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Synthesis of new half-sandwich ruthenium complexes containing 1,2-bis(diisopropylphosphino)ethane (dippe); crystal structures of $[Ru(C_5Me_5)Cl(dippe)]$ and $[Ru(C_5Me_5)(O_2)(dippe)][BPh_4]$

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The complex $[Ru(C_5H_5)Cl(PPh_3)_2]$ reacted with 1 equivalent of dippe [dippe = 1,2-bis(diisopropylphosphino)ethane] in refluxing toluene to yield $[Ru(C_5H_5)Cl(dippe)]$ **1**. The complex $[Ru(C_5Me_5)Cl(dippe)]$ **2** was obtained by reaction of $[\{Ru(C_5Me_5)(\mu_3\text{-}Cl)\}_4]$ with a stoichiometric amount of dippe in CH_2Cl_2. The crystal structure of **2** has been determined. Both **1** and **2** are non-electrolytes in non-polar solvents. In alcohols, compound **2** has a strong tendency to dissociate chloride. In the presence of air, this compound binds O_2 irreversibly, yielding the dioxygen complex $[Ru(C_5Me_5)(O_2)(dippe)]^+$, which is isolable as the $[BPh_4]^-$ salt (**3**). The crystal structure of this compound has also been determined. Both **1** and **2** reacted with $SnCl_2$ in CH_2Cl_2 to yield the insertion derivatives $[Ru(C_5R_5)(SnCl_3)(dippe)]$ (R = H **4** or Me **5**). All compounds were characterized by NMR spectroscopy and microanalysis.

The potential of the (cyclopentadienyl)bis(phosphine)-ruthenium system to act as an organometallic auxiliary not only for the development of new organic synthetic methods, but also for the binding and activation of small molecules is well documented.[1] Our research group has been studying the chemistry of transition-metal complexes containing the bulky diphosphine 1,2-bis(diisopropylphosphino)ethane (dippe), particularly those aspects related to the activation of small molecules.[2,3] We have prepared half-sandwich iron complexes of the type $[Fe(C_5R_5)Cl(dippe)]$ (R = H or Me),[4] which are reactive towards H_2 and N_2,[5] so we wanted to extend this work to ruthenium, in order to establish the effects of the bulky phosphine on the reactivity of the metal site, and also for comparing with the reactivity observed for the related iron system. In this paper we report the synthesis and characterization of $[Ru(C_5R_5)Cl(dippe)]$ (R = H or Me), and the study of their behaviour in solution, particularly some effects derived from the lability of the chloride ligand.

Results and Discussion

The complex $[Ru(C_5H_5)Cl(PPh_3)_2]$[6] reacts with a stoichiometric amount of dippe in refluxing toluene yielding the new half-sandwich derivative $[Ru(C_5H_5)Cl(dippe)]$ **1**. This material can be separated from the free PPh_3 formed during the reaction by column chromatography on silica gel, being isolated as an orange crystalline material in very good yields. Thermolysis of $[Ru(C_5H_5)Cl(PPh_3)_2]$ in the presence of diphosphines has been a method widely used for the general preparation of derivatives of the type $[Ru(C_5H_5)Cl(L\text{–}L)]$ (L–L = diphosphine), such as $[Ru(C_5H_5)Cl(dcpe)]$ [dcpe = 1,2-bis(dicyclohexylphosphino)-ethane][7] and $[Ru(C_5H_5)Cl(dppm)]$ [dppm = 1,1-bis(diphenylphosphino)methane],[8] although the yields of this reaction are very sensitive to the particular diphosphine, the amounts of solvent used and reaction times. At variance with this, the thermolysis of $[Ru(C_5Me_5)Cl(PPh_3)_2]$[9] in the presence of diphosphine is not a very convenient route for the preparation of the corresponding $[Ru(C_5Me_5)Cl(L\text{–}L)]$ derivatives. We have found that they are very easily accesible by reaction of the tetramer $[\{Ru(C_5Me_5)(\mu_3\text{-}Cl)\}_4]$[10] with a stoichiometric amount of phosphine in dichloromethane at room temperature, a method which has been used for the preparation of the co-ordinatively unsaturated complexes $[Ru(C_5Me_5)Cl(L)]$ [L = PPr^i_3 or $P(C_6H_{11})_3$].[11] In this fashion we have obtained $[Ru(C_5Me_5)Cl(dippe)]$ **2** in very good yields. The X-ray crystal structure of this compound was determined. The molecular structure of **2** is represented in Fig. 1. Atomic coordinates and selected bond lengths and angles are listed in Tables 1 and 2, respectively. Each unit cell contains two asymmetric units. The ruthenium atom is in a formally six-co-ordinate environment, and the molecule has a 'three-legged piano stool' geometry. The Ru–Cl bond distance is very similar to that found in $[Ru(C_5H_5)Cl(dppe)]$ [2.452 Å; dppe = 1,2-bis(diphenylphosphino)ethane][12] and in $[Ru(C_5H_5)Cl(dppp)]$ [2.443 Å; dppp = (*R*)-1,2-bis(diphenylphosphino)propane],[13] whereas the Ru–P separations are slightly longer, being similar to the average Ru–P bond distance found in complexes containing bulkier diphosphines, such as $[Ru(C_5H_5)Cl(dcpm)]$ [2.330 Å; dcpm = 1,2-bis(dicyclohexylphosphino)methane].[14] The C_5-ring of

