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Journal of Organometallic Chemistry 663 (2002) 127–133
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Reaction of $Cp^*RuCl(PPh_3)_2$ with dioxygen and formation of a neutral complex $Cp^*RuCl(O_2)(PPh_3)$

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Received 24 May 2002; accepted 25 September 2002

This paper is dedicated to Professor Pascual Royo with our best wishes for his 65th birthday

Abstract

Reaction of $Cp^*RuCl(PPh_3)_2$ (**1**) with atmospheric oxygen occurs at room temperature in the presence of acetone or methylene chloride leading to $Cp^*RuCl(O_2)(PPh_3)$ (**2**). This complex is remarkably stable in the solid state and it can also release, under not unduly harsh conditions, the activated oxygen molecule, which can oxidize the phosphite L = MeOP[$(OCHMe)_2CH_2$] to the corresponding phosphate, along with formation of the mono- and disubstituted $Cp^*RuCl(PPh_3)(L)$ (**5**), $Cp^*RuCl(L)_2$ (**6**) and $[Cp^*RuCl(PPh_3)(L)_2]Cl$ (**7**), complexes. Structural information of phosphite derivatives **5** and **6** has been obtained by X-ray diffraction.

Keywords: Dioxygen; Ruthenium neutral complexes; $Cp^*RuCl(PPh_3)_2$

1. Introduction

During studies directed towards the replacement of one triphenylphosphine in $Cp^*RuCl(PPh_3)_2$ (**1**) [1], we have made some interesting observations regarding the facile oxidation of compound **1** with atmospheric oxygen. Surprisingly, there has not been reports in the literature about how easily it goes to the corresponding oxidized compound $Cp^*RuCl(O_2)(PPh_3)$ (**2**).

The substitution of one or two triphenylphosphines in compound **1** has been carried out with a variety of ligands, where both, the effect on their corresponding steric strain and electron density have been analyzed [2].

The formation of analogue complexes with bidentate ligands, such as the coordinatively unsaturated species $[Cp^*Ru(P–P)]^+$ afforded, in the presence of oxygen, complexes of the type $[Cp^*Ru(O_2)(L\text{-}L)]^+$ (L-L = dppe [3,4], dppm [4], dippe [5] or $Me_2NCH_2CH_2NMe_2$ [6]. These oxygenated cationic complexes can be easily formed, and everything indicates that the dioxygen binding is irreversible.

A few examples containing a neutral dioxygen complex have been published: $Cp^*Ru(PPh_3)(C{\equiv}CR)(O_2)$, including the dioxygen molecule as a ligand, has been briefly mentioned by Bruce in the preparation of chiral ruthenium acetylides, by removal of the chlorine atom from $Cp^*Ru(CCHR)Cl(PPh_3)$ in a methanolic solution and adding excess of NaOMe [7]; the neutral peroxo compound $Cp^*Ru(O_2)[\eta^3\text{-}CH_2C(Me)CHC(Me)O]$ (**3**) [8], without PPh_3 as a ligand, and the synthesis and structural characterization of $RuCl(NO)(O_2)(PPh_3)_2$ [9] and $[Ru(H)(O_2)(dippe)_2]^+$ [10] in which the ligand Cp^* is not present. Finally, the isoelectronic rhodium complex $Cp^*Rh(PPh_3)(O_2)$ has been observed at low temperature [11].

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0022-328X/02/$ - see front matter
PII: S0022-328X(02)01978-2

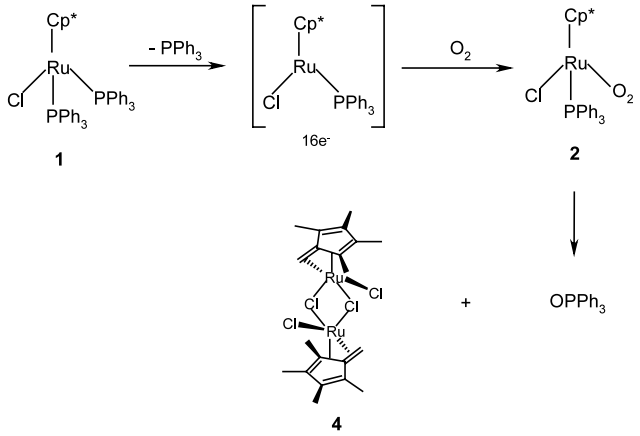
It has been reported that the $(Cp^*RuCl_2)_n$ complex reacts rapidly, in less than 5 min, with O_2 in air in $CHCl_3$ solution to give $(Cp^*RuCl_2)_2O$ and the molecular structure of the oxo complex was obtained, previously stabilized by dibenzothiophene [12]. Preliminary reactivity studies show that $(Cp^*RuCl_2)_2O$ reacts with excess PPh_3 to give $Ph_3P{=}O$, $Cp^*RuCl(PPh_3)_2$, and other unidentified metal complexes. We now know, that one of those unidentified species is compound **2**. The C–H cleavage in $(Cp^*RuCl_2)_n$ leads to the η^6-tetramethylfulvene complex $[(\eta^6\text{-}C_5Me_4CH_2)RuCl_2]_2$ (**4**); the μ-oxo complex $(Cp^*RuCl_2)_2O$ is an intermediate, which spontaneously transforms into **4** with loss of water [13].

