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Synthesis and derivative chemistry of $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-cymene})_2]^+$

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Abstract

The cationic diphenylphosphido-bridged compound $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (**2**) has been prepared by reaction of the tri-μ-hydroxo complex $[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (**1**) with diphenylphosphine. Complex **2** eliminates water on reaction with protic acids, incorporating the conjugate base of the added acid as a bridging ligand. Formic acid, acetic acid, phenol, and aniline react with **2** to give the monosubstituted compounds $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}L)(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (L = HCO_2, $MeCO_2$, OPh, or NHPh), whereas methanol, thiophenol, 1,2-benzenedithiol, hydrochloric acid and isopropanol afford the disubstituted derivatives $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}L)_2(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (L = OMe, SPh, 1/2 $S_2C_6H_4$, Cl, or H).

Key words: Ruthenium; Arene; Phosphide; Bridging ligand

1. Introduction

The synthesis of neutral phosphido-bridged transition-metal complexes has been extensively developed in the last 20 years and the study of their derivative chemistry has allowed the preparation of many compounds with interesting structures and chemical reactivities. The large number of such neutral compounds contrasts with the very few cationic phosphido-bridged derivatives reported to date [1–3]; in fact, as far as we are aware, only two cationic phosphido-bridged derivatives of ruthenium have been reported, namely $[Ru_2(\mu\text{-}PPh_2)(CO)_8]^+$ [1] and $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]^+$ [2].

This paper describes the synthesis of a new series of cationic diphenylphosphido-bridged ruthenium complexes containing no carbonyls. As the starting material, we have chosen the tri-μ-hydroxo-arenerutheniun(II) complex $[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (**1**) [4], a compound which contains labile hydroxo groups that can be easily replaced by the conjugate bases of protic acids [5,6]. This approach has allowed us to prepare the diphenylphosphido-bridged complex $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (**2**) and to study its reactivity with protic acids whose conjugate bases are potential anionic bridging ligands.

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2. Results and discussion

2.1. Preparation of $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (2)

The complex $[Ru_2(\mu\text{-}OH)_3(\eta\text{-}^6\text{-}p\text{-cymene})_2][PF_6]$ (**1**) reacted with diphenylphosphine in dichloromethane at room temperature to give the diphenylphosphido-bridged derivative $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ (**2**) (Scheme 1) quantitatively. This synthetic method has been previously used to prepare pyrazolato-bridged areneruthenium(II) complexes [6].

Complex **2** was characterized by analytical and spectroscopic methods. Its IR spectrum (Nujol mull) clearly shows a ν(OH) absorption at 3567 cm^{-1}, and its solution ^1H and $^{31}P\{^1H\}$ NMR spectra (Table 1) exhibit the characteristic resonances of the organic ligands, indicating the presence of a plane of symmetry which contains both ruthenium atoms, as expected if there were free rotation of the arene ligand [7].

Since each ruthenium atom in complex **1** is a coordinatively saturated 18-electron species, the mild conditions under which the transformation of **1** into **2** takes place suggest that the reaction mechanism should involve the protonation of a bridging hydroxo-ligand and the displacement of the water formed by the diphenylphosphido group.

All attempts to make the bis(diphenylphosphido-bridged) derivative $[Ru_2(\mu\text{-}PPh_2)_2(\mu\text{-}OH)(\eta^6\text{-}p\text{-cy-}$

