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The role of dioxygen in hydrosilylation of alkenes catalyzed by ruthenium phosphine complexes ☆

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Abstract

Catalytic hydrosilylation of C=C bonds in alkenes in the presence of Ru(II)–phosphine complexes takes place only for alkoxy-substituted silanes in the absence of solvent and in the presence of small amounts of O_2. The activation effect of "trace" O_2, noted previously for rhodium and other transition metal phosphine complex catalysts for several catalytic processes, has been little studied to date. In this work, oxygen is considered to cause removal of phosphine as its oxide, formation of intermediate dioxygen complexes (followed by oxygenation of Ru–Si≡ to an Ru–O–Si≡ moiety with elimination of disiloxane) and possible formation of Ru(IV) species. The studies include the characterization of isolated intermediates (well defined complexes or their mixtures) from an $RuCl_2(PPh_3)_3$–$HSi(OC_2H_5)_3$ system and general mechanisms for the hydrosilylation of alkenes in the presence of Ru(II) precursors are discussed.

Keywords: Hydrosilylation; Alkenes; Ruthenium; Catalysis; Silane; Dioxygen

1. Introduction

We reported previously our results on the hydrosilylation of C=C bonds in 1-alkenes in the presence of Ru(II) phosphine complexes as homogeneous catalysts [1]; the reaction takes place only for alkoxy-substituted silanes, in the absence of any solvent and in the presence of small amounts of molecular oxygen. The chemistry of the initial ternary component system $RuCl_2(PPh_3)_3$–$HSi(OC_2H_5)_3$–O_2 appeared to be key in the mechanism proposed. However, it was impossible to identify the species formed in the three-component system on the basis of analytical examinations of the isolated solid [2]. Because the preliminary investigations of the $RuCl_2(PPh_3)_3$–$HSi(OC_2H_5)_3$ system in aerobic conditions were incomplete, and different interpretations of the results found for similar systems under an inert atmosphere (and with C_6H_6 as solvent) were obtained by others [3–5], we undertook a more thorough examination of this system which proved to be complex, especially in the hydrosilylation reaction conditions (no solvent, air, 80–120°C).

The activation role of oxygen in different homogeneous catalytic processes catalyzed by transition metal phosphine complexes has been a subject of interest for many investigators [6]. It is known that dioxygen can oxidize the metal centre, change the ratio of phosphine to metal and also form dioxygen–metal complexes which can be intermediates in various reactions. $RuCl_2(PPh_3)_3$ reacts with trialkoxysilane in several different ways [2–5]. One involves a ruthenium-centered dehalogenation (partly or totally via Cl_2 or HCl elimination) with Ru–Si bond formation [3,4]. The presence of solvent (C_6H_6) and the use of elevated temperatures may facilitate some of the oxygen-based processes listed above.

The aim of this work was to understand better the ruthenium complex–trialkoxysilane reaction, including determination of the effects of the solvent, temperature and aerobic (anaerobic) conditions, in view of the previously discussed hydrosilylation mechanism. Despite the large number of papers on hydrosilylation catalyzed by platinum metal complexes [7], only a few have recently reported on such catalysis in the presence of ruthenium

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phosphine precursors [8,9]. Although the role of oxygen was not considered in these papers, the catalysis in a system using $RuHCl(CO)(P^iPr_3)_2$ and $HSi(C_2H_5)_3$ proceeds via the initial interaction of the Ru–complex with the silane [9]; triphenylphosphine–Ru complexes interact similarly with chloro-, alkyl- and alkoxysilanes [8].

2. Results and discussion

2.1. Synthesis in an oxygen-free atmosphere

Kono et al. [3] and Svroboda et al. [4] reported that reaction of $RuCl_2(PPh_3)_3$ with trialkoxysilanes, under argon at room temperature, and in the absence of solvent, gave mostly four-coordinate complexes of general formula $RuH[Si(OR)_3](PPh_3)_2$ [3], whereas a mixture of $Ru(H)Cl(PPh_3)_3$ and $RuH[Si(OR)_3](PPh_3)_2$ was produced when the reaction proceeded in benzene [4]. Later Haszeldine et al. [5] reported that $RuH_3[Si(OC_2H_5)_3](PPh_3)_3$ was obtained via the reaction of the ruthenium(II) complex with triethoxysilane (in benzene and under nitrogen) rather than the unusual four-coordinate Ru(II) complexes proposed by Kono et al. [3] or monohydridoruthenium(II) complexes suggested by Svroboda et al. [4].

