Transition-Metal Silyl Complexes, 43[1]

Preparation and Fluxionality of the Complexes $FeH_3(PPh_2R')_3ER_3$ (E = Si, Sn; R′ = Et, *n*Bu)

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The complexes $FeH_3(PPh_2R')_3ER_3$ (R′ = *n*Bu: ER_3 = $SnPh_3$, $SiMePh_2$; R′ = Et: ER_3 = $SnPh_3$) were prepared by reaction of $Fe(H)_2(H_2)(PPh_2R')_3$ with $HSnPn_3$ or $HSiMePh_2$. The heavy-atom skeleton of $FeH_3(PPh_2Et)_3SnPh_3$ shows an approximate C_3 symmetry in the crystalline state and a nearly tetrahedral FeP_3Sn core. However, the NMR spectra indicate the presence of Fe,H,Si(Sn) three-center two-electron bonds at low temperature in solution.

We recently obtained the trihydrido silyl complexes $FeH_3(CO)(dppe)SiR_3$ (dppe = $Ph_2PCH_2CH_2PPh_2$) by irradiation of some of the monohydrido silyl complexes $FeH(CO)_2(dppe)SiR_3$ with an excess of the corresponding silanes $HSiR_3$[2]. Although an X-ray structure analysis of the $Si(OEt)_3$ derivative was undertaken, the hydride ligands could not be unequivocally located. In the ^1H- and ^{31}P-NMR spectra only one set of signals was observed, and no coalescence was reached down to −95°C. Therefore, we were not able to answer the question on how the hydride ligands are bound (terminal hydrides, or η^2-H_2, or η^2-$HSiR_3$).

In order to prepare other derivatives, which might give a clearer picture of the bonding situation in complexes of the type $FeH_3L_3ER_3$ (E = Si, Sn), we treated $Fe(H)_2(H_2)(PPh_2R')_3$ (R′ = Et or *n*Bu) (**1**)[3] with several silanes and stannanes. Replacement of the H_2 ligand by HER_3 (E = Si, Sn) results in the formation of the trihydrido silyl or stannyl complexes $FeH_3(PPh_2R')_3ER_3$ (**2**) [Eq. (1)]. This reaction represents the first example of a novel method for preparing hydrido silyl or stannyl complexes.

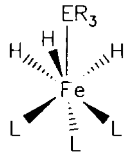
$$\underset{\mathbf{1}}{Fe(H)_2(\eta^2\text{-}H_2)(PPh_2R')_3} + HER_3 \rightarrow \underset{\mathbf{2}}{FeH_3(PPh_2R')_3ER_3} + H_2 \qquad (1)$$

	ER_3	R′
a	$SnPh_3$	*n*Bu
b	$SiMePh_2$	*n*Bu
c	$SnPh_2$	Et

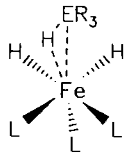
The room-temperature ^1H- and ^{31}P-NMR spectra of **2a, c** and **2b** in $[D_8]$toluene solution are different. The *stannyl* derivatives **2a, c** show quadruplets for the hydride ligands in the ^1H-NMR spectrum. Upon cooling of the solution, the inner lines of the quadruplet begin to broaden, and at 0°C an AA′A″XX′X″ pattern is observed. Further cooling results in a coalescing signal, and at ca. −60°C a single broad signal is observed. We were not able to obtain a resolved signal at the experimentally accessible temperature limit of −80°C. The *silyl* derivative **2b** has higher coalescence temperatures: at room temperature an AA′A″XX′X″ pattern is observed in the hydride signal region of the ^1H-NMR spectrum, and a single broad signal at ca. −30°C. It develops into two broad resonance lines at −60°C with a 1:2 intensity ratio.

While the $^{31}P\{^1H\}$-NMR spectra of both the silyl and stannyl derivatives show singlets at room temperature, the ^{31}P off-resonance spectra are different. Quadruplets are observed for the *stannyl* derivatives **2a, c**, and a doublet of triplets for the *silyl* derivative **2b**. Upon cooling of a solution of **2b**, the singlet in the $^{31}P\{^1H\}$-NMR spectrum broadens, then develops into a broad hump at −55°C, and finally gives two broad, unresolved signals with an approximate 1:2 ratio at −77°C.

