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# Iron, silicon, tin polymetallic complexes: formation of *trans*, *cis*, *cis*-[Fe(CO)<sub>2</sub>(dppm-*P,P*)(SnClPh<sub>2</sub>)<sub>2</sub>] by silicon–tin exchange and its crystal structure

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## Abstract

The reaction of the alkoxy-silylcarbonylferrate [Fe(CO)<sub>3</sub>(η<sup>1</sup>-dppm){Si(OMe)<sub>3</sub>}]<sup>−</sup> **1** (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) with [SnCl<sub>2</sub>Ph<sub>2</sub>] affords a Fe<sub>2</sub>Si<sub>2</sub>Sn chain complex **2** and a FeSn<sub>2</sub> complex **3** depending on the reaction conditions. Photochemical activation was found to trigger their transformation to another complex that has now been fully characterized by X-ray diffraction as *trans*, *cis*, *cis*-[Fe(CO)<sub>2</sub>(dppm-*P,P*)(SnClPh<sub>2</sub>)<sub>2</sub>] **6**, which results from CO elimination and chelation of the dppm ligand. **To cite this article:** P. Braunstein et al., C.R. Chimie 8 (2005).

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## Résumé

La réaction de l'alkoxy-silylcarbonylferrate [Fe(CO)<sub>3</sub>(η<sup>1</sup>-dppm){Si(OMe)<sub>3</sub>}]<sup>−</sup> **1** (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>) avec [SnCl<sub>2</sub>Ph<sub>2</sub>] conduit à un complexe en chaîne de cœur Fe<sub>2</sub>Si<sub>2</sub>Sn **2** et à un complexe FeSn<sub>2</sub> **3**, en fonction des conditions de réaction. Une activation photochimique favorise leur transformation en un nouveau complexe, qui a pu maintenant être complètement caractérisé par diffraction des rayons X comme étant le *trans*, *cis*, *cis*-[Fe(CO)<sub>2</sub>(dppm-*P,P*)(SnClPh<sub>2</sub>)<sub>2</sub>] **6**, qui résulte de l'élimination de CO et de la chélation du ligand dppm. **Pour citer cet article :** P. Braunstein et al., C.R. Chimie 8 (2005).

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**Mots clés :** Complexes Hétérométalliques ; Étain ; Fer ; Ligand alkoxy-silyle ; Ligand assembleur ; Silicium

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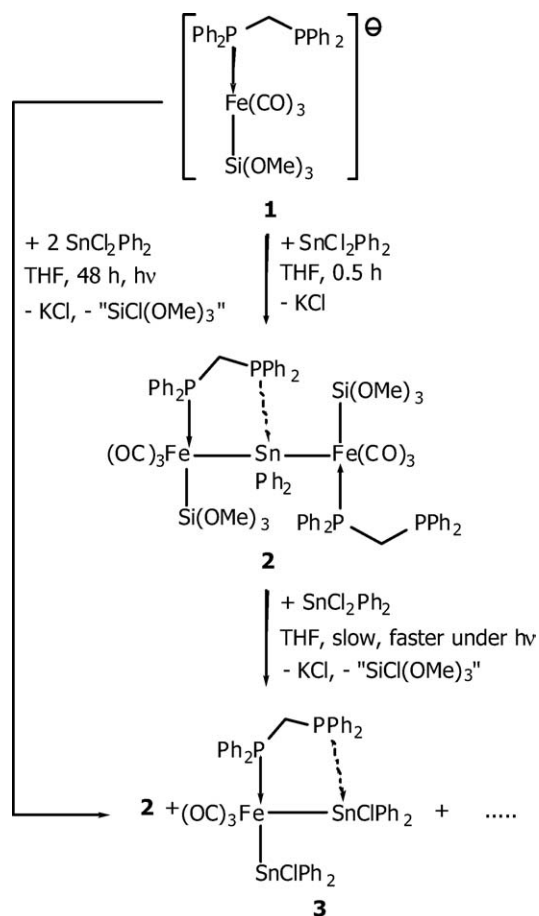
E-mail address: [braunst@chimie.u-strasbg.fr](mailto:braunst@chimie.u-strasbg.fr) (P. Braunstein).

Although the study of molecular compounds containing a metal-silicon or metal-tin bond has been the subject of much research, this topic remains of considerable interest owing to its implications in various aspects of synthetic, structural and catalytic chemistry and for the formation of advanced materials [1–15]. Following the discovery that  $-\text{Si}(\text{OR})_3$  ligands can form a  $\mu\text{-}\eta^2\text{-Si-O}$  bridge between two adjacent metals [16], which is thermodynamically stable but often displays hemilabile behaviour owing to the kinetic lability of the dative  $\text{SiO}\rightarrow\text{M}$  bond, and then of an analogous behaviour for aminosilyl ligands [17], we explored the reactivity of the alkoxy-silylcarbonylferrate  $\text{trans-}[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\eta^1\text{-dppm})]^-$  (dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) (**1**) towards a range of transition and post-transition metal complexes susceptible to form such a  $\text{Fe-Si-O}\rightarrow\text{M}$  moiety in order to study the scope of this phenomenon [2]. The presence of an assembling ligand such as dppm offers the possibility to increase the stability of the product by formation of a five-membered ring  $\text{Fe}(\mu\text{-dppm})\text{M}$ .

During our studies on the formation of mixed Fe-Si-Sn complexes, we noticed that the reactions of **1** with Sn(IV) precursors were very versatile and occurred with either retention of the silyl ligand or its exchange for a tin substituent. Thus, the reaction of  $\text{K}\cdot\mathbf{1}$  with  $[\text{SnCl}_2\text{Ph}_2]$  in THF, in a 1:1 ratio and under exclusion of light, led to the white product **2** in 89% yield (Scheme 1) [18].

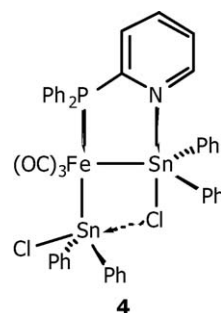
When this reaction was performed with a 1:2 stoichiometry and for a longer period of time, a new complex was isolated, **3**, which contained two stannyl ligands, and another product was detected which could not be identified. It was shown that **2** is an intermediate in the synthesis of **3**. Its formation may be explained by the greater stability of the Fe-Sn bond compared to that of the Fe-Si bond [1,19]. The silyl ligand in **1** may thus be viewed as a protecting group of a second negative charge on the iron centre [20].

The X-ray structure analysis of **3** indicated no bonding interaction in the solid state between the ‘dangling’  $\text{PPh}_2$  group and the  $\text{SnClPh}_2$  ligand cis to the  $\text{P}\rightarrow\text{Fe}$  bond, their separation being  $3.140(2)$  Å [18]. In solution, however, the presence in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of satellites for this resonance due to  $J(\text{P}^{117,119}\text{Sn})$  couplings suggested the occurrence of a  $\text{P}\rightarrow\text{Sn}$  interaction. It is noteworthy that when 2-(diphenylphosphino)pyridine was used as an assembling ligand, the



Scheme 1.

corresponding complex **4** clearly displayed a dative  $\text{N}\rightarrow\text{Sn}$  bond ( $2.499(7)$  Å), consistent with the preference of the tin centre for a nitrogen over a phosphine donor [21].



Whereas a complex analogous to **4** was obtained from  $[\text{SnCl}_2(n\text{-Bu})_2]$ , it is also important to remember that the nature of the anionic ligands on the Sn(IV) cen-

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