

CHELATING BEHAVIOUR OF BIS-(DIPHENYLPHOSPHINO)METHANE ON ARENE-RUTHENIUM COMPLEXES

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(Received September 25, 1992; Revised December 10, 1993)

ABSTRACT. The reaction of $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ or $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ with bis(diphenylphosphino)methane (dppm) in a mixture of methanol and dichloromethane in the presence of NH_4PF_6 or AgBF_4 , led to $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\text{dppm})]^+(\text{A})$ ($\text{A}=\text{PF}_6^-$ or BF_4^-) (1) or $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{dppm})]^+(\text{PF}_6^-)$ (2). The chelating behaviour of the ligand dppm and the non equivalent methylenic protons were evidenced by ^1H and ^{31}P NMR.

INTRODUCTION

Much of the chemistry of $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ and $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ is centred around the Ru-Cl bond. In polar solvent the chlorine is displaced by anionic or neutral ligands to give homoelectronic complexes or anionic moieties [1].

Stable species containing the dppm ligand could be obtained in the presence of a non co-ordinating anion such as hexafluorophosphate or tetrafluoroborate. This ligand is commonly used to bridge two metal atoms in forming stable binuclear or polynuclear complexes [2, 3]. Some complexes in which it is chelated have been described [4, 5]. In arene-ruthenium complexes, dppm acts as a monodentate or bridged ligand [1]. Thus, the cationic complex $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\text{dppm})]^+$ remains unknown. Although the analogous complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)(\text{dppm})]^+$ is obtained and characterised.

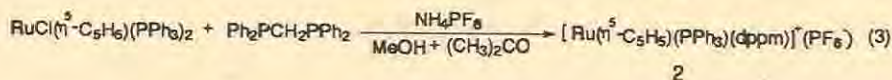
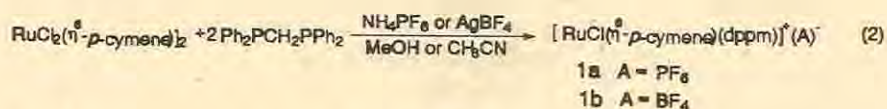
The chelating behaviour of bis-(diphenylphosphino)methane on arene-ruthenium complexes is reported herein.

RESULTS AND DISCUSSION

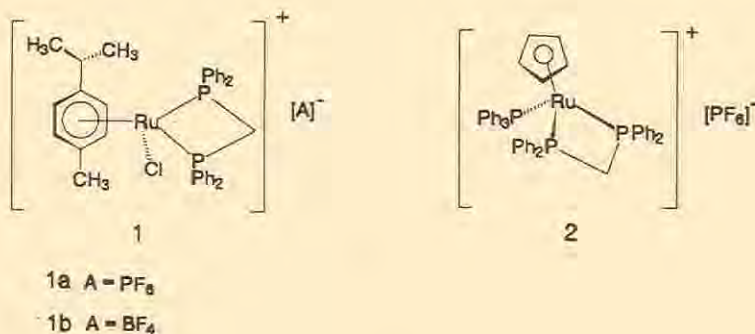
The formation of neutral complexes $\text{RuCl}_2(\eta^6\text{-arene})(\text{L})$ by reaction of a two-donor ligand with the complexes $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ is well known [7a, 7b] and happens with various ligands L. At room temperature a polar solvent (MeOH) is necessary to break the Ru-Cl bond and therefore the formation of an anionic moiety is favoured (Equation 1) [8].



The two-fold reaction of dppm with a binuclear complex $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})]_2$ or $\text{RuCl}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2$ in mixed solvent in the presence of NH_4PF_6 or AgBF_4 leads to derivatives of the type **1a**, **1b** and **2** containing one dppm chelated to the metal atom (Equations 2 and 3).



Complexes **1** and **2** were isolated in good yields, after addition of ether or hexane, as yellow (**1**) and green (**2**) microcrystalline solids which gave satisfactory analyses. They were fully characterised by IR, ^1H and ^{31}P NMR spectroscopy (Table 1).



The ^1H NMR spectra of (**1**) and (**2**) show, at room temperature, apart from the signals due to the arene and the cyclopentadienyl protons, two signals attributable to the two methylenic protons. The coupling of the methylenic protons with each other ($^2J_{\text{HH}} = 15.76$ Hz) and with the two nucleus phosphorus atoms results in an ABX_2 system corresponding to two doublet of triplets. Similar methylenic proton resonances have been reported earlier by Sherlock *et al.* [9]. However, the ^1H NMR spectrum of complex **2** shows an additional coupling of one of the methylenic protons with the phosphorus nuclei of the PPh_3 ligand ($^4J_{\text{PH}} = 1.39$ Hz) resulting in the splitting of each line of the doublet of triplets located at $\delta 4.3$. This shows the non equivalence of the methylenic protons of the dppm ligand chelated to the metal (Figure 1).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit a broad singlet in the range $\delta 2.5\text{-}3.5$ (**1**) and a doublet at $\delta 3$ for the phosphorus nucleus of the dppm, confirming that all the phosphorus atoms are linked to the metal. The phosphorus nuclei of the PPh_3 in complex (**2**) appears as a triplet at $\delta 49$ because of the coupling with dppm. The bands at 840 and 1055 cm^{-1} in the IR spectra of these complexes reveal the presence of PF_6^- and BF_4^- , respectively. These observations suggest that the complexes are cationic.

The present study of bis-(diphenylphosphino)methane-ruthenium(II) derivatives provides a new route to these complexes. We have also noted that attempts to link

more than one dpmm ligand to one metal atom were unsuccessful and led in all cases of stoichiometries to the ratio 1:1.

Table 1. ^1H and ^{31}P NMR* data of the arene-ruthenium and cyclopentadienyl-ruthenium complexes.

