Reactivity of Heterobimetallic Alkoxysilyl and Siloxyl Complexes in the Dehydrogenative Coupling of Stannanes

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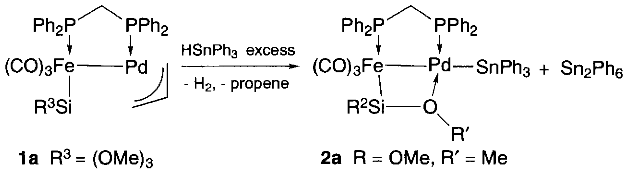
Heterobimetallic iron-palladium alkoxysilyl- and siloxyl-complexes catalyse the dehydrogenative tin–tin coupling reaction; high turnover numbers are obtained, whereas modifications of the silicon-containing ligand strongly influence the efficiency of the catalyst.

We have recently reported the synthesis of $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pd(SnPh_3)]$ **2a** from $(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Pd(\eta^3\text{-allyl})]$ **1a** and $HSnPh_3$. Interestingly, propene elimination was accompanied by evolution of H_2 and formation of Sn_2Ph_6 (*ca.* 10%) (Scheme 1).[1] We now report that heterobimetallic Fe–Pd siloxyl complexes are efficient catalysts for the dehydrogenative coupling of stannanes. The kinetics of the reaction and the catalytic activity are very sensitive to the nature of the silyl ligand.

Hexaorganoditin derivatives have a wide range of applications and are usually prepared by various organic methods.[2] Surprisingly, the dehydrogenative coupling of $HSnR_3$ has received little attention.[3] Only a few examples where this reaction is catalysed by organometallic complexes have been reported: $[PdCl_2(MeCN)_2]$, $[Pd(Ph)I(PPh_3)_2]$,[4] and $[Ph_3PCuH]_6$[5] have been used but low catalytic activities were observed. The oligomerisation of H_2SnBu_2 in the presence of metallocene derivatives of Ti and Zr has also been described.[6]

In an attempt to prepare the bimetallic siloxyl complex $(OC)_3Fe\{\mu\text{-}SiMe(OSiMe_3)(OSiMe_3)\}(\mu\text{-dppm})Pd(SnPh_3)]$ **2b** by treating $HSnPh_3$ (two to threefold excess) with a toluene solution of $[(OC)_3\{(Me_3SiO)_2MeSi\}Fe(\mu\text{-dppm})Pd(allyl)]$ **1b**, we noted a vigorous gas evolution with an immediate change from yellow to orange–red. ^1H and $^{31}P\{^1H\}$ NMR monitoring of the reaction (in $[^2H_8]$-toluene) only showed resonances due to **1b**, whereas Sn_2Ph_6 precipitated (Scheme 1). Further addition of a 10 to 15-fold excess of $HSnPh_3$ only led to the formation of more Sn_2Ph_6. A decrease in the intensity of the $^{31}P\{^1H\}$NMR resonances of **1b** was observed ($Ph_3P{=}O$ int. ref.) and no other product was evidenced. These observations indicate that **1b** is a catalyst (precursor) for the dehydrogenative tin–tin bond formation.

Increasing the ratio $[HSnPh_3]/[\mathbf{1b}]$ and keeping all other parameters unchanged† gave the turnover numbers (TON) reported in Table 1. In run 1, the TON found (490) already indicated a good catalytic activity. Addition of more $HSnPh_3$ to the final reaction mixture did not yield more Sn_2Ph_6 or H_2 and NMR and IR measurements showed the disappearance of **1b**. Owing to the high conversion (91%), we suspected that the catalysis did not proceed further because of the lack of substrate. Indeed, increasing the ratio $[HSnPh_3]/[\mathbf{1b}]$ led to a parallel rise of the TON (runs 2–6). Similar TON were obtained for runs 6–8, indicating that the maximum catalytic activity of **1b** in Et_2O had been reached (*ca.* 1560 TON).



1a $R^3 = (OMe)_3$
b $R^3 = Me(OSiMe_3)_2$

2a R = OMe, R′ = Me
b $R^2 = Me(OSiMe_3)$, R′ = $SiMe_3$
(not isolated)

Scheme 1

Under the conditions of run 6, the volume of H_2 released has been measured (TON *vs.* time is shown in Fig. 1). After *ca.* 1 h, a plateau was reached, which corresponds to the maximum catalytic activity of **1b** found above. A short induction period was noticed (see inset). The reaction rate rapidly increased and reached a maximum after 10–15 s, the turnover frequency being > 180 000 h^{-1}. It then decreases, presumably because of the relatively short lifetime of the catalyst. Identical kinetic data were obtained with larger quantities of $HSnPh_3$, thus showing no influence of the substrate concentration.

We reinvestigated the reaction between **1a** and $HSnPh_3$[1] in order to examine the difference in reactivity between **1a** and **1b** under similar reaction conditions‡ and therefore the influence of the alkoxysilyl group. When $HSnPh_3$ was added to an Et_2O solution of **1a** an immediate change from yellow to red was observed accompanied by a mild evolution of H_2. After three days, the solution was pale yellow and a precipitate of Sn_2Ph_6

Table 1 Catalytic activity of **1b** for the synthesis of Sn_2Ph_6 from $HSnPh_3$ in Et_2O

Run[a]	Mol ratio $[HSnPh_3]/[\mathbf{1b}]$	Turnover number (Δ)[b]	Conversion rate (%)[c]
1	1070	490 (30)	91
2	1275	600 (25)	94
3	1530	720 (40)	94
4	1710	815 (35)	95
5	3560	1350 (20)	76
6	5180	1560 (30)	60
7	6475	1560 (35)	48
8	7770	1560 (25)	40

[a] Data refer to the average values determined for 3–5 experiments/run; for the reaction conditions see footnotes; [b] *n* Sn_2Ph_6 formed/*n* catalyst. Δ = difference between highest and lowest values given in parentheses; [c] *n* $HSnPh_3$ consumed/*n* $HSnPh_3$ initially added.