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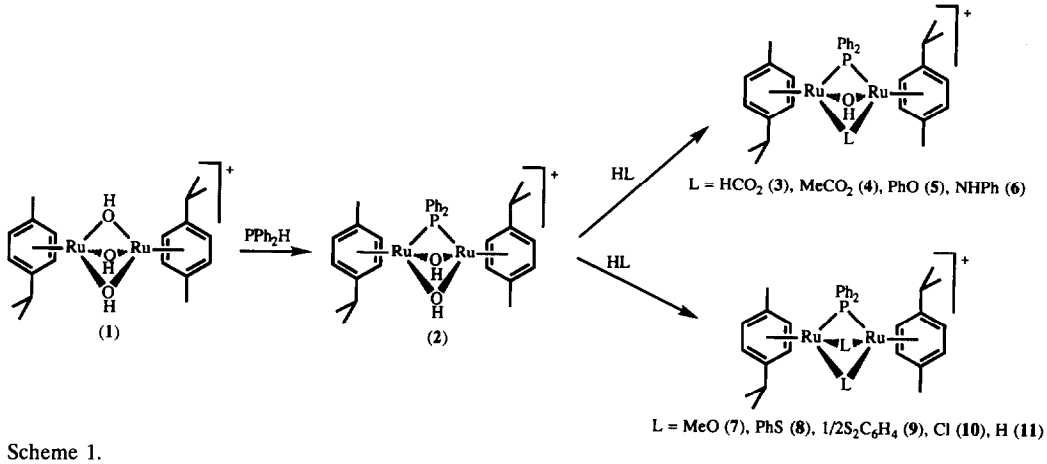


Scheme 1.

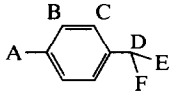
mene)$_2$][PF_6] failed, even using an excess of diphenylphosphine and higher temperatures. The low acidity of diphenylphosphine and the size of the diphenylphosphido group may account for the observed results.

2.2. *Monosubstituted derivatives of complex 2*

The reaction of complex **2** with formic or acetic acid in acetone-water at room temperature resulted in the compounds $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}RCO_2)(\eta^6\text{-}p\text{-}cy$-

TABLE 1. Selected NMR data

Compound	$\delta(H^1)$ [a]					$\delta(^{31}P\{^1H\})$ [a]
	A	B, C	D	E, F	Others [b]	
2 [c]	1.70 (s)	5.21 (s)	1.92 (sp, 6.9)	0.84 (d, 6.9)	1.26 (d, 7.0 (OH)	6.70 (s)
3 [c]	1.78 (s)	5.54 (d, 5.9), 5.23 (d, 5.8), 4.87 (d, 5.9), 4.64 (d, 5.8)	2.67 (sp, 6.8)	1.13 (d, 6.8), 1.07 (d, 6.8)	1.36 (br) (OH) [d]	−12.65 (s)
4 [e]	1.78 (s)	5.32 (d, 6.0), 5.08 (d, 5.5), 4.94 (d, 6.0), 4.58 (d, 5.5)	2.53 (sp, 6.8)	1.10 (d, 6.8), 1.07 (d, 6.8)	1.83 (s) (O_2CMe), 1.27 (br) (OH)	−8.44 (s)
5 [c]	1.59 (s)	5.24 (d, 5.8), 5.11 (d, 5.5), 4.86 (d, 5.8), 4.77 (d, 5.5)	1.78 (sp, 7.0)	0.78 (d, 7.0), 0.67 (d, 7.0)	3.75 (s) (OH)	16.82 (s)
6 [c]	1.69 (s)	5.50 (d, 5.9), 5.39 (d, 5.8), 5.05 (d, 5.8), 4.98 (d, 5.9)	2.17 (sp, 6.9)	0.87 (d, 6.9), 0.82 (d, 6.9)	[f]	9.59 (s)
7 [c]	1.71 (s)	5.18 (d, 5.8), 5.07 (d, 5.8)	2.39 (sp, 6.9)	1.03 (d, 6.9)	4.36 (s) (OMe)	3.61 (s)
8 [c]	1.92 (s)	5.45 (d, 5.4), 5.27 (d, 5.4)	2.06 (sp, 6.6)	0.78 (d, 6.6)		−25.0 (br)
9 [c]	1.83 (s)	5.11 (s)	2.03 (sp, 6.7)	0.82 (d, 6.7)		−30.89 (s)
10 [g]	1.74 (s)	5.73 (s)	2.14 (sp, 6.9)	0.92 (d, 6.9)		16.13 (s)
11 [c]	1.86 (s)	5.81 (d, 6.1), 5.77 (d, 6.1)	2.33 (sp, 7.0)	1.08 (d, 7.0)	−14.96 (d, 29.7) (μ-H)	117.21 (s)



