This article is published as part of the Dalton Transactions themed issue entitled:

Bridging the gap in catalysis *via* multidisciplinary approaches

Guest Editors: Christophe Coperet and Rutger van Santen Université de Lyon, France and Eindhoven University of Technology, The Netherlands



Published in issue 36, 2010 of Dalton Transactions

Image reproduced with the permission of Dieter Vogt

Articles in the issue include:

Molecular understanding of alkyne hydrogenation for the design of selective catalysts Javier Pérez-Ramírez, Blaise Bridier and Nuria Lopez Dalton Trans., 2010, DOI: 10.1039/C0DT00010H

<u>Molecular weight enlargement–a molecular approach to continuous homogeneous catalysis</u> Michèle Janssen, Christian Müller and Dieter Vogt, *Dalton Trans.,* 2010, DOI: 10.1039/C0DT00175A

<u>Structure Determination of Zeolites and Ordered Mesoporous Materials by Electron</u> <u>Crystallography</u> Xiaodong Zou, Junliang Sun, *Dalton Trans.*, 2010, DOI: 10.1039/C0DT00666A

Metal-Catalyzed Immortal Ring-Opening Polymerization of Lactones, Lactides and Cyclic Carbonates

Noureddine Ajellal, Jean-François Carpentier, Clémence Guillaume, Sophie M. Guillaume, Marion Helou, Valentin Poirier, Yann Sarazin and Alexander Trifonov, *Dalton Trans.,* 2010, DOI: 10.1039/C001226B

Visit the Dalton Transactions website for more cutting-edge inorganic and organometallic research www.rsc.org/dalton

Silyl and $\sigma\mbox{-silane}$ ruthenium complexes: Chloride substituent effects on the catalysed silylation of ethylene†

Sébastien Lachaize,^{*a,b*} Laure Vendier^{*a,b*} and Sylviane Sabo-Etienne^{*a,b*}

Received 3rd March 2010, Accepted 1st June 2010 DOI: 10.1039/c0dt00065e

Silylation of ethylene by the chlorosilanes HSiMe₂Cl and HSiMeCl₂ was catalysed by the bis(dihydrogen) complex RuH₂(η^2 -H₂)₂(PCy₃)₂ (1). Dehydrogenative silvlation leading to the formation of the corresponding vinylsilanes was in competition with hydrosilylation. The rate and selectivity of the reactions were influenced by the number of chloro substituents and the ethylene pressure. A comparative mechanistic study was performed in toluene- d_8 with the two chlorosilanes. Reaction of 1 with an excess of HSiMe₂Cl (10 equiv.) produced the σ -silane complexes RuH₂(η^2 -H₂)(η^2 -HSiMe₂Cl)(PCy₃)₂ $(2Me_2Cl)$, RuH₂(η^2 -HSiMe₂Cl)₂(PCy₃)₂ (3Me₂Cl) and the silvl complex RuCl(SiMe₂Cl)(η^2 -H₂)(PCy₃)₂ (4Me₂Cl), all characterised by multinuclear NMR spectroscopy. Complexes 2Me₂Cl and 3Me₂Cl adopt a cis configuration for the two bulky phosphine ligands as a result of stabilising SISHA (Secondary Interactions between Silicon and Hydrogen Atoms) interactions. Complex 4Me₂Cl resulted from the stoichiometric reaction of HSiMe₂Cl with 1 producing RuHCl(η^2 -H₂)(PCy₃)₂ in situ which further reacted with evolution of H₂ and formation of 4Me₂Cl. When reacting 1 with 10 equiv. of HSiMeCl₂, the corresponding complexes **3MeCl₂** and **4MeCl₂** were detected as well as traces of **2MeCl₂**. The reactivity toward ethylene was then examined. Under catalytic conditions (excess silane in toluene- d_8 , ethylene atmosphere) only two compounds could be characterised: free PCy_3 and the new $(\eta^6$ -aryl)(disilyl) complexes of the general formula Ru $(\eta^6$ -C₆D₅CD₃)(SiMe_{3-n}Cl_n)₂(PCy₃) (6Me_{3-n}Cl_n-d₈) n = 1.2). The X-ray structure of **6MeCl**₂ was obtained on a single-crystal at 160 K. When only 2 equiv. of $HSiMe_2Cl$ were added, the ethylene(silyl) complex $RuH(SiMe_2Cl)(C_2H_4)(PCy_3)_2$ (7Me₂Cl) was obtained in addition to the organic products resulting from catalytic hydrogenation, hydrosilylation and dehydrogenative silvlation, *i.e.* C_2H_6 (major one), $C_2H_3SiMe_2Cl$ and $C_2H_3SiMe_2Cl$. In the case of 2 equiv. of HSiMeCl₂, upon ethylene addition, 7MeCl₂ was formed in minority compared to a new disilyl complex Ru(SiMeCl₂)₂(PCy₃)₂ (8MeCl₂) characterised by NMR spectroscopy and X-ray diffraction on a single crystal at 160 K. In 8MeCl₂, a formal 14-electron species, stabilisation through two agostic C-H bonds of the cyclohexyl groups was ascertained by DFT calculations.

Introduction

Silane activation has attracted a lot of interest in the homogeneous and heterogeneous communities because of the importance of the silicon industry.¹ Hydrosilylation of alkenes is catalyzed by a variety of transition-metal complexes, and in some cases dehydrogenative silylation, a secondary reaction leading to the formation of the corresponding vinylsilanes, can be quite competitive. The Chalk–Harrod mechanism and its modified version are often invoked to explain these processes, with oxidative addition of the Si–H bond to the metal center being a key elementary step leading to the formation of the corresponding silyl species (Scheme 1).² However, in view of the knowledge gained on the properties of σ -complexes, an alternative mechanism involving the intermediacy of σ -silane and σ -dihydrogen complexes can take place, thus avoiding a change in the oxidation state of the metal center. Such a mechanism has been termed σ -CAM mechanism (σ -complex assisted metathesis mechanism) by Perutz and Sabo-Etienne.³ In the specific case of silanes, the establishment of secondary interactions between silicon and hydrogen atoms around the metal center (SISHA interactions) allows for isomerisation of various σ -intermediates leading to subsequent functionalization.⁴ It has been pointed out that the selectivity in vinylsilanes depends on different factors, among them ethylene pressure, order of addition of the reactants. The nature of the silicon substituents is also a key parameter. In this context, activation of chlorosilanes deserves a specific attention. Indeed chlorosilanes are good precursors for a wide variety of reagents in silicon chemistry (silane coupling agents, silicones, hybrid inorganic-organic materials, ceramics etc.).^{1,5} However, when using chlorosilanes one can face competition between Si-H and Si-Cl bond activation leading in particular to redistribution reactions.⁶ It is thus important to gain mechanistic information on elementary steps involved in catalytic reactions with chlorosilanes.