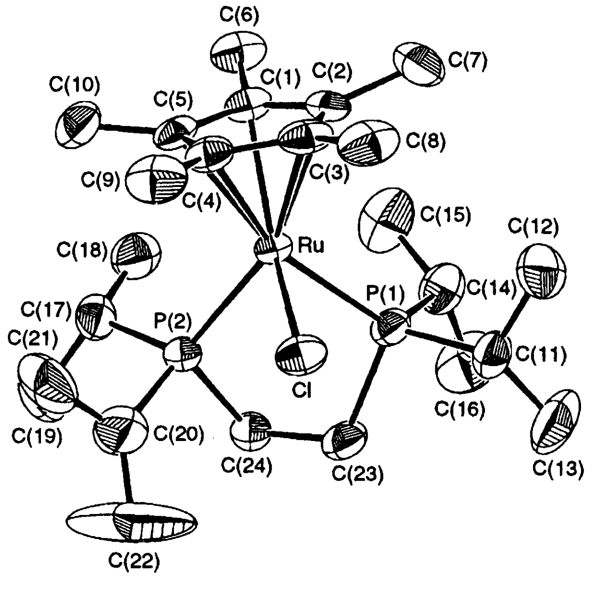

Fig. 1 Crystal structure of the complex $[Ru(C_5Me_5)Cl(dippe)]$; hydrogen atoms are omitted

Table 1 Atomic fractional coordinates for $[Ru(C_5Me_5)Cl(dippe)]$

Atom	*x*	*y*	*z*
Ru	0.090 06(5)	0.249 40(3)	0.268 75(5)
Cl	0.059 2(2)	0.301 7(1)	−0.007 3(2)
P(1)	0.328 2(2)	0.189 69(9)	0.273 9(2)
P(2)	0.235 0(2)	0.347 95(9)	0.393 6(2)
C(1)	−0.012 3(6)	0.194 6(3)	0.432 2(6)
C(2)	−0.034 0(6)	0.149 6(3)	0.288 6(7)
C(3)	−0.125 1(6)	0.195 7(4)	0.144 7(7)
C(4)	−0.164 2(6)	0.271 6(3)	0.197 0(7)
C(5)	−0.096 6(6)	0.269 8(3)	0.374 2(7)
C(6)	0.038 3(7)	0.161 6(4)	0.607 9(7)
C(7)	0.010 6(9)	0.063 4(4)	0.297 0(9)
C(8)	−0.186 4(8)	0.171 1(4)	−0.033 8(8)
C(9)	−0.273 1(7)	0.336 5(4)	0.084 1(9)
C(10)	−0.128 7(7)	0.330 0(4)	0.483 4(9)
C(11)	0.327 6(7)	0.143 6(4)	0.079 2(7)
C(12)	0.235(1)	0.076 8(4)	0.039 3(9)
C(13)	0.484(1)	0.120 4(6)	0.071(1)
C(14)	0.455 3(7)	0.115 9(4)	0.439 3(8)
C(15)	0.416 0(9)	0.114 4(5)	0.591 0(9)
C(16)	0.628 8(9)	0.117 2(5)	0.495(1)
C(17)	0.253 5(7)	0.376 6(4)	0.607 8(8)
C(18)	0.303 3(8)	0.307 2(4)	0.729 5(8)
C(19)	0.359(1)	0.438 0(4)	0.682(1)
C(20)	0.179(1)	0.441 1(4)	0.269(1)
C(21)	0.029(1)	0.480 5(4)	0.260(1)
C(22)	0.277(1)	0.474 2(9)	0.213(2)
C(23)	0.448 1(7)	0.267 1(4)	0.287 9(8)
C(24)	0.439 4(7)	0.320 4(3)	0.423 2(8)