[a] Multiplicity and coupling constants (Hz) in parentheses. [b] Excluding aromatic protons. [c] In $CDCl_3$. [d] The formate proton was not observed, probably because it overlaps with the aromatic protons. [e] In $CDCl_3$-C_6D_6 (3:1). [f] NH and OH protons not observed. [g] In $(CD_3)_2CO$.

mene)$_2$][PF_6] (R = H (**3**) or Me (**4**)) (Scheme 1). The low acidity of phenol and aniline may explain why the addition of these reagents to THF solutions of complex **2** at room temperature resulted in little or no reaction, even after a few hours; however, the monosubstituted derivatives [$Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}L)(\eta^6\text{-}p\text{-}cymene)_2$][$PF_6$] (L = PhO (**5**) or NHPh (**6**)) (Scheme 1) were easily obtained at reflux temperature. The use of an excess of formic acid, acetic acid, or phenol did not result in disubstituted products, whereas an excess of aniline produced a mixture of inseparable compounds.

The ^{1}H NMR spectra of these monosubstituted compounds (Table 1) are quite informative because not only do they exhibit the resonances of the added ligands, but they also clearly indicate that the metal atoms are chiral, as expected for monosubstituted derivatives (C_s symmetry), since they show the isopropyl methyls and the aromatic protons of the *p*-cymene group to be diastereotopic, giving rise to two doublets and two AB systems, respectively [7,8]. Their ^{31}P{^{1}H} NMR spectra are singlets, ranging from −12.65 ppm for complex **3** to 16.82 ppm for complex **5**; the low chemical shifts of these μ-PPh_2 resonances imply the absence of metal–metal bonds [9,10]. The vibrations of the OH groups can be observed in the IR spectra of all these compounds (see Experimental section).

Although there are two possible isomers for the aniline derivative **6** (the NH fragment may be pointing to the PPh_2 group or to the OH group), only one of them is observed. We think that the formation of a hydrogen bond between the nitrogen and the oxygen atoms should favour the isomer which allows this interaction.

2.3. Disubstituted derivatives of complex 2

Complex **2** reacted with methanol, thiophenol, 1,2-benzenedithiol, and hydrochloric acid to give the disubstituted derivatives [$Ru_2(\mu\text{-}PPh_2)(\mu\text{-}L)_2(\eta^6\text{-}p\text{-}cymene)_2$][$PF_6$] (L = MeO (**7**), PhS (**8**), 1/2 $S_2C_6H_4$ (**9**), or Cl (**10**)) (Scheme 1). The use of less than two equivalents of these reagents resulted in mixtures of the starting material **2** and the disubstituted compounds mentioned above, but in no case did we observe monosubstituted derivatives.

The IR spectra of compounds **7–10** do not show OH absorptions and the ^{1}H NMR spectra (Table 1) display, apart from the characteristic resonances of the added ligands, the aromatic and isopropyl methyls of the *p*-cymene groups as one AB system and one doublet, respectively, as expected for disubstituted derivatives (C_{2v} symmetry), indicating that the metal atoms are not chiral [7,8]. Again, the ^{31}P{^{1}H} NMR spectra consist of singlet resonances with low chemical shifts (Table 1).

The ^{31}P{^{1}H} NMR spectrum of the thiophenol derivative **8** merits some comments, since, unlike the other complexes, there is a very broad singlet (at −25.0 ppm) at room temperature. At −60°C, two sharp singlets are observed (at −13.3 and 31.8 ppm). These data indicate that a fluxional process that interconverts two isomers is taking place in solution at room temperature and that, at low temperature, the lifetime of each isomer is long on the NMR time scale. This fluxional process, which has been previously observed in other binuclear thiolato complexes [11], must be related to inversion at the pyramidal sulfur centre.