As part of our broad program on H–E bond activation,⁷ we became interested in ruthenium-catalysed silylation of ethylene. By using the bis(dihydrogen) complex precursor $RuH_2(\eta^2-H_2)_2(PCy_3)_2$ (1) (Cy = C₆H₁₁) we were able to favour the synthesis

^aCNRS, LCC (Laboratoire de Chimie de Coordination), 205 Route de Narbonne, F-31077 Toulouse, France

^bUniversité de Toulouse, UPS, INPT, F-31077 Toulouse, France. E-mail: sylviane.sabo@lcc-toulouse.fr

 $[\]dagger$ Electronic supplementary information (ESI) available: DFT data. CCDC reference numbers 765257 (**8MeCl**₂) and 765258 (**6MeCl**₂). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00065e



Scheme 1 The Chalk-Harrod and Chalk-Harrod modified catalytic cycles for alkene hydrosilation.

of vinylsilanes through dehydrogenative silylation. In the case of triethylsilane, very high selectivity into the corresponding vinylsilane was achieved at ambient temperature and under moderate ethylene pressure (1 to 20 bar).8 Total conversion of HSiEt₃ was achieved in 105 min under 1 bar of ethylene with a 78% selectivity in triethylvinylsilane. The selectivity increased up to 97% by introducing ethylene (1 bar) prior to the addition of HSiEt₃. We proved that the ethylene complex RuH[$(\eta^3 C_6H_8$)PCy₂](PCy₃)(C₂H₄) resulting from the reaction of 1 with ethylene was the catalyst resting state and that 1 served as an effective catalyst precursor. The reaction was subsequently extended to allyldimethylsilane,9 and disilanes.10 We also found an unexpected tolerance of our system for chlorosilanes.¹¹ However, in the presence of chloro substituents, the situation was much more complicated than in the case of triethylsilane. Several findings derived from our preliminary studies: (i) the catalyst efficiency was reduced by introduction of an electron-withdrawing group on the silane; (ii) the ethylene complex, which was the catalyst resting state in the case of HSiEt₃ silulation and led to very high selectivity in triethylvinylsilane, was not very efficient for HSiMe₂Cl activation; (iii) our studies highlighted the importance of SISHA interactions and led to the isolation of a wide variety of σ -silane complexes.⁴ In view of these previous results we now report a comparative study between HSiMe₂Cl and HSiMeCl₂ with the aim to better understand the influence of chloro substituents on the catalytic silulation of ethylene by using 1 as a catalyst precursor. We present the results of a mechanistic investigation through NMR monitoring and characterisation of key intermediates.

Results and discussion

Silylation of ethylene catalysed by **1** was tested with two chlorosilanes $\text{HSiMe}_n \text{Cl}_{3-n}$ (n = 1 or 2) (see eqn (1)). The order of addition of the substrates derives from our preliminary study showing that selectivity in vinylsilane when using HSiMe_2Cl was reduced when starting from the ethylene complex $\text{RuH}[(\eta^3-C_6\text{H}_8)\text{PCy}_2](\text{PCy}_3)(C_2\text{H}_4)$ or upon high pressure of ethylene.¹¹ We have thus conducted all our catalytic experiments by first adding the chlorosilanes to a toluene solution of **1**, followed by

Table 1 Silylation of C_2H_4 with $HSiMeCl_2$ and $HSiMe_2Cl,$ catalysed by 1 at ambient temperature

Entry	Silane ^a	P _{C2H4} / bar	Reaction time/h	Conversion (%) ^b	Selectivity (C_2H_3)SiMe _n Cl _{3-n} : EtSiMe _n Cl _{3-n} ^b
1	HSiMe ₂ Cl	1.5	40	99	54:46
2	HSiMe ₂ Cl	3	5	80	28:72
3	HSiMe ₂ Cl	20	2.5	80	10:90
4	HSiMeCl ₂	1.5	166	99	72:28
5	HSiMeCl ₂	3	96	94	64:36
6	HSiMeCl ₂	20	28	94	61:39

^{*a*} In toluene, with 100 equiv. of silane. ^{*b*} An error of 5% should be taken into account on the conversion and the selectivity as chlorosilanes decompose into heavier compounds—most probably polysiloxanes— along the capillary column. We checked that the reproducibility was not affected and that this decomposition also occurred when pure chlorosilanes were injected; less than 5% of decomposition into heavier compounds was measured in the latter case.

pressurization under ethylene. The experiments were performed at ambient temperature with ethylene pressure in the range 1.5-20 bar. Toluene was chosen in order to allow mechanistic investigation through NMR monitoring in toluene- d_8 . Conversion and selectivity with respect to vinylsilane vs. ethylsilane are reported in Table 1. They were determined by gas-chromatography (GC). Replacing HSiEt₃ by HSiMe₂Cl had a dramatic effect on the catalysis with longer reaction times for full conversion and reduced selectivity in the corresponding vinylsilane.^{8,11} In the case of HSiMeCl₂, thus replacing one Me group in HSiMe₂Cl by a second chlorine, the reaction rate is even more decreased. However, this effect can be limited by increasing ethylene pressure which this time, has a much lower impact on vinylsilane selectivity.

$$HSiMe_nCl_{3\cdot n} + C_2H_4 \xrightarrow{1} Cl_{3\cdot n}Me_nSi + Cl_{3\cdot n}Me_nSi$$

n = 1,2 (1)

The highest selectivities in vinylsilanes were 54% and 72% (entries 1 and 4) for $(C_2H_3)SiMe_2Cl$ and $(C_2H_3)SiMeCl_2$, respectively. These values were obtained at low ethylene pressure (1.5 bar). The



Scheme 2 Reactivity of the bis(dihydrogen) complex 1 with an excess of chlorosilanes.

change in selectivity as a function of ethylene pressure is quite surprising (entries 1 vs. 3 and 4 vs. 6). For a system in which hydrosilylation and dehydrogenative silvlation are in competition, a high alkene/silane ratio should favour the dehydrogenative pathway.1a This was indeed what we had observed previously in the case of HSiEt₃.⁸ Looking in more details, there is only a slight influence of the pressure in the case of HSiMeCl₂ (entries 4–6) and the reaction still preferentially produced the corresponding vinvlsilane at 20 bar. In the case of HSiMe₂Cl, the selectivity in vinylsilane dramatically dropped to 10% at high pressure (entry 3). This difference in behaviour is certainly linked to the change in the electronic properties of the silane when substituting a chlorine by a methyl group. One can thus postulate that several routes are possible in this catalytic system as a function of the silane and the ethylene pressure, especially in the case of HSiMe₂Cl. This prompted us to carry out a comparative mechanistic study with the two chlorosilanes.