Table 2 Selected bond distances (Å) and angles (°) for $[Ru(C_5Me_5)Cl(dippe)]$

Ru–Cl	2.456(2)	Ru–C(2)	2.251(5)
Ru–P(1)	2.336(2)	Ru–C(3)	2.225(5)
Ru–P(2)	2.331(2)	Ru–C(4)	2.218(5)
Ru–C(1)	2.253(5)	Ru–C(5)	2.253(5)
Cl–Ru–P(1)	84.30(6)	Cl–Ru–C(3)	88.2(2)
Cl–Ru–P(2)	89.68(6)	Cl–Ru–C(4)	89.4(1)
Cl–Ru–C(1)	149.0(1)	Cl–Ru–C(5)	123.0(2)
Cl–Ru–C(2)	119.9(1)	P(1)–Ru–P(2)	82.80(6)

the pentamethylcyclopentadienyl ligand is almost perfectly planar, with an average deviation of 0.0074 Å from the plane. The Ru atom is at 1.883 Å from the plane, whereas the five methyl substituents of the C_5Me_5 group are displaced away from the metal. All intermolecular contacts are van der Waals' type.

Both **1** and **2** exhibit ^1H, $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ NMR spectra in $CDCl_3$ or $(CD_3)_2CO$ which are in support of a 'three-legged piano stool' geometry in solution, consistent with the solid-state molecular structure found for **2** by X-ray diffraction. Thus, the $^{31}P-\{^1H\}$ NMR spectra in $(CD_3)_2CO$ display one sharp singlet, corresponding to the equivalent phosphorus atoms of the phosphine ligand. However, we have observed that the presence of small amounts of water in the solvent produces a considerable broadening of the $^{31}P-\{^1H\}$ NMR resonance of compound **2**. If the spectrum is recorded in a good donor solvent such as CD_3OD, a similar effect is observed. If the temperature is lowered, the broad resonance sharpens, but it remains rather broad even at −50 °C. The system is diamagnetic at all temperatures. We have attributed this behaviour to the occurrence in solution of an equilibrium, corresponding to the dissociation of the chloride ligand to some extent, equation (1).

$$[Ru(C_5Me_5)Cl(dippe)] \rightleftharpoons [Ru(C_5Me_5)(dippe)]^+ + Cl^- \quad (1)$$

The dissociation of chloride is a well precedented process for half-sandwich complexes of ruthenium of the type $[Ru(C_5H_5)ClL_2]$ (L = CO or PR_3),[15] being favoured by good donor solvents such as alcohols, as it has been noted for other halogeno–phosphine complexes such as $[Fe(C_5Me_5)Cl(dippe)]$,[3,4] $[RuHCl(dippe)_2]$[1] or $[FeCl_2(dmpe)_2]$.[16] No broadening of the NMR resonances is observed for compound **1** when the spectra are recorded in CD_3OD. This suggests that dissociation occurs to a lesser extent in this case, possibly due to the poorer donor properties of the C_5H_5 ligand compared to C_5Me_5. An increase in the electron-donating abilities of the co-ligands has been found to stabilise the 16-electron species formed as a consequence of the dissociation process,[4,15] shifting to the right the equilibrium shown in equation (1). Furthermore, 16-electron half-sandwich compounds of the type $[Ru(C_5Me_5)Cl(PR_3)]$ [$PR_3 = P(C_6H_{11})_3$ or $PPhPr^i_2$] have recently been shown to be quite stable, yet reactive.[17]

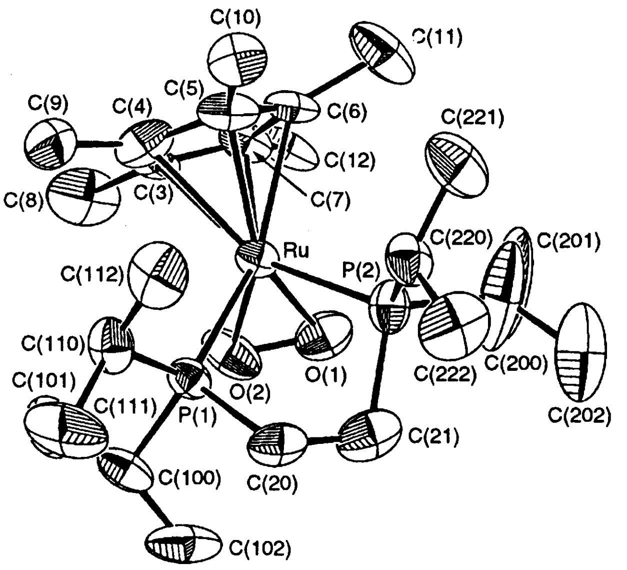

Fig. 2 Crystal structure of the cation $[Ru(C_5Me_5)(O_2)(dippe)]^+$; hydrogen atoms are omitted