We carried out the reaction of $RuCl_2(PPh_3)_3$ with triethoxysilane in the absence of solvent at both room temperature and at elevated temperature (100°C, the hydrosilylation reaction conditions) and obtained white solids **I** and **II**, respectively (for details, see Experimental). Both IR spectra show bands characteristic of the phosphine ligand (3000–3100 cm^{-1}) and an alkoxysilyl group (~ 1070 cm^{-1}). No ν(Si–H) or ν(Ru–Cl) stretching vibrations were detected. One broad band, corresponding to Ru–H stretching modes (1967–1978 cm^{-1}), was found for both solids. It results from the overlapping of two bands. Based on the IR data, solids **I** and **II** could correspond to $RuH_x[Si(OC_2H_5)_3]_y(PPh_3)_n$. Both complexes gave essentially the same ^1H NMR signals in the low-field region characteristic of the phosphine phenyl protons and the ethoxysilyl protons. Additionally, high-field signals of Ru–H species were observed at δ −12 to −13; these were broad with only partial resolution, probably due to exchange processes and fluxional rearrangement [5]. Integration of the proton signals for both solids **I** and **II** showed a ratio of Ru–H to $Ru–Si(OC_2H_5)_3$ between 2 and 3. The ^1H NMR spectra show signals similar to those previously assigned to $RuH_z[Si(OC_2H_5)_3](PPh_3)_y$ species ($z = 1$, $y = 2$; $z = y = 3$) [3,5] but with some differences in the Ru–H region (in this work, after 30 min in C_6D_6 only a doublet at δ −10.03 is observed, attributable to another hydride species). In the presence of $CDCl_3$, complex **I** decomposes; signals attributable to CH_3 and CH_2 protons split into two different positions, and free triethoxysilane (δ CH_3 0.79(t), CH_2O 3.29 (q) and SiH 4.26 (s) in $CDCl_3$ [10]) and $CHDCl_2$ protons (δ 5.28 (s)) appear, presumably as a result of dehydrosilylation from the Ru center and $RuH–CDCl_3$ exchange, respectively. $RuCl_2(PPh_3)_3$ is known to be an active catalyst in hydrodechlorination of $CDCl_3$ to $CHDCl_2$ by hydrosilanes [11]. A Ru–H signal at δ −10.54, as found here in $CDCl_3$, has been noted earlier in CD_2Cl_2 [5]. The detailed analysis of the ^1H NMR spectra permits the calculation of the integration ratio of the phenyl and alkoxy protons as close to 3 for the $PPh_3/Si(OC_2H_5)_3$ groups. In the ^{31}P [^1H] spectra of **I** and **II** in C_6D_6 (room temperature), surprisingly only the same relatively broad singlet at δ 47.4 was observed; this presumably results from exchange between coordinated and free PPh_3. No signals due to free PPh_3 or $OPPh_3$ were found. Electron impact (EI) mass spectra showed characteristic peaks for PPh_3 (m/z 262) and $Si(OC_2H_5)_3$ (m/z 163) ligands. Complex **II** has elemental analysis data similar to those reported previously for $RuH_3[Si(OC_2H_5)_3](PPh_3)_3$ [5]; for complex **I** a corresponding formulation but with two phosphine ligands is proposed.

On the basis of our analytical and spectroscopic results, and in the view of data published previously, it is concluded that under oxygen-free conditions, $RuCl_2(PPh_3)_3$ in the absence of solvent reacts with $HSi(OC_2H_5)_3$ to produce $RuH_3[Si(OC_2H_5)_3](PPh_3)_n$, where $n = 2$ or 3. In both cases hydridoruthenium silyl complexes are produced and the reaction conditions influence the number of phosphine ligands attached to the ruthenium center. The complexes are probably produced via a sequence of three steps. In the first, $Ru(H)Cl(PPh_3)_3$ is formed as established earlier [4,5].

$$RuCl_2(PPh_3)_3 + HSi(OC_2H_5)_3 \rightarrow Ru(H)Cl(PPh_3)_3 + ClSi(OC_2H_5)_3 \quad (1)$$

The same Ru–H complex can presumably be obtained using a range of hydrosilanes. With excess triethoxysilane, a dihydridoruthenium complex is probably produced in a subsequent dehalogenation step:

$$Ru(H)Cl(PPh_3)_3 + HSi(OC_2H_5)_3 \rightarrow Ru(H)_2(PPh_3)_3 + ClSi(OC_2H_5)_3 \quad (2)$$

Although GC–EIMS analysis of the reaction mixtures did not show directly the presence of $ClSi(OC_2H_5)_3$, the high-boiling pentaethoxy- and hexaethoxydisiloxanes were detected in solution (up to 10%); the highly reactive $ClSi(OC_2H_5)_3$ easily forms ethoxysiloxanes, especially at elevated temperatures. $Si(OC_2H_5)_4$, also present in the solution, derives from the well known redistribution of triethoxysilane [12].