Mechanistic study

We will first describe the reactivity of 1 with the chlorosilanes in toluene- d_8 for NMR analysis, and subsequently, the reaction of the resulting mixtures with C₂H₄. This procedure follows the order of addition of the reactants during the catalytic experiments.

Addition of chlorosilanes to 1

To mimic the catalytic conditions, we have chosen to examine the reactivity of 1 with 10 equiv. of chlorosilanes (see Scheme 2). In the case of HSiMe₂Cl, we had already reported that the reaction resulted in the formation of three silicon-containing complexes $\operatorname{RuH}_2(\eta^2-H_2)(\eta^2-HSiMe_2Cl)(PCy_3)_2$ (2Me₂Cl), $\operatorname{RuH}_2(\eta^2-HSiMe_2Cl)(PCy_3)_2$ (2Me₂Cl), $\operatorname{RuH}_2(\eta^2-HSiMe_2Cl)(PCy_3)_2$ HSiMe₂Cl)₂(PCy₃)₂ (3Me₂Cl) and RuCl(SiMe₂Cl)(η²-H₂)(PCy₃)₂ (4Me₂Cl) all characterised by NMR spectroscopy.¹¹ Complexes 2Me₂Cl and 3Me₂Cl adopt a *cis* configuration for the two bulky phosphine ligands as a result of stabilising SISHA interactions.⁴ The chemical shifts (δ_{si}) for the silicon atoms in 2Me₂Cl and 3Me₂Cl are 38 and 29 ppm, respectively. They are shielded compared to the free silane ($\delta_{s_i} = -11.1$ ppm) but it remains difficult to link the variation in chemical shift with the strength of the M-Si bond.^{4,12} The formation of complex 4Me₂Cl deserves a specific comment: we had previously shown that easy access to the known $RuHCl(\eta^2-H_2)(PCy_3)_2$ could be achieved by adding HSiMe₂Cl to 1 at 0 °C. Subsequent reaction of HSiMe₂Cl with RuHCl(η²- H_2)(PCy₃)₂ resulted in the isolation of RuCl(SiMe₂Cl)(η^2 - H_2)(PCy₃)₂ (4Me₂Cl) fully characterized by X-ray diffraction.¹³ It is not thus surprising that we observe 4Me₂Cl in our system.

The reaction of 1 with $HSiMeCl_2$ can also be depicted by Scheme 2. In addition to the hydride multiplets of the 3 complexes, **2MeCl_2** (traces), **3MeCl_2** and **4MeCl_2**, a new AA'A''XX'X''

multiplet at -8.55 ppm appeared in the ¹H NMR spectrum which was assigned to $RuH_3(SiMeCl_2)(PCy_3)_3$ (5). This complex is analogous to the complex RuH₃(SiMeCl₂)(PPh₃)₃ previously reported by Lemke et al.14 This type of complex has already been extensively studied with Fe, Ru and Os metal centers, so further characterisation was not carried out. We propose that 5 results from partial decomposition of the initial mixture: generation of free phosphine could then lead to substitution of one σ -ligand, H₂ in **2MeCl**₂ or HSiMeCl₂ in **3MeCl**₂, by the free phosphine. The ${}^{31}P{}^{1}H$ NMR spectrum of the mixture confirmed the presence of a small amount of free phosphine which resulted from the formation, in toluene- d_8 , of an aryl ruthenium complex $Ru(\eta^6-C_6D_5CD_3)(SiMeCl_2)_2(PCy_3)$ as it will be discussed below. Phosphine dissociation was only clearly observed in the case of HSiMeCl₂. The NMR data for 2MeCl₂, 3MeCl₂ and 4MeCl₂, very similar to those for the corresponding Me₂Cl complexes, allow us to propose the structures shown in Scheme 2. As mentioned above, we have already reported a detailed experimental and theoretical study on 4MeCl₂ and its analogue 4Me₂Cl.¹³ The relative ratio of complexes 2 and 3 indicates that, when adding more electronwithdrawing groups to the silicon atom, silane coordination is favored over H₂, leading thus to the bis(silane) complex as the major product in the case of HSiMeCl₂.

It is interesting to note that the reaction of **1** with 10 equiv of HSiEt₃ gave an equilibrium between **1** and **2Et**₃ in which no trace of **3Et**₃ was detected.⁸ This difference cannot be explained by steric considerations alone: the cone angle of HSiEt₃ (132°) is intermediate between those of HSiMe₂Cl, HSiMeCl₂ (120° and 122°, respectively) and HSiPh₃ (145°). In the last case, **2Ph**₃ was quantitatively produced.¹⁵ In the case of HSiEt₃, the equilibrium due to competition between σ -H₂ and σ -HSiEt₃ coordination agrees with the trend observed with HSiMe₂Cl and HSiMeCl₂. The presence of electron-withdrawing groups favours silane coordination.^{12b,16}

Reaction of the σ -silane and silyl complexes with ethylene

Ethylene was bubbled into a toluene- d_8 solution of **1** with 10 equiv. of the chlorosilanes. Catalysis proceeded and the organic compounds could be identified. We observed the elimination of free PCy₃ and the formation of a new η^6 -aryl complex of general formula Ru(η^6 -C₆D₅CD₃)(SiMe_{3-n}Cl_n)₂(PCy₃) (**6Me_{3-n}Cl_n-d₈**), as characterized by ¹H and ³¹P{¹H} NMR. In the case of HSiMeCl₂, other products were formed that remained unidentified. The ³¹P{¹H} NMR spectra gave chemical shifts for **6Me₂Cl-d₈** and **6MeCl₂-d₈** of δ 48.65 and δ 46.4, respectively. Irrespective of the nature of the silane, it appeared that complexes **6** were quite stable on the NMR time scale. The X-ray structure of **6MeCl₂** was obtained on a single-crystal at 160 K (Fig. 1). The complex



Fig. 1 X-ray structure of $Ru(\eta^6-C_6H_5CH_3)(SiMeCl_2)_2(PCy_3)$ (6MeCl_2) (ellipsoids are at 50% of probability). Selected bond lengths (Å): Ru–P 2.4069(9), Ru–Si1 2.3423(9), Ru–Si2 2.3645(9), and angles (°): P–Ru–Si1 97.30(3), P–Ru–Si2 96.25(3), Si1–Ru–Si2 83.67(3).

adopts a classical three legged piano-stool geometry for η^6 -arene complexes in agreement with the Ru(η^6 -C₆H₆)(SiR₃)₂(PPh₃) series (R₃ = Cl₃, MeCl₂ and Me₃) reported by Lemke *et al.*¹⁷ The phosphine is in the Si1–Ru–Si2 angle bisector plane. The two silicon atoms are in a pseudo-tetrahedral environment with Ru–Si1 and Ru–Si2 distances of 2.3423(9) Å and 2.3645(9) Å, respectively. Although the two methyl groups are in non-equivalent positions in the X-ray structure, fast rotation of the silyl groups was observed at ambient temperature by ¹H NMR in solution, as evidenced by the single resonance observed for the methyl groups.