When a methanolic solution of **2** was exposed to air, the colour changed from orange to yellow-brown. Under these conditions, the broad resonance in the $^{31}P-\{^1H\}$ NMR spectrum disappeared, being replaced by one sharp singlet. Addition of $Na[BPh_4]$ to this solution yielded a brown, crystalline precipitate, which was identified as the dioxygen complex $[Ru(C_5Me_5)(\eta^2-O_2)(dippe)][BPh_4]$ **3** by single-crystal X-ray diffraction and microanalysis.[18] A view of the cation $[Ru(C_5Me_5)(O_2)(dippe)]^+$ is shown in Fig. 2. Atomic coordinates and selected bond lengths and angles are listed in Tables 3 and 4, respectively. The dioxygen ligand is bound in the side-on manner, having an O(1)–O(2) separation of 1.37(1) Å, which is very similar to that found in $[RuH(O_2)(dippe)_2][BPh_4]$ [1.36(1) Å],[1] and in $[Ru(C_5Me_5)(L-L')_2(O_2)][BPh_4]$ [1.394(9) Å; L–L′ = 1,3-(dioxan-2-ylmethyl)diphenylphosphine],[19] and also in the closely related complex $[Ru(C_5Me_5)(O_2)(dppe)][PF_6]$ [1.398(5) Å].[20] All these distances are longer than in the free O_2 molecule, but shorter than in the ionic peroxide anion (1.49 Å). The Ru–O bond lengths are 2.028(9) and 2.021(9) Å, corresponding to a symmetrical arrangement of the dioxygen ligand, very similar to that found for $[Ru(C_5Me_5)(O_2)(dppe)][PF_6]$,[19] also having similar values for the Ru–O distances. The distance from Ru to the centroid of the C_5Me_5 ring is 1.921 Å, the methyl substituents being displaced away from the ring plane in the opposite direction to the metal centre. No bands in the IR spectrum can be unequivocally assigned to vibrational modes of the O_2 ligand, owing to overlapping with bands due to C_5Me_5, dippe and the $[BPh_4]^-$ counterion.

Table 3 Atomic fractional coordinates for $[Ru(C_5Me_5)(O_2)(dippe)][BPh_4]$

Atom	x	y	z
Ru	0.101 48(6)	0.052 91(5)	0.983 30(6)
P(1)	0.129 1(2)	−0.031 1(2)	1.104 4(2)
P(2)	0.172 6(2)	0.119 3(2)	1.100 0(3)
O(1)	0.212 4(5)	0.063 4(6)	0.916 5(6)
O(2)	0.184 6(6)	−0.000 7(5)	0.906 3(7)
C(3)	0.011 1(9)	0.022 3(7)	0.860(1)
C(4)	−0.034(1)	0.025 6(8)	0.950(1)
C(5)	−0.029 4(8)	0.090 4(7)	0.989(1)
C(6)	0.017 0(8)	0.129 6(7)	0.919(1)
C(7)	0.043 0(9)	0.085 9(7)	0.842(1)
C(8)	0.021(1)	−0.036(1)	0.792(1)
C(9)	−0.089 0(9)	−0.030 6(7)	0.986(1)
C(10)	−0.086 6(9)	0.117 3(8)	1.066(1)
C(11)	0.019(1)	0.205 5(8)	0.918(1)
C(12)	0.092(1)	0.106 7(7)	0.755(1)
C(20)	0.198 3(9)	0.001 3(8)	1.197(1)
C(21)	0.247(1)	0.060(1)	1.154(1)
C(51)	0.830 7(8)	0.129 2(7)	0.433(1)
C(52)	0.813(1)	0.193 8(6)	0.398(1)
C(53)	0.773(1)	0.205 8(8)	0.311(1)
C(54)	0.751(1)	0.154(1)	0.252(1)
C(55)	0.766(1)	0.090 0(8)	0.282(1)
C(56)	0.807(1)	0.080 7(7)	0.369(1)
C(61)	0.922 4(8)	0.043 3(7)	0.538 1(8)
C(62)	1.005 0(8)	0.033 4(6)	0.514(1)
C(63)	1.040 1(9)	−0.030 3(8)	0.506(1)
C(64)	0.992(1)	−0.087 3(7)	0.525(1)
C(65)	0.912(1)	−0.078 0(8)	0.548(1)
C(66)	0.877(1)	−0.014 1(7)	0.555(1)
C(71)	0.940 5(8)	0.179 0(6)	0.561(1)
C(72)	0.999 6(8)	0.197 3(6)	0.492(1)
C(73)	1.058(1	0.247 9(8)	0.509(2)
C(74)	1.057(1)	0.282 0(8)	0.597(1)
C(75)	1.001(1)	0.267 8(7)	0.664(1)
C(76)	0.943(1)	0.216 9(6)	0.648(1)
C(81)	0.806 9(8)	0.117 0(6)	0.627(1)
C(82)	0.726 2(9)	0.139 3(7)	0.618(1)
C(83)	0.670 3(8)	0.138 6(6)	0.696(1)
C(84)	0.694(1)	0.117 1(7)	0.788(1)
C(85)	0.774(1)	0.092 1(9)	0.799(1)
C(86)	0.826 0(9)	0.094 1(7)	0.722(1)
C(100)	0.182(1)	−0.106 0(7)	1.058(1)
C(101)	0.135(1)	−0.136 9(7)	0.975(1)
C(102)	0.273(1)	−0.098 3(9)	1.039(1)
C(110)	0.045(1)	−0.064 6(7)	1.179(1)
C(111)	0.070(1)	−0.122(1)	1.250(1)
C(112)	−0.002(1)	−0.008(1)	1.234(1)
C(200)	0.232(2)	0.190(1)	1.053(2)
C(201)	0.247(2)	0.200(2)	0.960(2)
C(202)	0.294(1)	0.219(1)	1.125(2)
C(220)	0.116(1)	0.151 7(7)	1.207(1)
C(221)	0.071(1)	0.216 0(8)	1.187(1)
C(222)	0.164(1)	0.157(1)	1.302(1)
B	0.876(1)	0.117 6(8)	0.541(1)

