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## First examples of $\eta^1$ -ligated halogenophosphaalkenes. Crystal structures of $trans$ -[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -PX=C(SiMe<sub>3</sub>)<sub>2</sub>}] (X = F or Cl)

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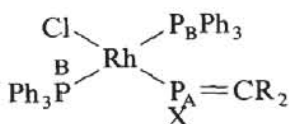
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### Abstract

Syntheses and single crystal X-ray diffraction studies of the  $\eta^1$ -halogenophosphaalkene complexes  $trans$ -[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -PX=C(SiMe<sub>3</sub>)<sub>2</sub>}] (X = F, Cl) are reported.

The field of coordination chemistry of compounds containing phosphorus–carbon multiple bonds is rapidly expanding and has been reviewed recently [1]. Although several  $\eta^1$ - and  $\eta^2$ -coordinated complexes of phosphalkenes RP=CR'<sub>2</sub> (R = Mes, R' = Ph; R = Xyl, R'<sub>2</sub> = Ph<sub>2</sub>; C<sub>12</sub>H<sub>8</sub>) have been reported, only one  $\eta^2$ -complex containing a ligated halogenophosphaalkene is known namely, [Ni(CO){ $\eta^2$ -P(Cl)=C(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub> (I) [2]. We now describe the preparation and structural characterisation of the first examples of  $\eta^1$ -complexes of halogenophosphaalkenes, namely  $trans$ -[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -PF=C(SiMe<sub>3</sub>)<sub>2</sub>}] (II) and  $trans$ -[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -P(Cl)=C(SiMe<sub>3</sub>)<sub>2</sub>}] (III).



(II, X = F;  
 III, X = Cl)

Treatment of a suspension of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] in toluene with one equivalent of PF=C(SiMe<sub>3</sub>)<sub>2</sub> (IV) [3] gave an orange solution from which orange crystals of II were isolated in quantitative yield. Similar treatment with P(Cl)=C(SiMe<sub>3</sub>)<sub>2</sub> (V) [4]

yielded III. Complexes II and III were identified from elemental analyses and multinuclear NMR studies\*.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of III exhibits the characteristic pattern of lines for a *trans*-square planar arrangement of ligands, with the phosphalkene phosphorus acting as a  $\sigma$ -donor. Its resonance appears 58 ppm upfield with respect to that of the free ligand (V). The value of the coupling constant  $^1J(\text{RhP}_A)$  (264 Hz) is characteristic of an  $\eta^1$ -ligated phosphalkene and is significantly larger than the corresponding value (218 Hz) found for *trans*-[RhCl(PPh<sub>3</sub>)<sub>2</sub>( $\eta^1$ -MesP=CPh<sub>2</sub>)] [5], reflecting the presence of the electronegative chlorine on the phosphorus.

Complex II shows a similar type of  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum to that of III together with additional coupling to the fluorine atom. The coordination chemical shift of the resonance from the ligated fluorophosphalkene is 45 ppm upfield with respect to that from free ligand. Interestingly the value of  $^1J(\text{PF})$  for III (1127 Hz) is the highest yet found for an  $sp^2$  hybridised phosphorus atom, and clearly indicates an increase in the *s*-character of the P–F bond on coordination.

The behaviour of phosphalkenes IV and V on Rh<sup>I</sup> contrasts with our recent observations on their reactions with olefin complexes of Ni<sup>0</sup> and Pt<sup>0</sup>, in which both  $\eta^2$ -coordination and oxidative addition reactions were observed [6]. Furthermore, whereas a decrease in the value of  $^1J(\text{PF})$  was observed in  $\eta^2$ -fluorophosphalkene complexes [Ni(PBu<sub>3</sub>)<sub>2</sub>{ $\eta^2$ -PF=C(SiMe<sub>3</sub>)<sub>2</sub>}] ( $^1J(\text{PF})$  872 Hz) and [Pt(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^2$ -PF=C(SiMe<sub>3</sub>)<sub>2</sub>}] ( $^1J(\text{PF})$  907 Hz) [6] with respect to that for PF=C(SiMe<sub>3</sub>)<sub>2</sub> ( $^1J(\text{PF})$  1090 Hz), the reverse effect was noted in the present work.

Confirmation of structures II and III was provided by single crystal X-ray diffraction studies\*\*.

The molecular structures of II and III, shown in Figs. 1 and 2 respectively, confirm the  $\eta^1$ -coordination of the halogeno phosphalkenes to rhodium within a square-planar geometry.

