work, the melting point found for **5** in a sealed capillary was 168–171 °C which differs from that previously reported (133–134 °C) [8]. Compound **5** was also prepared from **1** or **3**, requiring ten or five equivalents of $PHPh_2$ respectively in toluene at 100 °C for 5.5 h. Disubstituted compound **5**, mixed with **3**, was obtained in a 9:1 ratio as observed from ^{31}P NMR. Purification of these compounds by recrystallization or chromatography is very laborious and difficult owing to their similar solubilities.

The synthesis of **6** was carried out using $PHPh_2$ and different starting materials, such as $Cp^*Ru(PPh_3)_2Cl$ (**2**), $Cp^*Ru(NBD)Cl$ (**7**), $Cp^*Ru(COD)Cl$ (**8**), $[Cp^*RuCl]_4$ (**9**), $[Cp^*RuCl_2]_n$ (**10**) and $Cp^*Ru(PPh_3)Cl_2$ (**11**) (Scheme 2) (see Section 3.4). **8** was the most useful starting material, followed by **9**; these allowed the isolation of **6** in 90% and 75% yields respectively. Characterization of **6** is described in Tables 1 and 2; its identity was confirmed by an X-ray diffraction study (Fig. 3) (Section 2.2).

It is interesting to note that when **7** is used as starting material a very poor yield (1.5%) is obtained. The reason for this dramatic change between **7** and **8** could be explained from the thermodynamic studies performed on these species which shows COD to be less strongly bound to ruthenium than NBD. The labile nature of the COD ligand in **8** was used to gain access into the thermochemistry of ligand substitution for monodentate tertiary arsine, phosphine and phosphite ligands [6]. Indeed, reaction between complex **7** and two equivalents of PPh_3 (in spite of its estimated exothermic value, $\Delta H_{rxn} = -15.2\,\mathrm{kcal\,mol^{-1}}$) did not proceed quantitatively under calorimetric conditions (30 °C), while the reaction proceeded to completion under fairly mild conditions when compound **8** ($\Delta H_{rxn} =$

Table 1
^{1}H and ^{31}P NMR data for compounds **3–6** [a]

Compound	^{31}Pδ	^{1}H δ		
		Cp or Cp *	Phenyl groups	P–H
3	47.07 (d,46.7), 41.02 (d,46.7), $J_{PH} = 360$	4.34 (s)	6.80–7.80 (m,25H)	6.27 (dd) $J_{PH} = 359.5$ $^3J_{PH} = 2.44$
4	45.35 (d,42.9), 35.98 (d,42.9), $J_{PH} = 361.9$	1.26 (t), $^4J^{PH} = 1.65$	6.86–7.58 (m,25H)	5.86 (s,1H)
5	35.50 (s), $J_{PH} = 355$	4.51 (s)	7.18–7.50 (m,20H)	6.49 (d), $J_{PH} = 352.4$
	37.31 (s) [b]	4.52 (s)	7.24 (m,4H); 7.30 (m,4H) 7.36 (m,2H); 7.51 (m, 8H) 7.81 (m,1H); 8.09 (m,1H)	6.40 (d), $J_{PH} = 359.0$
	35.71 (s) [c]	4.42 (s)	7.46–7.58 (m); 7.32–7.40 (m) 6.97–7.12 (m)	6.52 (d), $J_{PH} = 358.3$
6	37.17 (s), $J_{PH} = 350.6$	1.35 (t), $^4J_{PH} = 1.45$ 1.41 (t), [c] $^4J_{PH} = 1.98$	7.03–7.55 (m,20H) 7.54–7.72 (m,H_o) 7.04–7.12 (m,H_m,H_p) 6.82–6.90 (m,H_m,H_p)	6.34 (d) $J_{PH} = 351.0$ 6.54 (d) $J_{PH} = 351.0$

[a] $CDCl_3$; [b] acetone-d_6 [8]; [c] C_6D_6.

Table 2
^{13}C NMR data for compounds **3–6** [a]

Compound	δ(C$_p$ or C$_p$ *)	Phenyl groups			
		C$_i$	C$_o$	C$_m$	C$_p$
3	80.1 (t,2.2 Hz)	135.1 (m)	132.5 (d,8.8)	127.7 (d,9.9)	129.2 (d,2.2)
		135.7 (s,br)	132.9 (d,11)	128.0 (d,10)	129.3 (d,2.2)
		136.5 (d,41.9)	133.7 (d,9.9)	128.4 (d,8.8)	129.4 (s)
4	89.0 (s)	133.2 (s,br)	132.5 (d,10)	127.3 (d,8.8)	128.7 (s)
	9.7(s)	135.2 (d,35.3)	133.9 (d,8.8)	127.4 (d,8.8)	129.4 (s)
		135.3 (d,35.3)	— [b]	128.0 (d,7.7)	— [b]
5	79.7 (t, 2.2 Hz)	134.6(t, ≈ 24)	132.1(t,5.5)	128.0(t,4.4)	129.1(s)
		135.7(t, ≈ 23)	133.3 (t,5.5)	128.3(t,4.4)	129.5(s)
	80.5 [c]	138.1	132.0	128.7	129.9
		134.2	132.2	129.1	130.3
6	89.0(s)	133.9 (t, ≈ 21)	131.9 (t,4.4)	127.6 (t,4.4)	128.4 (s)
	9.4 (s)	135.5 (t, ≈ 21)	134.1 (t,4.4)	128.0 (t,4.4)	129.3 (s)
	89.3 (s) [d]	134.8 (t,21)	132.4 (t,4.4)	127.8 (t,4.4)	128.6 (s)
	9.7 (s)	136.2 (t,21)	134.7 (t,5.5)	128.2 (t,5.5)	129.5 (s)

[a] CDCl$_3$; [b] not observed; [c] C$_6$D$_6$; [d] acetone-d_6 [8].

-18 kcal mol^{-1}) was used. According to thermodynamic calculations, compound **8**, in the presence of NBD, should give compound **7** via an exothermic process (3.1 kcal mol^{-1}) [6]. These results suggest that the dominant factor behind the inability to observe transformation from **7** to **2** or **6**, in the presence of PPh$_3$ or PHPh$_2$ respectively, must be a kinetic one. Other reported reactions with preferential binding of NBD over COD have been observed in the Mo(CO)$_4$(diene) [14] and CpCo(diene) [15] species.