$Ru(H)_2(PPh_3)_n$ ($n = 3$ or 4) is known to be very reactive toward hydrosilanes, even forming seven-coordinate complexes of Ru(IV) [5]. Therefore, in the presence of triethoxysilane, an appropriate $Ru(H)_3[Si(OC_2H_5)_3](PPh_3)_n$ can be obtained via a formal oxidative addition:

$$Ru(H)_2(PPh_3)_3 + HSi(OC_2H_5)_3 \rightarrow \underset{\substack{\mathbf{I,\,II} \\ n = 2 \text{ or } 3}}{Ru(H)_3[Si(OC_2H_5)_3](PPh_3)_n} \qquad (3)$$

All these reactions appear to occur at room temperature under an inert gas in C_6H_6 or in the absence of solvent; elevated temperatures (100°C) cause no major difference in the basic reaction routes mentioned above. The only gas evolved (several cm^3) during the preparation of the complex **I** (for details, see Experimental) was dihydrogen, probably originating from Si–H bond cleavage and/or from decomposition of the ruthenium hydride intermediates. In view of the work of Haszeldine et al. [5] and our new results, the earlier proposed dehalogenation route

$$RuCl_2(PPh_3)_3 + HSi(OC_2H_5)_3 \xrightarrow{-Cl_2} RuH[Si(OC_2H_5)_3](PPh_3)_n + (3-n)PPh_3 \qquad (4)$$

reported by Kono et al. [3] ($n = 2$) and by Svroboda et al. [4] ($n = 3$) appears unlikely.

2.2. Synthesis in air

It is known that in air $RuCl_2(PPh_3)_3$ dissolves in C_6H_6 at room temperature, absorbing O_2, and the initially red–brown solution turns green in a few minutes. Cenini et al. [13], following the oxygen uptake at constant pressure, proposed the initial dissociation of phosphine:

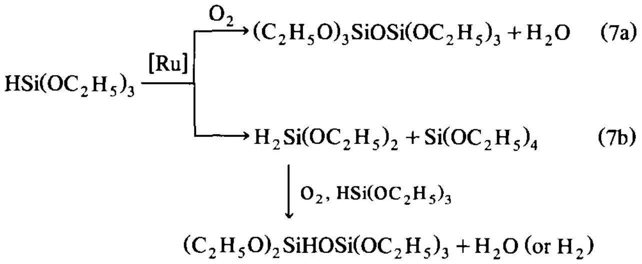
$$RuCl_2(PPh_3)_3 \xrightarrow{-PPh_3} \text{“}RuCl_2(PPh_3)_2\text{”} \xrightarrow{O_2} Ru(O_2)Cl_2(PPh_3)_2 \qquad (5)$$

and subsequent formation of an oxygen complex (however, without any analytical evidence). A more detailed examination [14,15] showed that 1.5 mol of O_2 is absorbed per Ru complex; triphenylphosphine oxide and a green complex were isolated according to the stoichiometry of Eq. (6).

$$n\ RuCl_2(PPh_3)_3 + \tfrac{3}{2}n\ O_2 \rightarrow 2n\ OPPh_3 + [RuCl_2(OPPh_3)]_n \qquad (6)$$

Despite the difficulty in the characterization of the Ru species, there is no doubt that O_2 promotes the $RuCl_2(PPh_3)_3$ dissociation due to oxidation of the PPh_3 ligands to free $OPPh_3$. The “$RuCl_2(PPh_3)_2$” species exists in benzene as a chloro-bridged dimer [15].