In order to gain information on the reactivity of species 2-4, resulting from the reaction of 1 with the chlorosilanes, we have conducted additional experiments. As previously described, the reaction of 4 with C_2H_4 led to the formation of the ethylene(chloro) complex $RuHCl(C_2H_4)(PCy_3)_2$ and the corresponding organic compounds.¹³ With 2Me₂Cl preferentially formed upon reaction of 1 with 2 equiv. of HSiMe₂Cl, the ethylene(silyl) complex $RuH(SiMe_2Cl)(C_2H_4)(PCy_3)_2$ (7Me_2Cl) was obtained in addition to the organic products resulting from catalytic hydrogenation, hydrosilylation and dehydrogenative silvlation, *i.e.* C₂H₆ (major), $C_2H_3SiMe_2Cl$ and $C_2H_5SiMe_2Cl$ (Scheme 3). The ¹H NMR spectrum of 7Me₂Cl gave a well-resolved triplet at δ -5.14 (²J_{PH} = 32.5 Hz) integrating for one hydride and a broad signal at δ 3.17 corresponding to the 4 protons of the coordinated C_2H_4 . The ¹³C{¹H} NMR spectrum showed a broad signal at δ 44.9, significantly shielded compared to free C_2H_4 (δ 123.1) and the ²⁹Si-¹H-{³¹P} HMQC spectrum showed a correlation between the hydride and the silicon at δ 79.7 (d, ${}^{2}J_{\text{SiH}} = 15$ Hz). These data are in perfect agreement with the formulation of 7Me₂Cl as an unsaturated 16-electron hydrido silyl complex, with the silyl trans to the vacant site, as a result of it being the strongest trans influence ligand.¹⁸ The analogous complex 7MeCl₂ displays similar data except that the silicon atom is more shielded at δ 61.2 (d, ${}^{2}J_{\text{SiH}} =$ 17.8 Hz). The small $J_{\rm SiH}$ values for the two complexes are consistent with a formulation as hydrido(silyl) species.⁴ These unsaturated complexes are stable over one day in toluene- d_8 under a C₂H₄ atmosphere. Such a stability might be explained by the strong trans influence of the silvl group trans to the vacant site, which does not favour the coordination of an additional C_2H_4 ligand or any further reaction.



Scheme 3 Addition of chlorosilanes to the bis(dihydrogen) complex 1, followed by ethylene bubbling.



Fig. 2 X-Ray structure of $Ru(SiMeCl_2)_2(PCy_3)_2$ (**8MeCl_2**) (ellipsoids are at 50% of probability). Only the two hydrogen atoms possibly involved in an agostic interaction with Ru are represented, for clarity.

In contrast with the bis(silane) species 3MeCl₂, the major species formed upon reaction of 1 with 2 equiv. of HSiMeCl₂, 7MeCl₂ was formed in minority upon addition of ethylene, compared to the new species Ru(SiMeCl₂)₂(PCy₃)₂ (8MeCl₂) characterized as a disilyl complex (Scheme 3). Ethane was again the main organic product formed in this reaction, indicating that the Ru-Si bonds were less reactive than the Ru-H ones. Complex 8MeCl, was characterised by NMR spectroscopy and X-ray diffraction on a single-crystal at 160 K. Its structure showed the ruthenium centre in a pseudo-octahedral environment with two vacant sites (Fig. 2 and Table 2). The two silyl groups are in a cis position because of their trans influence. The Ru-Si distances differ insignificantly (2.259(2) Å and 2.270(2) Å) and are in the range reported for silvl complexes.^{12b,14,19} These values are shorter than those in 6MeCl₂ which is consistent with an unsaturated ruthenium center. The quality of the data does not allow us to really discuss the possible stabilisation, of this formally 14-electron complex, by two agostic C-H bond interactions. However, the two phosphines are bent away from the pair of silvl ligands with a P-Ru-P angle of 157.11(7)° and two ortho CH₂ groups of the PCy₃ ligands displaying Ru-C and Ru-H distances of ca. 3.01 Å and 2.26 Å,

Table 2 Relevant distances (Å) and angles (°) for $8MeCl_2$ (X-ray) and $8MeCl_2\text{-}a$ (DFT)

	X-Ray	DFT
Ru–P1	2.392(2)	2.428
Ru–P2	2.424(2)	2.479
Ru-Si1	2.259(2)	2.279
Ru-Si2	2.270(2)	2.286
$Ru \cdots H_a$	2.28	2.364
$Ru \cdots H_b$	2.26	2.373
$Ru \cdots C_a$	3.014(7)	3.134
$Ru \cdots C_b$	3.008(7)	3.178
P1–Ru–P2	157.12(7)	156.89
P1-Ru-Si1	97.35(7)	95.60
P1-Ru-Si2	96.52(8)	96.79
P2-Ru-Si1	101.40(8)	102.64
P2-Ru-Si2	97.37(8)	97.93
Si1-Ru-Si2	87.21(8)	87.93

respectively. These values are consistent with agostic interactions. Indeed, 14-electron four-coordinate Ru(II) complexes have already been disclosed in particular by Caulton, Eisenstein *et al.* and shown to be stabilised by double agostic interactions.²⁰ More recently, an unsaturated Ru(II) complex incorporating a Xantsil ligand (*i.e.* disilyl) was shown to be stabilised by an agostic interaction from the PCy₃ ligand (Ru–H distances of 2.89 Å and 3.06 Å).²¹ The NMR data of **8MeCl₂** are in agreement with a symmetrical structure in which the silyl groups are free to rotate. NMR monitoring of a C₇D₈ solution of **8MeCl₂** showed no change in the presence of dissolved C₂H₄ in excess.

The structures of three **8MeCl**₂ rotamers were optimised by DFT calculations using the B3PW91 functional.²² They differ in the number of silyl based chloride substituents located in the equatorial plane, that is to say two, one or none (see ESI).† Importantly, each structure is stabilised by two C–H agostic interactions, as inferred by the X-ray crystal structure of **8MeCl**₂ (keeping in mind the poor quality of the data). The most stable optimised geometry **8MeCl**₂-**a** compares actually very well with the X-ray data (Table 2). The C–H agostic interactions are characterised by Ru…H contact distances close to 2.4 Å, and Ru…C distances around 3.1 Å. The impact of the chloride positions, through silyl rotation (in agreement with NMR data), on the overall stability of the complex is very limited.