Also, activation of the Cp* ligand to give the aldehyde $[\eta^5\text{-}C_5Me_4CHO]Ru[\eta^5\text{-}CH_2C(Me)CHC(Me)O]$ had been previously observed after heating compound **3** [8], which supports that oxygen-promoted cleavage of a CH to take place. The same behavior, described by Maitlis, occurs with conspicuous facility in Cp^*Ru^{III} complexes [13]. In the electrochemical study of the formation of compound **3**, the proposed mechanism is initiated by a fast one-electron transfer reaction, allowing the oxidation of a Ru^{II} into a Ru^{III} complex [14], which is a reactive intermediate between the formation of Ru^{IV} from Ru^{II} [14,15].

The reactivity of compound **2** in front of a cyclic phosphite $L = (MeO)P[(OCHMe)_2CH_2]$, was explored, giving evidence of an easy release of O_2 and formation of mono- and disubstituted products $Cp^*RuCl(PPh_3)(L)$ (**5**), $Cp^*RuCl(L)_2$ (**6**) and $[Cp^*Ru(PPh_3)(L)_2]Cl$ (**7**), along with the corresponding cyclic phosphate $(MeO)OP[(OCHMe)_2CH_2]$.

2. Results and discussion

Exposure of acetone solutions of $Cp^*RuCl(PPh_3)_2$ (**1**) to air produced a brown solution from which the dioxygen neutral monosubstituted chiral complex $Cp^*RuCl(O_2)(PPh_3)$ (**2**) was isolated (Scheme 1). The



Scheme 1.

^{31}P-NMR spectrum [$\delta = 39.7$ (s)] of the reaction mixture showed that the only product of the reaction is **2**. Similar results were obtained when pure oxygen gas, instead of air, was used. Compound **2** was also produced when chloroform or methylene chloride solutions of **1** were exposed to air. However, **2** decomposes faster in these solvents (4 h). The yields of **2** from the oxidation reactions appear to be solvent dependent.

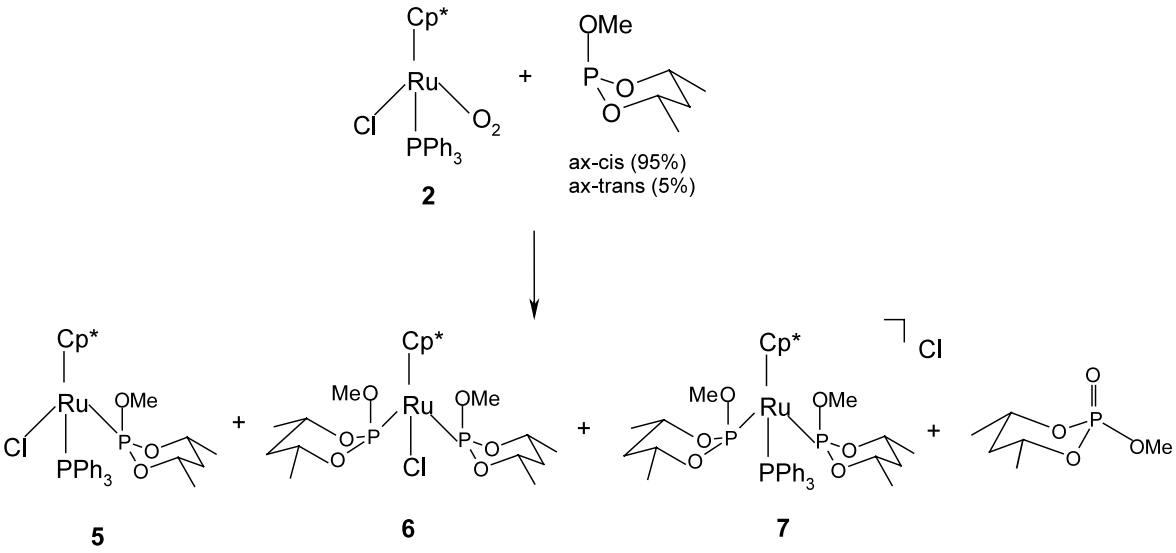
Several attempts to get suitable crystals from acetone, chloroform and methylene chloride solutions failed due to the low stability of **2** in solution, recovering in some cases crystals of **1**, as a result of partial dissociation of O_2 and PPh_3 from decomposition of compound **2**, suggesting the presence of the μ-oxo complex $(Cp^*RuCl_2)_2O$ [13] in the reaction mixture.