Complex		^1H NMR	^{31}P NMR
	<i>p</i> -cymene or cyclopentadienyl	dpmm or PPh ₃	
1a	5.99, AB, 4H, C ₆ H ₂ ($^3J_{\text{HH}}=6.30$) 2.40, <i>m</i> , 1H, CHMe ₂ 1.50, <i>s</i> , 3H, CH ₃ -Ar 1.10, <i>d</i> , 6H, (CH ₃) ₂ C ($^3J_{\text{HH}}=6.80$)	7.80-7.30, <i>m</i> , 20H, C ₆ H ₂ 4.90, <i>dt</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=15.20$, $^2J_{\text{PH}}=4.97$) 4.50, <i>dt</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=15.20$, $^2J_{\text{PH}}=2.43$)	2.78, <i>s</i> , PCH ₂ P
1b	6.49, AB, 4H, C ₆ H ₂ ($^3J_{\text{HH}}=6.43$) 2.50, <i>m</i> , 1H, CHMe ₂ 1.50, <i>s</i> , 3H, CH ₃ -Ar 1.01, <i>d</i> , 6H, (CH ₃) ₂ C ($^3J_{\text{HH}}=6.90$)	7.80-7.30, <i>m</i> , 20H, C ₆ H ₂ 5.60, <i>dt</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=15.76$, $^2J_{\text{PH}}=5.31$) 4.70, <i>dt</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=15.76$, $^2J_{\text{PH}}=2.63$)	3.17, <i>s</i> , PCH ₂ P
2	5.10, <i>s</i> , 5H, C ₅ H ₅	7.80-7.20, <i>m</i> , 35H, C ₆ H ₂ 5.50, <i>dt</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=13.93$, $^2J_{\text{PH}}=4.95$) 4.30, <i>m</i> , 1H, PCH ₂ P ($^2J_{\text{HP}}=13.93$, $^2J_{\text{PH}}=3.28$, $^4J_{\text{HP}}=1.39$)	49.33, <i>t</i> , PPh ₃ ($^2J_{\text{PP}}=35.47$) 2.02, <i>d</i> , PPh ₂ ($^2J_{\text{PP}}=35.47$)

* Solvent (CD₃)₂CO; 297 K; ^1H at 300.135 MHz and ^{31}P at 121.497 MHz. Resonances of PF₆⁻ anion are omitted.

EXPERIMENTAL

General: All reactions were carried out under nitrogen by Schlenk techniques. Solvent were dried by conventional methods. NMR spectra were recorded on Bruker AM300 spectrometer and elemental analyses were performed at the "Service de Microanalyses du CNRS" Vernaison France. The starting materials RuCl₃·3H₂O (Johnson-Matthey), triphenylphosphine and α -terpinene (Aldrich) were used without further purification. [RuCl₂(η^5 -*p*-MeC₆H₄CHMe₂)₂] was prepared according to published methods [7a] using α -terpinene instead of α -phellandrene. RuCl(η^5 -C₅H₅)(PPh₃)₂ was prepared following the method of Bruce *et al.* [10].

[RuCl(η^5 -*p*-MeC₆H₄CHMe₂)(Ph₂PCH₂PPh₂)](PF₆) (1a): In a typical run, [RuCl₂(η^5 -*p*-MeC₆H₄CHMe₂)₂] (0.5 g, 0.80 mmol), dpmm (0.65 g, 1.6 mmol) and NH₄PF₆ (0.27 g, 1.6 mmol) were stirred with 10 ml of MeOH and 40 ml of dichloromethane during 3 days at room temperature. The resulting yellow mixture was evaporated to dryness and the residue extracted with 20 ml of acetone. The extract was filtered and the yellow filtrate covered with a layer of 30 ml of diethyl ether. The yellow crystal resulting from the slow diffusion of ether were separated by decantation, washed twice with hexane and dried under vacuum (0.92 g; 71%).

Elemental analysis % calculated (% found): C 52.53 (53.31), H 4.50 (4.90), P 11.63 (10.14).

$[RuCl(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)(Ph_2PCH_2PPh_2)](BF_4)$ (**1b**): In a typical run, $[RuCl_2(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2]$ (0.13 g, 0.20 mmol), dppm (0.24 g, 0.6 mmol) and $AgBF_4$ (0.24 g, 1 mmol) were stirred with 20 ml of acetonitrile during four hours at room temperature. The resulting mixture was filtered, evaporated to dryness and the residue extracted with 10 ml of acetone. The extract was filtered and the filtrate reduced to 5 ml and covered with a layer of 40 ml of hexane. The resulting yellow crystal were separated by decantation, washed twice with hexane and dried under vacuum (0.16 g; 57%). *Elemental analysis* % calculated (% found): C 56.63 (56.32), H 4.8 (4.93), P 8.36 (8.65).

$[Ru(\eta^5\text{-C}_5\text{H}_5)(PPh_3)(Ph_2PCH_2PPh_2)](PF_6)$ (**2**)

In a typical run, $RuCl(\eta^5\text{-C}_5\text{H}_5)(PPh_3)_2$ (1 g, 1.4 mmol), dppm (0.58 g, 1.5 mmol) and NH_4PF_6 (0.26 g, 1.6 mmol) were stirred with 20 ml of methanol and 30 ml of acetone during three days at room temperature. The resulting yellow mixture was filtered and evaporated to dryness and the residue extracted with 10 ml of acetone. The extract was filtered and evaporated to dryness. The residue was washed several times with methanol to remove triphenylphosphine displaced by bis-(diphenylphosphino)-methane ligand. The resulting green powder was dried under vacuum (0.82 g, 62%).

Elemental analysis % calculated (% found): C 60.14 (60.75); H 4.38 (4.15); P 12.94 (12.30).

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