Palladium-induced rearrangement of a Fe_2Sn_2 metal core leading to the first Fe–Pd–Sn cluster $[(OC)_3Fe(\mu\text{-}SnBu^n{}_2)(\mu\text{-dppm})Pd(\mu\text{-dppm})Fe(CO)_3]$†

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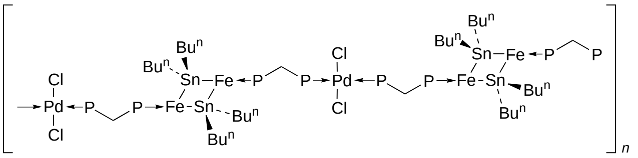
A new tetranuclear FePdFeSn four-membered ring cluster, which could be viewed as a bent chain complex FePdFe bridged by a stannylene ligand, is obtained from a Fe_2Sn_2 precursor by $Ph_2PCH_2PPh_2$ (dppm)-assisted palladium incorporation; it provides the first example of a Sn–Fe–Pd linkage.

Molecules which associate transition metals with group 14 elements currently enjoy increased attention because they provide opportunities for the formation of unusual structures and new bonds between transition metals and main-group elements, they are used as single-source precursors for new materials and display interesting catalytic properties.[1]

We have recently reported the synthesis of $[Fe(CO)_3(\eta^1\text{-dppm})(SnBu^n{}_2)]_2$ **1** (dppm = $Ph_2PCH_2PPh_2$) from $K[Fe(CO)_3\{Si(OMe)_3\}(\eta^1\text{-dppm})]$ and $[Sn(OAc)_2Bu^n{}_2]$ where a silicon/tin exchange reaction has taken place.[2] The silyl ligand may be considered as a protecting group for the unknown dianion $[Fe(CO)_3(\eta^1\text{-dppm})]^{2-}$.[3] Since the uncoordinated phosphorus lone pair in **1** can be used for further metal complexation,[2] we considered using a palladium educt with two labile ligands which could lead to an inorganic cyclic or a linear polymer.



Addition of 1 equiv. of $[PdCl_2(SEt_2)_2]$ to the solution of **1** in CH_2Cl_2 at −40 °C, gave after 2 h a dark-red solution which was filtered at −30 °C and yielded a bright-red powder which should be kept below −30 °C.‡ Its IR spectrum [ν(CO) region] is similar to that found for **1**. However two main products, in approximately 1 : 1 ratio, were detected by $^{31}P\{^1H\}$ NMR and have very similar data. The former is characterized by two doublets at δ 58.0 and 35.3 with $^2J(PP)$ 70.5 Hz and the latter by two other doublets at δ 56.7 and 34.7 with $^2J(PP)$ 69.1 Hz. Further stirring of this red solution for 2 h at −30 °C did not result in any change and there was no evolution from one product to the other. However, if the reaction mixture is left standing in CH_2Cl_2 at room temp. for 2 d, $^{31}P\{^1H\}$ NMR monitoring shows the progressive formation of two new products and the disappearance of those described above. After one week, the solution became bright-green and contained only the two new products. Product **2** is characterized by a pair of doublets at δ 64.2 and 28.8 with $^2J(PP)$ 107.2 Hz, and product **3** by a pair of triplets centered at δ 63.1 and 21.7 with $^2J(PP)$ 99.8 Hz. Very dark single crystals of **2** were obtained by fractional crystallisation (slow diffusion of hexane into a concentrated solution in CH_2Cl_2) and their structure was determined by X-ray diffraction (Fig. 1).§

This rhombus-like molecule provides the first structure of a SnFePd ring. The Pd, two Fe and four P atoms are nearly coplanar and the four membered ring $PdFe_2Sn$ is folded by 9.97(9)° along the Fe–Fe axis. The sum of the angles around the Pd atom is exactly 360°, *i.e.* the coordination sphere around this atom is perfectly planar. The Fe(1)–Pd–Fe(2) angle is 93.51(8)° whereas the opposite Fe(1)–Sn–Fe(2) angle of 106.89(8)° reflects the nearly tetrahedral arrangement around the Sn atom. The coordination sphere around the Fe atoms is distorted octahedral.[1l,n,4] The Fe–Sn distances are 2.517(3) and 2.520(3) Å and are smaller than those found in **1** [2.6736(9) and 2.645(1) Å]. The Fe–Pd distances [2.763(3), 2.791(3) Å] are longer than those found in related dppm bridged complexes such as $[Fe(CO)_3\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})PdCl]$ [2.582(1) Å] or $[Fe(CO)_3\{Si(OMe)_3\}(\mu\text{-dppm})Pd(\eta^3\text{-}C_3H_4Me\text{-}2)]$ [2.6994(7) Å] or $[Fe(CO)_3\{Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pd(SnPh_3)]$ [2.6655(5) Å].[5] Neither the Pd–Sn (3.389(2) Å) nor the Fe(1)–Fe(2) distances [4.046(3) Å] indicate a metal–metal interaction across the ring.