However, the NBD ligand in **7** could be replaced by an excess of tertiary phosphines or t-butylisonitrile, giving compounds (η^5-C$_5$Me$_5$)Ru(PR)$_2$Cl (R = Me$_3$, Me$_2$Ph, MePh$_2$) [16] or (η^5-C$_5$Me$_5$)Ru(NC^{t}Bu)$_2$Cl [12] respectively. Alternatively, the synthesis of **2** has been described [16] using **10** and PPh$_3$ in the presence of a catalytic amount of NBD. However, using COD, we observed that formation of **11** competes in this reaction, producing **2** in low yield. **2** has also been reported to be synthesized by a method similar to the published proce-

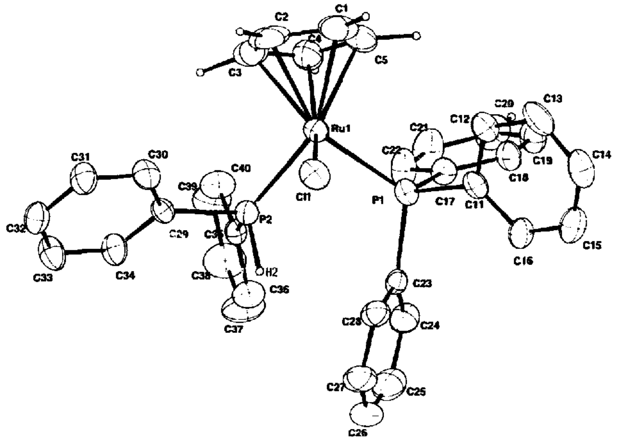


Fig. 1. An ORTEP plot of the molecular structure of **3** with atomic numbering scheme.

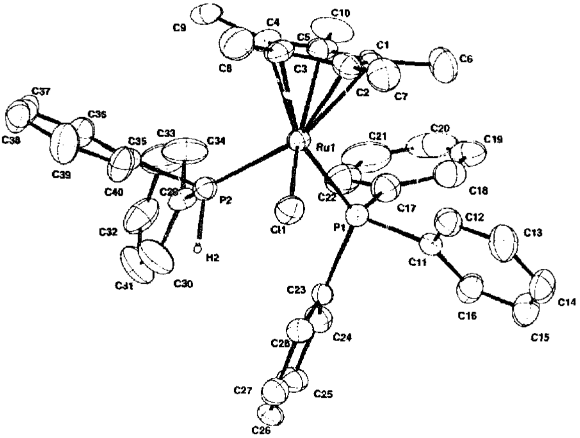
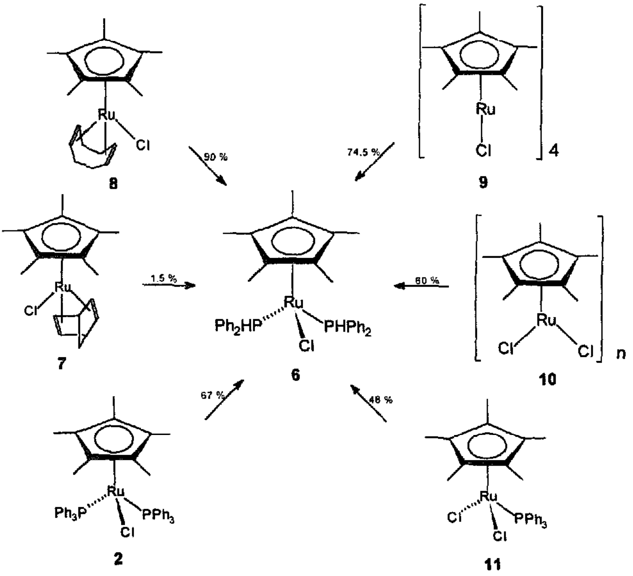


Fig. 2. An ORTEP plot of the molecular structure of 4 with atomic numbering scheme.



Scheme 2.

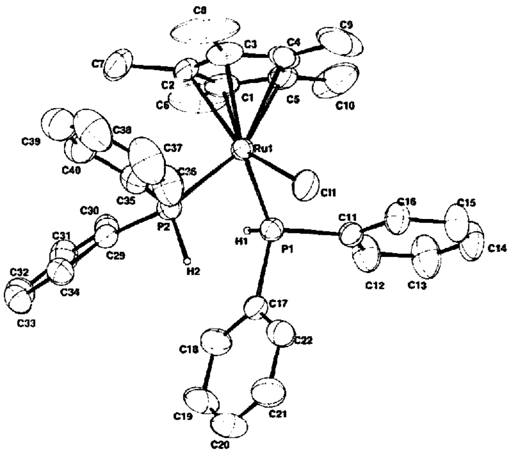


Fig. 3. An ORTEP plot of the molecular structure of **6** with atomic numbering scheme.

dure [16] but without NBD [17]. Some of the resulting compounds when **7** was treated with $AgBF_4$ are the η^6-6-methylfulvene complex $[Cp^*Ru(\eta^6$-$C_5H_4CHMe)]BF_4$ [18] or $[Cp^*Ru(NBD)(CH_3OH)]BF_4$ [10], depending on the solvent used. The latter afforded $[Cp^*Ru(NBD)(PPh_3)]BF_4$ quantitatively in the presence of one equivalent of PPh_3 [10]. Reduction of **7** with lithium powder in DME gave the anionic $[Cp^*Ru(NBD)]Li(DME)$ [13]. We were able to obtain single-crystals of **7**, and here we will describe its structure (see Fig. 4) (Section 2.2).

The formation of Cp^* derivatives **2** and **4** is faster than that of the corresponding Cp analogues **1** and **3**. This difference is attributed to an increase of electron density, as well as steric shielding, at the metal center [3,19]. The difference in reactivity between the two Cp and Cp^* series opens up a wide range of chemical reactions. Some examples have been described in the literature [4,12,19]. The disubstituted compounds **5** and **6** are respectively more reactive than the corresponding mixed species **3** and **4** owing to the presence of two PH functions. In particular, the chemistry of **6** has been studied, and it turns out to be exceptionally versatile in the preparation of new $Cp^*Ru(II)$ and $Cp^*Ru(IV)$ compounds. This chemistry will be described in future contributions [20].

2.2. Molecular structures

Single-crystal X-ray structure determinations were carried out for compounds **3**, **4**, **6** and **7**. The molecular geometries of these compounds are depicted in Figs. 1–4 respectively. Atom positional parameters are given in Tables 3–6, selected bond angles and bond distances are listed in Tables 7 and 8 respectively for **3**, **4** and **6**.