Table 4 Selected bond distances (Å) and angles (°) for $[Ru(C_5Me_5)(O_2)(dippe)][BPh_4]$

Ru–P(1)	2.407(3)	Ru–C(4)	2.31(1)
Ru–P(2)	2.377(4)	Ru–C(5)	2.25(1)
Ru–O(1)	2.028(9)	Ru–C(6)	2.24(1)
Ru–O(2)	2.021(9)	Ru–C(7)	2.25(1)
Ru–C(3)	2.31(1)	O(1)–O(2)	1.37(1)
P(1)–Ru–P(2)	80.8(1)	P(2)–Ru–O(1)	79.4(3)
P(1)–Ru–O(1)	102.6(3)	P(2)–Ru–O(2)	109.9(3)
P(1)–Ru–O(2)	82.1(3)	P(2)–Ru–C(3)	160.7(3)
P(1)–Ru–C(3)	115.6(4)	P(2)–Ru–C(4)	136.5(4)
P(1)–Ru–C(4)	98.4(4)	P(2)–Ru–C(5)	104.2(4)
P(1)–Ru–C(5)	112.6(4)	P(2)–Ru–C(6)	100.0(4)
P(1)–Ru–C(6)	149.8(4)	P(2)–Ru–C(7)	128.0(4)
P(1)–Ru–C(7)	151.1(4)	O(1)–Ru–O(2)	39.6(4)

Complex **3** is remarkably stable, it being impossible to remove co-ordinated O_2 either thermally, or by substitution using ligands such as CO or MeCN. Therefore, the co-ordination of dioxygen must be regarded as irreversible, as has been found for other Ru–O_2 complexes.[1,19] The formation of the dioxygen adduct $[Ru(C_5Me_5)(O_2)(dippe)]^+$ drives the equilibrium in equation (1) to the right. However, this does not seem to be the case for the cyclopentadienylruthenium derivative, since the dioxygen complex $[Ru(C_5H_5)(O_2)(dippe)]^+$ has not been isolated nor detected. However, it has been possible to prepare other cationic derivatives containing neutral ligands including ethylene, N_2 and H_2 using $AgBF_4$ as halide scavenger. These and others will be reported elsewhere.[21]