The formation of **7MeCl₂** and **8MeCl₂** in a ratio close to the ratio of the silane precursors **2MeCl₂** and **3MeCl₂** before C_2H_4 bubbling and in addition, the absence of any trace of **8Me₂Cl** when using HSiMe₂Cl (2 equiv.), allow for the postulate that mono(silane) complexes **2** are directly responsible for the formation of silyl complexes **7**, and bis(silane) complexes **3** directly responsible for disilyl complexes **8**. Moreover, it should be noted that the disilyl complex **8MeCl₂** can be prepared by adding an excess of HSiMeCl₂ to the ethylene complex RuH[(η^3 - C_6H_8)PCy₂](PCy₃)(C₂H₄) whereas in the case of triethylsilane we never observed the formation of a disilyl species.

It is important to note that $8MeCl_2$ is very air-sensitive and it was impossible to isolate it in any decent yield, thus preventing any test as a catalyst precursor. Decomposition occurred leading to the formation of the arene complex $6MeCl_2-d_8$ as monitored by NMR in toluene- d_8 solution. One can regret the choice of toluene as a solvent for the catalysis, as it rendered the comparison with the $HSiEt_3$ system in pentane quite difficult and led to the formation of arene complexes, but it was a convenient solvent for the characterization of very unstable species.

Conclusion

The introduction of chloro substituents on silanes has a strong effect both on activity and selectivity when using the ruthenium bis(dihydrogen) complex 1 as a catalyst precursor for ethylene silvlation. At low ethylene pressure, it is still possible to favour the formation of vinylsilanes, but surprisingly, higher pressures are detrimental to the dehydrogenative silvlation pathway, particularly in the case of HSiMe₂Cl. Our mechanistic investigation shows that the systems are quite complex with several organometallic species in competition. The reactivity of chlorosilanes with 1 led to a mixture of complexes incorporating one or two silane ligands obonded to the metal (complexes 2 and 3, respectively), as well as chloro(silyl) species resulting from Si-Cl bond cleavage (complexes 4). The ratio of the different species depends on the starting silane: in HSiMeCl₂, the Si–H bond has a better π -acceptor character than in HSiMe₂Cl, thus favouring the formation of the bis(silane) 3MeCl₂. When adding ethylene to the mixture of products resulting from the reaction of 1 with 2 equiv of chlorosilanes, different complexes were observed together with the organic products resulting from catalysis. In the case of HSiMe₂Cl, the unsaturated hydrido(silyl) complex 7Me₂Cl was the major product. In contrast, with HSiMeCl₂, the corresponding complex 7MeCl₂ became a minor product and the new complex 8MeCl₂ was produced and identified as a disilyl species. This formally 14-electron complex was characterised by X-ray diffraction and convincing evidence came from DFT calculations that agostic C-H interactions could stabilise the ruthenium centre. Thus, the addition of electron-withdrawing groups at silicon pushes the reactions toward the formation of disilyl complexes. In order to better model the catalytic conditions, we used a large excess of silanes and subsequent exposure to ethylene led to the observation of arene species still incorporating two silvl ligands. The arene complex 6MeCl₂ could be characterised by X-ray crystallography. The formation of arene products is due to the catalytic conditions involving toluene as the solvent. Such a choice was made to allow for easy NMR monitoring of the catalysis, but with the drawback of producing arene species from decomposition of the unsaturated disilyl complexes. In any case, the presence of disilyl species in the catalytic cycle, never observed in the case of HSiEt₃, might explain the differences observed in terms of activity and selectivity. A key factor favouring either hydrosilylation or dehydrogenative silvlation is the competition between ethylene insertion into M-H vs. M-Si bonds in the Chalk-Harrod or Chalk-Harrod modified mechanism or in the σ -CAM mechanism. In the case of HSiMeCl₂, we form strong Ru-Si bonds within bis(o-silane) and subsequently disilyl species upon ethylene pressure: long reaction times are needed to obtain a good conversion but selectivity is in favour of vinylsilane formation (as a result of ethylene insertion into the Ru-Si bond), and the influence of ethylene pressure is minimized (in the absence of Ru-H bonds). In contrast, in the case of triethylsilane, we had previously shown that a mechanism involving a partially dehydrogenated phosphine was operating. There, the formation of disilyl species is not possible as one phosphine acts as a bifunctional ligand with an allylic coordination to the



Scheme 4 Role of the bis(silyl) species in the catalysed silylation of ethylene

metal center and vinylsilanes are logically preferred with high pressures of ethylene. Indeed, assuming that Ru–H bonds are favourably consumed through ethylene hydrogenation, insertion of ethylene into a Ru–Si bond and subsequent β -H elimination can occur, the vinylsilane being then replaced by ethylene (see Scheme 4). The case of HSiMe₂Cl is more puzzling as we observe a detrimental effect of ethylene pressure on the selectivity towards vinylsilanes. We have seen that monosilane *vs.* disilane species are preferred when using HSiMe₂Cl instead of HSiMeCl₂. Ethylene insertion into the M–H bond could now be competitive leading to hydrosilylation and hydrogenation of ethylene as major processes.

Our study clearly shows that depending on the silicon substituents, we are facing different catalytic pathways, and it is thus very difficult to draw a general picture of a mechanism for homogeneous silylation reactions. Not only can the silane be either oxidatively added to the metal center leading to the corresponding M–H and M–Si bonds, but it can also coordinate to the metal center in a σ -bond fashion and mono or bis(silane) species are then stabilized (and subsequently silyl and disilyl species), or also the phosphine can interfere and become a "noninnocent" ligand, complicating even more the situation. However, it appears that the Ru–Si bond strength, tuned by the silicon substituents, is a key parameter that guides the reactivity of the potential intermediates irrespective of whether they contain σ -silane or silyl ligands.

Experimental

General methods

All reactions were performed using standard Schlenk or drybox techniques under argon. Solvents were dried and distilled prior to use. All reagents were purchased from Aldrich, except RuCl₃·3H₂O, which was obtained from Johnson Matthey Ltd., and were used without further purification. Complex RuH₂(η^2 -H₂)₂(PCy₃)₂ (1) was synthesised using a previously published procedure.²³ All NMR solvents were dried using appropriate methods and degassed prior to use. NMR samples of sensitive compounds were all prepared in an inert atmosphere glovebox. NMR spectra were recorded on Bruker DPX 300 (with ¹H at 300,13 MHz, ³¹P at 121,49 MHz and ¹³C at 75,46 MHz) and AMX 400 (with ¹H at 400,13 MHz, ³¹P at 161,98 MHz, ¹³C at 100,71 MHz, ²⁹Si at 79,50 MHz) spectrometers.