2.2.1. Molecules 3, 4, and 6

These molecules have a piano-stool structure that contains a Cp or Cp^* ring, a chlorine ligand and two

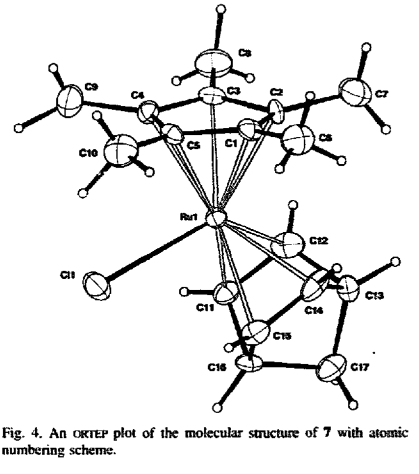


Fig. 4. An ORTEP plot of the molecular structure of **7** with atomic numbering scheme.

phosphines bonded to ruthenium in a distorted octahedral geometry. Bond angles Cl–Ru–P1, Cl–Ru–P2 and P1–Ru–P2 for compounds **3** (89.27(5), 88.43(5), 92.38(5)°), **4** (93.13(8), 84.25(8), 91.33(8)°) and **6** (91.20(4), 84.71(5), 90.67(5)°) reflect the fact that octahedral distortion decreases in the following order **3** < **6** < **4**. The respective angles for **1** (89.05(3), 90.41(4), 103.99(4)°) [21], $CpRu(PMe_3)_2Cl$ (**12**) (89.7(2), 90.1(2), 94.7(2)°) [21], $CpRu(PEt_3)_2Cl$ (**13**) (90.43(3), 90.50(3), 94.71(3)°) [4], $(\eta^5\text{-}C_5H_7)Ru(PEt_3)_2Cl$ (**14**) (93.93(6), 87.17(6), 97.25(5)°) [22], $(\eta^5\text{-}C_5H_7)Ru(PEt_2Ph)_2Cl$ (**15**) (92.88(6), 88.14(5), 97.93(5)°) [22], $(\eta^5\text{-}C_5H_7)Ru(PEt_3)(PPh_3)Cl$ (**16**) (93.38(2), 87.94(2), 98.70(2)°) [22], $(\eta^5\text{-}C_5H_7)Ru(PHPh_2)(PPh_3)Cl$ (**17**) (91.73(3), 96.70(3), 93.34(3)°) [2] and $(\eta^5\text{-}2,4\text{-}Me_2C_5H_7)Ru(PHPh_2)(PPh_3)Cl$ (**18**) (85.81(2), 85.92(2), 92.45(2)°) [2] allowed us to compare the influence of the phosphine ligands in these half-sandwich compounds. Analyzing angles Cl–Ru–P1 and Cl–Ru–P2 in disubstituted species **1**, **12** and **13** for Cp derivatives, there is no significant difference in their bond angles. In contrast, Cp* derivative **6** presents an important variation (ca. 6.5°), such as that observed in disubstituted complexes with acyclic pentadienyl ligands **14** (ca. 6.8°) and **15** (ca. 4.7°); this reflects the higher steric congestion on Cp* and η^5-pentadienyl

Table 3
Atom positional parameters for compound **3**

Atom	x	y	z	U_{eq}	Occ
Ru(1)	0.18489(7)	0.20657(4)	0.07909(4)	0.0383	1.0000
P(1)	0.3387(2)	0.2766(1)	0.0421(1)	0.0409	1.0000
P(2)	0.3309(2)	0.1764(1)	0.1881(1)	0.0396	1.0000
Cl(1)	0.1264(2)	0.3092(1)	0.1516(1)	0.0556	1.0000
C(1)	0.0596(8)	0.1821(6)	−0.0353(5)	0.0448	1.0000
C(2)	−0.0206(8)	0.2019(6)	0.0105(5)	0.0512	1.0000
C(3)	−0.0009(9)	0.1472(5)	0.0696(5)	0.0515	1.0000
C(4)	0.0939(9)	0.0956(5)	0.0573(5)	0.0502	1.0000
C(5)	0.1360(9)	0.1177(5)	−0.0048(6)	0.0492	1.0000
C(6)	0.057(1)	0.2193(7)	−0.1090(5)	0.0695	1.0000
C(7)	−0.1208(9)	0.2627(6)	−0.0034(6)	0.0690	1.0000
C(8)	−0.078(1)	0.1428(7)	0.1243(6)	0.0770	1.0000
C(9)	0.125(1)	0.0244(5)	0.0967(6)	0.0654	1.0000
C(10)	0.215(1)	0.0729(6)	−0.0444(6)	0.0649	1.0000
C(11)	0.2818(9)	0.3651(5)	−0.0057(5)	0.0406	1.0000
C(12)	0.1565(9)	0.3867(6)	−0.0165(5)	0.0557	1.0000
C(13)	0.113(1)	0.4521(7)	−0.0523(6)	0.0728	1.0000
C(14)	0.195(1)	0.4977(6)	−0.0776(6)	0.0699	1.0000
C(15)	0.323(1)	0.4765(6)	−0.0665(6)	0.0719	1.0000
C(16)	0.366(1)	0.4109(6)	−0.0309(5)	0.0579	1.0000
C(17)	0.417(1)	0.2296(6)	−0.0243(6)	0.0625	1.0000
C(18)	0.393(1)	0.2492(6)	−0.0993(6)	0.0734	1.0000
C(19)	0.455(1)	0.2114(7)	−0.1459(6)	0.0600	1.0000
C(20)	0.532(2)	0.159(1)	−0.128(1)	0.0940	1.0000
C(21)	0.563(1)	0.1346(7)	−0.054(1)	0.0890	1.0000
C(22)	0.504(1)	0.1703(6)	−0.0016(7)	0.0748	1.0000
C(23)	0.4821(8)	0.3130(4)	0.1107(4)	0.0376	1.0000
C(24)	0.6091(9)	0.3003(6)	0.1094(5)	0.0527	1.0000
C(25)	0.7102(9)	0.3310(6)	0.1629(6)	0.0579	1.0000
C(26)	0.685(1)	0.3742(6)	0.2184(6)	0.0534	1.0000
C(27)	0.560(1)	0.3884(5)	0.2199(6)	0.0597	1.0000
C(28)	0.4599(9)	0.3559(5)	0.1665(5)	0.0492	1.0000
C(29)	0.4825(9)	0.1294(5)	0.1908(5)	0.0424	1.000
C(30)	0.598(1)	0.1518(7)	0.2397(6)	0.0633	1.0000
C(31)	0.712(1)	0.1161(8)	0.2440(6)	0.0723	1.0000
C(32)	0.713(1)	0.0554(7)	0.2033(8)	0.0701	1.0000
C(33)	0.606(1)	0.0292(6)	0.1574(8)	0.0814	1.0000
C(34)	0.491(1)	0.0676(6)	0.1512(7)	0.0715	1.0000
C(35)	0.2741(8)	0.1241(5)	0.2580(4)	0.0391	1.0000
C(36)	0.316(1)	0.0538(5)	0.2827(5)	0.0586	1.0000
C(37)	0.268(1)	0.0170(6)	0.3333(6)	0.0601	1.0000
C(38)	0.180(1)	0.0492(6)	0.3641(6)	0.0642	1.0000
C(39)	0.138(1)	0.1192(7)	0.3422(6)	0.0661	1.0000
C(40)	0.183(1)	0.1567(5)	0.2888(6)	0.0594	1.0000