Compound **2** is presumably formed by displacement of PPh_3 in **1** with O_2, as indicated by monitoring the reaction with ^{31}P-NMR spectroscopy.

A plausible mechanism for the formation of **2** is shown in Scheme 1, which involves a 16 e^- intermediate formed and oxygen completing the 18 e^- complex **2**. Subsequent activation of C–H in the Cp* by the coordinated ruthenium–dioxygen complex **2**, as previously described for a neutral peroxo compound $Cp^*Ru(O_2)[\eta^3\text{-}CH_2C(Me)CHC(Me)O]$ (**3**) [8], gives a fulvene **4**, which in the case of compound **3** continues reacting until it produces the aldehyde compound $[\eta^5\text{-}C_5(Me_4)CHO]Ru[\eta^5\text{-}CH_2C(Me)CHC(Me)O]$ [8]. The ^1H-NMR of **4**, product of the reactivity of compound **2** in solution, is quite complex [16], as previously described by Maitlis for the mixture of tetramethylfulvenes in $[(C_5Me_4CH_2)RuCl_2]_2$ (**4**) [13].

As already mentioned, compound **2** is much more stable in acetone, than in chloroform, methylene chloride, or benzene (partially soluble). However, in all solvents, if compound **2** remains in solution sometime (vide supra), the final products are $OPPh_3$ and the fulvene derivative **4**, except in presence of the phosphite ligand $MeOP[(OCHMe)_2CH_2]$. Interestingly, when **2** is in $CDCl_3$, in the presence of one equivalent of the phosphite ligand, there is no evidence of decomposition of compound **2**, even after 24 h. Once the phosphite is consumed giving the monosubstituted compound $Cp^*RuCl(PPh_3)[MeOP(OCHMe)_2CH_2]$ (**5**) and the disubstituted phosphite compounds $Cp^*RuCl[MeOP(OCHMe)_2CH_2]_2$ (**6**) and $\{Cp^*RuCl(PPh_3)[MeOP(OCHMe)_2CH_2]_2\}Cl$ (**7**), there is clear evidence of quick consumption of compound **2**, giving $OPPh_3$ and the isomers of fulvene complex **4**.

Replacement of the dioxygen ligand in compound **2** occurred under phosphite $L = (MeO)P[(OCHMe)_2CH_2]$ (mixture of *cis*- and *trans-axial* isomers in a ratio 95:5, respectively) addition, in 1:2 and 1:5 ratios, respectively, to give the chiral and prochiral compounds $Cp^*RuCl(PPh_3)(L)$ (**5**), $Cp^*RuCl(L)_2$ (**6**) and $[Cp^*RuCl(PPh_3)(L)_2]^+$ (**7**) (Scheme 2). The half-sandwich compounds **5**



Scheme 2.

and **6** were obtained as yellow crystalline solids in 18 and 73% yield, respectively. Compound **5** was obtained in low yield, due to the formation of the disubstituted phosphite compounds **6** and **7** (vide infra), even when the synthesis was carried out with less than two equivalents of L. Compound **5** can be separated from **6** and **7**, by column chromatography and by solubility, respectively. Structures of **5**, **6** and **7** have been established by ^{1}H-, ^{13}C-, ^{31}P-NMR, mass spectrometry and those of **5** and **6** by single-crystal X-ray diffraction studies. The crystal data are described in Table 1. Compounds **5** and **6** have a piano-stool structure that contains η^5-pentamethylcyclopentadienyl ring, a chlorine ligand and the phosphine and phosphite or two phosphites, respectively, bonded to ruthenium through phosphorus. An ORTEP representation is shown in Figs. 1 and 2. Atom positional parameters are given in Tables 2 and 3.

