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Note

Transition-metal silyl complexes
51[☆]. Preparation of the mixed silyl/stannyl complexes $(\pi\text{-}C_5H_5)Fe(CO)(SnPh_3)(SiR_3)H$

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Abstract

The mixed silyl/stannyl complexes $(\pi\text{-}C_5H_5)Fe(CO)(SnPh_3)(SiR_3)H$ ($SiR_3 = SiPh_3$, $SiPh_2Me$, $SiPh_2H$) were prepared by photochemical reaction of $(\pi\text{-}C_5H_5)Fe(CO)_2SnPh_3$ with $HSiR_3$. The H, SiR_3 and $SnPh_3$ ligands are classically bonded to the metal.

Keywords: Iron complexes; Silyl complexes; Stannyl complexes; Cyclopentadienyl complexes; Carbonyl complexes

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1. Introduction

The chemistry of complexes containing two different Group 4 ligands, $L_nM(ER_3)E'R'_3$ (E = C, Si, Sn; E' = Si, Sn), is hardly exploited. For example, very little is known about reductive eliminations leading to E–E' bonds, although this may be an important step in metal-mediated transformations of silicon or tin compounds [2]. This is partly due to the fact that the preparative routes leading to such complexes are not well investigated.

In this paper we report the preparation and characterisation of the new mixed silyl/stannyl complexes $(\pi\text{-}C_5H_5)Fe(CO)(SnPh_3)(SiR_3)H$. Symmetric compounds of the general formula $CpFe(CO)(SiR_3)_2H$ (R = alkyl, aryl, halide) were first prepared by Jetz and Graham by reaction of $[CpFe(CO)_2]_2$ or $CpFe(CO)_2SiR_3$ with $HSiR_3$ [3]. More recently an equivalent tin analogue was obtained by the reaction of $CpFe(CO)_2CH_2CH_2Ph$ with $HSnPh_3$ [4]. A principal difficulty associated with most preparation methods for mixed silyl/stannyl complexes is to avoid the formation of symmetrical compounds by ligand exchange.

The mixed silyl/stannyl complexes $(\pi\text{-}C_5H_5)$-$Fe(CO)(SnPh_3)(SiR_3)H$ are also interesting with regard to bonding. NMR data of the complexes $CpFe(CO)(ER_3)_2H$ (E = Si, Sn) exclude η^2-EH interactions [4,5], i.e. all complexes contain conventional hydride ligands. However, a different bonding situation is found in the isoelectronic complexes $CpMn(CO)(SiR_3)(PR'_3)H$. Except for the $SiCl_3$ derivative, the occurrence of Mn,H,Si three-centre bonds is proven by structural, NMR and photoelectron spectroscopic data [6,7]. There was a chance that unsymmetric substitution in the iron complexes would favour an η^2-SiH interaction as in the Mn complexes.

2. Synthesis and characterisation of $CpFe(CO)(SiR_3)(SnR'_3)H$ (2)

The most effective synthesis of $CpFe(CO)(ER_3)_2H$ complexes has been found to be the photochemical reaction of $CpFe(CO)_2ER_3$ with HER_3. The starting materials are easily accessible, and few side-products are observed (as is often not so in the case of thermal reactions). Therefore, there are two possible routes for the preparation of a mixed Si/Sn species $CpFe(CO)(SiR_3)(SnR'_3)H$, provided that no exchange leading to symmetrical products occurs: $CpFe(CO)_2SnR'_3 + HSiR_3$ (Eq. (1)) or $CpFe(CO)_2SiR_3 + HSnR'_3$.

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The first route was chosen due to the greater number of easily obtainable silanes. $CpFe(CO)_2SnPh_3$ (**1**), easily prepared by the reaction of $Na[CpFe(CO)_2]$ with $ClSnPh_3$ [8], was reacted with $HSiPh_3$, $HSiMePh_2$ and H_2SiPh_2.

$$\underset{\mathbf{1}}{CpFe(CO)_2SnPh_3} + HSiR_3 \longrightarrow \underset{\mathbf{2}}{CpFe(CO)(SnPh_3)(SiR_3)H} + CO \quad (1)$$

$SiR_3 = SiPh_3$ (**2a**), $SiMePh_2$ (**2b**), $SiHPh_2$ (**2c**).