Catalyses were performed in a 100 mL stainless steel autoclave equipped with an anti-vortex mechanical stirring system (1000 tr min⁻¹). The autoclave was equipped with several valves for liquid and gas introduction and sample withdrawing. All the catalyses were performed at ambient temperature, using 12 mL of solvent. GC spectra were recorded on a HP 5890 spectrometer, and GC-MS spectra (EI, 70 eV) on a HP 6890 spectrometer coupled with an HP 5970 MSD ion detector. A SE30 column (50 m, \emptyset 0.32 mm) was used, with a flow of helium (1.5 mL min⁻¹). Acquisition and treatment of the data were performed using the GC ChemStation software. To check the reliability of the GC analysis, we also monitored the reaction by NMR in C₆D₆ under analogous experimental conditions as entry #2, Table 1. ¹H NMR spectral integration gave a (C₂H₃)SiMeCl₂ : EtSiMeCl₂ ratio of 23 : 77 that compared quite well with the results of entry #2.

It was impossible to isolate the new compounds in a pure form and get reliable microanalytical data as they were always contaminated by traces of other species as attested by NMR.

 $RuH_2(\eta^2-H_2)(\eta^2-HSiMe_2Cl)(PCy_3)_2$ (2Me₂Cl). Addition of 6.7 µL of HSiMe₂Cl (0.060 mmol) to a solution of 1 (19.9 mg,

0.030 mmol) in 0.5 mL of toluene- d_8 , resulted in gas evolution and total dissolution. ¹H NMR (C₇D₈, 288 K, 400.13 MHz): -8.51 (br, RuH₅), 1.44 (s, SiMe₂). T_{1min} (C₇D₈, 253 K, 300.13 MHz): 32 ms for the high field resonance. All the hydrides remained in fast exchange from 193 K to 293 K. ³¹P-{¹H} NMR (C₇D₈, 288 K, 161.97 MHz): 57.74 (s). ²⁹Si-{¹H}-{³¹P} NMR (C₇D₈, 288 K, 79.49 MHz): 38 (s).

RuH₂(**η**²-**H**₂)(**η**²-**HSiMeCl**₂)(**PCy**₃)₂ (2MeCl₂). Addition of 3.1 μL of HSiMeCl₂ (0.030 mmol) to a suspension of 1 (20.1 mg, 0.030 mmol) in 0.5 mL of toluene- d_8 , resulted in gas evolution and total dissolution. ¹H NMR (C₇D₈, 288 K, 400.13 MHz): -8.37 (br, RuH₅). *T*₁ (C₇D₈, 253 K, 300.13 MHz): 20 ms for the high field resonance. All the hydrides remained in fast exchange from 193 K to 293 K. ³¹P-{¹H} NMR (C₇D₈, 253 K, 161.97 MHz): 54.92 (br). The resonance of the silicon atom could not be located in the ²⁹Si NMR spectrum.

RuH₂(**η**²-**HSiMe**₂**Cl**)₂(**PCy**₃)₂ (**3Me**₂**Cl**). Addition of 33.3 μL of HSiMe₂Cl (0.300 mmol) to a solution of **1** (20.0 mg, 0.030 mmol) in 0.5 mL of toluene-*d*₈, resulted in rapid gas evolution and total dissolution. ¹H NMR (C₇D₈, 233 K, 400.13 MHz): -7.90 (br t, ²*J*_{PH} = 10 Hz, 2H, Ru-**η**²-H–Si), -10.69 (AA'XX' pattern, ²*J*_{PH} = 27 and 46 Hz, 2H, RuH), 1.36 (s, SiMe₂). ³¹P-{¹H} NMR (C₇D₈, 233 K, 161.97 MHz): 50.03 (s). ²⁹Si-{¹H}-{³P} NMR (C₇D₈, 233 K, 79.49 MHz): 29 (s).

RuH₂(**η**²-**HSiMeCl**₂)₂(**PCy**₃)₂ (**3MeCl**₂). Addition of 6.1 μL of HSiMeCl₂ (0.059 mmol) to a suspension of **1** (18.9 mg, 0.028 mmol) in 0.5 mL of toluene- d_8 , resulted in rapid gas evolution and total dissolution. ¹H NMR (C₇D₈, 233 K, 400.13 MHz): -6.56 (br t, ²J_{PH} = 9.8 Hz, 2H, Ru-η²-H–Si), -9.59 (broad AA'XX' pattern, 2H, RuH), 1.79 (s, SiMe). ³¹P-{¹H} NMR (C₇D₈, 253 K, 161.97 MHz): 49.46 (br s). HMQC ²⁹Si-¹H-{³¹P} NMR (C₇D₈, 193 K, 79.49 MHz): 33 (br s).

RuH₃(SiMeCl₂)(PCy₃)₃ (5MeCl₂). Complex **5MeCl₂** was observed in an NMR sample of **1** + excess of HSiMeCl₂. ¹H NMR (C_7D_8 , 253 K, 400.13 MHz): -8.56 (AA'A''XX'X'' pattern, 3H, RuH₃), 1.57 (s, SiMe). T_1 (C_7D_8 , 400.13 MHz): over 200 ms from 243 to 283 K for the high field resonance. ³¹P-{¹H_{cyclohexyl}} NMR (C_7D_8 , 253 K, 161.97 MHz): 39.74 (AA'A''XX'X'' pattern). HMQC ²⁹Si-¹H-{³¹P} NMR (C_7D_8 , 193 K, 79.49 MHz): 63 (s).

Ru(η^6 -C₆**D**₅**CD**₃)(**SiMe**₂**Cl**)₂(**PCy**₃) (**6Me**₂**Cl**-*d*₈). Complex **6Me**₂**Cl**-*d*₈ was characterised from an NMR sample of **3Me**₂**Cl** (see above), into which C₂H₄ was bubbled. ¹H NMR (C₇D₈, 293 K, 300.13 MHz): 1.08 and 1.11 (s, SiMe₂), 1.0–2.3 (m, PCy₃). ³¹P-{¹H} NMR (C₇D₈, 293 K, 121.49 MHz): 48.6 (s).

Ru(η^6 -C₆H₅CH₃)(SiMeCl₂)₂(PCy₃) (6MeCl₂). Addition of 8.8 µL of HSiMeCl₂ (0.084 mmol) to a solution of RuH[(η^3 -C₆H₈)PCy₂](PCy₃)(C₂H₄) (28.7 mg, 0.042 mmol) in 0.7 mL of toluene, resulted in a colour change from beige to intense orange. The resulting orange solution kept at ambient temperature for 1 month, gave yellow crystals suitable for X-ray measurements. NMR spectra were obtained from the crystalline material dissolved in toluene- d_8 . ¹H NMR (C₇D₈, 293 K, 300.13 MHz): 5.0–5.7 (m, toluene), 2.27 (s, 3H, toluene–Me), 1.46 (s, SiMe), 1.0–2.1 (m, 33H, PCy₃). ³¹P-{¹H} NMR (C₇D₈, 293 K, 121.49 MHz): 46.3 (s).