Reactions of triethoxysilane with $RuCl_2(PPh_3)_3$ in the presence of dry air (dioxygen) were examined, these were carried out without solvent at room temperature and also at an elevated temperature closer to the typical hydrosilylation process conditions used. In all the reactions, no green ruthenium complex (see above) was observed. Some gases were evolved during the reactions, and O_2 must have been absorbed to generate the detected $OPPh_3$. Room temperature experiments from which **III** and **IV** were isolated showed for the first hour a net gas evolution (mainly H_2, with no Cl_2 or HCl being detected). Up to 22 cm^3 of H_2 (ca. 10^{-3} mol) were produced (for details, see Experimental). Detailed GLC analysis detected some C_2H_4 and C_2H_6 (in a ratio close to 2 : 1), but neither CH_4 nor CO was found. No substantial net gas absorption or desorption was noted after the first hour. The initial suspension changes color from dark to light brown, and then yellowish in the yellow silane solution. GC–EIMS analysis of this liquid showed significant amounts of $Si(OC_2H_5)_4$, $(C_2H_5O)_3SiOSiH(OC_2H_5)_2$ and $(C_2H_5O)_3SiOSi(OC_2H_5)_3$ (up to 15%). After 2 weeks of additional stirring of the reaction mixture, the amount of $Si(OC_2H_5)_4$ present is greater than that of $HSi(OC_2H_5)_3$. Both catalytic redistribution (observed previously under argon atmosphere) and oxidation of $HSi(OC_2H_5)_3$ (eventually to siloxanes) occur under the conditions used [5] (see Eq. (7)). Once again, $ClSi(OC_2H_5)_3$ was not detected directly in the reaction mixture.



$$HSi(OC_2H_5)_3 \xrightarrow{[Ru]} \begin{cases} \xrightarrow{O_2} (C_2H_5O)_3SiOSi(OC_2H_5)_3 + H_2O & (7a) \\ \rightarrow H_2Si(OC_2H_5)_2 + Si(OC_2H_5)_4 & (7b) \end{cases}$$

$$H_2Si(OC_2H_5)_2 \xrightarrow{O_2,\ HSi(OC_2H_5)_3} (C_2H_5O)_2SiHOSi(OC_2H_5)_3 + H_2O \text{ (or } H_2)$$

The yellowish suspension **III** is only slightly soluble in C_6H_6. The IR spectrum showed a broad band at 1970 cm^{-1} (assigned to the Ru–H bond), characteristic Si–O–C stretching bands (ca. 1000–1100 cm^{-1}) and a broad signal in the 2245–2250 cm^{-1} region, attributed to a shifted, coordinated Si–H bond [10]. A weak band is seen at ca. 850 cm^{-1}, attributed previously to $\nu Ru(O_2)$ [2]. Two sets of signals characteristic of CH_3 and CH_2O protons in the ^1H NMR spectrum, and the shifted Si–H signal (δ 4.49 (s)), in comparison with δ 4.26 for free $HSi(OC_2H_5)_3$ [10], demonstrate the presence of solvating $HSi(OC_2H_5)_3$ and a coordinated triethoxysilyl substituent. The ^{13}C NMR spectra support these conclusions. A high-field signal at δ −10.5 and the presence of $CHDCl_2$ protons (δ 5.27 (s)) in the $CDCl_3$ ^{1}H NMR spectrum provide further evidence for the presence of an Ru–H bond. The ^{31}P [^{1}H] NMR spectrum of **III** showed only a signal characteristic of free $OPPh_3$, possibly because of a very limited solubility of the compound in benzene. The EI mass spectrum shows neither molecular ions nor ions derived from the simple loss of PPh_3; however, the presence of Ru-containing ions was detected by a characteristic pattern, resulting from seven stable isotopes present in naturally abundant ruthenium [16]. A high-intensity peak at *m/z* 277 is characteristic of triphenylphosphine oxide. A peak at *m/z* 297, attributed previously [2] to the ruthenium–oxygen species $\{Ru(O_2)[Si(OC_2H_5)_3]\}^+$, is observed. On the basis of spectroscopic data, we conclude that **III** contains free $OPPh_3$ and a phosphine-triethoxysilyl–ruthenium complex solvated by $HSi(OC_2H_5)_3$ molecules, or a mixture of similar complexes containing an Ru–H bond. No direct evidence for the presence of a dioxygen–Ru complex was found except for the $\nu Ru(O_2)$ band of low intensity in the IR spectrum.

The yellow solid **IV**, precipitated from the reaction filtrate by adding n-hexane, is thought to be $Ru\{Si(OC_2H_5)_3\}_2(PPh_3)_2$. That this formulation is correct is supported by the absence of Ru–H and Si–H bands in the IR spectrum, one set of CH_3CH_2O protons and the lack of Ru–H signals in the ^{1}H NMR spectrum and especially a $Si(OC_2H_5)_3$-to-PPh_3 ratio of about 1.0, calculated from integration of the ^{1}H NMR spectrum. The elemental analysis data are considered to be in reasonable agreement.