As already observed from **7**, the reaction also promotes halide ionization and the eventual generation of [Cp*Ru(PPh$_3$)L$_2$]Cl as deduced from ^{31}P-NMR, δ ($CDCl_3$) = 149.5 (d, 15.3 Hz), 16.7 (t, 15.3 Hz). The isolation of compound **7** as a strong yellow solid was possible after exchanging the counterion Cl^- for BF_4^- in methylene chloride. The excess of phosphite is required in order to get shorter reaction times, and it is interesting to comment that only the *cis*-axial isomer reacts. The easy formation of the phosphate MeOOP[(OCHMe)$_2$CH$_2$] (^{31}P δ ($CDCl_3$) = −5) is clear from ^{31}P-NMR through the corresponding oxidation of the ax-*cis*-phosphite [^{31}P ($CDCl_3$, ppm): δ = 128.83 (ax-*cis*, 95%), 133.13 (ax-*trans*, 5%)], as well as formation of compound **5** [^{31}P ($CDCl_3$, ppm): δ = 49.5 (d, 79.8), 151.5 (d, 79.2)]. If a larger excess of phosphite ligand is used, formation of compound **6** is preferred [^{31}P ($CDCl_3$, ppm): δ = 152.5 (s)], along with evidence of oxidation of some phosphite ligands. Also, formation of **7** competes in the reaction mixture, and this product can be isolated preferentially if, at least, a 1:3 ratio of **2**–phosphite is used. Finally, it was observed that replacement of dioxygen ligand in **2** for CO gave the well-known Cp*RuCl(PPh$_3$)(CO) [1b] and Cp*RuCl(CO)$_2$ complexes [17].

Table 1
Crystal data for compounds **5** and **6**

	5	**6**
Empirical formula	$C_{34}H_{43}ClO_3P_2Ru$	$C_{22}H_{41}ClO_6P_2Ru$
Molecular weight	698.14	600.01
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	12.0272 (10)	16.273 (3)
b (Å)	15.6258 (10)	21.001 (4)
c (Å)	17.5719 (10)	16.197 (3)
α (°)	90.00	90.00
β (°)	94.62 (2)	92.74 (3)
γ (°)	90.00	90.00
V (Å^3)	3291.6 (4)	5529.0 (18)
Z	4	8
Crystal size (mm)	0.22 × 0.17 × 0.15	0.32 × 0.16 × 0.16
Absorption coefficient (mm^{-1})	0.687	0.812
D_{calc} (g cm^{-3})	1.409	1.442
Scan type	$\omega/2\theta$	$\omega/2\theta$
Data	6882	10 106
Unique data	6665	9725
Variables	370	579
Observed data, $F > 4\sigma(F)$	3369	6293
Final R_1	0.0622	0.0459
Final wR_2	0.1428	0.1283

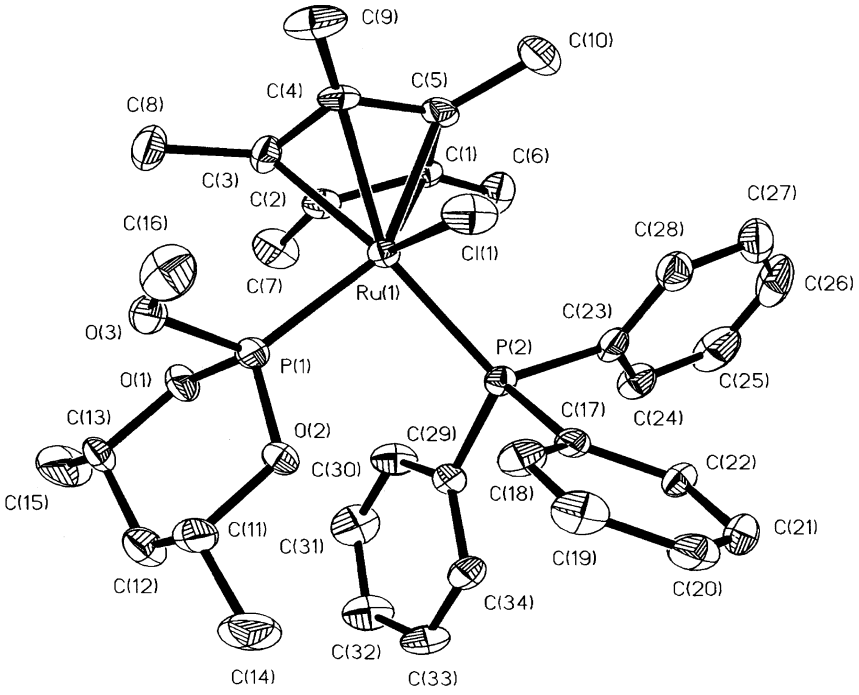


Fig. 1. Molecular structure of $Cp^*RuCl(PPh_3)[MeOP(OCHMe)_2CH_2]$ (**5**).

