

Mechanistic studies on ethylene silylation with chlorosilanes catalysed by ruthenium complexes†

Sébastien Lachaize, Sylviane Sabo-Etienne,* Bruno Donnadieu and Bruno Chaudret

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 04, France. E-mail: sabo@lcc-toulouse.fr

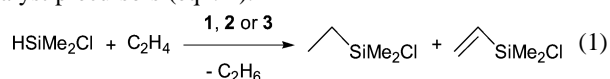
Received (in Cambridge, UK) 29th October 2002, Accepted 29th November 2002

First published as an Advance Article on the web 11th December 2002

Silylation of ethylene by chlorosilanes is catalysed by ruthenium complexes. Mechanistic investigations reveal the presence of a complicated network of reactions leading to new σ -silane, ethylene and silyl complexes.

Vinylsilanes are useful reagents in organic chemistry and chlorovinylsilanes are important monomers for polyorganosiloxane and ceramic production.¹ Dehydrogenative silylation of olefins catalysed by transition metal complexes can be an interesting alternative to the various methods available for their preparation. In some cases, it can compete favourably with hydrosilylation to produce vinylsilanes in rather good yields. We have previously reported an efficient synthesis of triethylvinylsilane by using the bis(dihydrogen) complex $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$ (**1**)² as catalyst precursor and shown that the best results were obtained when using the ethylene complex $\text{RuH}(\text{C}_2\text{H}_4)\{\eta^3\text{-C}_6\text{H}_8\text{PCy}_2\}(\text{PCy}_3)$ (**2**) deriving from **1**, and a high pressure of ethylene.^{3a} We have recently extended the scope of our system to disilane activation. In that case, a more complicated system is obtained and the selectivity and activity are highly dependent on the chain length n of the disilane $\text{HSiR}_2(\text{CH}_2)_n\text{SiR}_2\text{H}$.^{3b} We now report an unexpected tolerance of our system for chlorosilane activation by ethylene. Mechanistic studies allow the identification of new σ -chlorosilane and chlorosilyl complexes which generate different catalytic cycles. Our findings evidence the competition between Si–H and Si–Cl bond activation.

The catalytic experiments were performed at room temperature with ethylene pressure in the range 1.5–20 bar and **1**, **2** or the chloro complex $\text{RuHCl}(\eta^2\text{-H}_2)(\text{PCy}_3)_2$ (**3**)⁴ were tested as catalyst precursors (eqn. 1).



Analysis of the results concerning chlorodimethylsilane activation are described in Table 1. We were surprised to find

Table 1 Reaction^a of ethylene with HSiMe_2Cl catalysed by the compounds **1**, **2** and **3**

Entry no.	Catalyst	$P_{\text{C}_2\text{H}_4}$ /bar	$\text{C}_2\text{H}_3\text{SiMe}_2\text{Cl}/$ $\text{C}_2\text{H}_5\text{SiMe}_2\text{Cl}^b$
1	1	1.5	54:46
2	1	3	27:73
3	1	20	10:90
4 ^c	2	1.5	45:55
5 ^c	2	3	24:76
6 ^c	2	20	15:85
7	3	1.5	41:59
8	3	3	31:69
9	3	20	8:92

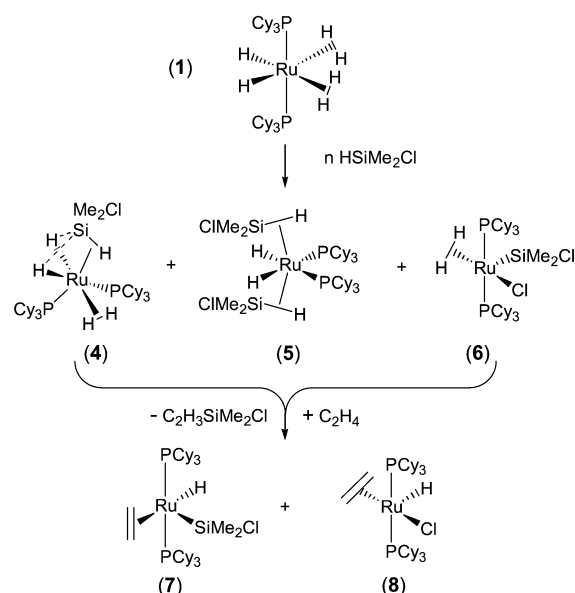
^a In toluene, with 100 equiv. of HSiMe_2Cl . ^b Determined by GC; in all cases, HSiMe_2Cl was totally consumed. ^c C_2H_4 atmosphere before HSiMe_2Cl addition.