The reaction of **1** and **2** with $SnCl_2$ in CH_2Cl_2 yields the complexes derived from the insertion of $SnCl_2$ into the Ru–Cl bond, namely $[Ru(C_5H_5)(SnCl_3)(dippe)]$ **4** and $[Ru(C_5Me_5)(SnCl_3)(dippe)]$ **5**. The related iron complex $[Fe(C_5H_5)(SnCl_3)(dippe)]$ has been obtained recently by the same method,[4] although no characterizable product was obtained from the reaction between $[Fe(C_5Me_5)Cl(dippe)]$ and $SnCl_2$ in CH_2Cl_2. Other half-sandwich trichlorostannyl–ruthenium complexes are also known.[22,23] Compounds **4** and **5** are orange or yellow-orange crystalline materials, which exhibit similar NMR spectral properties. The $^{31}P-\{^1H\}$ NMR spectra for both compounds consist of one singlet with small satellites due to coupling with the NMR-active nuclei ^{117}Sn and ^{119}Sn. The ^{119}Sn NMR spectra display one triplet, as expected for one ^{119}Sn coupled to two equivalent phosphorus atoms. Again, a 'three-legged piano stool' geometry is expected for complexes **4** and **5**, according to spectral data. The formation of these insertion derivatives is consistent with the lability of the chloride ligand in the starting complexes **1** and **2**. However, it has been found that the dissociation of either chloride or phosphine is not really necessary for the formation of insertion derivatives. The fact that the reaction of $SnCl_2$ with the chiral complex $[Ru(C_5H_5)Cl(dppp)]$[22] proceeds with net retention of configuration at the metal centre shows that, at least in this case, there is no need for dissociation. According to this an associative mechanism, involving the formation of a tight ion pair, has been proposed for this type of reaction.

Experimental

All synthetic operations were performed under a dry dinitrogen atmosphere following conventional Schlenk techniques, unless otherwise stated. Tetrahydrofuran, diethyl ether and light petroleum (b.p. 40–65 °C) were distilled from the appropriate drying agents. All solvents were deoxygenated immediately before use. 1,2-Bis(diisopropylphosphino)ethane,[24] $[Ru(C_5H_5)Cl(PPh_3)_2]$[6] and $[\{Ru(C_5Me_5)(\mu_3\text{-}Cl)\}_4]$[10] were prepared according to literature methods. The IR spectra were recorded in Nujol mulls on a Perkin-Elmer 881 spectrophotometer; NMR spectra were taken on Varian Unity 400 MHz or Varian Gemini 200 MHz instruments. Chemical shifts are given in ppm relative to $SiMe_4$ (^1H and $^{13}C-\{^1H\}$), 85% H_3PO_4 ($^{31}P-\{^1H\}$) or $SnBu^n_4$ (^{119}Sn). The phosphine protons for all the compounds appeared in the corresponding ^1H NMR spectra as a series of overlapping multiplets in the range δ 1–3, and were not assigned. Microanalyses were by Dr. Manuel Arjonilla at the CSIC-Instituto de Ciencias Marinas de Andalucía.

[1,2-Bis(diisopropylphosphino)ethane]chloro(cyclopentadienyl)ruthenium(II) [Ru(C_5H_5)Cl(dippe)] 1

The complex [Ru(C_5H_5)Cl(PPh_3)$_2$] (0.74 g, *ca.* 1 mmol) was dissolved in toluene (25 cm^3), and dippe (0.3 cm^3, 1 mmol) was added. The mixture was heated under reflux for 2 h and then allowed to cool and taken to dryness. An orange-brown oil was obtained. It was dissolved in the minimum amount of pentane, and passed through a silica gel chromatographic column, in order to remove triphenylphosphine. This can be done in the air. The column was eluted with light petroleum–diethyl ether (3:1, v/v). The fraction corresponding to the orange band was collected. The solvent of the orange solution was removed *in vacuo*, leaving orange crystals of complex **1**, the purity of which were checked by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy, and found to be high enough for synthetic purposes. Analytically pure samples were obtained by recrystallisation from diethyl ether–light petroleum. Yield: essentially quantitative (Found: C, 49.5; H, 8.00. $C_{19}H_{37}ClP_2Ru$ requires C, 49.2; H, 8.00%). NMR ($CDCl_3$): ^{1}H, δ 4.63 (s, C_5H_5); ^{31}P-{^{1}H}, δ 93.52 (s); ^{13}C-{^{1}H}, δ 18.68, 19.75, 19.95, 20.58 {s, P[CH(CH_3)$_2$]}, 22.68 (m, PCH_2), 25.32 {m, P[CH(CH_3)$_2$]}, 29.40 {m, P[CH(CH_3)$_2$]} and 76.10 (s, C_5H_5).