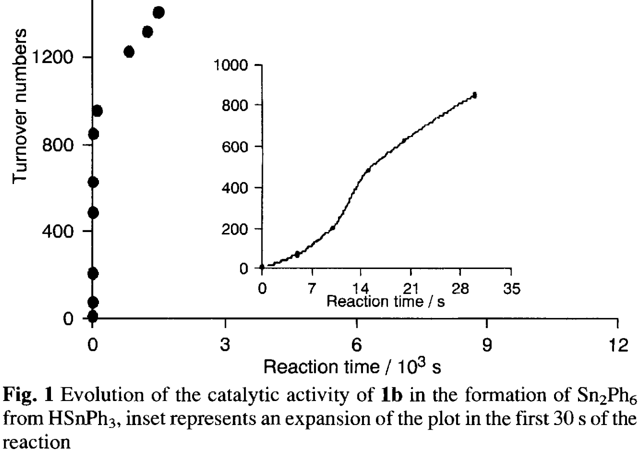


Fig. 1 Evolution of the catalytic activity of **1b** in the formation of Sn_2Ph_6 from $HSnPh_3$, inset represents an expansion of the plot in the first 30 s of the reaction

was formed (0.500 g, TON: 650), whereas $^{31}P\{^1H\}$ NMR or IR measurements gave no evidence for **1a** or **2a**. These data indicate that **1a** also catalyses the formation of Sn_2Ph_6, but much more slowly and less effectively than **1b**. Monitoring the formation of Sn_2Ph_6[§] gave the plot shown in Fig. 2 (○). The general aspect of the curve is similar to that obtained with **1b** (●). The maximum turnover frequency is 80 h^{-1} (between 1 and 4.5 h). The plateau is only reached after more than 48 h (*cf.* 1 h for **1b**).

The change from yellow to red described above being characteristic of the formation of **2**, the latter was used instead of **1a**: a comparable catalytic activity was observed, indicating that **2** is certainly an intermediate in the catalytic process. Rapid formation of a catalytically active trimetallic Fe–Pd–Sn complex **2b** is strongly suggested by the similar colour change observed with **1b**, although the former could not be isolated owing to its high reactivity under the reaction conditions of the catalysis.

We suggest that the considerable difference of reactivity between **1a** and **1b** is related to the nature of the μ_2-η^2-SiO bridge.[3] This interaction is more stabilizing in **2a** than in **2b**, and therefore decreases the reactivity of the complex (by masking more effectively the coordination site on the palladium atom required for the catalysis to proceed). The O-donor capacity of the siloxyl ligand is reduced compared with that of an alkoxysilyl ligand owing to the more electropositive charactrer of the Si atom in the former.[7] A possible mechanism would involve the hemilability of the bridging μ_2-η^2-SiO ligand, and proceed *via* the alternate opening and closing of the Fe–Si–O–Pd four-membered ring and the transient formation of Pd^{IV} species.[8] Although the elementary transformations during catalysis would take place at the palladium centre,[¶] the function of the iron fragment is to provide the appropriate coordination environment through metal–metal bonding and the Si-containing ligand.

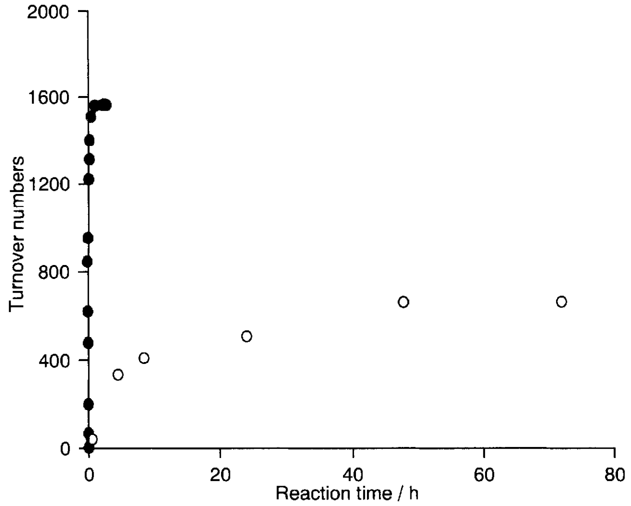


Fig. 2 Comparison between the catalytic activities of **1a** (○) and **1b** (●)

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Footnotes

[†] In a typical experiment, a large excess of $HSnPh_3$ was added at 25 °C to an Et_2O (15 ml) solution of **1b**. The mixture was stirred for 1 h after which time no more evolution of H_2 was observed. Most of the Sn_2Ph_6 (>90%) was collected by filtration and dried under reduced pressure. The filtrate was evaporated to dryness and the residue washed with 2 × 3 ml of cold Et_2O (−10 °C), thus allowing the recovery of the remaining Sn_2Ph_6 (<10%); mp > 225 °C.

[‡] Reaction conditions for which the optimum catalytic activity of **1b** had been obtained.

[§] A set of 18 experiments was started at $t = t_o$ using standard solutions of **1a** (8.8 mg, 1.1 10^{-6} mol) and a large excess of $HSnPh_3$ (5000 equiv.) in 15 ml of Et_2O. At t = 1, 4.5, 8.5, 24, 48 and 72 h, three reactions were stopped and the Sn_2Ph_6 formed isolated and weighed. The average TONs were used for the plot.

[¶] This is supported by the work of Beletskaya[4] and other reactions we have carried out with palladium and iron mononuclear complexes.[9]

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