3. Conclusions

The steric strain between the two bulky triphenylphosphine ligands together with the high electron density localized at the ruthenium center result in the ready dissociation of one triphenylphosphine ligand from **1**, which in the presence of air yields compound **2**. The dioxygen ligand can be coordinated and uncoordinated with relative facility, as already demonstrated by the formation of chiral compounds **2** and **5**. Complex **5** can undergo a second substitution of the remaining bulky triphenylphosphine ligand. The preference of the co-

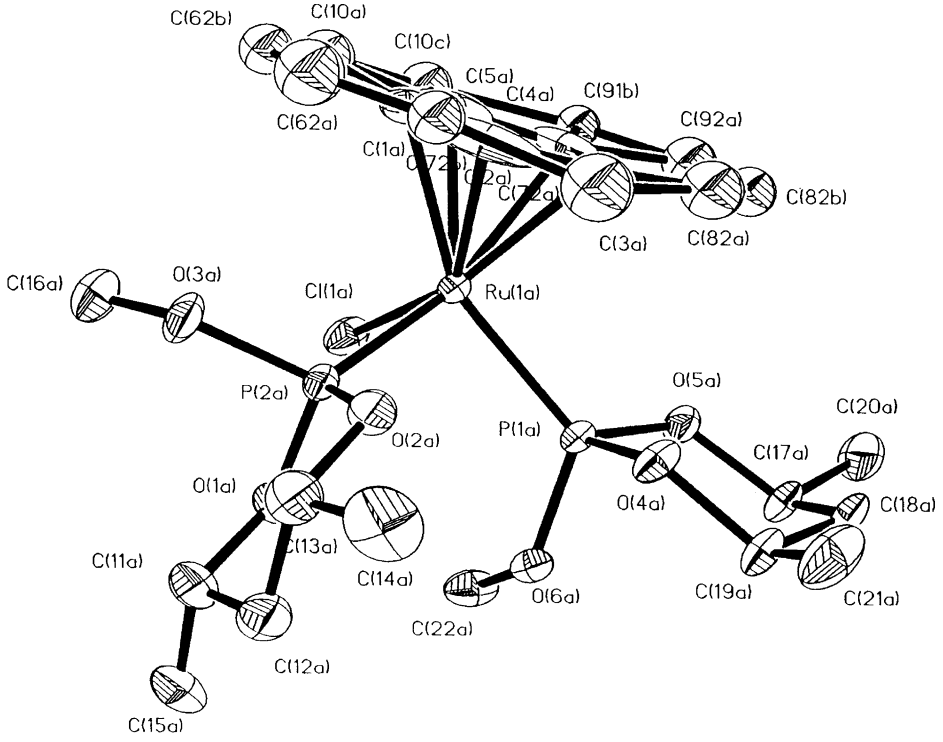


Fig. 2. Molecular structure of $Cp^*RuCl[MeOP(OCHMe)_2CH_2]_2$ (**6**).

Table 2
Selected bond lengths (Å) and bond angles (°) for compound **5**

Bond lengths			
Ru–P1	2.205(2)	Ru–Cl	2.427(2)
Ru–P2	2.322(2)	P1–O1	1.604(6)
Ru–C1	2.287(7)	P1–O2	1.606(6)
Ru–C2	2.243(7)	P1–O3	1.623(6)
Ru–C3	2.235(8)	O1–C13	1447(10)
Ru–C4	2.228(8)	O2–C11	1.442(10)
Ru–C5	2.264(8)	O3–C16	1.430(11)
C1–C2	1.451(11)	P2–C17	1.867(7)
C2–C3	1.457(12)	P2–C23	1.825(8)
C3–C4	1.407(12)	P2–C29	1.834(9)
C4–C5	1.444(12)	C5–C10	1.517(12)
C1–C6	1.379(11)	C19–C18	1.356(11)
Bond angles			
P1–Ru–C4	115.6(3)	C4–Ru–P2	154.2(3)
P1–Ru–C3	90.3(2)	C3–Ru–P2	152.0(2)
C4–Ru–C3	36.8(3)	C5–Ru–P2	1117.1(2)
P1–Ru–C2	100.3(2)	C3–Ru–Cl	119.2(3)
C3–Ru–C2	38.0(3)	C4–Ru–Cl	87.4(2)
C4–Ru–C2	62.7(3)	P1–Ru–Cl	100.41(9)
P1–Ru–C5	151.3(2)	P2–Ru–Cl	88.19(8)
C4–Ru–C5	37.5(3)	C3–Ru–P2	152.0(2)
C3–Ru–C5	61.5(3)	C4–Ru–P2	154.2(3)
C2–Ru–C5	61.5(3)	C2–Ru–Cl	148.9(2)
P1–Ru–C1	136.6(2)	C5–Ru–Cl	89.9(2)
P1–Ru–P2	90.14(8)	O1–P1–Ru	114.3(2)