At room temperature, in the presence of air, in addition to the processes illustrated by Eqs. (1)–(3), other transformations possibly occur starting from "$RuCl_2(PPh_3)_2$", e.g.

$$\text{“}RuCl_2(PPh_3)_2\text{”} + 2\ HSi(OC_2H_5)_3 \xrightarrow[-H_2]{-ClSi(OC_2H_5)_3} RuCl[Si(OC_2H_5)_3](PPh_3)_2 \quad (8)$$

and consequently with excess silane, leading to **IV**:

$$RuCl[Si(OC_2H_5)_3](PPh_3)_2 + HSi(OC_2H_5)_3 \xrightarrow[-\frac{1}{2}H_2]{-ClSi(OC_2H_5)_3} \underset{\textbf{IV}}{Ru[Si(OC_2H_5)_3]_2(PPh_3)_2} \quad (9)$$

It is difficult to propose a structure for **IV** with untypically, for Ru(II), a coordination number of four. It seems probable that the aerobic nature of the reaction is reflected in the formation of intermediate ruthenium–oxygen species and/or of dimeric species with μ-$O[Si(OC_2H_5)_3]$ bonds.

A suspension of $RuCl_2(PPh_3)_3$ in $HSi(OC_2H_5)_3$, when warmed at 100°C for 0.5 h, turned light brown in a few minutes. The isolated white solid **V**, washed with diethyl ether, was examined. The IR spectrum showed bands characteristic of Si–H, Ru–H and P=O stretching vibrations, similar in part to those observed for **III**; the ^{1}H NMR spectrum (C_6D_6) showed $Si(OCH_2CH_3)_3$ protons, those characteristic of phenyl groups and a high-field signal (δ −10.5). In addition to EIMS peaks at *m/z* 262 and 183 (due to PPh_3), higher mass peaks due to $OPPh_3$ (*m/z* 277) and to the fragments with Ru (*m/z* 297, 362, 440) are present. The peak at *m/z* 297, attributed previously [2] to the ruthenium–oxygen species $\{Ru(O_2)[Si(OC_2H_5)_3]\}^+$, is observed, but with a lower intensity (12%), as for **III**. The carbon and hydrogen contents are very similar to those expected for $Ru[Si(OC_2H_5)_3]_2(PPh_3)_3$, but the product consists partly of $OPPh_3$. We conclude that **V** is $Ru[Si(OC_2H_5)_3]_2(PPh_3)_2$, accompanied by $OPPh_3$ and admixtures of $RuH_x[Si(OC_2H_5)_3]_y(PPh_3)_n$. Unfortunately, attempts to precipitate some products from the filtrate failed.

Thus, under dry air, $RuCl_2(PPh_3)_3$ reacts with triethoxysilane, probably yielding at room temperature a mixture of **III**, $OPPh_3$, $Ru[Si(OC_2H_5)_3]_2(PPh_3)_2$, $RuH_x[Si(OC_2H_5)_3](PPh_3)_y$ and some "$Ru(O_2)$" species; a similar product **V** is obtained at elevated temperatures.

Under more extreme conditions of refluxing triethoxysilane, the $RuCl_2(PPh_3)_3$–$HSi(OC_2H_5)_3$–O_2 system becomes homogeneous, changing colour from gray to yellow, red and finally yellow. The elemental analysis of the white compound **VI** (m.p. > 360°C), which was precipitated from the yellow reaction solution, does not allow for any reasonable formulation. The high m.p., high mass peaks observed in the EI mass spectra (*m/z* 362, 369, 440, 604) and the lack of Si–H and Ru–H bands in the IR spectrum (ν(Si–O–C, Si–O–Si) and ν(OH) are present) suggest that **VI** consists of di- or higher nuclearity Ru complexes (clusters) with triethoxysilyl and possibly hydroxyl substituents. Unfortunately, insolubility in all common NMR solvents made spectroscopic investigations on **VI** impossible.

All the ruthenium complexes isolated under oxygen-containing conditions (**III**–**VI**) appear to contain an Ru–$Si(OC_2H_5)_3$ bond in mono- or polynuclear compounds. Formation of hexaethoxydisiloxane can be accounted for by oxygenation of one Ru–Si≡ bond to a Ru–O–Si≡ moiety, followed by elimination of disiloxane according to the following reaction:

$$Ru^{II}[Si(OC_2H_5)_3]_2(PPh_3)_n \xrightarrow{O_2} Ru(O_2)[Si(OC_2H_5)_3]_2(PPh_3)_n$$

$$\xrightarrow[-\mathrm{OPPh_3}]{} [\mathrm{Ru^{IV}O[Si(OC_2H_5)_3]_2(PPh_3)_{\mathit{n}-1}}]$$

$$\longrightarrow \mathrm{Ru[OSi(OC_2H_5)_3][Si(OC_2H_5)_3](PPh_3)_{\mathit{n}-1}}$$

$$\xrightarrow[-\mathrm{(C_2H_5O)_3SiOSi(OC_2H_5)_3}]{\mathrm{HSi(OC_2H_5)_3}} \mathrm{RuH[Si(OC_2H_5)_3](PPh_3)_{\mathit{n}-1}}$$

$$\xrightarrow[-\mathrm{H_2},\ -\mathrm{OPPh_3}]{\mathrm{HSi(OC_2H_5)_3,\ O_2}} \underset{\textit{cluster}}{[\mathrm{Ru}]_x[\mathrm{Si(OC_2H_5)_3}]_y} \qquad (10)$$