In all cases a solution containing **1** along with an excess of silane was irradiated with UV light at −10 °C, and the progress of the reaction monitored using IR spectroscopy. When no further decrease in starting material, and/or increase in product ν(CO) band intensity was observed, the reaction was stopped.

With toluene as the solvent, in which **1** was readily soluble, photolysis occurred rapidly (good conversion usually achieved after 2 h irradiation), but the product proved difficult to separate from the reaction mixture. Complex **1** was only sparingly soluble in petroleum ether, particularly at −10 °C, and so completion of the photolysis reaction took more time than with toluene. The products are also relatively insoluble, however, and so product separation was easier. The best results were obtained when diethyl ether solutions were photolysed. In this case both **1** and the silane are soluble, but the pale yellow product formed simply precipitates from the solution on formation, making separation and purification relatively straightforward.

An attempt was also made to produce product **2b** by the irradiation of $CpFe(CO)_2SiPh_2Me$ with $HSnPh_3$ in petroleum ether. Even after 400 min photolysis only a small amount of **2b** had been formed. Therefore, the other route (Eq. (1)) is more efficient.

By far the most stable product is $CpFe(CO)(SnPh_3)(SiPh_3)H$ (**2a**). The pale yellow solid is very air stable, although only stable in hydrocarbon solution at room temperature for a few hours. As might be expected, **2a** is fully soluble only in relatively polar solvents such as THF, and reasonably soluble in toluene and benzene.

The products **2b** and **2c** are considerably less stable. Photolyses in toluene solution resulted in almost complete reaction of **1**, along with the appearance of a single ν(CO) band, indicating formation of **2b** or **2c** (Eq. (1)). On removal of solvent, however, the complexes partially decomposed. Attempts to separate the complexes from their decomposition products were unsuccessful.

The spectroscopic data for the compounds **2** are mainly as expected. The most interesting is the J(SiFeH) coupling constant of 23 Hz for compound **2a**. This suggests that there is very little, if any, interaction between the Si and H atoms [9], and thus that **2a** is a conventional metal hydride. By way of comparison, a value of 20 Hz was found for J(SiFeH) in $CpFe(CO)(SiCl_3)_2H$ [3] and 12.9 Hz in $CpFe(CO)(SiMe_2H)_2H$ [5]. These coupling constants clearly indicate that the complexes have conventionally bonded hydride ligands. Values of 38–46.5 Hz were observed in the analogous complexes $Cp'Mn(CO)(SiHPh_2)(PR_3)H$ [6], having Mn,Si,H three-centre bonds. The value of 20 Hz for J(SnFeH) in compound **2a** indicates that there is also no interaction between the Sn and H atoms. This value can be compared with a coupling of 15.8 Hz in $CpFe(CO)(SnPh_3)_2H$ [4] (conventional bonds) and 270 Hz in $MeCpMn(CO)_2(SnPh_3)H$ [3] (three-centre bond).

Unfortunately, the corresponding couples were not observed in compounds **2b** and **2c**, due to their instability in solution and the difficulties encountered in producing pure samples. However, previous investigations on M,E,H three-centre bonds suggest that substitution of one phenyl group of **2a** for Me or H would not change the bonding situation decisively [9].

3. Experimental

All operations were performed in an atmosphere of dry and oxygen-free argon, using dried and nitrogen-saturated solvents. IR spectra: Perkin-Elmer 283, CaF_2 cuvettes. ^1H NMR spectra: Jeol FX 90 Q and Bruker WM 400. ^{119}Sn NMR: Jeol FX 90 Q (35.35 MHz). ^{29}Si NMR: Bruker WM 400 (79.49 MHz).

