

Preliminary communication

**ATTACK OF TRIMETHYLPHOSPHITE UPON A η^6 -BENZENE
 LIGAND TO GIVE 2-6- η -1-*exo*-DIMETHOXYPHOSPHORYLCYCLO-
 HEXADIENYL(η^5 -ETHYLTETRAMETHYLCYCLOPENTADIENYL)-
 RHODIUM(III) HEXAFLUOROPHOSPHATE**

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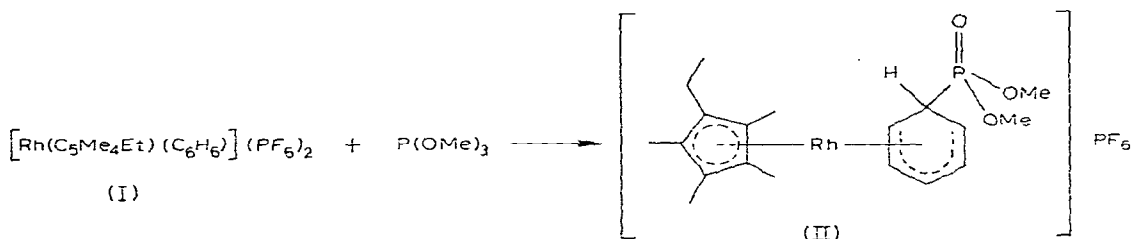
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Summary

The title compound has been prepared by reaction of trimethylphosphite with η^6 -benzene(η^5 -ethyltetramethylcyclopentadienyl)rhodium(III) hexafluorophosphate. IR and ^1H , ^{13}C and ^{31}P NMR spectra of the product are reported.

Although it has been recognised for many years that ligands coordinated to transition metal cations are susceptible to nucleophilic attack, there has been only one report of attack by phosphites upon coordinated ligands [1]. In this communication we report that trimethylphosphite reacts with η^6 -benzene-(η^5 -ethyltetramethylcyclopentadienyl)rhodium(III) hexafluorophosphate [2] to give 2-6- η -1-*exo*-dimethylphosphorylcyclohexadienyl(η^5 -ethyltetramethylcyclopentadienyl)rhodium(III) hexafluorophosphate in 72% yield.



Microanalysis of the yellow crystalline product is consistent with the proposed formulation (Found: C, 39.1; H, 4.8. $\text{C}_{19}\text{H}_{29}\text{F}_6\text{O}_3\text{P}_2\text{Rh}$ calcd.: C, 39.1; H, 5.0%). Integration of the ^1H NMR spectrum confirmed that only two methoxy groups were present and both the ^{13}C and ^1H NMR spectra were characteristic of a cyclohexadienyl compound (Table 1). Evidence that

TABLE 1

NMR DATA FOR $[\text{Rh}(\text{C}_5\text{Me}_4\text{Et})\{\text{C}_6\text{H}_6\text{P}(\text{O})(\text{OMe})_2\}]\text{PF}_6^a$

^1H NMR		$^{13}\text{C}\{^1\text{H}\}$ NMR		^{31}P NMR		
Assignment	δ (ppm)	Assignment	δ (ppm)	Assignment	δ (ppm)	
$\text{C}_5\text{Me}_4\text{Et}$	2.08(s), 2.10(s)	$\text{C}_5\text{Me}_4\text{Et}$	9.9,10.1	$\text{P}(\text{O})(\text{OMe})_2$	+20.3(s)	
$\text{C}_5\text{Me}_4\text{Et}$	1.11[t, $J(\text{CH}_3-\text{CH}_2)$ 7.5 Hz] 2.50(q)	$\text{C}_5\text{Me}_4\text{Et}$	14.5,19.2	PF_6	-144.3 (septet) $J(\text{F}-\text{P})$ 713 Hz	
H(2,6)	3.71 ^c	$\text{C}_5\text{Me}_4\text{Et}$	$\left\{ \begin{array}{l} 103.2(6)^b \\ 104.1(6)^b \\ 108.3(8)^b \end{array} \right.$			
H(3,5)	5.39(dd) $J(2,6-3,5)$ 5 Hz	C(2,6)		50.2(8) ^b		
H(4)	6.56(t) $J(3,5-4)$ 5 Hz	C(3,5)		95.4(3) ^b		
H(1,endo)	3.53 ^c	C(4)	92.3(6) ^b			
$\text{P}(\text{O})(\text{OMe})_2$	3.65(d) $J(\text{P}-\text{H})$ 10.5	C(1)	35.4(131) ^d			
		$\text{P}(\text{O})(\text{OMe})_2$	53.4(8) ^d			

^aRecorded in [^2H]chloroform; J quoted in Hz. ^b $J(^{13}\text{C}-^{103}\text{Rh})$. ^cSignal partly obscured. ^d $J(^{13}\text{C}-^{31}\text{P})$.

the phosphorus atom is directly bonded to the six-membered ring comes from the ^{13}C NMR spectrum ($J(^{31}\text{P}-^{13}\text{C}(1))$ 131 Hz) and the absence of rhodium coupling in the ^{31}P NMR spectrum. In addition to $\nu(\text{P}-\text{O})$ bands at 1025 and 1075 cm^{-1} , the IR spectrum (Nujol) contained a doublet at 1258 and 1266 cm^{-1} which is assigned to $\nu(\text{P}=\text{O})$. The doubling of the phosphoryl absorption peak probably arises from the presence of different spatial isomers [3].

Preliminary X-ray crystallographic studies support the proposed structure and have shown that the dimethoxyphosphoryl substituent occupies the *exo*-position [4].

It is suggested that the product (II) is formed by attack of trimethylphosphite upon the benzene complex (I) to give a phosphonium intermediate $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\{\eta^5\text{-C}_6\text{H}_6\text{P}(\text{OMe})_3\}](\text{PF}_6)_2$ which then undergoes a Michaelis-Arbuzov type elimination reaction. Compounds containing tertiary phosphite ligands coordinated to metal atoms have been reported to undergo similar elimination reactions [5,6,7]. Although we have not been able to detect a phosphonium intermediate we have observed that free benzene and $[\text{Rh}(\text{C}_5\text{Me}_4\text{Et})\{\text{P}(\text{OMe})_3\}_3](\text{PF}_6)_2$ are also present in the reaction mixture, indicating that attack at the metal centre is a competing but minor pathway in this reaction.

The reactions of the benzene compound $[\text{Rh}(\text{C}_5\text{Me}_4\text{Et})(\text{C}_6\text{H}_6)](\text{PF}_6)_2$ with other nucleophiles are being investigated.

Acknowledgements

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