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Journal of Organometallic Chemistry 493 (1995) 261–266

Journal of Organometallic Chemistry

Synthesis, characterization and some reactions of $[(\text{diene})Rh(\mu\text{-}OSiMe_3)]_2$

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Received 16 November 1994

Abstract

The rhodium(I) complexes of general formula $[(\text{diene})Rh(\mu\text{-}OSiMe_3)]_2$, (where diene = cod (I) and nbd) were synthesized in the reaction of $[(\text{diene})RhCl]_2$ with sodium trimethylsilanolate. The reactions of I with triphenylphosphine gave monomeric and dimeric products, which formula depends on the [Rh]:[P] ratio (i.e. $Rh(\mu\text{-}OSiMe_3)(cod)PPh_3$ and $[(PPh_3)_2Rh(\mu\text{-}OSiMe_3)]_2$ for [Rh]:[P] = 1:1 and $[(PPh_3)_2Rh(\mu\text{-}OSiMe_3)]_2$ when [Rh]:[P] = 1:2). The reaction of (I) with triethylsilane after eliminating triethyltrimethyldisiloxane yielded tetrameric hydride, $[codRhH]_4$ but, when there was an excess of triethylsilane, also $Rh(H)_2SiEt_3(cod)$. The reactions of I with both PPh_3 and Et_3SiH furnish a mixture of the products mentioned above. All the rhodium complexes were characterized by ^{1}H, ^{13}C, ^{31}P and ^{29}Si NMR spectroscopy.

Keywords: Rhodium; Silicon

1. Introduction

Simple metal silanolates and other compounds and complexes of main group elements as well as early transition elements containing silyloxy ligands are well known and have been well characterized [1–3]. Some of them can be utilized as precursors of ceramic materials [4–6]. Of particular interest are the preparation and characterization of molecular complexes incorporating M–O–Si bonds (where M = transition metal) as models for metal complexes supported on silica surface [7,8]. However, there is a little information about the group VIII transition metal–silyloxy complexes prepared and characterized in molecular form.

Among them there are $[\mu\text{-}OSi(O^{t}Bu)_3]_2Ni_2(\eta^{5}\text{-}C_3H_5)_2$ [9], $(PPh_3)_2Pt(OSiMe_3)_2$ [10], $[Co(OSiMe_3)_2(THF)]_2$ [11], $Co(OSiMe_3)L_3$ [12], $[Rh(CO)_2(OSiR_3)]_2$, where R = Ph [13] or Me [13,14], $NX_4[RuN(OSiMe_3)_4]$, where X = PPh_3 or *n*-Bu [15], $Ru(CO)_2(OCOCF_3)(\mu\text{-}OSiMe_2CH_2PPh_2)_2$ [16], $RuHX(CO)L_2$, where $L{\equiv}PBu_2Me$, X = $OSiPh_3$, $OSiMe_3$ or, $OSiMe_2Ph$ [17], $HOs_3CO_{10}(OSiR_3)$, where R = Et or Ph [18], $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiEt_3)$ [19] and silyloxy-bridged Fe–In complexes [20]. Polymetallasilsesquioxanes of sandwich type containing Ni–O–Si bond were synthesized and the crystal structure was determined [21,22].

In the present paper we provide all synthetic details for $[(\text{diene})Rh(\mu\text{-}OSiMe_3)]_2$, where diene = 1,5 cyclooctadiene or norborna-2,5-diene, and its reactivity with tertiary phosphines and trisubstituted silanes.

2. Experimental details

All manipulations were carried out under argon using standard Schlenk techniques and a glove-box. All solvents (POCh, Merck) were freshly distilled under argon and dried prior to use. C_6D_6 (Dr. Glaser AG) was distilled under argon and kept over 4A molecular sieves. NMR spectra were recorded on a Varian 300 MHz instrument, using 5 mm Wilmad tubes with silicon septa. The ^{1}H and ^{13}C NMR spectra are reported against C_6D_6. Visible spectra were recorded using a Specord UV–visible spectrophotometer (Carl Zeiss Jena) in quartz cells of 1 cm thickness hermetically sealed with silicon rubber. IR spectra were recorded in Nujol kept over molecular sieves, using Fourier transform IR Bruker JFS-113v.

Triphenylphosphine (Fluka AG.) and sodium trimethylsilanolate (Huls-Petrarch) were used as purchased. Triethylsilane (Fluka AG) was distilled under argon

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Elsevier Science S.A.
SSDI 0022-328X(95)05352-9

before use. [codRhCl]$_2$, [nbdRhCl]$_2$, RhCl(cod)PPh$_3$ and RhCl(PPh$_3$)$_3$ were prepared according to the literature procedures [23–25].