Table 4
Atom positional parameters for compound **4**

Atom	*x*	*y*	*z*	U_{eq}	Occ
Ru(1)	0.11606(4)	0.23350(3)	0.93145(3)	0.0426	1.0000
Cl(1)	0.1326(1)	0.2301(1)	0.79413(8)	0.0539	1.0000
P(1)	0.2690(1)	0.1355(1)	0.94962(8)	0.0381	1.0000
P(2)	0.2293(1)	0.3609(1)	0.93917(8)	0.0377	1.0000
C(1)	−0.0489(7)	0.1635(7)	0.9275(6)	0.0766	1.0000
C(2)	−0.0667(5)	0.2611(8)	0.9203(6)	0.0750	1.0000
C(3)	−0.0198(7)	0.3025(6)	0.9874(6)	0.0753	1.0000
C(4)	0.0295(6)	0.2331(6)	1.0361(4)	0.0718	1.0000
C(5)	0.0087(8)	0.1482(6)	0.9988(6)	0.0749	1.0000
C(11)	0.2634(6)	0.0286(4)	0.8925(3)	0.0390	1.0000
C(12)	0.1593(6)	−0.0096(5)	0.8686(4)	0.0523	1.0000
C(13)	0.1518(7)	−0.0926(5)	0.8273(4)	0.0586	1.0000
C(14)	0.2480(9)	−0.1355(4)	0.8102(4)	0.0554	1.0000
C(15)	0.3516(7)	−0.0989(5)	0.8349(4)	0.0587	1.0000
C(16)	0.3591(5)	−0.0176(4)	0.8767(3)	0.0478	1.0000
C(17)	0.2917(5)	0.0923(4)	1.0484(3)	0.0396	1.0000
C(18)	0.3011(5)	−0.0002(4)	1.0663(3)	0.0463	1.0000
C(19)	0.3115(6)	−0.0279(5)	1.1426(4)	0.0582	1.0000
C(20)	0.3113(6)	0.0347(6)	1.2008(4)	0.0576	1.0000
C(21)	0.3045(7)	0.1271(6)	1.1834(4)	0.0637	1.0000
C(22)	0.2940(6)	0.1558(4)	1.1083(4)	0.0584	1.0000
C(23)	0.4087(5)	0.1805(4)	0.9307(4)	0.0390	1.0000
C(24)	0.4984(6)	0.1920(4)	0.9860(4)	0.0580	1.0000
C(25)	0.5966(6)	0.2348(6)	0.9678(6)	0.0738	1.0000
C(26)	0.6068(6)	0.2654(5)	0.8957(7)	0.0766	1.0000
C(27)	0.5204(7)	0.2521(5)	0.8389(5)	0.0687	1.0000
C(28)	0.4223(5)	0.2092(4)	0.8558(4)	0.0538	1.0000
C(29)	0.1716(5)	0.4686(4)	0.8976(3)	0.0371	1.0000
C(30)	0.0792(5)	0.4683(4)	0.8420(4)	0.0503	1.0000
C(31)	0.0433(5)	0.5491(5)	0.8052(4)	0.0563	1.0000
C(32)	0.0978(6)	0.6305(5)	0.8228(4)	0.0528	1.0000
C(33)	0.1876(6)	0.6324(4)	0.8780(4)	0.0561	1.0000
C(34)	0.2242(5)	0.5520(5)	0.9160(3)	0.0487	1.0000
C(35)	0.2965(5)	0.3983(4)	1.0317(3)	0.0359	1.0000
C(36)	0.4124(6)	0.4064(4)	1.0440(3)	0.0504	1.0000
C(37)	0.4635(6)	0.4308(6)	1.1160(5)	0.0719	1.0000
C(38)	0.4004(8)	0.4473(6)	1.1751(4)	0.0734	1.0000
C(39)	0.2857(7)	0.4397(5)	1.1638(4)	0.0654	1.0000
C(40)	0.2336(5)	0.4149(5)	1.0922(4)	0.0564	1.0000

species compared with the Cp analogue. Also, variations in the corresponding bond angles Cl–Ru–P1, Cl–Ru–P2 in **3** (ca. 0.84°) and **4** (ca. 8.9°) clearly reflect the influence of the bulky Cp* in **4**. Interestingly, the small difference found in **3** is also observed in the 2,4-dimethylpentadienyl complex **18** (ca. −0.11°), which achieves the most symmetric piano-stool structure for the acyclic species; this contrasts with the higher angle values found in disubstituted pentadienyl complexes **14–15** and also the mixed phosphine compound **16** (vide supra). These results reflect the similarity between the $PHPh_2$ and PPh_3 in **3** and **18**, even though their cone angles are different ($PHPh_2$ (128°), PPh_3 (145°)) [23]. Furthermore, comparison between Cp* species **4** (ca. 8.9°) and **6** (ca. 6.5°) reinforces the similarity between $PHPh_2$ and PPh_3, the highest steric requirements being for the mixed species.

The Ru–Cl bond length in **3**, 2.434(2) Å, is significantly shorter than the corresponding distances in **6**, 2.454(1) Å, and **4**, 2.462(2) Å. According to analogous species, which include cyclic **1** (2.453(2) Å), **12** (2.451(6) Å), **13** (2.4502(8) Å) and acyclic ligands **14** (2.478(2) Å), **15** (2.471(2) Å), the trend observed for Ru–Cl is longer for Cp < Cp* < η^5-C_5H_7.

As expected, Ru–P bond lengths in **3** and **4** decrease, by approximately 0.02 Å and 0.026 Å respectively, upon replacement of the P-bound H atom by phenyl groups. The Ru–$PHPh_2$ bond length for **3**, **4** and **6** is significantly shorter (average 2.281 Å) than the corresponding distances in *trans*-$RuCl_2(PHPh_2)_4$ (average 2.3585 Å) [24], **17** (2.3083(6) Å) and **18** (2.2973(9) Å) [2].

The Ru–PPh_3 bond length in **3** and **4** (average 2.3055 Å) is also shorter than those in **1** (average 2.336 Å) [21], **17** (2.3565(6) Å) and **18** (2.3403(9) Å) [2], reflecting the lower steric requirement of the mixed phosphine compounds **3** and **4**.

