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## Organometallic complexes of the diphosphene [2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>P<sub>2</sub>

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### Abstract

Complexes of the symmetrical diphosphene [2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>P<sub>2</sub> (ArP=PAR) containing the transition metal fragments Mo(CO)<sub>5</sub>, W(CO)<sub>5</sub> and Pt(PEt<sub>3</sub>)Cl<sub>2</sub> have been synthesised, and characterised by <sup>31</sup>P NMR spectroscopy. The ligand is coordinated in an η<sup>1</sup>-fashion in each case.

### Introduction

Since the first diphosphene was reported by Yoshifuji *et al.* in 1981 [1], many compounds of the type RP=PR' have been prepared. They are usually stabilised by the presence of bulky substituents in the R groups, such as 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (mesityl), 2,4,6-<sup>t</sup>BuC<sub>6</sub>H<sub>2</sub> (supermesityl) or (Me<sub>3</sub>Si)<sub>3</sub>C [1,2]. These help to prevent dimerisation, and are capable of coordinating to transition metal fragments either in an η<sup>1</sup>-fashion, via a lone pair on phosphorus, or in an η<sup>2</sup>-mode, via the π system of the double bond. More recently, diphosphenes have been synthesised with strongly electron-withdrawing substituents such as 2,6-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (Ar') [3,4] or 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Ar) [5,6]. The effect of these substituents is to deactivate the diphosphene, so that its coordination properties are considerably reduced [6,7], and no transition metal derivatives have been reported. The compound ArP=PAR, for example, does not form an adduct with vanadocene, and is not protonated by HBF<sub>4</sub> [6]. We now describe the synthesis and characterisation of the first organometallic complexes of ArP=PAR, with the transition metal fragments Mo(CO)<sub>5</sub>, W(CO)<sub>5</sub> and Pt(PEt<sub>3</sub>)Cl<sub>2</sub>.

### Results and discussion

The diphosphene ArP=PAR (Ar = 2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) was prepared either (in 68% yield) by the reaction of equimolar quantities of ArPCL<sub>2</sub> and ArPH<sub>2</sub> [5] with

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two mol equivalents of DBU [6], or (in 72% yield) by the direct reaction of two mol equivalents of  $\text{ArP}=\text{PAr}$  with one mol equivalent of 1,3,1',3'-tetraethyl-2,2'-bis(imidazolidine). (The latter was made as described previously [8].)  $\text{ArP}=\text{PAr}$  is a pale yellow air-stable [6] solid, m.p.  $185^\circ\text{C}$ ,  $\delta(^{31}\text{P})$  ( $\text{CDCl}_3$ ) 473.9 ppm (13-line multiplet,  $J(\text{PF})$  45.0 Hz),  $\delta(^{19}\text{F})$  ( $\text{CDCl}_3$ )  $-56.5$  (apparent t,  $J(\text{PF})$  45.0 Hz, 12F) and  $-63.8$  (s, 6F) ppm. Found: C, 35.0;  $\text{C}_{18}\text{H}_4\text{F}_{18}\text{P}_2$  calc.: C, 34.6%. A solid state  $^{31}\text{P}$  NMR shift of 466.7 ppm was also recorded.

The complex  $\text{ArP}=\text{PAr} \cdot \text{Mo}(\text{CO})_5$  was prepared by adding  $\text{ArP}=\text{PAr}$  (0.61 g, 1.0 mmol) in THF (10  $\text{cm}^3$ ) to a stirred suspension of  $\text{Mo}(\text{CO})_6$  (0.53 g, 2.0 mmol) in THF (15  $\text{cm}^3$ ), in a quartz tube. This mixture was irradiated for 12 h at 254 nm, giving a dark red solution. The volatile material was removed in vacuo and the reddish oil was extracted with pentane (20  $\text{cm}^3$ ). The extract was cooled to  $-40^\circ\text{C}$  to give dark red crystals of the product in 66% yield. (Found: C, 32.4;  $\text{C}_{23}\text{H}_4\text{F}_{18}\text{O}_5\text{P}_2\text{Mo}$  calc.: C, 32.1%.)  $\delta(^{31}\text{P})$  ( $\text{CDCl}_3$ ) 412.7(d), 407.7(d) ppm ( $^1J(\text{PP})$  510 Hz).  $\delta(^{19}\text{F})$  ( $\text{CDCl}_3$ )  $-54.9$  (6F),  $-58.9$  (m, 6F),  $-65.1$  (6F) ppm. The observation of two doublets in the  $^{31}\text{P}$  spectrum shows unequivocally that the diphosphene is bonded in an  $\eta^1$ -fashion to the  $\text{Mo}(\text{CO})_5$  moiety, via a lone pair on one of the phosphorus atoms. The complex was also prepared by irradiating a solution of  $\text{Mo}(\text{CO})_6$  in THF at 254 nm for 4 h, then adding a THF solution of  $\text{ArP}=\text{PAr}$  and stirring for 20 h at room temperature, but the yield was lower (30%).