We interpret the temperature dependence of the NMR spectra as follows: in the low-temperature spectrum the hydride and phosphane ligands are inequivalent, probably because one of the hydride ligands in engaged in an Fe,H,E three-center two-electron bond. The complexes are octahedrally coordinated having *facial* phosphorus atoms, two terminal hydrides and an η^2-coordinated $H-ER_3$ ligand (**B**). This bonding situation corresponds to a triple energy minimum, and therefore an increasing temperature causes the averaging of the hydride sites with respect to the ER_3 ligand. This may be due to a dynamic process, in which the three hydrogen atoms alternate in the three-center bond, or to formation of a symmetric structure **A**, in which the ER_3 ligand caps an octahedral, static *fac*-$FeH_3(PR_3)_3$ unit. The high-temperature spectrum of **2a** corresponds to a situation in which the hydride ligands are chemically and magnetically equivalent with respect to both the ER_3 *and* the PR_3 ligands. A rapid interchange of sites is not unusual for polyhydride complexes.



A



B

(L = $PBuPh_2$)

The assumption of a three-center Fe,H,E bond is qualitatively supported by the coupling constant *J*(SnFeH) in **2a**. In complexes

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with an M,H,E three-center two-electron bond the values of the NMR coupling constants are between ^1J(EH) and ^2J(EMH) and correlate for a given type of complex with the degree of three-center bonding[4]. In the complexes (π-1,3,5-$C_6H_3Me_3$)$(CO)_2$Cr(H)$SnPh_3$[5] and MeCp$(CO)_2$Mn(H)$SnPh_3$[6], in which the occurrence of M,H,Sn three-center bonds was established by structure analyses, J(SnMH) of 327.6 Hz and 270 Hz were found. In $(CO)_3(Ph_3P)$Fe(H)$SnPh_3$, having classical Fe–H and Fe–Sn bonds, ^2J(SnFeH) is 101 Hz[7]. J(SnFeH) in **2a** is 174.2 Hz, which could be the average of two classical SnFeH coupling constants (ca. 100 Hz) and the coupling constant in an Fe,H,Sn three-center bond (ca. 325 Hz).

Complex **2c** has a symmetric structure in the crystalline state (Figure 1; Table 1) corresponding to the intermediate form **A**.

Although the hydride positions could not be refined, the heavy-atom skeleton with an approximate C_3 symmetry does not indicate a special position of one of the hydride ligands. This solid-state structure of **2c** is no contradiction to the proposed three-center bond of **2a** and **2b** in solution at low temperatures, because the energy difference between **A** and **B** is small enough to be compensated by packing forces in the solid state or solvation effects in solution.