Table 5
Atom positional parameters for compound **6**

Atom	x	y	z	U_{eq}	Occ
Ru(1)	0.40922(2)	0.63099(2)	0.18934(2)	0.0406	1.0000
Cl(1)	0.26457(6)	0.69675(8)	0.23518(6)	0.0579	1.0000
P(1)	0.49086(6)	0.76867(7)	0.24420(5)	0.0441	1.0000
P(2)	0.42570(7)	0.54431(8)	0.30515(6)	0.0474	1.0000
C(1)	0.4976(3)	0.5986(4)	0.0970(2)	0.0570	1.0000
C(2)	0.4542(3)	0.5064(3)	0.1158(2)	0.0515	1.0000
C(3)	0.3575(3)	0.5201(4)	0.0985(3)	0.0614	1.0000
C(4)	0.3450(4)	0.6209(5)	0.0672(2)	0.0680	1.0000
C(5)	0.4297(4)	0.6696(4)	0.0669(2)	0.0660	1.0000
C(6)	0.6023(5)	0.613(1)	0.0976(5)	0.0985	1.0000
C(7)	0.5051(8)	0.4072(6)	0.1397(4)	0.0932	1.0000
C(8)	0.2841(9)	0.437(1)	0.1051(7)	0.1100	1.0000
C(9)	0.250(1)	0.666(2)	0.0389(7)	0.1249	1.0000
C(10)	0.447(1)	0.7736(6)	0.0303(5)	0.1144	1.0000
C(11)	0.4631(2)	0.8987(3)	0.2058(2)	0.0478	1.0000
C(12)	0.5341(3)	0.9697(4)	0.1979(3)	0.0744	1.0000
C(13)	0.5139(4)	1.0677(4)	0.1680(4)	0.0881	1.0000
C(14)	0.4237(4)	1.0954(4)	0.1461(3)	0.0812	1.0000
C(15)	0.3534(4)	1.0264(4)	0.1537(3)	0.0740	1.0000
C(16)	0.3725(3)	0.9281(3)	0.1824(3)	0.0613	1.0000
C(17)	0.5020(3)	0.7924(3)	0.3489(2)	0.0499	1.0000
C(18)	0.5864(3)	0.7816(4)	0.3929(3)	0.0675	1.0000
C(19)	0.5926(5)	0.7942(5)	0.4735(3)	0.0854	1.0000
C(20)	0.5165(5)	0.8215(5)	0.5092(3)	0.0927	1.0000
C(21)	0.4322(5)	0.8321(5)	0.4661(3)	0.0885	1.0000
C(22)	0.4256(4)	0.8162(4)	0.3874(3)	0.0693	1.0000
C(29)	0.5407(3)	0.5038(3)	0.3490(2)	0.0492	1.0000
C(30)	0.6184(3)	0.5370(3)	0.3155(3)	0.0575	1.0000
C(31)	0.7070(3)	0.5195(4)	0.3520(3)	0.0729	1.0000
C(32)	0.7177(4)	0.4699(4)	0.4223(3)	0.0783	1.0000
C(33)	0.6412(4)	0.4339(4)	0.4556(3)	0.0749	1.0000
C(34)	0.5527(3)	0.4504(4)	0.4191(2)	0.0643	1.0000
C(35)	0.3506(3)	0.4320(3)	0.3159(2)	0.0599	1.0000
C(36)	0.2589(4)	0.4510(5)	0.3290(3)	0.0838	1.0000
C(37)	0.1957(4)	0.3694(7)	0.3315(4)	0.1014	1.0000
C(38)	0.2250(6)	0.2699(6)	0.3204(4)	0.1015	1.0000
C(39)	0.3143(6)	0.2491(5)	0.3086(4)	0.0901	1.0000
C(40)	0.3781(4)	0.3306(4)	0.3062(3)	0.0738	1.0000

Table 6
Atom positional parameters for compound **7**

Atom	x	y	z	U_{eq}	Occ
Ru(1)	0.01227(8)	0.27448(7)	0.24920(5)	0.0227	1.0000
Cl(1)	0.2125(3)	0.4273(2)	0.2191(2)	0.0439	1.0000
C(1)	−0.2466(9)	0.388(1)	0.2064(6)	0.0263	1.0000
C(2)	−0.2619(9)	0.2910(9)	0.3050(7)	0.0242	1.0000
C(3)	−0.2476(9)	0.378(1)	0.4008(7)	0.0272	1.0000
C(4)	−0.2045(9)	0.5153(9)	0.3578(7)	0.0260	1.0000
C(5)	−0.2019(9)	0.5199(9)	0.2361(7)	0.0221	1.0000
C(6)	−0.279(1)	0.357(1)	0.0946(7)	0.0472	1.0000
C(7)	−0.331(1)	0.153(1)	0.3149(8)	0.0535	1.0000
C(8)	−0.282(1)	0.335(1)	0.5267(7)	0.0480	1.0000
C(9)	−0.185(1)	0.643(1)	0.4270(8)	0.0494	1.0000
C(10)	−0.175(1)	0.654(1)	0.1607(7)	0.0484	1.0000
C(11)	0.228(1)	0.0864(9)	0.3005(6)	0.0292	1.0000
C(12)	0.094(1)	0.027(1)	0.3171(7)	0.0357	1.0000
C(13)	0.145(1)	−0.087(1)	0.2040(8)	0.0383	1.0000
C(14)	0.112(1)	0.049(1)	0.1213(7)	0.0319	1.0000
C(15)	0.246(1)	0.1063(9)	0.1015(7)	0.0387	1.0000
C(16)	0.3598(9)	0.0103(9)	0.1751(7)	0.0279	1.0000
C(17)	0.348(1)	−0.1635(9)	0.1666(7)	0.0404	1.0000

