H/D Exchange of Organosilanes catalysed by Heterogenised Zirconium Hydride Complexes

Béatrice Coutant, Françoise Quignard and Agnès Choplin*

Institut de Recherches sur la Catalyse, conventionné à l'Université Cl. Bernard, Lyon-1, 2 avenue A. Einstein, 69 626 Villeurbanne Cedex, France

Silica supported zirconium hydride complexes activate stoichiometrically and catalytically the Si–H bond of primary, secondary and tertiary organosilanes, $R_{4-x}SiH_x$, R = alkyl, aryl.

The catalytic reaction of dehydrogenative coupling of silanes could substitute the industrial synthesis of polysilanes from chlorosilanes *via* a Wurtz-type reaction. This is confirmed by the recent results of Corey, Harrod and Tilley *et al.*[1] The most efficient catalysts of this reaction so far described in the literature are complexes of elements of Group 4, such as $(\eta^5\text{-}C_5H_5)_2MR_2$ (R = H, alkyl). The first step of the presumed catalytic cycle is the activation of the Si–H bond on the electrophilic metal centre.[2]

We have recently described the synthesis of silica supported zirconium hydrides, $[Zr]_s$–H, from tetraneopentylzirconium and a silica, partially dehydroxylated at 773 K under vacuum [eqn. (1)].[3]

$$Zr(CH_2CMe_3)_4 + \geqslant SiOH \rightarrow \geqslant SiO\text{–}Zr(CH_2CMe_3)_3 \xrightarrow{H_2} (\geqslant SiO)_xZrH_{4-x} \quad x = 2 \text{ or } 3 \quad (1)$$

These zirconium hydride complexes show chemical properties which are related to the fact that they are immobilized at the solid surface *via* a strong covalent bond (stabilization of the active mononuclear complex) and to the presence of electron-attracting siloxy ligands in the coordination sphere of Zr. Their most interesting property is their capacity to activate alkanes, including methane, under very mild conditions.[3–4] We now report that these supported zirconium hydrides are able to activate, at room temperature, the Si–H bond of primary, secondary and tertiary organosilanes.

The introduction of $PhSiH_3$ (1.8 Pa, 298 K) on a self-supported disk of $[Zr]_s$–H, generated *in situ* following a described procedure,[3] leads to an instantaneous colour change from light pink to red–brown; this strongly suggests the onset of a reaction leading to the formation of a silicon–zirconium bond.[5] This reaction clearly involves the Zr–H bond as indicated by the disappearance of its characteristic stretching vibrational band at 1635 cm^{-1}. Clearly this phenomenon is not due to accidental hydrolysis as shown by the absence of ν(Zr–OH) bands in the 3700 cm^{-1} region.[3] Qualitative analysis by chromatography of the gas phase reveals the evolution of hydrogen. Evacuation of the gas phase leaves a surface complex, characterized by vibrational bands in the 3000 cm^{-1} region [$\nu(C\text{–}H)_{ar}$] and at 2161 cm^{-1} [ν(Si–H)]. All these data are in agreement with the occurrence of the reaction shown in eqn. (2):

$$PhH_2Si\text{–}H + [Zr]_s\text{–}H \rightarrow [Zr]_s\text{–}SiH_2Ph + H_2 \quad (2)$$

When the same type of experiment is performed under D_2 [$p(D_2)$ 5 × 10^4 Pa, 298 K, silane/Zr (mol/mol) = 20] with a larger sample of solid (100 mg), analysis of the gas phase by IR spectroscopy indicates that only a trace amount of $PhSiH_3$ remains after 5 min, and that deuteriated phenylsilanes, characterized by ν(Si–D) bands centred at 1597 cm^{-1}, are formed. GC–MS analysis shows essentially perdeuteriated phenylsilane, $PhSiD_3$ [*m*/*z* 111 (d_3), no peak at 108 (d_0)]. Although these reaction conditions would not favour Si–Si coupling (large excess of D_2), other deuteriated silylated products are formed, most probably oligomers; this is in agreement with the complexity of the IR spectrum (Table 1) and the intensity decrease of the ν(C–H) vibrational bands.