Many of the complexes and products presented in this scheme were identified in the reaction mixtures examined under oxygen conditions. Additionally, it was found previously that **I** and **II** react with oxygen in the presence of excess $HSi(OC_2H_5)_3$ at elevated temperatures to form complexes corresponding to **III**–**VI** [2].

In discussing the role of oxygen in the processes described above, it should also be mentioned that Ru(II) complexes can easily be converted in to Ru(IV)O species [17] according to the following pathway:

$$\mathrm{Ru^{II}(L) + O_2 \rightarrow Ru^{III}(L)O_2 \rightarrow LRu^{III}\text{–}O\text{–}O\text{–}Ru^{III}L} \\ \rightarrow \mathrm{2LRu^{IV}O} \qquad (11)$$

However, the analytical possibilities to provide evidence for the formation of such an Ru(IV)O species (e.g. ν(RuO) occurs in the IR region at 785–890 cm^{-1} [18]) are limited. The possible presence of RuO species in **VI** cannot be excluded; however, under the preparative conditions (reflux, 6 h), activation of the Si–O–C bond of the silane is more likely.

2.3. Catalytic activity

It has been reported previously that the $RuCl_2(PPh_3)_3$-catalyzed hydrosilylation of the C=C bond in 1-alkenes by trialkoxysilanes takes place only in the absence of solvent and in the presence of a small amount of oxygen [1]. Preliminary identification of an isolated ruthenium–silyl phosphine complex (corresponding to **V**) and its activity in this reaction helped us to rationalize the role of oxygen in the catalysis [2]. Therefore, we tested all the isolated solids (**I**–**VI**) as precursors for the hydrosilylation reaction.

The results, based on GLC data, are presented below. All the isolated solids from a "$RuCl_2(PPh_3)_3$ + $HSi(OC_2H_5)_3$ + O_2" system (i.e. **III**, **IV**, **V** and **VI**) reveal a catalytic activity close to that observed for their precursor $RuCl_2(PPh_3)_3$, yielding n-hexyltriethoxysilane (from 69 to 72%). Complexes **I** and **II** are not catalytically active, whereas other ruthenium complexes with an Ru–H bond show some reactivity: for $Ru(H)Cl(PPh_3)_3$ and $Ru(H)_2(PPh_3)_4$, a 16% yield of product was determined and additionally hexane was detected in the reaction product mixture. The activity of complex **V** and the inactivity of complexes **I** and **II** are in accord with our preliminary results [2]. More surprising is that, under oxygen-free conditions, none of the solids **I**–**VI** or the hydrides noted above show catalytic activity in the test reaction. It is concluded that during the hydrosilylation process taking place in oxygen-free conditions, catalytically inactive hydride ruthenium complexes are probably formed; these could be similar to or identical with **I** or **II**, which are the six- and seven-coordinate species $RuH_3[Si(OC_2H_5)_3](PPh_3)_n$ ($n = 2$ or 3). The results of additional studies on hydridoruthenium complexes with 1-hexene [2] indicated that the alkene does not add to the Ru–H bond under the conditions applied.

In air (and especially at elevated temperature), catalytically active species are produced (presumably similar to **III**–**VI**) from the $RuCl_2(PPh_3)_3$ precursor. However, oxygen is needed during the catalytic process, probably partly because of its irreversible consumption to form $OPPh_3$ (which could be reduced back to PPh_3 by the silane [19]) but mainly because of the formation of oxygen-stabilized Ru intermediates of high catalytic activity that lead to oxygenation of Ru–Si≡ to Ru–O–Si≡ species; these eliminate disiloxane and form in situ coordinatively unsaturated Ru–H complexes which are directly active in the hydrosilylation.

3. Experimental

3.1. Materials

$RuCl_2(PPh_3)_3$ was prepared by a standard procedure [20] from $RuCl_3 \cdot 3H_2O$ obtained from Johnson Matthey. Other ruthenium complexes were purchased from Strem Chemicals or Ventron. 1-Hexene and triethoxysilane were obtained from Aldrich and were distilled prior to use.