† Electronic supplementary information (ESI) available: full characterisation data. See <http://www.rsc.org/suppdata/cc/b2/b210552g/>

that the vinyl product was favoured with a low pressure of ethylene. This is in contrast to our previous results on triethylsilane activation and prompted us to carry out mechanistic investigation. In a first stage, we have examined the results of the addition of HSiMe_2Cl to **1** and then the behaviour of the new mixture under ethylene. In a second set of experiments, we have changed the order of addition of the reactants, adding ethylene to **1** and then the silane.

Reaction of **1** with an excess of HSiMe_2Cl (2 or 10 equiv.) gives a mixture of three silicon-containing complexes **4–6** characterised by NMR studies (see Scheme 1). $\text{RuH}_2(\eta^2\text{-H}_2)(\eta^2\text{-H-SiMe}_2\text{Cl})(\text{PCy}_3)_2$ (**4**) and $\text{RuH}_2(\eta^2\text{-H-SiMe}_2\text{Cl})_2(\text{PCy}_3)_2$ (**5**) are formulated as σ -silane complexes⁵ by comparison with analogous mono and bis(silane) complexes,⁶ previously characterised by NMR and X-ray structures. Complexes **4** and **5** adopt a *cis* configuration for the two bulky PCy_3 ligands as a result of stabilising Secondary Interactions between Silicon and Hydrogen Atoms (SISHA interactions).[‡]§ The third complex **6** results from Si–Cl bond breaking and is formulated as a 16-electron dihydrogen(silyl) complex $\text{RuCl}(\eta^2\text{-H}_2)(\text{SiMe}_2\text{Cl})(\text{PCy}_3)_2$ on the basis of multinuclear NMR data and deuteration experiment.¶ **6** can be directly generated by addition of 1 equiv. HSiMe_2Cl to **3**. It is noteworthy that traces of **3** were detected in the reaction mixture of **1** with one equiv. of HSiMe_2Cl .

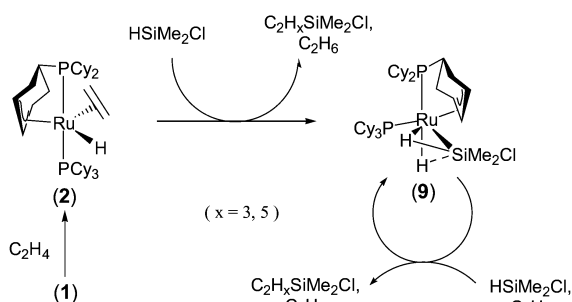
The C_7D_8 solution containing **4–6**, obtained by addition of 2 equiv. of HSiMe_2Cl to **1**, was then saturated with C_2H_4 and the reaction was monitored by multinuclear NMR spectroscopies (^1H , ^{31}P , ^{13}C and ^{29}Si). The starting silane was totally consumed and chlorodimethylvinylsilane was detected as a result of dehydrogenative silylation. Two new ethylene complexes, $\text{RuH}(\text{C}_2\text{H}_4)(\text{SiMe}_2\text{Cl})(\text{PCy}_3)_2$ (**7**) and $\text{RuHCl}(\text{C}_2\text{H}_4)(\text{PCy}_3)_2$ (**8**), were characterised. It is likely that **8** arises from the reaction



Scheme 1

of **6** with C₂H₄. This was confirmed by adding HSiMe₂Cl to **3**, thus generating **6 in situ**, and then bubbling C₂H₄. This resulted in quantitative formation of **8**.|| Complex **7** should play a major role in catalysis as the three key ligands, *i.e.* a hydride, a silyl and an ethylene, are linked to the ruthenium.