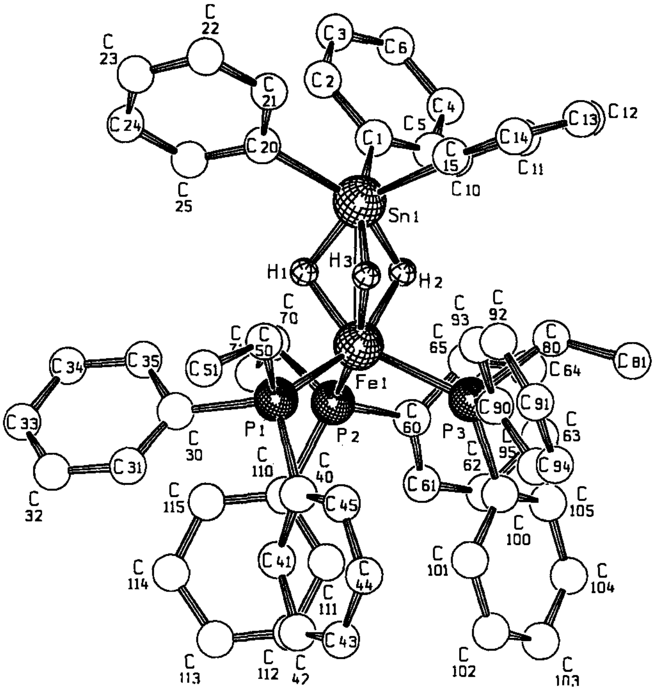

Figure 1. Solid-state structure of **2c**; the positions of the hydride ligands were calculated by the program HYDEX[11] but not refined; although the calculation places the hydrogen atoms in bridging positions (Fe–H 165 pm, Sn–H 165 pm; Fe–H–Sn 100°) the exact hydrogen positions still have to be verified by additional structural investigations; selected bond lengths [pm] and angles [°] Fe–Sn 252.7(1), Fe–P(1) 223.9(2), Fe–P(2) 223.2(2), Fe–P(3) 224.7(2); Fe–Sn–C(1) 118.8(2), Fe–Sn–C(10) 112.1(2), Fe–Sn–C(20) 117.7(2), Sn–Fe–P(1) 114.02(7), Sn–Fe–P(2) 118.74(7), Sn–Fe–P(3) 113.68(6), P(1)–Fe–P(2) 103.40(8), P(1)–Fe–P(3) 103.31(8), P(2)–Fe–P(3) 101.78(8)

There are two complexes with related structures: The ruthenium complex $RuH_3(PMe_3)_3SiMe_3$[8] has the same pseudotetrahedral heavy-atom skeleton as **2a**[9]. In the dinuclear complex $(EtPh_2P)_3Fe(\mu\text{-}H)_3Cu(PEtPh_2)$, prepared by reaction of $Fe(H)_2(\eta^2\text{-}H_2)(PEtPh_2)_3$ with $[CuOtBu]_4$, a *fac*-$FeH_3(PR_3)_3$ moiety is symmetrically bridged by three hydride ions to a $CuPR_3$ fragment[10]. The Cu–P-decoupled NMR signal of the bridging hydride ligands at 25°C has an AA′A″XX′X″ pattern as in the medium-temperature case of **2**.

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Table 1. Atomic coordinates and B(equ.) values [Å^2] of **2c**