The P–C bond lengths for the parent phosphalkenes PF=CH<sub>2</sub> and PCl=CH<sub>2</sub> have been determined by microwave spectroscopic methods and found to be 1.645 and 1.660 Å, respectively [8], and are slightly shorter than those in stable organo phosphalkenes [9]. The P=C distance in II (1.633(10) Å) is one of the shortest ever found. Similar shortening was observed in (<sup>1</sup>Pr<sub>2</sub>N)P=C(Ph)(SiMe<sub>3</sub>) (1.641(7) Å) [7].

\* NMR data for complexes (II) and (III). For II,  $^{31}\text{P}\{^1\text{H}\}$ (relative to H<sub>3</sub>PO<sub>4</sub>)(toluene),  $\delta(\text{P}_A)$  322.2,  $\delta(\text{P}_B)$  19.0 ppm;  $^1J(\text{RhP}_A)$  258 Hz,  $^1J(\text{P}_A\text{F})$  1127 Hz,  $^1J(\text{RhP}_B)$  125 Hz,  $^2J(\text{P}_A\text{P}_B)$  63 Hz,  $^{19}\text{F}$  (relative to CCl<sub>3</sub>F)(C<sub>6</sub>D<sub>6</sub>),  $\delta(\text{F})$  6.5 ppm,  $^1J(\text{P}_A\text{F})$  1128 Hz,  $^2J(\text{RhF})$  22 Hz.  $^1\text{H}$  (relative to TMS)(C<sub>6</sub>D<sub>6</sub>),  $\delta$  -0.11(d,9H,SiMe<sub>3</sub>),  $\delta$  0.47(d,9H,SiMe<sub>3</sub>),  $\delta$  7.07(m,15H,Ph),  $\delta$  7.97(m,15H,Ph).

For III,  $^{31}\text{P}\{^1\text{H}\}$ ,  $\delta(\text{P}_A)$  287.0,  $\delta(\text{P}_B)$  7.0 ppm;  $^1J(\text{RhP}_A)$  264 Hz,  $^1J(\text{RhP}_B)$  127 Hz,  $^2J(\text{P}_A\text{P}_B)$  59 Hz.  $^1\text{H}$ ,  $\delta$  -0.24(s,9H,SiMe<sub>3</sub>), 0.23(s,9H,SiMe<sub>3</sub>),  $\delta$  7.1–7.7 (m,30H,Ph).

\*\* Crystal data for II: C<sub>43</sub>H<sub>48</sub>ClF<sub>3</sub>RhSi<sub>2</sub>, triclinic, space group  $P\bar{1}$  *a* 9.206(8), *b* 13.170(5), *c* 18.211(6) Å,  $\alpha$  93.79(3),  $\beta$  90.03(5),  $\gamma$  101.21(5)°, *Z* = 2. The structure was solved by heavy atom methods and refined to *R* = 0.059 by least squares based on 5204 reflections measured on CAD4 diffractometer with Mo-K $\alpha$  radiation.

Crystal data for III: C<sub>43</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>3</sub>RhSi<sub>2</sub>, monoclinic, space group  $P2_1/c$ , *a* 11.904(3), *b* 20.083(5), *c* 18.485(8) Å,  $\beta$  98.12(3)°, *Z* = 4. The structure was solved by heavy atom methods and refined to *R* = 0.046 by least squares based on 5493 reflections measured on CAD4 diffractometer with Mo-K $\alpha$  radiation.

Tables of atom coordinates and bond lengths and angles, have been deposited with the Cambridge Crystallographic Data Centre.