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **6**

Bond lengths			
Ru1A–C2A	2.149(8)	Ru–C2	2.199(6)
Ru1A–C3A	2.172(7)	Ru–C1	2.171(7)
Ru1A–C1A	2.193(10)	Ru–C3	2.234(6)
Ru1A–P2A	2.206(2)	Ru–C4	2.243(7)
Ru1A–P1A	2.2146(15)	Ru–C5	2.263(7)
Ru1A–C4A	2.222(7)	Ru–Cl	2.432(2)
Ru1A–C5A	2.234(10)	P1–O1	1.603(4)
Ru1A–Cl1A	2.440(2)	P1–O2	1.599(4)
P2A–O2A	1.584(4)	P2–O4	1.584(4)
P2A–O1A	1.595(4)	P2–O6	1.625(4)
P2A–O3A	1.618(4)	P1A–O5A	1.601(4)
P1A–O4A	1.591(4)	P1A–O6A	1.622(4)
Bond angles			
C2A–Ru1A–C3A	38.3(5)	C1–Ru–C2	37.5(3)
C2A–Ru1A–C1A	34.3(6)	C1–Ru–P2	109.6(3)
C3A–Ru1A–C1A	59.6(4)	C1–Ru–P1	102.8(2)
C2A–Ru1A–P2A	95.8(3)	P1–Ru–P2	90.05(6)
C3A–Ru1A–P2A	125.4(4)	C2–Ru–P1	136.8(3)
C1A–Ru1A–P2A	101.4(5)	C1–Ru–C3	61.9(3)
C2A–Ru1A–P1A	120.5(5)	C2–Ru–C3	37.8(3)
C3A–Ru1A–P1A	94.0(2)	P1–Ru–C3	157.42(2)
C1A–Ru1A–P1A	152.9(5)	C2–Ru–C4	61.6(3)
P2A–Ru–P1A	88.90(6)	P1–Ru–C4	121.6(3)
O1–P1–O2	102.7(2)	P2–Ru–Cl	93.79(6)
O5–P2–Ru	118.9(2)	P1–Ru–Cl	93.57(6)

ordination of the phosphite indicates that this ligand is sterically less demanding and a better π ligand than the triphenylphosphine.

Conversion of **2** to the tetramethylfulvene derivative **4** and $OPPh_3$ is achieved simply by dissolution of **2**. Further developments in the chemistry of **2** will be based on its reactivity trends.

4. Experimental

4.1. General procedures

All reactions were performed under a nitrogen atmosphere, except those for compound **2**, in reagent grade solvents using Schlenk techniques. THF was distilled from Na–benzophenone, while acetone and CH_2Cl_2 were dry from $CaSO_4$ and CaH_2, respectively. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on JEOL GSX-270, JEOL Eclipse-400 or Bruker 300 spectrometers using deuterated solvents and Me_4Si and H_3PO_4 (85%) as internal and external references, respectively, in $CDCl_3$ at ambient temperature. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. Mass spectra were measured on a Hewlett Packard HP-5990A (EI, 70 eV), Finigan MAT 95 (FAB) and at the Washington University (MALDI-MS). IR spectra were measured on a Perkin–Elmer/6FPC-FT spectrophotometer using KBr. Melting points were recorded on compounds in sealed nitrogen-filled capillaries and are uncorrected.

$Cp^*RuCl(PPh_3)_2$ [1e], *axial*-2-methoxi-4,6-dimethyl-1,3,2-λ^3-dioxaphosphorinanes [18] were prepared by literature methods.

4.2. Preparation of $Cp^*RuCl(O_2)(PPh_3)$ (2)

4.2.1. Chloro(dioxygen)(η^5-pentamethylcyclopentadienyl)(triphenylphosphine)ruthenium(IV)

a) A dry acetone solution (60 ml) containing 520 mg of compound **1** (0.65 mmol) was bubbled with pure O_2 during 45 min. The initial orange–yellow solution turn brown–orange and finally brown. The brown precipitate is filtered and the solid washed twice with acetone and dry under vacuum. After reducing the volume of the acetone solution, more brown solid is obtained, giving 261 mg (0.46 mmol, 71%) of compound **2**. M.p. 124–125 °C, ^{1}H-NMR ($CDCl_3$): δ 1.34 (d, $J = 1.47$ Hz, 15H, Cp*), 7.28–7.85 (m, 30H, PPh_3). ^{31}P-NMR: δ 39.70 (s). ^{13}C-NMR: δ 131.40 (d, $J = 9.9$ Hz, o), 131.39 (s, p), 127.91 (d, $J = 12.1$ Hz, m) 104.7 (s, Cp*), 7.91 (s, Cp*), MS: 531 $[M-Cl]^+$(50), 515 $[M-Cl-O]^+$(100), 499 $[M-Cl-O_2]^+$ (24). IR ($CHCl_3$,

cm^{-1}): 926. Anal. Found: C, 59.61; H, 5.28. Calc. for $C_{28}H_{30}ClO_2PRu$: C, 59.49; H, 5.31%.