RuH(SiMe₂Cl)(C_2H_4)(**P**C y_3)₂ (7**Me₂Cl)**. A solution of complex 7**Me₂Cl** was prepared from an NMR sample of 2**Me₂Cl** (see above), by bubbling C₂H₄ into the solution for 1 min. ¹H NMR (C₇D₈, 293 K, 400.13 MHz): -5.14 (t, ²J_{PH} = 32.6 Hz, 1H, RuH), 3.17 (br, 4H, RuC₂H₄), 0.91 (s, SiMe₂). ³¹P-{¹H} NMR (C₇D₈, 293 K, 161.97 MHz): 53.14 (s). ¹³C-{¹H} NMR (C₇D₈, 293 K, 100.62 MHz): 44.9 (br, C₂H₄). ²⁹Si-{³¹P} NMR (C₇D₈, 293 K, 79.49 MHz): 79.7 (br d, ²J_{SiH} = 15 Hz).

RuH(SiMeCl₂)(C₂H₄)(PCy₃)₂ (7MeCl₂). A solution of complex **7MeCl₂** was prepared from an NMR sample of **2MeCl₂** (see above), by bubbling C₂H₄ into the solution for 1 min. ¹H NMR (C₇D₈, 273 K, 400.13 MHz): -4.82 (t, ²J_{PH} = 30.2 Hz, 1H, RuH), 3.23 (br, 4H, RuC₂H₄), 1.16 (s, SiMe). ³¹P-{¹H} NMR (C₇D₈, 273 K, 161.97 MHz): 51.28 (s). ¹³C-{¹H} NMR (C₇D₈, 273 K, 100.62 MHz): 47.5 (br, C₂H₄). HMQC ²⁹Si-¹H-{³¹P} NMR (C₇D₈, 273 K, 79.49 MHz): 61.2 (br d, ²J_{SiH} = 17.4 Hz).

Ru(SiMeCl₂)₂(PCy₃)₂ (8MeCl₂). Addition of 17.0 μ L of HSiMeCl₂ (0.163 mmol) to a suspension of RuH[(η³-C₆H₈)PCy₂](PCy₃)(C₂H₄) (27.0 mg, 0.039 mmol, prepared according to published procedure)²³ in 2 mL of pentane, resulted in slow dissolution of the solid. The resulting orange solution kept at ambient temperature for 5 days, gave intense orange/red crystals suitable for X-ray measurements. NMR spectra were obtained from the crystalline material dissolved in toluene-*d*₈. ¹H NMR (C₇D₈, 293 K, 300.13 MHz): 1.81 (s, SiMe), 1.0–2.8 (m, PCy₃). ³¹P-{¹H} NMR (C₇D₈, 293 K, 121.49 MHz): 28.3 (s). HMQC ²⁹Si-¹H-{³¹P} NMR (C₇D₈, 273 K, 79.49 MHz): 72.2 (br).

X-Ray crystallography

Table 3 summarizes the crystal data for 6MeCl₂ and 8MeCl₂. Data were collected at low temperature (160 K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Instrument Cooler Device. The structures have been solved by Direct Methods using SIR-92,²⁴ and refined by means of leastsquares procedures on F^2 with the aid of the program SHELXL-97²⁵ include in the software package WinGX version 1.63.²⁶ The atomic scattering factors were taken from international tables for X-ray crystallography.²⁷ All hydrogen atoms were geometrically placed and refined using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where P = $(F_o^2 + 2F_c^2)/3$. Drawing of the molecules was performed with the program Mercury with 50% probability displacement ellipsoids for non-hydrogen atoms.²⁸ The two complexes present statistic disorders between two Cl and CH₃, over two sites. These disorders have been treated using the PART command of SHELX-97. Moreover, in the case of 8MeCl₂, we were not able to grow superior single crystals. For this reason, we collected poor quality data, resulting after data reduction in high R_{int} and R_{σ} values (13.1 and 27.8%, respectively). Indeed, for a 1.49–1.19 Å resolution, the R_{int} is already at 12.6% and R_{σ} at 19.5%.

Table 3 Crystal data for 6MeCl₂ and 8MeCl₂

Compound	$Ru(\eta^{6}-C_{6}H_{5}CH_{3})(SiMeCl_{2})_{2}(PCy_{3}) (6MeCl_{2})$	Ru(SiMeCl ₂) ₂ (PCy ₃) ₂ (8MeCl ₂)
Empirical formula	$C_{27}H_{47}Cl_4PRuSi_{2}\cdot\frac{1}{2}C_7H_8$	$C_{38}H_{72}Cl_4P_2RuSi_2$
Formula weight	747.74	889.95
Crystal size/mm	$0.25 \times 0.17 \times 0.07$	$0.2 \times 0.12 \times 0.05$
T/K	160(2)	160(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/c$
a/Å	10.1180(8)	9.7901(8)
b/Å	11.3620(10)	44.9570(7)
c/Å	14.9910(9)	10.1672(9)
$\alpha /^{\circ}$	94.278(5)	90
$\beta/^{\circ}$	94.911(3)	105.977(3)
$\gamma/^{\circ}$	92.777(6)	90
$V/Å^3$	1709.7(2)	4302.1(5)
Ζ	2	4
$\rho_{\rm c}/{\rm cm}^{-3}$	1.453	1.374
Reflections collected/unique	$23632/5653[R_{\rm int}=0.0311]$	$28188/7865[R_{\rm int}=0.1095]$
Data/restraints/parameters	5653/31/371	7865/0/414
GOF on F^2	1.056	1.137
Final R indices	$R_1 = 0.0391,$	$R_1 = 0.0867,$
	$wR_2 = 0.0954 [I > 2\sigma(I)]$	$wR_2 = 0.1397 [I > 2\sigma(I)]$
	$R_1 = 0.0409,$	$R_1 = 0.133,$
	$wR_2 = 0.0971$ (all data)	$wR_2 = 0.1532$ (all data)
Largest difference peak and	1.96 and -3.06	0.82 and -0.815
hole/e Å ⁻³		

Computational details

DFT calculations were performed with the GAUSSIAN 03 series of programs,²⁹ using the hybrid functional denoted as B3PW91.^{22,30} The structures were fully optimised in the gas-phase without any symmetry constraints by using the gradient method available in GAUSSIAN 03. A double-zeta plus polarization valence basis set (6-31G**) was employed for C and H.³¹ The energy-consistent pseudo-potentials of the Stuttgart/Cologne group were used to represent the core electrons of the other atoms *via* the SDDALL keyword in GAUSSIAN 03. The polarization function exponents for each associate basis set were $\alpha_{Ru} = 1.235$, $\alpha_{Si} = 0.287$, α_{P} = 0.387 and $\alpha_{CI} = 0.640$. Calculations of harmonic vibrational frequencies were performed to confirm that all the optimised structures were local minima.