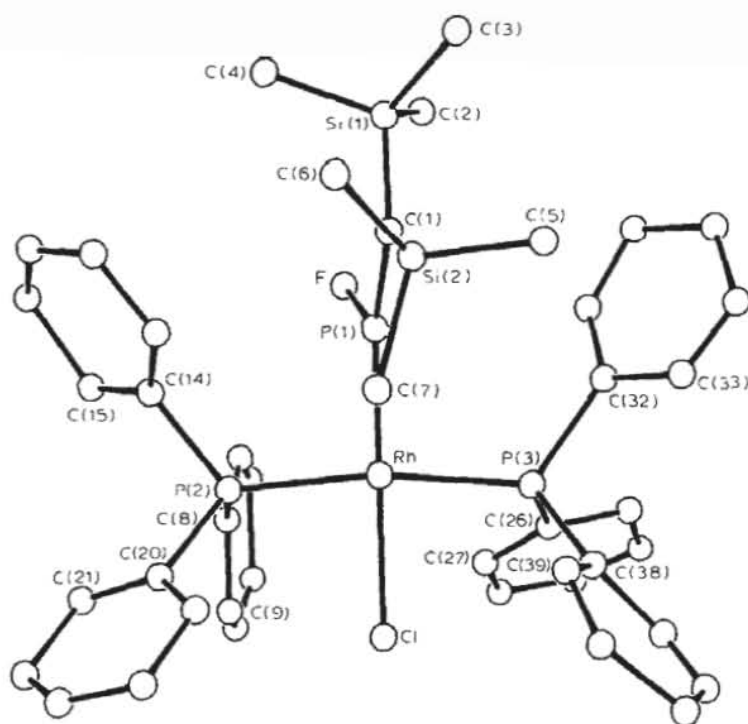


Fig. 1. The molecular structure of *trans*-[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -PF=C(SiMe<sub>3</sub>)<sub>2</sub>}], (II). Selected dimensions are: P(1)–C(1) 1.633(10), P(1)–F 1.608(6), Rh–P(1) 2.112(2), Rh–P(2) 2.302(2), Rh–P(3) 2.321(1) Rh–Cl 2.369(2)Å; C(1)–P(1)–F 105.0(4) Rh–P(1)–F 113.8(3), Rh–P(1)–C(1) 141.1(3)°.

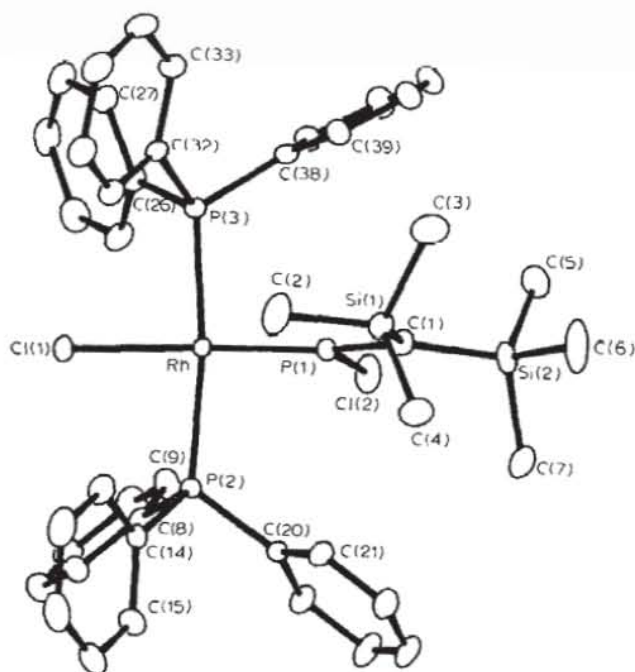


Fig. 2. The molecular structure of *trans*-[RhCl(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^1$ -PCl=C(SiMe<sub>3</sub>)<sub>2</sub>}], (III). Selected dimensions are: P(1)–C(1) 1.644(5), P(1)–Cl(2) 2.086(2), Rh–P(1) 2.136(1), Rh–P(2) 2.310(1), Rh–P(3) 2.315(1) Rh–Cl(1) 2.364(1)Å; C(1)–P(1)–Cl(2) 107.4(2), Rh–P(1)–Cl(2) 109.97(7), Rh–P(1)–C(1) 142.6(2)°.

Interestingly the halogenophosphaalkenes follow the trend observed in other phosphoalkenes and their complexes, namely P=C bond lengthening on  $\eta^2$ -coordination and shortening on  $\eta^1$ -coordination; compare: 1.692(3) Å in MesP=CPh<sub>2</sub> [10]; 1.679(4) Å in [Cr(CO)<sub>5</sub>( $\eta^1$ -MesP=CPh<sub>2</sub>)] [11]; 1.660(9) Å in *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>( $\eta^1$ -MesP=CPh<sub>2</sub>)] [12]; 1.814(4) Å in [Pt(PPh<sub>3</sub>)<sub>2</sub>{ $\eta^2$ -XylP=C(C<sub>12</sub>H<sub>8</sub>)}] [13]; and 1.832(6) Å in [Ni(bpy)( $\eta^2$ -XylP=CPh<sub>2</sub>)] [14].

The other features of interest in complexes II and III are the very short Rh–P(halogenophosphaalkene) bond lengths (2.112(2) and 2.136(1) Å, respectively) which may be compared with those related for the fluorophosphinerhodium(I) complexes (Rh–PF<sub>3</sub> 2.141 Å in [RhH(PF<sub>3</sub>)<sub>3</sub>] [15]; 2.245 Å in [Rh(PF<sub>3</sub>)<sub>3</sub>(NO)] [16]; 2.219 Å (average) in [Rh<sub>2</sub>(PF<sub>3</sub>)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>(PhC<sub>2</sub>Ph)] [17].

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