[1,2-Bis(diisopropylphosphino)ethane]chloro(pentamethylcyclopentadienyl)ruthenium(II) [Ru(C_5Me_5)Cl(dippe)] 2

To [{Ru(C_5Me_5)(μ_3-Cl)}$_4$] (0.66 g, *ca.* 0.6 mmol) in dichloromethane (20 cm^3), dippe (0.75 ml, *ca.* 2.5 mmol) was added. A deep red solution was obtained and was stirred at room temperature for 30 min. Then the solvent was removed *in vacuo*, and an orange-brown crystalline product was obtained. It was dissolved in diethyl ether, and the solution filtered if necessary. Addition of light petroleum, concentration and cooling to −20 °C afforded orange-brown crystals. Yield: 1.2 g, 91% (Found: C, 53.9; H, 8.80. $C_{24}H_{47}ClP_2Ru$ requires C, 54.0; H, 8.80%). NMR [(CD_3)$_2$CO]: ^{1}H, δ 1.58 [s, $C_5(CH_3)_5$]; ^{31}P-{^{1}H}, δ 80.07 (s); ^{13}C-{^{1}H}, δ 11.12 [s, $C_5(CH_3)_5$], 19.26, 19.57, 19.79 {s, P[CH(CH_3)$_2$]}, 22.57 (t, J_{CP} = 21.4, PCH_2), 28.79 {t, J_{CP} = 9.4, P[CH(CH_3)$_2$]}, 29.23 {t, J_{CP} = 21 Hz, P[CH(CH_3)$_2$]} and 87.82 [s, $C_5(CH_3)_5$].

[1,2-Bis(diisopropylphosphino)ethane](dioxygen)(pentamethylcyclopentadienyl)ruthenium(II) tetraphenylborate [Ru(C_5Me_5)(O_2)(dippe)][BPh_4] 3

Complex **2** (0.5 mmol) was dissolved in MeOH in the air. Addition of an excess of solid Na[BPh_4] (0.3 g) produced a golden brown precipitate, which was filtered, washed with ethanol and light petroleum and dried *in vacuo*. The product was dissolved in acetone, and the solution filtered. Addition of ethanol, concentration and cooling to −20 °C afforded brown crystals, suitable for X-ray crystal structure analysis. Yield: 83% (Found: C, 64.9; H, 7.80. $C_{48}H_{67}BO_2P_2Ru$ requires C, 65.1; H, 7.60%). NMR ($CDCl_3$): ^{1}H, δ 1.57 [s, $C_5(CH_3)_5$]; ^{31}P-{^{1}H}, δ 75.14 (s); ^{13}C-{^{1}H}, δ 10.30 [s, $C_5(CH_3)_5$], 18.18, 19.23, 19.41, 19.78 {s, P[CH(CH_3)$_2$]}, 20.40 (t, J_{CP} = 19.7, PCH_2), 24.59 {t, J_{CP} = 9.4, P[CH(CH_3)$_2$]}, 27.39 {t, J_{CP} = 15 Hz, P[CH(CH_3)$_2$]} and 106.51 [s, $C_5(CH_3)_5$].

[1,2-Bis(diisopropylphosphino)ethane](cyclopentadienyl)(trichlorostannyl)ruthenium(II) [Ru(C_5H_5)($SnCl_3$)(dippe)] 4

An excess of $SnCl_2$ (0.2g) was added to **1** (0.23 g, *ca.* 0.5 mmol) in CH_2Cl_2 (20 cm^3) and the mixture was stirred at room temperature for 2 h and a yellow solution was obtained. This was centrifuged and the solvent removed *in vacuo*. A yellow, microcrystalline solid was obtained, which was washed with light petroleum and dried *in vacuo*. This compound can be recrystallized from dichloromethane–light petroleum. Yield: quantitative (Found: C, 34.5; H, 5.80. $C_{19}H_{37}Cl_3P_2RuSn$ requires C, 34.3; H, 5.65%). NMR ($CDCl_3$): ^{1}H, δ 4.96 (s, C_5H_5); ^{31}P-{^{1}H}, δ 93.46 (s, with ^{117}Sn/^{119}Sn satellites, $J_{^{117}SnP}$ = 373, $J_{^{119}SnP}$ = 389 Hz); ^{13}C-{^{1}H}, δ 19.54, 19.63, 20.12, 20.20 {s, P[CH(CH_3)$_2$]}, 23.37 (t, J_{CP} = 20, PCH_2), 31.49 {t, J_{CP} = 10, P[CH(CH_3)$_2$]}, 35.06 {t, J_{CP} = 14 Hz, P[CH(CH_3)$_2$]} and 77.10 (s, C_5H_5); ^{119}Sn, δ −24.474 (t, J_{SnP} = 390 Hz).