Secondary alcohols are useful sources of hydride ligands [8,12,13]. Consistent with this, thermolysis of complex **2** in refluxing isopropanol for 2 h afforded the dihydride [$Ru_2(\mu\text{-}PPh_2)(\mu\text{-}H)_2(\eta^6\text{-}p\text{-}cymene)_2$][$PF_6$] (**11**) as a black solid. Its IR spectrum shows no bands in the OH stretching region and its ^{1}H NMR spectrum is characteristic of a disubstituted compound (Table 1); it also shows the hydride ligand signals as a doublet at −14.96 ppm (J_{P-H} = 29.7 Hz). Its ^{31}P{^{1}H} NMR spectrum consists of a singlet at 117.21 ppm, indicating some metal–metal interaction [9,10], as expected for a 32-electron binuclear complex. The analogous dihydrido compound [$Ru_2(\mu\text{-}MeCO_2)(\mu\text{-}H)_2(\eta^6\text{-}C_6Me_6)_2$][$PF_6$], which contains a bridging acetato ligand in place of the phosphido-group, has been reported previously [13].

Further reactions of the complexes described here, including catalytic applications, are currently being investigated.

3. Experimental details

Solvents were dried and distilled under dinitrogen prior to use [14]. Compound **1** was prepared from [$Ru_2Cl_2(\mu\text{-}Cl)_2(\eta^6\text{-}p\text{-}cymene)_2$] [15], following the procedure described for the synthesis of the analogous osmium complex [$Os_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-}cymene)_2$][$PF_6$] [8]. All other reagents (reagent or analytical grade) were used as received from commercial suppliers. All reactions were carried out under dinitrogen using standard Schlenk techniques, although the products did not seem to be air-sensitive. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer FT 1720-X spectrophotometer. ^{1}H and ^{31}P{^{1}H} NMR spectra (Table 1) were run at 23°C with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ (^{1}H) or external 85% H_3PO_4 (^{31}P) as standards (δ = 0 ppm). Microanalyses were obtained by the University of Oviedo Analytical Service.

3.1. [$Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)_2(\eta^6\text{-}p\text{-}cymene)_2$][$PF_6$] (2)

Diphenylphosphine (61.4 mg, 0.330 mmol) was added dropwise to a dichloromethane solution (10 ml) of

complex **1** (200 mg, 0.300 mmol). The solution was stirred for 1 h at room temperature and then concentrated to *ca.* 3 ml. Addition of diethyl ether (10 ml) led to the precipitation of a dark yellow solid, which was washed with diethyl ether and dried under vacuum (234 mg, 93%). Anal. Found: C, 46.5; H, 4.9. $C_{32}H_{40}F_6O_2P_2Ru_2$ calc.: C, 46.0; II, 4.8%. IR: ν(OH) 3567s cm^{-1}.

3.2. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}HCO_2)(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (3)

A solution of formic acid (0.160 mmol) in water (10 ml) was added to a solution of complex **2** (100 mg, 0.120 mmol) in acetone (3 ml) and the mixture stirred at room temperature for 4 h. The acetone solvent was removed under vacuum and the aqueous suspension filtered, washed with water and air-dried. The yellow-orange solid was recrystallized from dichloromethane-diethyl ether (54.8 mg, 53%). Anal. Found: C, 46.5; H, 4.6. $C_{33}H_{40}F_6O_3P_2Ru_2$ calc.: C, 45.9; H, 4.6%. IR: ν(OH) 3567m, br; $\nu(CO_2)$ 1565s, 1378s cm^{-1}.

3.3. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}MeCO_2)(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (4)

This compound was prepared in 55% yield from complex **2** and acetic acid, using the synthetic procedure described above for compound **3**. Anal. Found: C, 46.7; H, 4.7. $C_{34}H_{42}F_6O_3P_2Ru_2$ calc.: C, 46.0; H, 4.8%. IR: ν(OH) 3597m; $\nu(CO_2)$ 1547m, 1462m cm^{-1}.