All these data demonstrate that the supported zirconium hydride complexes catalyse the reaction of H/D exchange of a primary silane such as $PhSiH_3$ [eqn. (3)].

$$PhSiH_3 \xrightarrow[D_2,\ 298\ K]{[Zr]_s\text{–}H} PhSiD_3 + \text{oligomers} \quad (3)$$

Secondary silanes, such as $PhMeSiH_2$, present the same type of reactivity under similar conditions as evidenced by gas phase IR spectroscopy (Table 1). Partial and full deuteriation is further confirmed by MS [*m*/*z* 123 (d_1), 124 (d_2)].

Most interesting is the case of the tertiary silane, Et_3SiH. First, the Si–H bond is deuteriated and this with a rate close to that observed with secondary silanes: the gas phase IR spectrum is characterized by the appearance and increase of a ν(Si–D) band at 1536 cm^{-1} (Table 1). Second, a C–H bond of the ethyl group is concomitantly deuteriated, as evidenced by the simultaneous intensity increase of two bands at 2218 and 2187 cm^{-1}, respectively, assigned to ν(C–D) stretching vibrations (Fig. 1).

Table 1 Vibrational stretching frequencies of Si–H and Si–D bonds

Silane	ν(Si–H)/cm^{-1}	ν(Si–D)/cm^{-1}
$PhSiH_3$ [a]	2161	
$PhSiH_3 + D_2$ [a]		1597–1564, 1559, 1554
$PhSiD_3$ [b]		1555, 1575
$PhMeSiH_2$ [a]	2141	
$PhMeSiH_2 + D_2$ [a]	2141	1557
Ph_2SiH_2	2145	
Ph_2SiD_2 [b]		1565, 1549
Et_3SiH [a]	2109	
$Et_3SiH + D_2$ [a]	2109	1536
Ph_3SiH [b]	2128	
Ph_3SiD [b]		1545

[a] This work, Si/Zr = 20, *T* = 298 K, $p(D_2)$ 5 × 10^4 Pa. [b] Ref. 6.

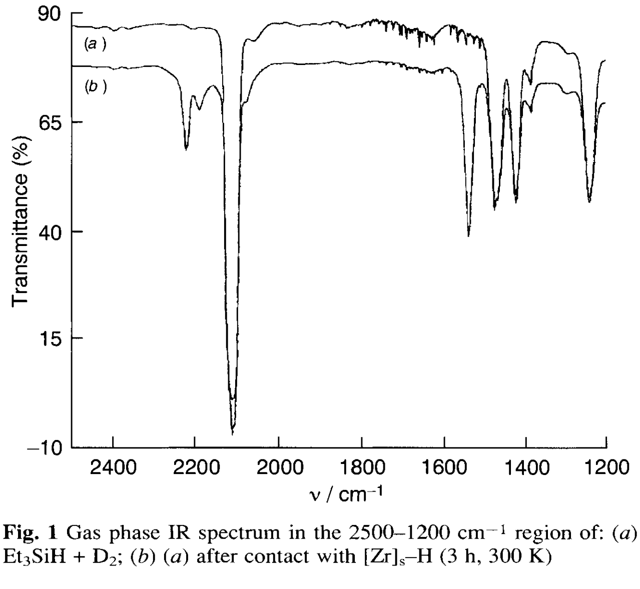

Fig. 1 Gas phase IR spectrum in the 2500–1200 cm^{-1} region of: (*a*) $Et_3SiH + D_2$; (*b*) (*a*) after contact with $[Zr]_s$–H (3 h, 300 K)

The fact that C–H and Si–H activation occur under the same conditions with a substrate like triethylsilane is currently under investigation in order to capitalize on the special properties of this kind of catalyst for the synthesis of polycarbosilanes.

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