During attempts to optimize the yield of **2**, we have reacted a solution of **1** with 1 equiv. of $[PdCl_2(SEt_2)_2]$ in refluxing

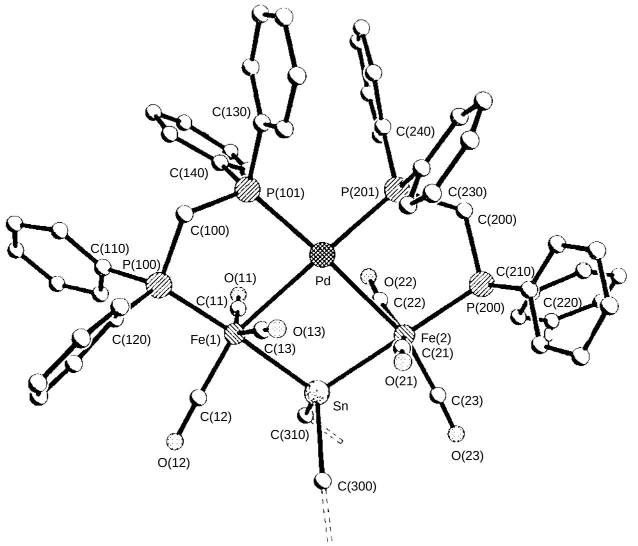
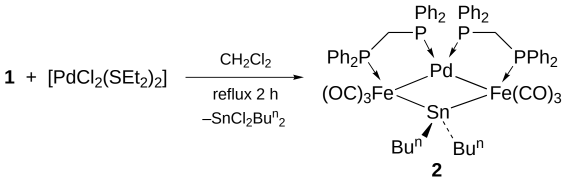


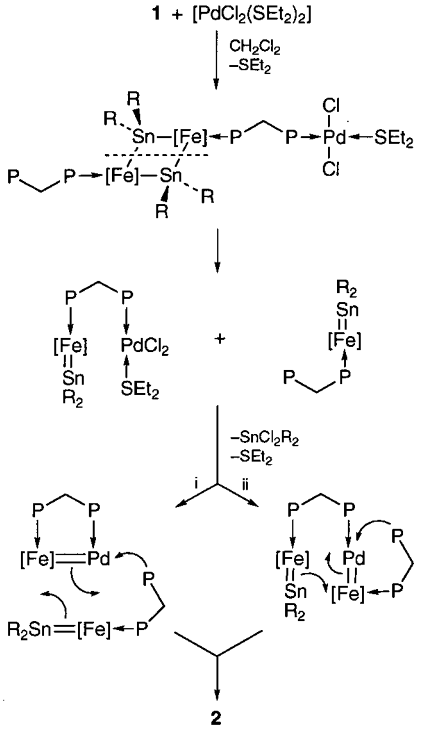
Fig. 1 View of the structure of **2**. The dotted lines at C(300) and C(310) indicate the disorder of the butyl groups. Selected bond distances (Å) and angles (°): Pd–Fe(1) 2.763(3), Pd–Fe(2) 2.791(3), Sn–Fe(1) 2.520(3), Sn–Fe(2) 2.517(3), Pd–P(101) 2.347(4), Pd–P(201) 2.325(4), Sn–C(300) 2.421(12), Sn–C(310) 2.31(2), Fe(1)–C(11) 1.79(2), Fe(1)–C(12) 1.74(2), Fe(1)–C(13) 1.79(2), Fe(1)–P(100) 2.210(5), Fe(2)–C(21) 1.76(2), Fe(2)–C(22) 1.78(2), Fe(2)–C(23) 1.76(2), Fe(2)–P(200) 2.201(5); Fe(1)–Pd–Fe(2) 93.51(8), Fe(1)–Sn–Fe(2) 106.89(8), Sn–Fe(1)–Pd 79.69(7), Sn–Fe(2)–Pd 79.20(7), P(201)–Pd–P(101) 97.1(2), P(101)–Pd–Fe(1) 83.52(12), P(201)–Pd–Fe(2) 85.91(11), C(300)–Sn–C(310) 106.9(8), C(13)–Fe(1)–C(11) 147.6(8), C(21)–Fe(2)–C(22) 149.7(8).



Scheme 1

CH_2Cl_2 for 2 h. The solution became green and a dark-green powder of **2** was isolated in 51% yield (Scheme 1).

The first step of this unusual reaction is likely to be palladium coordination to a phosphorus lone pair of **1** (Scheme 2). The subsequent steps can only be speculative at this stage. Fragmentation of the Fe_2Sn_2 ring would occur and it is conceivable that replacement of one 'Fe=SnR$_2$' unit with an isolobal 'Fe=PdLL' moiety with elimination of $SnCl_2Bu^n_2$ would be followed by combination of this moiety with the remaining equivalent iron–stannylene.



Scheme 2 Tentative pathways to the formation of **2**. Alternatives i and ii correspond to formal intra- or inter-molecular elimination of $SnCl_2R_2$. R = Bu^n; [Fe] = Fe(CO)$_3$.