Atom	x	y	z	B(equ.)
Sn1	0.00630(4)	0.20633(4)	0.14956(2)	2.39(1)
Fe1	0.18814(8)	0.24062(8)	0.12831(3)	2.03(2)
P1	0.2795(2)	0.3434(2)	0.17183(6)	2.45(4)
P2	0.2888(2)	0.0942(2)	0.11683(6)	2.32(4)
P3	0.2008(1)	0.3360(2)	0.07052(6)	2.11(4)
C1	-0.0631(6)	0.0436(6)	0.1369(3)	3.1(2)
C2	-0.1119(7)	-0.0130(8)	0.1682(3)	4.9(2)
C3	-0.1653(9)	-0.1113(9)	0.1600(4)	7.3(3)
C4	-0.1675(8)	-0.1532(8)	0.1219(4)	6.7(3)
C5	-0.1171(8)	-0.1013(9)	0.0915(4)	6.5(3)
C6	-0.0649(7)	-0.0027(7)	0.1001(3)	4.5(2)
C10	-0.1015(6)	0.3189(6)	0.1194(2)	2.8(2)
C11	-0.1518(6)	0.2875(8)	0.0850(3)	4.1(2)
C12	-0.2116(7)	0.362(1)	0.0626(3)	5.7(3)
C13	-0.2212(7)	0.4701(9)	0.0761(3)	6.4(3)
C14	-0.1746(7)	0.5023(8)	0.1107(4)	5.8(3)
C15	-0.1150(6)	0.4282(7)	0.1324(3)	4.0(2)
C20	-0.0292(6)	0.2287(7)	0.2122(3)	3.7(2)
C21	-0.1091(9)	0.2970(9)	0.2254(3)	6.5(3)
C22	-0.130(1)	0.310(1)	0.2653(3)	9.3(3)
C23	-0.073(1)	0.262(1)	0.2938(3)	8.0(4)
C24	0.0025(8)	0.192(1)	0.2830(3)	7.6(3)
C25	0.0244(7)	0.176(1)	0.2420(3)	6.4(3)
C30	0.3430(6)	0.2755(7)	0.2149(2)	3.3(2)
C31	0.4281(7)	0.3182(9)	0.2345(3)	4.9(2)
C32	0.4723(8)	0.265(1)	0.2673(3)	7.2(3)
C33	0.4309(9)	0.168(1)	0.2815(3)	7.6(3)
C34	0.3451(9)	0.1266(9)	0.2639(3)	6.2(3)
C35	0.3012(7)	0.1772(8)	0.2308(3)	4.2(2)
C40	0.3819(5)	0.4330(6)	0.1530(2)	2.3(2)
C41	0.4800(6)	0.3907(6)	0.1480(2)	2.8(2)
C42	0.5573(6)	0.4527(7)	0.1311(3)	3.4(2)
C43	0.5366(6)	0.5600(7)	0.1179(2)	3.3(2)
C44	0.4396(6)	0.6034(6)	0.1216(3)	3.2(2)
C45	0.3635(6)	0.5414(7)	0.1398(2)	2.9(2)
C50	0.1983(6)	0.4452(7)	0.1984(2)	3.4(2)
C51	0.2490(7)	0.5148(8)	0.2318(3)	5.0(2)
C60	0.2841(6)	0.0287(6)	0.0666(2)	2.5(2)
C61	0.3692(6)	-0.0126(6)	0.0461(3)	3.1(2)
C62	0.3590(6)	-0.0545(7)	0.0078(3)	3.7(2)
C63	0.2646(7)	-0.0599(7)	-0.0115(3)	3.8(2)
C64	0.1798(7)	-0.0261(7)	0.0098(3)	4.0(2)
C65	0.1898(6)	0.0194(6)	0.0476(3)	3.0(2)
C70	0.2512(6)	-0.0287(6)	0.1469(2)	3.0(2)
C71	0.3098(7)	-0.1376(7)	0.1398(3)	3.9(2)
C80	0.0929(6)	0.3039(7)	0.0362(2)	2.9(2)
C81	0.0820(7)	0.3671(7)	-0.0030(3)	3.9(2)
C90	0.1816(6)	0.4906(6)	0.0722(2)	2.6(2)
C91	0.1050(6)	0.5304(6)	0.0960(2)	2.7(2)
C92	0.0802(6)	0.6426(7)	0.0968(3)	3.4(2)
C93	0.1347(6)	0.7175(7)	0.0748(3)	3.6(2)
C94	0.2114(6)	0.6792(7)	0.0501(3)	3.8(2)
C95	0.2343(6)	0.5660(6)	0.0481(2)	2.9(2)
C100	0.3123(5)	0.3226(6)	0.0373(2)	2.4(2)
C101	0.4020(6)	0.3801(6)	0.0470(2)	2.9(2)
C102	0.4866(6)	0.3707(7)	0.0226(3)	3.3(2)
C103	0.4860(6)	0.3038(7)	-0.0113(3)	3.7(2)
C104	0.3976(7)	0.2445(7)	-0.0200(3)	3.9(2)
C105	0.3116(6)	0.2529(6)	0.0042(2)	3.1(2)
C110	0.4268(5)	0.1032(6)	0.1268(2)	2.4(2)
C111	0.4893(6)	0.1534(6)	0.0984(2)	2.8(2)
C112	0.5926(6)	0.1657(7)	0.1052(3)	4.0(2)
C113	0.6361(7)	0.1309(8)	0.1399(3)	5.3(3)
C114	0.5751(7)	0.0823(8)	0.1697(3)	5.1(2)
C115	0.4707(6)	0.0688(7)	0.1625(3)	3.8(2)
H1	0.124	0.170	0.162	4.0*
H2	0.083	0.179	0.112	4.0*
H3	0.087	0.310	0.143	4.0*

* Fixed atomic parameters.

Experimental

All operations were performed in dry and oxygen-free argon or hydrogen by using dried and argon-saturated solvents. – IR: Perkin-Elmer 283 (NaCl cuvettes). – ^1H NMR: Bruker AM400 and AMX400 (400 MHz). For tin-containing compounds only the coupling constants for the isotop ^{119}Sn are given. – ^{31}P NMR: Jeol FX-90Q (36.23 MHz) rel. ext. 85% H_3PO_4. – Melting points were determined by differential thermal analysis using a DuPont Thermal Analyzer 990.

General Procedure for the Preparation of the Complexes Fe-$H_3(PPh_2R')_3ER_3$ (**2**): To a suspension of ca. 2.5 mmol of Fe-$(H)_2(H_2)(PPh_2R')_3$ (R' = Et or *n*Bu) (**1**)[3] in 10 ml of ethanol (isolation of the complex is not necessary for these reactions; it can be used as obtained) a solution of ca. 6 mmol of silane or stannane in 40 ml of toluene was added at room temp. with stirring. When gas evolution was no longer observed, the dark solution was stirred for one additional hour. Then the solvent was removed in vacuo, and the residue was extracted with several portions of toluene. The combined solutions were filtered, and the solvent was removed. Upon washing of the yellow, oily residue with several portions of pentane at −30°C yellow solids were obtained.