3.4. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}OPh)(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (5)

A solution of complex **2** (100 mg, 0.120 mmol) and phenol (14.1 mg, 0.150 mmol) in THF (20 ml) was stirred at reflux temperature for 4 h. The solution was taken to dryness and the residue redissolved in dichloromethane (3 ml). On addition of diethyl ether (10 ml) a yellow-brown precipitate was obtained. The supernatant liquid was decanted and the solid washed with diethyl ether and dried *in vacuo* (73 mg, 67%). Anal. Found: C, 50.7; H, 4.9. $C_{38}H_{43}F_6O_2P_2Ru_2$ calc.: C, 50.2; H, 4.8%. IR: ν(OH) 3558m; ν(OC) 1225s cm^{-1}.

3.5. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OH)(\mu\text{-}NHPh)(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (6)

This brown compound was prepared as complex **5**, except that **2** (200 mg, 0.240 mmol) and aniline (30 mg, 0.323 mmol) were used. Yield 136.4 mg, 63%. Anal. Found: C, 48.6; H, 4.9; N, 1.51. $C_{38}H_{44}F_6NOP_2Ru_2$ calc.: C, 50.2; H, 4.8; N, 1.5%. IR: ν(OH) 3536w; ν(NH) 3374w, br cm^{-1}.

3.6. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}OMe)_2(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (7)

A solution of complex **2** (100 mg, 0.120 mmol) in methanol (20 ml) was stirred for 2 h at a room temperature. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane (3 ml). On addition of diethyl ether, an orange microcrystalline precipitate was obtained. The solid was washed with diethyl ether and dried under vacuum (96.1 mg, 93%). Anal. Found: C, 47.7; H, 5.1. $C_{34}H_{44}F_6O_2P_2Ru_2$ calc.: C, 47.3; H, 5.1%. IR: ν(OC) 1024s cm^{-1}.

3.7. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}SPh)_2(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (8)

A solution of complex **2** (108 mg, 0.129 mmol) and thiophenol (31.3 mg, 0.280 mmol) in THF (10 ml) was stirred at reflux temperature for 4 h. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane (3 ml). On addition of diethyl ether a brown solid precipitated. The supernatant liquid was decanted and the solid recrystallized from dichloromethane-diethyl ether (103 mg, 18%). Anal. Found: C, 51.1; H, 4.7. $C_{44}H_{48}F_6P_2Ru_2S_2$ calc.: C, 51.7; H, 4.7%.

3.8. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}S_2C_6H_4)(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (9)

A solution of complex **2** (150 mg, 0.180 mmol) and 1,2-benzenedithiol (28 mg, 0.200 mmol) in THF (10 ml) was stirred at room temperature for 2 h. The solution was concentrated under reduced pressure to *ca.* 3 ml and pentane added to give a dark brown precipitate. The solid was washed several times with diethyl ether and recrystallized from dichloromethane-diethyl ether (159 mg, 94%). Anal. Found: C, 47.9; H, 4.5. $C_{38}H_{42}F_6P_2Ru_2S_2$ calc.: C, 48.5; H, 4.5%.

3.9. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}Cl)_2(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (10)

A 0.1 M solution of hydrochloric acid (2 ml, 0.200 mmol) was added to a solution of complex **2** (100 mg, 0.120 mmol) in a mixture of water (10 ml) and acetone (3 ml). The solution was stirred at room temperature for 4 h. The acetone solvent was removed under reduced pressure and the resulting orange suspension was filtered, washed with water, air-dried and recrystallized from dichloromethane-diethyl ether (89 mg, 85%). Anal. Found: C, 43.8; H, 4.7. $C_{32}H_{38}Cl_2F_6P_2Ru_2$ calc.: C, 44.1; H, 4.4%.

3.10. $[Ru_2(\mu\text{-}PPh_2)(\mu\text{-}H)_2(\eta^6\text{-}p\text{-}cymene)_2][PF_6]$ (11)

A suspension of complex **2** (314 mg, 0.376 mmol) in isopropanol (20 ml) was stirred at reflux temperature for 2 h. The dark brown solution was concentrated to *ca.* 3 ml and diethyl ether added to give a black precipitate, which was recrystallized from dichloro-

methane-diethyl ether (229 mg, 76%). Anal. Found: C, 47.4; H, 4.5. $C_{32}H_{40}F_6P_2Ru_2$ calc.: C, 47.9; H, 5.0%.

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