b) A CH_2Cl_2 solution (15 ml) containing 200 mg of compound **1** (0.25 mmol) was bubbled with air (20 ml syringe) and stirring during 60 min. The initial orange solution turn brown–red. After reducing the volume of the CH_2Cl_2 solution, hexane is added and brown–red needles precipitate giving after filtration, 100 mg (0.18 mmol, 71%) of compound **2**.

*4.3. Preparation of Cp*RuCl(PPh$_3$)[MeOP(OCHMe)$_2$CH$_2$] (**5**)*

4.3.1. Chloro(2-methoxi-4,6-dimethyl-1,3,2-λ^3-dioxaphosphorinane)(η^5-pentamethylcyclopentadienyl)-(triphenylphosphine)ruthenium(II)

Compound **2** (143 mg, 0.25 mmol) in THF (20 ml) gave a brown solution after addition, at room temperature (r.t.) of 0.1 ml (0.66 mmol) of the mixture of phosphite isomers. After heating under reflux for 1 h, the color of the solution changed from dark-brown to bright-yellow. The bright-yellow solution was evaporated under vacuum and the fraction soluble in Et_2O was chromatographed under silica with Et_2O–hexane (2/8) affording two yellow bands. The first band gave yellow needles of compound **5** (32 mg, 0.05 mmol, 18.3% yield) after reducing volume and adding hexane and maintaining this solution at −15 °C. The second fraction correspond to compound **6** which precipitates from hexane at −15 °C in 3.3% yield (15.2 mg, 0.03 mmol). Compound **5**: M.p. 169–172 °C, ^{1}H-NMR ($CDCl_3$): δ 0.53 (d, $J = 6.2$ Hz, Me4), 1.20 (d, $J = 6.4$ Hz, Me6), 1.56 (m, H5a,b), 1.34 (d, $J = 1.8$ Hz, Cp*), 3.57 (d, $J = 11.3$ Hz, OMe), 4.52 (m, H4) (4.22, m, H6), 7.56–7.68 (m, 30H, PPh_3). ^{31}P-NMR: δ 49.5 (d, $J = 79.8$ Hz, PPh_3), 151.5 (d, $J = 79.2$ Hz, phosphite). ^{13}C-NMR: δ 21.54 (d, $J = 6.2$ Hz, Me4), 22.47 (d, $J = 7.7$ Hz, Me6), 70.1 (d, $J = 8.8$ Hz, C4), 41.62 (s, C5), 68.7 (d, $J = 8.0$ Hz, C6), 51.67 (s, OMe), 91.68 (s, Cp*), 9.58 (s, Cp*), 126.9 (d, $J = 8.5$ Hz, Cm), 128.5 (s,Cp), 132.1 (d, $J = 9.2$ Hz, Co), 135.0 (s,Ci). MS: 548 (2), 436 $[M-PPh_3]^+$ (7), 332 (5), 301 (3), 236 (7), 262 (100). Anal. Found: C, 58.79; H, 6.40. Calc. for $C_{34}H_{43}ClO_3P_2Ru$: C, 58.49; H, 6.16%.

*4.4. Preparation of Cp*RuCl[MeOP(OCHMe)$_2$CH$_2$]$_2$ (**6**)*

4.4.1. Chloro-bis-(2-methoxi-4,6-dimethyl-1,3,2-λ^3-dioxaphosphorinane)(η^5-pentamethylcyclopentadienyl)-ruthenium(II)

Compound **2** (60 mg, 0.11 mmol) in THF (10 ml) gave a brown solution after addition, at r.t. of 80 μl (0.53 mmol) of the mixture of phosphite isomers. After heating under reflux for 15 min, the color of the solution changed from dark-brown to yellow–brown. The reaction mixture was stirred 1 h at r.t. and filtered. The light-yellow solution was evaporated under vacuum and the fraction soluble in Et_2O was chromatographed under silica with Et_2O–hexane (2/8) affording compounds **5** and **6**. Recrystallization of **6** in C_5H_{12} at r.t. gave 47 mg (0.08 mmol, 71% yield). M.p. 116–119 °C, ^{1}H-NMR ($CDCl_3$): δ 1.21 (dd, $J = 6.3$, 4.6 Hz, Me4, Me6), 1.38 (m, 2H, H5), 1.65 (s, Cp*), 3.62, t, $J = 5.7$ Hz, OMe), 4.52 (m, H4, H6). ^{31}P-NMR: δ 152.5 (s). ^{13}C-NMR: δ 9.5 (s, Cp*), 15.23 (s, C4α, C6α, Me), 65.8 (s, C4, C6, CH), 41.9 (d, 3.8 Hz, C5, CH_2), 51.83 (s, OMe), 92.73 (s, Cp*). MS: 600 $[M]^+$(83), 436 $[M-L2]^+$(100), 332 (52), 300 (13), 236 (63). Anal. Found: C, 44.39; H, 7.22. Calc. for $C_{22}H_{41}ClO_6P_2Ru$: C, 44.03; H, 6.83%.