During attempts to extend the formation of this complex to other metal centers we have found that reaction of **1** with [PtCl$_2$(NCPh)$_2$] under similar conditions (CH_2Cl_2, 2 h, reflux) appears less selective but yields a product **4** similar to **2** on the basis of spectroscopic data.‡

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Footnotes and References

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† Dedicated to Professor Pascual Royo (Universidad de Alcala) on the occasion of his 60th birthday.

‡ All reactions were performed under purified nitrogen, using carefully dried solvents.

Syntheses: [(OC)$_3$Fe(μ-SnBu$^n_2$)(μ-dppm)Pd(μ-dppm)Fe(CO)$_3$] **2**: to a solution of **1** in CH_2Cl_2 (0.258 g, 0.17 mmol) was added [PdCl$_2$(SEt$_2$)$_2$] (0.061 g, 0.17 mmol). The solution was refluxed for 2 h, then filtered and concentrated. Yield: 51%. IR (CH_2Cl_2) ν(C≡O) 1980m, 1949m, 1918vs cm^{-1}; (KBr) 1959m, 1925s, 1895vs, 1884vs cm^{-1}. NMR ^{1}H (CD_2Cl_2): δ 0.88 (t, 3 H, CH$_2$C*H*$_3$), 0.98 (t, 3 H, CH$_2$C*H*$_3$), 1.20–2.05 (m, 12 H, CH$_2$), 3.56 [t, 2 H, PCH$_2$P, ^2J(PH) 9.48 Hz], 3.57 [t, 2 H, PCH$_2$P, ^2J(PH) 9.56 Hz], 6.79–7.40 (m, 40 H, Ph). NMR ^{31}P{^{1}H} (CD_2Cl_2): δ 64.2 [d, P(Fe), ^2J(PP) 107.2, ^2J(P^{117,119}Sn) 212.9 Hz], 28.8 [d, P(Pd), ^2J(PP) 107.3 Hz].

[(OC)$_3$Fe(μ-SnBu$^n_2$)(μ-dppm)Pt(μ-dppm)Fe(CO)$_3$] **4**: to a solution of **1** in CH_2Cl_2 (0.300 g, 0.20 mmol) was added [PtCl$_2$(NCPh)$_2$] (0.095 g, 0.20 mmol). The solution was refluxed for 2 h, then filtered and concentrated. The brown powder was precipitated by addition of hexane. Yield: 55%. IR (CH_2Cl_2) ν(C≡O) 1990w, 1955m, 1920s cm^{-1}. NMR ^{31}P{^{1}H} (CD_2Cl_2): δ 77.5 [d, P(Fe), ^2J(PP) 49.3 Hz], 20.5 [d, P(Pd), ^2J(PP) 49.3 Hz].

§ *Crystal data* for **2**. Dark red crystals (0.4 × 0.3 × 0.2 mm) were mounted on a Siemens SMART CCD area detector diffractometer. Mo-Kα radiation (λ = 0.710 73 Å, graphite monochromated). Monoclinic, space group $P2_1/n$, a = 17.5349(7), b = 18.6137(7), c = 17.8860(7) Å, β = 90.781(1)°, U = 5837.3(4) Å^3, Z = 4, D_c = 1.797 g cm^{-3}. The cell dimensions were refined with all unique reflections. The data collection at 303(2) K covered a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different ϕ angle for the crystal and each exposure took 20 s and covered 0.3° in ω. The collected data range was $1.58 \leqslant \theta \leqslant 23.00°$ ($-25 \leqslant h \leqslant 24$, $-22 \leqslant k \leqslant 26$, $-16 \leqslant l \leqslant 25$) with a crystal-to-detector distance of 5.85 cm. 27 071 reflections were collected, and 8134 unique reflections (R_{int} = 0.136) were obtained after correction of polarization and Lorentz effects (μ = 2.09 mm^{-1}). An empirical absorption correction with the program SADABS was carried out.[5] The structure was solved by direct methods (SHELXS86). Refinement was performed by the full-matrix least-squares method based on F^2 (SHELXL93). All non-hydrogen atoms were refined with anisotropic thermal parameters with exception of the Bu^n carbon atoms. The hydrogen atoms were added in idealized positions and were refined with a riding model. We were not able to refine the two Bu^n groups due to their strong disorder. Only the anchor C atoms were found and were refined isotropically. The positions C(2)–C(4) were totally smeared over the whole cone angle opened by the vector originating in the Sn atom. Various routines and ways of modelling the disorder of the Bu groups were attempted without success. There was neither convergence of the refinements nor an improvement of the R factors. The missing Bu^n groups cause the relatively high R values [R = 0.103, R_w = 0.28 for 5265 reflections with $I \geqslant 2.0\,\sigma(I)$; $w = 1/[\sigma^2(F_o^2) + (0.1437\,P)^2 + 118.83\,P]$ [$P = (F_o^2 + 2\,F_c^2)/3$]. The largest residual electron density was 2.486 e Å^{-3}. CCDC 182/588.

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