Table 7
Selected bond angles (deg) for **3**, **4** and **6**

	3	**4**	**6**
Cl(1)–Ru(1)–P(1)	89.27(5)	93.13(8)	91.22(3)
Cl(1)–Ru(1)–P(2)	88.43(5)	84.25(8)	84.70(4)
P(1)–Ru(1)–P(2)	92.13(5)	91.33(8)	90.68(4)
Cl(1)–Ru(1)–C(1)	96.6(3)	119.7(3)	151.6(1)
P(1)–Ru(1)–C(1)	113.9(3)	96.7(2)	97.7(1)
P(2)–Ru(1)–C(1)	153.2(3)	154.1(3)	121.8(1)
Cl(1)–Ru(1)–C(2)	95.0(3)	89.6(3)	97.8(1)
P(1)–Ru(1)–C(2)	152.0(3)	121.0(3)	129.8(1)
P(2)–Ru(1)–C(2)	115.3(3)	147.4(3)	97.8(1)
C(1)–Ru(1)–C(2)	38.2(3)	36.4(3)	37.4(1)
Cl(1)–Ru(1)–C(3)	125.5(3)	93.3(3)	102.2(1)
P(1)–Ru(1)–C(3)	144.9(3)	158.0(3)	157.9(1)
P(2)–Ru(1)–C(3)	93.2(2)	110.2(3)	107.8(1)
C(1)–Ru(1)–C(3)	62.5(3)	62.0(3)	62.5(1)
C(2)–Ru(1)–C(3)	36.8(3)	38.1(3)	37.6(2)
Cl(1)–Ru(1)–C(4)	156.7(2)	128.1(3)	91.9(1)
P(1)–Ru(1)–C(4)	108.0(2)	138.5(3)	126.1(2)
P(2)–Ru(1)–C(4)	105.8(2)	96.6(3)	143.1(2)
C(1)–Ru(1)–C(4)	62.5(3)	61.6(3)	61.1(2)
C(2)–Ru(1)–C(4)	62.4(3)	62.8(4)	61.8(2)
C(3)–Ru(1)–C(4)	37.5(3)	37.7(3)	37.3(2)
Cl(1)–Ru(1)–C(5)	128.7(3)	152.5(2)	115.2(2)
P(1)–Ru(1)–C(5)	93.8(2)	103.9(3)	96.2(1)
P(2)–Ru(1)–C(5)	142.4(3)	116.2(3)	158.7(1)
C(1)–Ru(1)–C(5)	36.7(3)	37.9(3)	37.3(2)
C(2)–Ru(1)–C(5)	62.2(3)	63.2(3)	62.4(2)
C(3)–Ru(1)–C(5)	62.1(3)	63.3(3)	62.3(2)
C(4)–Ru(1)–C(5)	37.4(3)	37.1(3)	36.1(2)
Ru(1)–P(1)–C(11)	117.2(2)	116.4(3)	118.3(1)
Ru(1)–P(1)–C(17)	112.5(2)	115.1(3)	122.2(1)
C(11)–P(1)–C(17)	102.7(3)	102.6(4)	101.5(2)
Ru(1)–P(1)–C(23)	117.8(2)	120.8(3)	
C(11)–P(1)–C(23)	100.8(3)	98.0(4)	
C(17)–P(1)–C(23)	103.8(3)	100.9(4)	
Ru(1)–P(2)–C(29)	118.2(2)	122.2(3)	120.9(1)
Ru(1)–P(2)–C(35)	119.9(2)	118.8(3)	117.6(1)
C(29)–P(2)–C(35)	102.4(3)	101.3(4)	104.9(2)
Ru(1)–C(1)–C(2)	70.7(4)	71.2(5)	71.5(2)
Ru(1)–C(1)–C(5)	71.6(4)	69.3(5)	72.9(2)
C(2)–C(1)–C(5)	107.1(7)	109.5(9)	109.0(4)
Ru(1)–C(2)–C(1)	71.1(4)	72.4(5)	71.1(2)
Ru(1)–C(2)–C(3)	72.0(4)	70.2(5)	71.7(2)
C(1)–C(2)–C(3)	108.0(8)	107.4(9)	107.6(4)
Ru(1)–C(3)–C(2)	71.2(4)	71.6(5)	70.6(2)
Ru(1)–C(3)–C(4)	70.5(4)	70.9(5)	72.3(2)
C(2)–C(3)–C(4)	108.3(7)	106.7(8)	106.5(4)
Ru(1)–C(4)–C(3)	72.0(4)	71.4(5)	70.4(2)
Ru(1)–C(4)–C(5)	71.8(4)	71.2(5)	71.7(2)
C(3)–C(4)–C(5)	107.5(7)	109.8(9)	109.8(4)
Ru(1)–C(5)–C(1)	71.7(4)	72.8(5)	69.8(2)
Ru(1)–C(5)–C(4)	70.8(4)	71.7(5)	72.1(3)
C(1)–C(5)–C(4)	109.2(7)	106.5(8)	107.0(4)
P(1)–C(11)–C(12)	119.2(5)	120.4(7)	119.9(3)
P(1)–C(11)–C(16)	122.4(5)	121.1(7)	121.5(3)

The bond parameters (Ru–C(1–5) average) for coordinated Cp (**3** (2.195 Å)) or Cp* (**4** (2.222 Å), **6** (2.196 Å)) do not differ much from published data: **1** (2.213 Å) [21,25], [CpRu(NBD)(PPh$_3$)]ClO$_4$ (**19**) (2.224 Å) [26], CpRu(PEt$_3$)$_2$Cl (**20**) (2.209 Å) [4], [Cp*Ru(NBD)(H$_2$O)]BF$_4$ (**21**) (2.205 Å) [18], Cp*Ru(COD)H (**22**) (2.231 Å) [27], [Cp*Ru(py)Cl]$_2$PF$_6$ (**23**) (2.166 Å) [28], [Cp*Ru(η^6-C$_6$H$_6$)]$^+$ (**24**) (2.174 Å) [29].

The P–C distances in the phosphine compounds **3**, **4** and **6** are similar to those in analogous compounds [26]. The disubstituted diphenylphosphine compound **6** observed the shortest C–C ring bond distance for C26–C27 (1.346(8) Å).

The P–H distances for **3**, **4** and **6** are not significantly different (1.296(1) Å, 1.32(8) Å and 1.31(3) Å, 1.31(3) Å respectively). The non-bonding distances H(2) ··· Cl(1) are also very similar (3.31, 3.02, 3.15 Å) for **3**, **4** and **6**. Interestingly, H(1)...Cl(1) in **6** is significantly longer (4.66 Å). These facts, suggest to us that the higher reactivity of the disubstituted compound **6**, which has been attributed to the presence of two PH functions, is due to the labile P–H bond, but not necessarily because of formation of HCl, which would afford phosphide species that have never been observed.

2.2.2. *The diene complex 7*

This crystallizes in the triclinic form. The Ru(II) complex has a distorted octahedral geometry with the Cp* ligand occupying three sites, a chlorine atom and two olefinic bonds from the NBD ligand. Distances relating to the coordination of Ru with the Cp* ring are within the normal range, Ru–C(1–5) average 2.221(7) Å (vide supra). However, a significant variation is observed for **7** in Ru–C2 (2.154(7) Å) and Ru–C1

Table 8
Selected bond distances (Å) for **3**, **4** and **6**

	3	**4**	**6**
Ru(1)–Cl(1)	2.434(2)	2.462(2)	2.4542(9)
Ru(1)–P(1)	2.302(2)	2.309(2)	2.282(1)
Ru(1)–P(2)	2.282(2)	2.283(3)	2.277(1)
Ru(1)–C(1)	2.198(7)	2.249(9)	2.174(4)
Ru(1)–C(2)	2.193(6)	2.234(8)	2.180(3)
Ru(1)–C(3)	2.204(7)	2.216(9)	2.194(4)
Ru(1)–C(4)	2.184(7)	2.210(9)	2.218(4)
Ru(1)–C(5)	2.197(7)	2.203(9)	2.213(4)
P(1)–C(11)	1.841(6)	1.848(9)	1.830(4)
P(1)–C(17)	1.837(6)	1.86(1)	1.820(4)
P(1)–C(23)	1.839(6)	1.842(8)	
P(2)–C(29)	1.828(6)	1.813(9)	1.833(4)
P(2)–C(35)	1.820(6)	1.833(8)	1.827(4)
C(1)–C(2)	1.44(1)	1.40(1)	1.395(6)
C(1)–C(5)	1.38(1)	1.45(1)	1.402(6)
C(2)–C(3)	1.39(1)	1.45(1)	1.410(6)
C(3)–C(4)	1.41(1)	1.43(1)	1.410(7)
C(4)–C(5)	1.41(1)	1.40(1)	1.375(7)
P(2)–H(2)	1.296(1)	1.32(8)	1.31(3)
P(1)–H(1)			1.31(3)
Ru–Cp*	1.841	1.861	1.845

(2.252(7) Å) which gives evidence of the deformation of the ring. Compound **21**, with a more symmetric Ru–C (C1–C4) interaction, showed similar behavior for Ru–C5 (2.148(8) Å) [18], as did **23**, which showed two short bond lengths for Ru–C3 (2.155(4) Å) and Ru–C4 (2.149(5) Å) [28].