In a second set of experiments, we have inverted the addition order of the reactants to our precursor **1**, and first produced the ethylene complex (**2**). We then added 2 equiv. of HSiMe₂Cl to **2** and detected vinylsilane, ethane and the formation of a new complex RuH(η²-H-SiMe₂Cl){(η³-C₆H₈)PCy₂}(PCy₃) (**9**) that was fully characterised by multinuclear NMR and X-ray data (see Scheme 2).†



Scheme 2

We have already reported analogous complexes in the case of HSiEt₃ and HSiMe₂(CH₂)₂SiMe₂H activation.³ The corresponding complexes, RuH(η²-H-SiEt₃){(η³-C₆H₈)PCy₂}(PCy₃) (**10**) and RuH(η²-H-SiMe₂(CH₂)₂SiMe₂H){(η³-C₆H₈)PCy₂}(PCy₃) (**11**), were formulated as dihydride(silyl) ruthenium (iv) complexes as a result of oxidative addition of the silane. In view of the X-ray and Si NMR data obtained for **9**, we now propose a ruthenium (ii) formulation as we have evidenced the presence of a σ-Si-H bond. The X-ray structure of **9** is shown in Fig. 1.** The phosphines are in a *cis* position, favouring the formation of a σ-Si-H bond and a SISHA interaction.⁷ The distance H1-Si is 1.91(2) Å, at the higher limit for σ-Si-H bonds.⁵ The SISHA interaction H2...Si is characterised by a distance of 1.99(2) Å. These data are in agreement with the results obtained from a 1D HMQC ²⁹Si-¹H-³¹P NMR experiment allowing the determination of two J_{Si-H} constants of 37 Hz for H1 and 24 Hz for H2.

Remarkably, **9** is stable under C₂H₄ whereas the analogous complex **10** regenerates **2** and eliminates ethyl and vinylsilane. Thus **9** generates another catalytic cycle as seen by NMR monitoring after mixing **9** and HSiMe₂Cl under C₂H₄ atmos-

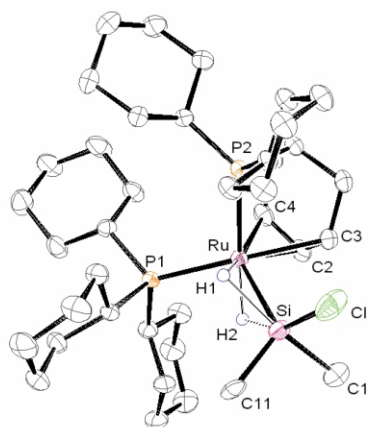


Fig. 1 ORTEP drawing of compound **9**. Selected bond lengths (Å): Ru-Si, 2.3534 (11); Ru-H(1), 1.57 (2); Ru-H(2), 1.62 (3); Si-Cl, 2.110 (5); Si-C(1), 1.924 (17); Si-C(11), 1.919 (2); Si-H(1), 1.91 (2); Si-H(2), 1.99 (2); H(1)-H(2), 2.33 (3). Selected bond angles (deg): P(1)-Ru-P(2), 107.80 (3); P(2)-Ru-H(2), 175.2 (9); P(2)-Ru-H(1), 83.2 (9); H(1)-Ru-H(2), 94.0 (13); Si-Ru-P(1), 110.67 (3); Si-Ru-P(2), 118.71 (2); Si-H(1)-Ru, 84.5 (10); Si-H(2)-Ru, 80.7 (10).

phere: formation of vinylsilane was observed, **9** remaining the only detected organometallic species. The reaction occurs at a much lower rate compared to the system with **10**. We note that **9** and **10** present the same overall structure, but the main difference is a more electropositive Si atom on **9**. This might be one of the factors responsible for the difference of activity and selectivity between HSiMe₂Cl and HSiEt₃.

In summary, activation of chlorosilane by ethylene is achieved by using RuH₂(η²-H₂)₂(PCy₃)₂ as catalyst precursor. However, chloro substituents induce a dramatic influence on selectivity and activity. A better selectivity in chlorovinylsilane might be reached by a control of the factors favouring Si-H versus Si-Cl bond breaking. It is remarkable that σ-Si-H and SISHA interactions play a major role in the process, as highlighted by the characterisation of **9**. This complex can be considered as an intermediate between arrested Ru(II) and Ru(IV) structures which are normally invoked in the elementary step of oxidative addition of a silane in catalysis. Further investigation including a full theoretical analysis and comparative experiments with HSiMeCl₂ are in progress.