3.2. Physical techniques

Infrared spectra were recorded for CsBr or CsI pellets using Perkin-Elmer 180 and Niclolet 5 DXFT spectrometers. ^1H NMR and ^{31}P [^1H] NMR spectra were obtained using Bruker WH-270 (270 MHz, TMS as external standard) and Bruker WP-80 FT (32.44 MHz, room temperature) instruments, respectively. ^{31}P data are reported with respect to 85% H_3PO_4 as reference. ^1H and ^{13}C NMR spectra were additionally recorded on a Varian XL300 spectrometer (300 MHz). EI mass spectra were recorded on Kratos MS 50 (70 eV), Finnigan Mat 800 and Jeol JMS D-100 mass spectrometers. Gas chromatographic analyses were carried out on a Hewlett-Packard Model 5830A chromatograph using SE-30/Chrom R and a thermal conductivity detector.

3.3. Preparation of complexes

3.3.1. Complex **I**: $RuH_3[Si(OC_2H_5)_3](PPh_3)_2$

A 0.25 g (0.27 mmol) amount of $RuCl_2(PPh_3)_3$ was treated with excess triethoxysilane (10 ml) at room temperature under dry argon. H_2 evolved as the ruthenium complex reacted with the silane. After being stirred for 7 days, the suspension changed color from brown to white; hexane was then added and the white solid product (0.15 g) was filtered, washed with hexane and dried under vacuum. All operations were carried out under a nitrogen atmosphere.

$RuH_3[Si(OC_2H_5)_3](PPh_3)_2$: m.p. 128–130°C. IR (cm^{-1}): 1070(s), Si–O–C, 1968, 1979(m), Ru–H, 3000–3100(m) C_6H_5. ^{1}H NMR (C_6D_6): δ 1.18(t) CH_3, 3.80(q) CH_2O, 6.8–7.8(m) C_6H_5, -12.4 to -13.1 (m) Ru–H (-10.03 (d) after 0.5 h). ^{1}H NMR ($CDCl_3$): δ 0.79(t) CH_3, 1.16(t) CH_3, 3.29(q) CH_2O, 3.88(q) CH_2O, 4.26(s) Si–H, 5.28(s) $CHDCl_2$, 6.8–7.8(m) C_6H_5, -10.54(d) Ru–H. ^{31}P [^{1}H] NMR (C_6D_6): δ 47.4. EIMS (*m/z* relative intensity (%)): 78(100), 163(23), 183(40), 262(45), 277(7). Elemental analysis (%): C 64.0, H 5.8, P 8.0, Cl 0.1 (Calc. 63.7, 6.1, 7.8 and 0.0, respectively).

3.3.2. Complex **II**: $RuH_3[Si(OC_2H_5)_3](PPh_3)_3$

A 0.5 g (0.54 mmol) amount of $RuCl_2(PPh_3)_3$ and 4.5 ml (25 mmol) of triethoxysilane were placed in a 50 ml Schlenk tube equipped with a condenser. The reaction mixture was stirred and warmed to 100°C (H_2 was evolved at the beginning of the reaction) and kept at this temperature for 0.5 h under dry argon. The resulting white product was filtered, washed with n-hexane and dried under vacuum (0.37 g). All operations were carried out under dry argon.

$RuH_3[Si(OC_2H_5)_3](PPh_3)_3$: m.p. 132–134°C. IR (cm^{-1}): 1068(s), Si–O–C, 1967, 1978(m), Ru–H, 3000–3100(m) C_6H_5. ^{1}H NMR (C_6D_6): δ 1.17(t) CH_3, 3.78(q), CH_2O, 6.8–7.8(m) C_6H_5 -12.4 to -13.1(m) RuH (-10.03 after 0.5 h). ^{31}P [^{1}H] NMR (C_6D_6): δ 47.4. EIMS (*m/z*, relative intensity (%)): 78(94), 163(46), 183(66), 262(100), 277(5). Elemental analysis (%): C 67.2, H 5.9,P 8.6, Cl 0.1 (Calc. 68.4, 6.0, 8.8 and 0.0, respectively).

3.3.3. *Solid* **III** and complex **IV**

A 0.25 g (0.27 mmol) amount of $RuCl_2(PPh_3)_3$ was treated with excess triethoxysilane (10 ml) at room temperature under dry air. Gases evolved as the ruthenium complex reacted with the silane. After being stirred for 7 days, the suspension changed color from brown to white–yellowish. The yellowish suspension **III**, washed with several portions of diethyl ether, was isolated (0.16 g); a yellow complex **IV** was subsequently precipitated from the filtrate by addition of n-hexane, washed and dried under vacuum.