2a: Yield 75%; m.p. 118°C (dec.). – IR (toluene): ν(FeH) = 1822 cm^{-1} (m, br.). – ^1H NMR (C_6D_6, 30°C): δ = −13.85 [q, 3H, FeH, ^2J(PFeH) = 32.2 Hz, ^2J($^{117/119}$SnFeH) = 174.2 Hz], 2.13 (m, 2H, PCH_2), 1.48−0.89 (m, 4H, CCH_2), 0.71 (m, 3H, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6, 30°C): δ = 60.55 [s, ^2J(^{119}SnFeP) = 146.5 Hz].

$C_{66}H_{75}FeP_3Sn$ (1135.8)	Calcd.	C 69.80	H 6.66
	Found	C 70.14	H 6.92

2b: Yield 78%; m.p. 82°C (dec.). – IR (toluene): ν(FeH) = 1900 cm^{-1} (m, br). – ^1H NMR ($CD_3C_6D_5$, 30°C): δ = −14.45 (AA'A''XX'X'', 3H, FeH), 2.11−0.63 (m, 12H, PBu and SiMe). – $^{31}P\{^1H\}$ NMR (toluene/C_6D_6, 30°C): δ = 62.6 [s, ^2J(SiFeP) = 44 Hz]; (−77°C): δ = 66.0 (br.), 63.6 (br.).

$C_{61}H_{73}FeP_3Si$ (983.1)	Calcd.	C 74.53	H 7.48
	Found	C 74.33	H 7.55

2c: Yield 68%; m.p. 67°C (dec.). – IR (toluene): ν(FeH) = 1828 cm^{-1} (m, br.). – ^1H NMR (C_6D_6, 30°C): δ = −13.80 [q, 3H, FeH, ^2J(PFeH) = 32.4 Hz, ^2J($^{117/119}$SnFeH) = 174.2 Hz], 2.05 (m, 2H, PCH_2), 0.38 (m, 3H, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6, 30°C): δ = 62.85 [s, ^2J(^{119}SnFeP) = 140.7 Hz].

$C_{60}H_{63}FeP_3Sn$ (1051.6)	Calcd.	C 68.53	H 6.04
	Found	C 68.11	H 6.17

X-ray Structure Analysis of **2c**: Crystals were obtained from a toluene/pentane solution at 20°C. A crystal (0.3 × 0.3 × 0.3 mm) was mounted on an Enraf-Nonius CAD4 four-circle diffractometer in a sealed tube. Mo-K_α radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. Crystal data: monoclinic; $P2_1/c$; a = 1310(8), b = 1199(8), c = 3331(3) pm; β = 90.65(1)°; V = 5233 × 10^6 pm^3; Z = 4; $D_{calcd.}$ = 1.44 g cm^{-3}; μ = 8.87 cm^{-1}. Cell dimensions were determined from 25 reflections with high diffraction angles from different parts of the reciprocal space. 5192 unique reflections were measured between 2° ≤ 2θ ≤ 40° by the ω/θ method at −20°C. The reflections were corrected for polarization and Lorentz effects, and by an empirical absorption (min. transmission 90.6%) and a decay correction (0.8% loss of intensity). The structure was solved by the Patterson method. The positions of the hydrogen atoms were calculated according to an idealized geometry. The positions of the hydride ligands were calculated by the program HYDEX[11]. Refinement was performed by full-matrix least squares (Enraf-Nonius SDP) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were not refined. The final R was 0.043 and R_w was 0.049 (w = 1), using 4064 observed reflections with $F_0 \geq 3.96\sigma(F_0)$. Final atomic coordinates are given in Table 1, selected bond lengths and angles in Figure 1[12].

CAS Registry Numbers

1 (R' = Bu): 138858-78-3 / **1** (R' = Et): 102149-40-6 / **2a**: 138858-79-4 / **2b**: 138858-80-7 / **2c**: 138858-81-8

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[12] Further details of the crystal-structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55886, the names of the authors, and the journal citation.

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