The analogous complex with the  $\text{W}(\text{CO})_5$  fragment was similarly prepared by irradiation of a mixture of  $\text{ArP}=\text{PAr}$  and an excess of  $\text{W}(\text{CO})_6$  in THF at 254 nm for 12 h;  $^{31}\text{P}$  NMR spectroscopy showed that the desired complex had been formed in low yield (ca. 30% conversion from the peak intensities),  $\delta(^{31}\text{P})$  386.5 (d), 359.9 (d) ppm ( $^1J(\text{PP})$  478 Hz). Satellites were also observed for the latter doublet from  $^{183}\text{W}-^{31}\text{P}$  coupling,  $^1J(\text{PW})$  293 Hz. The compound could not be isolated pure in this instance, but the  $^{31}\text{P}$  NMR data are again compatible only with the formation of an  $\eta^1$ -bonded complex. A comparable result was obtained when the  $\text{W}(\text{CO})_6$  solution was irradiated initially and the  $\text{ArP}=\text{PAr}$  added afterwards.

Complex formation also took place with the dimer  $[\text{Pt}(\text{PEt}_3)\text{Cl}_2]_2$ , resulting in cleavage of the bridges. The platinum complex was added to a stirred solution of an excess of  $\text{ArP}=\text{PAr}$  ( $> 2/1$  molar ratio) in  $\text{CH}_2\text{Cl}_2$  at room temperature. Stirring was continued for 1 h, and the  $^{31}\text{P}$  spectrum in the high frequency region of the resulting solution is shown in Fig. 1. (The singlet at 473.9 ppm is from unchanged diphosphene.) For the complex,  $\delta(^{31}\text{P})$  ( $\text{P}_1$ ) 346.6 ppm (d,  $^1J(\text{PP})$  534 Hz); the satellites from coupling with  $^{195}\text{Pt}$  are clearly visible,  $^1J(\text{PPt})$  2603 Hz;  $\delta(^{31}\text{P})$  ( $\text{P}_2$ ) 337.2 ppm (d,  $^1J(\text{PP})$  534 Hz). Hence  $\text{P}_1$  is evidently coordinated to platinum in the complex, and the ligand is again attached in an  $\eta^1$ -fashion. A signal was also seen for the  $\text{PEt}_3$  ligand ( $\text{P}_3$ ) at 9.5 ppm, with platinum satellites (d,  $^1J(\text{PPt})$  4024 Hz). The spectra show that the diphosphene and  $\text{PEt}_3$  groups are in *cis* positions, since no large coupling was apparent between  $\text{P}_1$  and  $\text{P}_3$ , such as would be expected for a *trans* complex [9,10]. The complex was isolated as pale yellow crystals in 64% yield by cooling the solution to  $-40^\circ\text{C}$ ; unfortunately these proved unsuitable for X-ray analysis [11]. Not surprisingly, no reaction was observed between  $\text{ArP}=\text{PAr}$  and  $\text{PtCl}_2(\text{PhCN})_2$ .

The results clearly indicate that  $\text{ArP}=\text{PAr}$  will coordinate with suitable transition metal fragments, although these must be reactive and/or forcing conditions

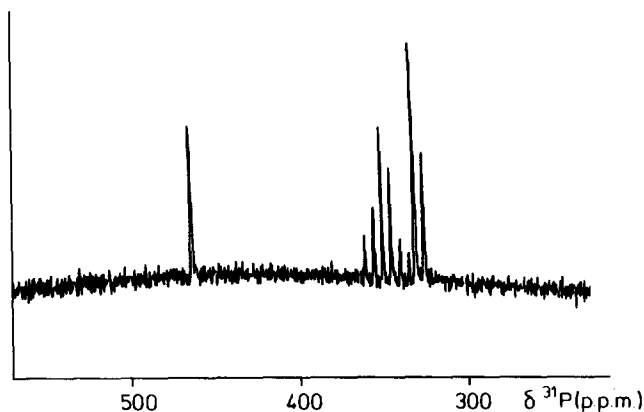


Fig. 1. High frequency region of the  $^{31}\text{P}$  NMR spectrum from the reaction of  $\text{ArP}=\text{PAr}$  with  $[\text{Pt}(\text{PET}_3)\text{Cl}_2]_2$ .

may be required. The resistance of the diphosphene to both oxidation and complexation confirms that the strongly electron-withdrawing  $\text{CF}_3$  groups confer considerable stability on the system, as suggested by Edlmann and co-workers [6].

### Experimental

Unless indicated otherwise, all manipulations were carried out either under an atmosphere of dry nitrogen or in vacuo.  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker AC250 instrument at 101.256 ( $^{31}\text{P}$ ) and 235.360 ( $^{19}\text{F}$ ) MHz. Chemical shifts were measured relative to external 85%  $\text{H}_3\text{PO}_4$  and  $\text{CFCl}_3$  respectively, with the high frequency (downfield) direction taken as positive.

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