Acknowledgements

This work was supported by the CNRS and the European network IDECAT. S. L. thanks the French Ministery "Education Nationale, Enseignement Supérieur, Recherche" for his AMN grant. A generous allocation of computer time was given by CALMIP (Toulouse, France).

References

- (a) B. Marciniec, Coord. Chem. Rev., 2005, 249, 2374–2390; (b) T. D. Tilley, in The chemistry of Organic Silicon Compounds, ed. S. Patai and Z. Rappoport, John Wiley & Sons, New York, 1989, vol. 3, pp. 1415–1477, 1153–1156; (c) J. Y. Corey, Adv. Organomet. Chem., 2004, 51, 1–52; (d) M. A. Brook, in Silicon in Organic, Organometallic, and Polymer Chemistry, ed., Wiley, New York, 2000; (e) B. Marciniec, in Applied Homogeneous Catalysis with Organometallic Compounds, ed. B. Cornils and W. A. Herrmann, 2nd edn, 2002, p. 491.
- 2 (a) S. Sakaki, N. Mizoe and M. Sugimoto, *Organometallics*, 1998, 17, 2510–2523; (b) A. M. LaPointe, F. C. Rix and M. Brookhart, *J. Am. Chem. Soc.*, 1997, 119, 906–917.

- 3 R. N. Perutz and S. Sabo-Etienne, Angew. Chem., Int. Ed., 2007, 46, 2578–2592.
- 4 S. Lachaize and S. Sabo-Etienne, Eur. J. Inorg. Chem., 2006, 2115-2127.
- 5 (a) S. Calmettes, B. Albela, O. Hamelin, S. Menage, F. Miomandre and L. Bonneviot, New J. Chem., 2008, 32, 727–737; (b) J. O. Krause, S. Lubbad, O. Nuyken and M. R. Buchmeiser, Adv. Synth. Catal., 2003, 345, 996–1004; (c) H. Metz, Spec. Chem. Mag., 2007, 27, 38–40; (d) J. Terao, K. Torii, K. Saito, N. Kambe, A. Baba and N. Sonoda, Angew. Chem., Int. Ed., 1998, 37, 2653–2656; (e) J. Terao and N. Kambe, Chem. Rec., 2007, 7, 57–67.
- 6 (a) M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, 1981, **19**, 213–232; (b) J. Gavenonis and T. D. Tilley, *Organometallics*, 2004, **23**, 31–43.
- 7 (a) S. Sabo-Etienne and B. Chaudret, *Coord. Chem. Rev.*, 1998, 178–180, 381–407; (b) G. Alcaraz, M. Grellier and S. Sabo-Etienne, *Acc. Chem. Res.*, 2009, 42, 1640–1649.
- 8 M. L. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1995, 14, 1082–1084.
- 9 F. Delpech, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Organometallics*, 1998, **17**, 4926–4928.
- 10 F. Delpech, J. Mansas, H. Leuser, S. Sabo-Etienne and B. Chaudret, Organometallics, 2000, 19, 5750–5757.
- 11 S. Lachaize, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 2003, 214–215.
- 12 (a) G. Alcaraz and S. Sabo-Etienne, *Coord. Chem. Rev.*, 2008, 252, 2395–2409; (b) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, 99, 175–292.
- 13 S. Lachaize, A. Caballero, L. Vendier and S. Sabo-Etienne, Organometallics, 2007, 26, 3713–3721.
- 14 N. M. Yardy, F. R. Lemke and L. Brammer, Organometallics, 2001, 20, 5670–5674.
- 15 (a) S. Sabo-Etienne, M. Hernandez, G. Chung, B. Chaudret and A. Castel, *New J. Chem.*, 1994, **18**, 175–177; (b) K. Hussein, C. J. Marsden, J. C. Barthelat, V. Rodriguez, S. Conejero, S. Sabo-Etienne, B. Donnadieu and B. Chaudret, *Chem. Commun.*, 1999, 1315–1316.
- 16 G. J. Kubas, Metal Dihydrogen and σ-Bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001.
- 17 J. Burgio, N. M. Yardy, J. L. Petersen and F. R. Lemke, *Organometallics*, 2003, **22**, 4928–4932.
- 18 J. L. Mc Bee, J. Escalada and T. D. Tilley, J. Am. Chem. Soc., 2009, 131, 12703–12713.
- 19 (a) V. K. Dioumaev, B. R. Yoo, L. J. Procopio, P. J. Carroll and D. H. Berry, J. Am. Chem. Soc., 2003, **125**, 8936–8948; (b) D. V. Gutsulyak, A. V. Churakov, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov,

Organometallics, 2009, **28**, 2655–2657; (c) D. V. Gutsulyak, A. L. Osipov, L. G. Kuzmina, J. A. K. Howard and G. I. Nikonov, *Dalton Trans.*, 2008, 6843–6850.

- 20 (a) D. Huang, W. E. Streib, O. Eisenstein and K. G. Caulton, Angew. Chem., Int. Ed. Engl., 1997, 36, 2004–2006; (b) D. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter and T. Scheiring, J. Am. Chem. Soc., 1999, 121, 8087–8097; (c) W. Baratta, E. Herdtweck and P. Rigo, Angew. Chem., Int. Ed., 1999, 38, 1629–1631; (d) A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein and K. G. Caulton, J. Am. Chem. Soc., 1999, 121, 97–106.
- 21 M. Okazaki, N. Yamahira, J. J. G. Minglana, T. Komuro, H. Ogino and H. Tobita, *Organometallics*, 2008, 27, 918–926.
- 22 J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, 1992, **45**, 13244–13249.
- 23 A. F. Borowski, S. Sabo-Etienne, M. L. Christ, B. Donnadieu and B. Chaudret, *Organometallics*, 1996, 15, 1427–1434.
- 24 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, J. Appl. Crystallogr., 1993, 26, 343–350.
- 25 G. M. Sheldrick, SHELX97, Universität Göttingen, Göttingen, Germany, 1998.
- 26 L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.
- 27 in International tables for X-raycrystallography, Kynoch press, Birmingham, 1974, vol. 4.

- 28 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, 39, 453–457.
- 29 M. J. T. Frisch, G. W., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji , M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, in Gaussian 03Gaussian, Inc.: Wallingford, CT., 2004.
- 30 A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 31 W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972, 56, 2257–2261.