[1,2-Bis(diisopropylphosphino)ethane](pentamethylcyclopentadienyl)(trichlorostannyl)ruthenium(II) [Ru(C_5Me_5)($SnCl_3$)(dippe)] 5

This complex was obtained following a procedure analogous to that for compound **3**, starting from **2** in dichloromethane. The

Table 5 Summary of data for the crystal structure analysis of **2** and **3**[a]

Compound	**2**	**3**
Formula	$C_{24}H_{47}ClP_2Ru$	$C_{48}H_{67}BO_2P_2Ru$
M	534.11	849.88
Crystal size/mm	0.13 × 0.18 × 0.45	0.30 × 0.55 × 0.45
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)
a/Å	9.401(2)	16.210(8)
b/Å	17.444(4)	20.067(6)
c/Å	8.636(2)	13.687(5)
α/°	90.17(2)	—
β/°	111.93(2)	—
γ/°	83.03(2)	—
U/Å^3	1303(1)	4452(5)
Z	2	4
D_c/g cm^{-3}	1.362	1.268
μ(Mo-Kα)/cm^{-1}	8.20	4.50
F(000)	2080	1944
Range of transmission coefficients	0.92–1.00	0.84–1.00
Scan speed ω/° min^{-1}	8	16
Unique reflections (R_{int})	4921 (0.142)	3313 (0.079)
Observed reflections ($I > 3\sigma_I$)	3636	2382
R[b]	0.044	0.048
R' ($w = \sigma_F^{-2}$)[c]	0.054	0.060
S[d]	1.85	2.12

[a] Details in common: T = 290 K; λ(Mo-Kα) = 0.710 69 Å; range 2θ/° 5–45. [b] $R = ||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] $S = \Sigma[(|F_o| - |F_c|)/\sigma]/(n - p)$ where n is the number of observations and p the number of parameters.

complex was obtained as an orange microcrystalline solid, in essentially quantitative yield (Found: C, 39.5; H, 6.80. $C_{24}H_{47}Cl_3P_2RuSn$ requires C, 39.8; H, 6.50%). NMR ($CDCl_3$): ^1H, δ 1.92 [s, $C_5(CH_3)_5$]; $^{31}P-\{^1H\}$, δ 79.75 (s, with $^{117}Sn/^{119}Sn$ satellites, $J_{^{117}SnP} = 365$, $J_{^{119}SnP} = 380$ Hz); $^{13}C-\{^1H\}$, δ 11.89 [s, $C_5(\mathit{C}H_3)_5$], 19.15, 19.78, 20.24, 20.63 {s, $P[CH(\mathit{C}H_3)_2]$}, 22.03 (t, $J_{CP} = 19.6$, PCH_2), 26.68 {t, $J_{CP} = 8.5$, $P[\mathit{C}H(CH_3)_2]$}, 40.69 {t, $J_{CP} = 14.1$ Hz, $P[\mathit{C}H(CH_3)_2]$} and 91.48 [s, $\mathit{C}_5(CH_3)_5$]; ^{119}Sn, δ −43.37 (t, $J_{SnP} = 381$ Hz).

Experimental data for the X-ray crystal structure determinations

A summary of crystallographic data for compounds **2** and **5** is given in Table 5. X-Ray measurements were made on crystals of the appropriate size, which were mounted onto a glass fibre, and transferred to an AFC6S-Rigaku automatic diffractometer, using Mo-Kα graphite-monochromated radiation. Cell parameters were determined from the settings of 25 high-angle reflections. Data were collected by the ω–2θ scan method. Lorentz, polarization and absorption (ψ-scan method) corrections were applied. Three standard reflections were intensity controlled, in order to establish a decay correction. Decay was negligible during data collection for compound **3**, but a deterioration correction was applied in the case of compound **2** (0.55%). Reflections having $I > 3\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution and refinement were carried out on a VAX 3520 computer at the Servicio Central de Ciencia y Tecnología de la Universidad de Cádiz, using the TEXSAN[25] software system and ORTEP[26] for plotting. All the structures were solved by the Patterson method, and anisotropically refined by full-matrix least-squares methods for all non-hydrogen atoms. All hydrogen atoms were included at idealised positions and not refined. The thermal parameters for C(22) in compound **2**, and for C(202) in compound **3** evidence some disorder at these isopropyl groups, but it was not possible to solve it. Maximum and minimum peaks in the final Fourier-difference maps were +0.62 and +1.11 e Å^{-3} for **2**, and +0.68 and −0.71 e Å^{-3} for **3**. Atomic coordinates and selected bond lengths and angles for each compound are listed in Tables 1–4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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