3.1. Preparation of CpFe(CO)(SnPh₃)(SiPh₃)H (2a)

A solution of 1.08 g (2.05 mmol) of **1** and 1.13 g (4.35 mmol) of $HSiPh_3$ in 80 ml Et_2O was cooled to −10 °C maintaining a slow flow of argon to allow for contraction of the solution. The solution was then photolysed for 240 min until the intensity of the product ν(CO) band had ceased to increase in intensity. At this stage there was only a very small trace of **1**, as identified by the ν(CO) band, remaining in the solution. The supernatant solution which had been yellow at the beginning of photolysis was now dark green–brown, and a large amount of pale yellow solid had precipitated. The solution was decanted off, and the solid dried under vacuum. The solid was then washed with Et_2O and petroleum ether to remove remaining traces of silane and **1**, and dried. Pale yellow solid, yield 1.05 g (67%). *Anal.* Found: C, 66.61; H, 4.66. Calc. for $C_{42}H_{36}FeOSiSn$ (759.4): C, 66.43; H, 4.78%. IR (toluene): $\nu(CO) = 1941\ cm^{-1}$. ^1H NMR (400 MHz, benzene-d_6): $\delta = 4.14$ (s, 5H, C_5H_5), −11.69 (s, 1H, FeH, $^2J(^{117/119}SnFeH)$ 20 Hz). ^{29}Si NMR (benzene-d_6):

$\delta = 26.17$ (^2J(SiFeH) = 23 Hz). ^{119}Sn NMR (benzene-d$_6$): $\delta = 40.83$.

3.2. Preparation of CpFe(CO)(SnPh$_3$)(SiPh$_2$Me)H (2b)

1.0 g of **1** (1.9 mmol) and 2 ml of HSiPh$_2$Me (10.0 mmol) were photolysed as described for compound **2a** above, with toluene as the solvent. After 120 min photolysis, no further change in the intensity of the ν(CO) bands could be seen. The solution, now being dark green–brown in colour, was filtered into a Schlenk tube, and the solvent removed, leaving a green oil. An attempt was made to purify the compound by column chromatography on silica gel at −10 °C, with a mixture of toluene and petroleum ether used as eluent. Only a small amount of oily, brown product was obtained, the remainder decomposing on the column. On addition of a small amount of petroleum ether a dirty yellow solid precipitated, which was then dried and washed again with petroleum ether. The overall yield of solid was very low (~50 mg). The IR spectrum indicated that it was relatively pure **2b**, but with a small amount of **1** present as impurity. Attempts to remove this impurity by further washing were unsuccessful since decomposition to a green solid was observed. IR (toluene): ν(CO) = 1942 cm^{-1}. ^{1}H NMR (90 MHz, benzene-d$_6$): $\delta = 4.23$ (s, 5H, C$_5$H$_5$), 0.83 (s, 3H, CH$_3$), −11.98 (s, 1H, FeH). ^{119}Sn{^{1}H} NMR (benzene-d$_6$): $\delta = 46.61$.

3.3. Preparation of CpFe(CO)(SnPh$_3$)(SiPh$_2$H)H (2c)

The experimental details are the same as for **2b**. IR (toluene): ν(CO) = 1944 cm^{-1}. ^{1}H NMR (90 MHz, benzene-d$_6$): $\delta = 6.25$ (d, 1H, SiH), 4.26 (s, 5H, C$_5$H$_5$), −11.90 (s, 1H, FeH, ^3J(HSiFeH) = 1 Hz). ^{119}Sn{^{1}H} NMR (benzene-d$_6$): $\delta = 50.92$.

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References

[1] S. Gilbert, M. Knorr, S. Mock and U. Schubert, *J. Organomet. Chem.*, in press.
[2] U. Schubert, *Angew. Chem., 106* (1994) 435; *Angew. Chem., Int. Ed. Engl., 33* (1994) 419.
[3] W. Jetz and W.A.G. Graham, *Inorg. Chem., 10* (1971) 1159, and refs. therein.
[4] M. Akita, T. Oku, M. Tanaka and Y. Moro-oka, *Organometallics, 10* (1991) 3080.
[5] W. Malisch and H. Käb, personal communication.
[6] U. Schubert, G. Scholz, J. Müller, K. Ackermann, B. Wörle and R.F.D. Stansfield, *J. Organomet. Chem., 306* (1986) 303; U. Schubert, K. Bahr and J. Müller, *J. Organomet. Chem., 327* (1987) 357.
[7] D.L. Lichtenberger and A. Rai-Choudhuri, *J. Am. Chem. Soc., 111* (1989) 3583; *112* (1990) 2492; *Inorg. Chem., 29* (1990) 975; *Organometallics, 9* (1990) 1686.
[8] R.D. Gorsich, *J. Am. Chem. Soc., 84* (1962) 2486.
[9] U. Schubert, *Adv. Organomet. Chem., 30* (1990) 151.