The Ru–Cl distance has a value of 2.443(2) Å; this is similar to those of the analogous compounds Ru(NBD)(dppb)Cl$_2$ (**25**) (2.4371(10), 2.4374(9) Å) [30] and [Ru(NBD)(CO)Cl$_3$]$^-$ (**26**) (2.445(2), 2.422(2) 2.429(2) Å) [31] which are longer than the amine derivatives Ru(NBD)L$_2$Cl$_2$ (L = C$_5$H$_{11}$N (**27**), 2.4263(4), 2.4200(4) Å, [32]; L = C$_6$H$_5$NH$_2$ (**28**) 2.415(2), 2.407(1) Å [33]).

The average bond distance of **7** (2.18 Å) between Ru and the olefinic carbons of norbornadiene is similar to **27** (2.185 Å), **28** (2.179 Å) [32], Ru(NBD)(L-his)Cl (**29**) (2.170 Å) [34], and slightly longer than [Ru(NBD)(O$_2$CCCl$_3$)]$_2$(μ-H$_2$O)(μ-O$_2$CCCl$_3$)$_2$ (**30**) (2.164 Å) [35], Ru(NBD)[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]X (X = Cl (**31**) (2.153 Å); X = OSO$_2$CF$_3$ (**32**) (2.166 Å) [36]) and Ru(NBD)(L-phe) (**33**) (2.163 Å) [37]. These structures showed the lowest distortion in the NBD–Ru interaction, whereas **19** (2.235 Å), **21** (2.201 Å), **25** (2.284 Å), **26** (2.220 Å), Ru(NBD)(diimine)I(CH$_3$) (**34**) (2.201 Å) [38] and [Ru(NBD)(aminoacid)]$_2$ (**35**) [39] are less symmetrically bonded.

3. Experimental details

3.1. *General procedures*

All reactions were carried out by use of standard procedures for manipulation of air-sensitive materials, either under dry nitrogen using Schlenk tubes, syringe and/or high vacuum techniques. Solvents were dried, freshly distilled under dinitrogen, and degassed prior to use.

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Jeol GSX-270 spectrometer at 270 MHz, 67.80 MHz and 109.25 MHz respectively, with TMS and H$_3$PO$_4$ (85%) as internal and external references, in benzene-d_6 or CDCl$_3$ at ambient temperature. Mass spectra were obtained with Finnigan MAT 95 or Hewlett Packard 5989A instruments. Carbon and hydrogen analyses were carried out by Oneida Research Services Inc., Whitesboro, NY.

The triphenyl- and diphenylphosphines were used as received from Aldrich. The following metal complexes were made by published methods: **1** [40], **5** [8], (**7**, **8**, **9**) [13], **10** [10], **11** [41].

Complex **2** was synthesized by reduction of **11**. A mixture of **11** (400 mg, 0.7 mmol) and PPh$_3$ (0.2 g, 0.76 mmol) in THF (25 ml) was stirred at room temperature. Addition of zinc powder (0.5 g) showed that partially soluble **11** in THF dissolves completely without color change in the brick-red solution after 1 h. The solution was filtered and the volume reduced to 5 ml: addition of hexane gave a pale yellow precipitate. Recrystallization with CH$_2$Cl$_2$–hexane (1:2) afforded a microcrystalline orange-yellow powder in 85% (475 mg, 0.60 mmol).

3.2. *Preparation of CpRu(PHPh$_2$)(PPh$_3$)Cl (3)*

A stirred suspension of compound **1** (480 mg, 0.66 mmol) in toluene (30 ml) was treated with PHPh$_2$ (0.23 ml, 1.32 mmol) for 2 h at 60 °C under dinitrogen atmosphere. The resulting solution was concentrated in vacuo and the residue of the reaction was purified by column chromatography over silica, firstly with hexane and then with diethyl ether:hexane (1:1) as eluents. PHPh$_2$ and PPh$_3$ were eluted with the former solvent and compound **3** with the mixed solvents and isolated as an orange-red solid after concentration of the solution in 81.4% (350 mg, 0.54 mmol), m.p. 175–205 °C without decomposition. Elemental Anal. Found: C, 64.07; H, 4.68. C$_{35}$H$_{31}$ClP$_2$Ru. Calc.: C, 64.67; H, 4.77%. MS (70 eV) *m/z* (rel. int. (%)): 650 (3) [M$^+$], 536(1), 464(3), 427(8), 352(5), 262 (100), 183(75), 186(30), 108(91).

3.3. *Preparation of Cp* Ru(PHPh$_2$)(PPh$_3$)Cl (4)*

PHPh$_2$ (11.5 ml, 0.64 mmol) was added at room temperature to a suspension of **2** (424 mg, 0.53 mmol) in toluene (20 ml) and the mixture was stirred for 30 min. The solvent was evaporated under reduced pressure to leave an orange oil, which was purified by chromatography on silica with diethyl ether:hexane (3:7) to afford compound **4** (which is contaminated with **6** in a 20:1 ratio according to ^{1}H NMR) in approximately 56% (215 mg, 0.3 mmol). Careful crystal separation by hand allowed characterization of **4**, m.p. 185–190 °C. MS *m/z* (rel. int. (%)). LR/FAB (CH$_2$Cl$_2$–3NBA) 720(48) [M$^+$], 685(46), 534(92), 499(100), 458(87), 422(74), 271(16), 262(21), 236(14).

3.4. *Preparations of Cp* Ru(PHPh$_2$)$_2$Cl (6)*

3.4.1. *From compound 8*

A stirred suspension of **8** (230 mg, 0.6 mmol) in 30 ml of cyclohexane was treated with PHPh$_2$ (0.23 ml, 1.32 mmol). After 1 h the starting material was not observed in solution. After stirring for 16 h at room temperature the cyclohexane was removed under vacuum. The golden yellow powder was recrystallized twice from toluene–hexane to give pure orange-red crystals of **6** in 90% yield (350 mg, 0.54 mmol) m.p. 190–200 °C. Elemental Anal. Found: C, 63.02; H, 5.72; Cl, 5.20. C$_{34}$H$_{37}$ClP$_2$Ru. Calc.: C, 63.40; H, 5.75; Cl, 5.52%. MS (70 eV) m/z (rel. int. (%)): 644(5) [M$^+$], 543(5), 470(4), 458(11), 422(11), 236(4), 186(60), 108(100).