Notes and references

† Their geometry is supported by DFT calculations that will be published elsewhere. The role of SISHA interactions has been recently demonstrated in σ-silane ruthenium complexes. They represent the key factor for the stabilisation of several complexes and play a major role in the exchange processes.⁷

§ The complex RuH₃(SiMeCl₂)(PPh₃)₃ analogous to **4**, has been reported from the reaction of HSiMeCl₂ with RuCl₂(PPh₃)₃.⁸ The authors describe this complex as a trihydride stabilised by Ru-H...Si-E (E = Cl or C) interactions, closely related to the IHI theory developed by Nikonov.⁹

¶ The dihydrogen ligand in **6** is characterized by a triplet at -13.8 ppm with a very short J_{H-P} constant of 10 Hz and a T_{1min} value of 29 ms at 253 K (300 MHz). The HD isotopomer was generated from the addition of HSiMe₂Cl to **3d**. The measurement of a coupling constant J_{HD} of 12 Hz in RuCl(η²-HD)(SiMe₂Cl)(PCy₃)₂, leads to a calculated distance r_{HD} of 1.24 Å, in favor of a stretched dihydrogen ligand.

|| The analogous PiPr₃ complex was previously reported.¹⁰

** Crystal data for **9**: C₃₈H₇₁ClP₂SiRu, M = 754.50, triclinic, space group P $\bar{1}$, T = 180(2) K, a = 10.702(5), b = 10.739(5), c = 18.617(5) Å, α = 90.882(5), β = 91.127(5), γ = 112.928(5)°, V = 1969.6(14) Å³, Z = 2, μ = 0.602 mm⁻¹, reflections collected/unique = 19343/7182, R₁ = 0.0300, wR₂ = 0.0645, GOF = 1.027. In the silyl group, one methyl and the chlorine were disordered. CCDC 196457. See <http://www.rsc.org/suppdata/cc/b2/b210552g/> for crystallographic files in CIF format.

- (a) T. C. Kendrick, B. Parbhoo and J. W. White, *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, John Wiley & Sons, New York, 1989, Chapter 21; (b) C. Rucker, *Chem. Rev.*, 1995, **95**, 1009; (c) E. Langkopf and D. Schinzer, *Chem. Rev.*, 1995, **95**, 1375.
- (a) S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, **178-180**, 381; (b) A. F. Borowski, B. Donnadiou, J. C. Daran, S. Sabo-Etienne and B. Chaudret, *Chem. Commun.*, 2000, 543.
- (a) M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1995, **14**, 1082; (b) F. Delpech, J. Mansas, H. Leuser, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 2000, **19**, 5750.
- M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800.
- (a) For recent reviews on σ-silane complexes, see: G. J. Kubas, *Metal Dihydrogen and σ-Bond complexes*, Kluwer Academic/Plenum Publishers, New York, 2001; (b) Z. Lin, *Chem. Soc. Rev.*, 2002, **31**, 239; (c) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175.
- (a) K. Hussein, C. J. Marsden, J. C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadiou and B. Chaudret, *Chem. Commun.*, 1999, 1315; (b) F. Delpech, S. Sabo-Etienne, J. C. Daran, B. Chaudret, K. Hussein, C. J. Marsden and J. C. Barthelat, *J. Am. Chem. Soc.*, 1999, **121**, 6668.
- I. Atheaux, F. Delpech, B. Donnadiou, S. Sabo-Etienne, B. Chaudret, K. Hussein, J. C. Barthelat, T. Braun, S. B. Duckett and R. N. Perutz, *Organometallics*, 2002, **21**, 5347.
- N. M. Yardy, F. R. Lemke and L. Brammer, *Organometallics*, 2001, **20**, 5670.
- G. I. Nikonov, *J. Organomet. Chem.*, 2001, **635**, 24.
- J. N. Coalter, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gerard, E. Clot and O. Eisenstein, *New J. Chem.*, 2000, **24**, 9.