*4.5. Preparation of {Cp*Ru(PPh$_3$)[MeOP(OCHMe)$_2$CH$_2$]$_2$]BF$_4$ (**7**)*

4.5.1. Bis(2-methoxi-4,6-dimethyl-1,3,2-λ^3-dioxaphosphorinane)(η^5-pentamethylcyclopentadienyl)-(triphenylphosphine)ruthenium(II)tetrafloroborate

Compound **2** (180 mg, 0.32 mmol) in THF (20 ml) gave a brown solution after addition, at r.t. of 0.16 ml (1.1 mmol) of the mixture of phosphite isomers. After heating under reflux for 15 min, the color of the solution changed from dark-brown to bright-yellow. The yellow solution was evaporated under vacuum and the fraction soluble in Et_2O was removed. The solid insoluble in Et_2O was dissolved in $CHCl_3$ and hexane was added for precipitation at −15 °C, affording an oily residue which under vacuum gives a bright yellow powder, but at r.t. remains as a oily solid **7-Cl** in 38.3% (105 mg, 0.12 mmol). Compound **7-Cl** (100 mg, 0.12 mmol) in CH_2Cl_2 (15 ml) gave a yellow solution after addition, at r.t. of $AgBF_4$ (22.6 mg, 0.12 mmol) in CH_2Cl_2 (2 ml). Immediately a white precipitated of AgCl was observed. After stirring for 5 min, the solid was filtered and the solution evaporated until 5 ml, and adding hexane. The filtration of the yellow precipitate gave 50 mg (0.05 mmol, 47.2% yield) of compound **7**. M.p. 136–138 °C. ^{1}H-NMR ($CDCl_3$): δ 1.2 (m, Me4, Me6), 1.5 (s, br, Cp*, H5), 3.5 (t, 5.7 Hz, OMe), 4.8 (m, H4, H6). ^{11}B-NMR ($CDCl_3$): δ −1.3. ^{31}P-NMR($CDCl_3$): δ 16.7 (t, $J = 15.3$ Hz, PPh_3), 149.5 (d, $J = 15.3$ Hz, phosphite). ^{13}C-NMR: δ 9.85 (s, Cp*), 22.50 (s, C4α, C6α, Me), 70.00 (s, C4, C6, CH), 41.80 (d, 3.8 Hz, C5, CH_2), 52.20 (s, OMe), 91.90 (s, Cp*), 130.72 (10.40, C*m*), 134.60 (d, 12.50, C*p*), 136.20 (s, C*o*), n.o. (C*i*).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 186379 and 186378 for compounds **5** and **6**. Copies of the information may be obtained free

of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ca.uk or www: http://www.ccdc.cam.ac.uk). Structural comparison of **5** and **6** with analogous molecules are described in the supplementary material.

Acknowledgements

This work was supported by grants from Conacyt. The authors also acknowledge Conacyt for financial support in the acquisition of the X-ray diffractometer (No. F0084) and project 26352-E. Thanks to Washington University Mass Spectrometry Research Resource (NIH, No. P41RR0954) for recording the mass spectra and Marco Antonio Leyva and Ma. Luisa Rodriguez for helping us with some X-ray diffraction studies and NMR spectra, respectively.

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[16] ^{1}H-NMR showed signals for CH_2: doublets at 6.15 (2.1 Hz), 6.08 (2.0 Hz) and singlets at 5.98, 5.24, 5.23, 5.20, 5.13, 4.82, 4.66 ppm. The signals for methyl groups observed were more (underline) than those observed and described by Maitlis, et al. at: *1.41*, 1.44, 1.46, 1.48, 1.50, 1.52, *1.54*, 1.64, 1.65, 1.68, 1.70, *1.79*, 1.81, 1.84, 1.86, *1.88*, *1.91*, *1.96*, 2.17, *2.20*, 2.26, 2.31, *2.36*.

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