Solid **III**: IR (cm^{-1}): 850(w) Ru(O_2), 1000–1100(s) Si–O–C, 1195(s) P=O, 1970(m,br) Ru–H, 2245(m) Si–H. ^{1}H NMR (C_6D_6): δ 0.78(t) CH_3, 1.24(t)CH_3, 3.30(q) CH_2O, 3.86(q) CH_2O, 4.49(s) SiH, 6.8–7.8(m) C_6H_5, -10.5(d) RuH. ^{13}C NMR (C_6D_6): δ 18.09 (CH_3), 18.47(CH_3), 58.42 (CH_2O), 59.14 (CH_2O), 118–122 (C_6H_5). ^{31}P [^{1}H] NMR (C_6D_6): δ 12($OPPh_3$). EIMS (*m/z*, relative intensity (%)): 78 (100), 163(20), 183(60), 262(85), 277(100), 297(12). Elemental analysis (%): C 64.8, H 5.6, P 6.5, Cl 0.1.

$Ru[Si(OC_2H_5)_3]_2(PPh_3)_2$: m.p. 135–137°C. IR-(cm^{-1}): 1000–1100(s) Si–O–C, 3000–3100(m) C_6H_5. ^{1}H NMR (C_6D_6): δ 1.25(t) CH_3, 3.86(q) CH_2O, 6.8–7.8(m) C_6H_5. ^{31}P [^{1}H] NMR (C_6D_6): δ -1.24. EIMS (*m/z*, relative intensity (%)): 78 (80), 163(17), 183(60), 262(77). Elemental analysis (%): C 59.4, H 6.3, P 6.3 (calculated 60.5, 6.4, and 6.5; respectively).

3.3.4. Solid V

Solid **V** (0.41 g) was synthesized analogously to complex **II**, but all operations were carried out under dry air. The resulting light-brown suspension was collected and washed several times with diethyl ether to yield a white solid.

IR(cm^{-1}) 1000–1100(s) Si–O–C, 1195(m) P=O, 1970(w) Ru–H, 2245(w) Si–H. ^{1}H NMR (C_6D_6): δ 1.24(t) CH_3, 3.85(q) CH_2O, 6.8–7.8(m) C_6H_5, -10.5(d) Ru–H. EIMS (*m/z*, relative intensity (%)): 163(15), 183(100), 262(43), 277(27), 297(12), 362(5), 440(12). Elemental analysis (%): C 65.8, H 6.0, P 6.3, Cl 0.1.

3.3.5. Solid VI

Solid **VI** was prepared analogously to solid **V** but the reaction mixture was stirred at reflux temperature (130–135°C) for 6 h. From the yellow homogeneous reaction mixture, a white solid **VI** (0.05 g) was precipitated by the addition of n-hexane; this was collected, washed and dried under vacuum.

IR (cm^{-1}): ~ 1100(br) Si–O–C, Si–O–Si, 3400 (br) OH. EIMS (*m/z*, relative intensity (%)): 262(22), 277(100), 362(4), 369(2), 440(14), 604(5). Elemental analysis (%): C 45.2, H 4.15, P 5.4.

3.4. Manometric measurements

The net gas evolution (H_2 evolved minus the O_2 absorbed) during the reaction was followed manometrically using a Datametrics Type 1173 electronic manometer with a Barocel Model 570 D-100, T-1A1 V1 pressure sensor equipped with solvent shields and connected to a servorecorder. The reactants were placed in a two-necked, round-bottomed flask with a pressure-equalizing pipette in one neck and the sample side of the pressure sensor attached through the other. 2.5×10^{-4} mol of $RuCl_2(PPh_3)_3$ and excess triethoxysilane

(2.5×10^{-2} mol) was stirred magnetically in a reaction flask at room temperature under dry argon (or air).

3.5. Hydrosilylation test

Hydrosilylation experiments were carried out in sealed ampoules under air or nitrogen without solvent. The reaction mixture (1-hexane, triethoxysilane and the appropriate Ru complex) was heated to 120°C and kept at temperature for 6 h in sealed glass ampoules ($[\equiv\text{SiH}]:[>\text{C}=\text{C}<]:[\text{cat.}] = 1:1:\sim 2 \times 10^{-4}$). In the case of solids **III**, **V** and **VI** the same amount of precursor was weighed (0.003 g) and sealed in the reaction mixture. Then the reaction mixtures were analyzed by GLC. A standard sample of the hydrosilylation product (n-hexyltriethoxysilane) was prepared in separate experiments and was isolated and identified [21].

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