3.4.2. *From compound 7*

Complex **6** was prepared in a similar manner to above, but using compound **7** (150 mg, 0.41 mmol) in 20 ml of cyclohexane and $PHPh_2$ (0.17 ml, 0.9 mmol). The unreacted **7** was separated by chromatography on silica with diethyl ether–hexane after the first orange-red fraction of **6** which was eluted with diethyl ether:hexane (3:7). Recrystallization of **6** in hexane at −5 °C gave 1.5% yield (4 mg, 6.2×10^{-3} mmol) and recrystallization of **7** in dichloromethane:hexane (1:2) at room temperature gave 134 mg (0.37 mmol) of recovered starting material.

3.4.3. *From compound 9*

Compound **9** (340 mg, 0.31 mmol) in THF (20 ml) was treated with $PHPh_2$ (0.5 ml, 2.87 mmol) and the resulting mixture was stirred at room temperature for 2 h. The solution is filtered from a black thin powder and the THF was evaporated. The golden yellow solid was recrystallized three times with toluene:hexane (1:1) at room temperature to give orange-red crystals in 74.5% yield (600 mg, 0.93 mmol).

3.4.4. *From compound 10*

Compound **10** (300 mg, 0.96 mmol) in EtOH (15 ml) gave a brown suspension which was treated with two equivalents of $PHPh_2$ (0.34 ml, 1.92 mmol) at room temperature, changing drastically from a brown to a yellow-green solution. After stirring 1 h the reaction mixture was filtered, giving a black powder and a wine-red solution. The EtOH was removed and the crude product was dissolved in chloroform, then filtered and the volume of solvent reduced. Addition of hexane gave a yellow powder (385 mg) which is a mixture of **6**, $Cp'Ru(PHPh_2)(POEtPh_2)Cl$ and $Cp'Ru(POEtPh_2)_2Cl$, in an approximate ratio 60:35:5

Table 9
Crystallographic data collection and structure refinements for compounds 3, 4, 6 and 7

	$C_{35}H_{31}P_2ClRu$ (3)	$C_{40}H_{41}ClP_2Ru$(4)	$C_{34}H_{37}P_2ClRu$ (6)	$C_{17}H_{23}RuCl$ (7)
Fw	650.1	720.23	644.13	363.89
Space group	$P2_1/c$	$P2_1/n$	$P2_1/a$	$P\bar{1}$
a (Å)	11.844(1)	10.653(1)	14.470(2)	8.467(2)
b (Å)	14.512(1)	17.988(4)	12.870(2)	8.510(3)
c (Å)	17.523(1)	18.650(4)	17.207(1)	11.839(4)
α (deg)	90.0	90.0	90.0	89.10(4)
β (deg)	95.589	105.0	95.48(9)	71.74(2)
γ (deg)	90.0	90.0	90.0	60.74(3)
V (Å^3)	3019.3(1)	3452.6(1.1)	3190(1)	740(1)
Z	4	4	4	2
$F(000)$	1328	1488	1328	372
Diffractometer	CAD4 Enraf–Nonius	CAD4 Enraf–Nonius	CAD4 Enraf–Nonius	CAD4 Enraf–Nonius
Radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
Linear abs coeff (cm^{-1})	7.29	6.41	6.86	12.07
ρ(calc) (g cm^{-3})	1.44	1.39	1.34	1.63
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Scan range (deg)	0.80 + 0.34 tan θ	0.80 + 0.34 tan θ	0.50 + 0.6 tan θ	0.8 + 0.345 tan θ
θ limits (deg)	1–25	1–25	1–25	2–18
Measurement temperature	room temperature	room temperature	room temperature	room temperature
Octants collected	−10, 10; 0, 14; 0, 15	−12, 12; 0, 21; 0, 22	0, 15; 0, 13; −18, 18	−6, 7; −7, 7; 0, 10
No. of data collected	4880	6480	4312	1097
No of unique data collected	2332	6055	3902	1026
No of unique data used	2063 $(F_o)^2 > 3\sigma(F_o)^2$	2476 $(F_o)^2 > 3\sigma(F_o)^2$	3582 $(F_o)^2 > 3\sigma(F_o)^2$	986 $(F_o)^2 > 3\sigma(F_o)^2$
R(int)	4.56	4.12	1.12	0.01
Decay (%)	< 1	< 1	< 1	< 1
Absorption correction	DIFABS (min = 0.86, max = 1.17)	(min = 0.90, max = 1.06)	DIFABS (min = 0.86, max = 1.09)	DIFABS (min = 0.83, max = 1.08)
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.029	0.040	0.036	0.026
$Rw = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.031, w = 1.0	0.045, w = 1.0	0.037, w = 1.0	0.030, w = 1.0
Goodness of fit s	3.43	1.58	6.39	4.18
No. of variables	353	401	351	173
$\Delta\rho$ min (e Å^{-3})	−2.8	−0.315	−0.43	−0.28
$\Delta\rho$ max (e Å^{-3})	0.26	0.625	0.42	0.520

according to ^{31}P NMR spectroscopy. Attempts to isolate pure samples were not successful.

3.4.5. *From compound 11*

To a suspension of **11** (1.32 mg, 2.32 mmol) in THF (70 ml) at room temperature was added three equivalents of $PHPh_2$ (1.21 ml, 6.9 mmol). The color of the solution changed from wine-red to red-yellow. The mixture was heated under reflux for 4 h. The solution was filtered and the solvent was removed in vacuo and the residue was dissolved in toluene. Chromatography on silica with hexane afforded $PHPh_2$ and PPh_3; a second orange-red band was eluted with diethyl ether:hexane (3:7) giving **6** in 48% yield (715 mg, 1.11 mmol). Two more bands were eluted, giving hydrolysis products.

3.4.6. *From compound 2*

Compound **2** (150 mg, 0.189 mmol) in 30 ml of THF was treated with $PHPh_2$ (0.083 ml, 0.48 mmol) and the resulting mixture was stirred under reflux for 2.5 h. The THF was evaporated and a yellow oily solid was purified by chromatography on silica with hexane eliminating excess of $PHPh_2$; a second yellow band was eluted with diethyl ether:hexane (1:9). After concentration of the solution, a yellow solid precipitates. Recrystallization from CH_2Cl_2–hexane gave **6** in 67% yield (100 mg, 139 mmol).

3.5. *Crystal structure determinations*

Details of crystal data and intensity collection parameters are given in Table 9. Unit cell dimensions with estimated standard deviations were obtained from least squares refinement of the setting angles of 25 well-centered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods using CRYSTALS and refined by full matrix least squares cycles. Anisotropic temperature factors were introduced for all non-hydrogen atoms. The hydrogen atoms were found on difference electron density maps and refined isotropically.

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