2.1. Synthesis of bis-(1,5 cyclooctadiene)-di-μ-trimethylsiloxy-dirhodium(I)

([codRhCl]$_2$) (0.375 g, 0.76 mmol) was dissolved in 3 ml of C_6H_6 and added to a suspension of NaOSiMe$_3$ (0.170 g, 1.52 mmol) in 5 ml of C_6H_6 and stirred for 24 h. Then the benzene was carefully evaporated to dryness under vacuum and 7 ml of pentane was added. The mixture was stirred for 1 h and filtered from NaCl (AgNO$_3$ test). Pentane solution was evaporated under reduced pressure and finally [codRh(μ-OSiMe$_3$)]$_2$ (I) (0.35g, 0.56 mmol) precipitated as yellow–orange powder (yield, 77%).

Anal. Found: C, 43.59; H, 6.96. $C_{22}H_{42}O_2Si_2Rh_2$ calc.: C, 43.98; H, 6.99. ^{1}H NMR (C_6D_6,): δ 0.31 (s, –SiCH$_3$, 18H), 1.52 (m, cod-aliph., 4H), 1.65 (m, cod-aliph., 4H), 2.20 (s, cod-aliph., 4H), 2.55 (s, cod-aliph., 4H), 3.85 (s, cod-olef., 4H), 4.15 (s, cod-olef., 4H), ppm. ^{13}C NMR (C_6D_6,): δ 6.51 (s, –SiCH$_3$), 31.55 (s, cod-aliph.), 32.22 (s, cod-aliph.), 72.70 (d, JRh-C 14.4 Hz, cod-olef.), 76.65 (d, JRh-C 13.9 Hz, cod-olef) ppm. ^{29}Si NMR(C_6D_6): δ 10.46 (s) ppm. IR: ν(O–Si) 910 (vs) cm^{-1}. Visible (C_6D_6): λ_{max}28 × 10^3 cm^{-1}.

2.2. Synthesis of bis-(norborna-2,5-diene)-di-μ-trimethylsilyloxy-dirhodium(I)

[nbdRhCl]$_2$ (0.277 g, 0.60 mmol) was dissolved in 5 cm^3 of benzene and filtrated through a porous-glass filter into Schlenk flask. Then suspension of NaOSiMe$_3$ (0.135 g, 1.20 mmol) in 5 cm^3 of C_6H_6 was added and the mixture was rapidly stirred overnight. The precipitated NaCl was filtrated and benzene was evaporated to dryness under vacuum. The final product was extracted into 5 ml of *n*-pentane, filtrated and collected under reduced pressure as a yellow powder (0.25 g., 0.44 mmol) (yield, 73%).

Anal. Found: C, 42.26; H, 5.98%. $C_{20}H_{34}O_2Si_2Rh_2$ calc.: C, 42.23; H, 5.98%. ^{1}H NMR (C_6D_6): δ 0.15 (s, –SiCH$_3$), 0.87 (t, nbd-aliph, 4H), 3.45 (s, nbd-bridge, 4H), 3.64 (s, nbd-olef, 8H) ppm. ^{13}C NMR (C_6D_6,): δ 5.81 (s, –Si–CH$_3$), 47.44 (s, nbd-aliph), 50.49 (t, nbd-bridge), 60.68 (d, J(Rh-C)6.45 Hz, nbd-olef): ppm. IR: ν(O–Si) 913 (s) cm^{-1}. Visible 27 × 10^3 cm^{-1}.

2.3. Reaction of RhCl(cod)PPh$_3$ with NaOSiMe$_3$

RhCl(cod)PPh$_3$ (0.43 g, 0.84 mmol) was added to a suspension of NaOSiMe$_3$ (0.099 g, 0.88 mmol) in 10 cm^3 of benzene and stirred rapidly. The reaction was monitored by ^{31}P NMR until the doublet resonance at $\delta = 30.8$ ppm, J(Rh–P) = 152 Hz, disappeared and the resonance at $\delta = 24.55$ ppm (d, J(Rh–P) = 160.2 Hz) was detected. The precipitated NaCl was filtrated; the reaction mixture evaporated to one third of the volume and kept at 0°C overnight. The yellow crystals precipitated on the walls of the flask were dissolved in C_6D_6.

^{1}H NMR (C_6D_6): δ 0.119 (s, –OSiCH$_3$ terminal), 0.14 (s, –OSiCH$_3$ bridged), 1.61 (m, cod-aliph), 2.93 (s, cod-olef), 5.57 (s, cod-olef), 6.90, 7.70 (m, –Ph), 6.9 (m, Ph), 7.7 (m, Ph) ppm. ^{13}C NMR (C_6D_6): δ 33.29 (s, cod-aliph), 64.71 (d, J(Rh–C) = 13.04 Hz, cod-olef), 103.10 (d, J(Rh–C) = 7.9 Hz, cod-olef) ppm. ^{31}P NMR (C_6D_6): δ 24.5 (d), J(Rh–P) = 160.2 Hz, 57.1 (d, J(Rh–P) = 189.1 Hz) ppm.

2.4. Reaction of [codRh(μ-OSiMe$_3$)]$_2$ with four equivalents of PPh$_3$

[codRh(μ-OSiMe$_3$)]$_2$ (0.102 g, 0.16 mmol) in 5 cm^3 of C_6H_6 was added to a solution of PPh$_3$ (0.175 g, 0.67 mmol) in 7 cm^3 of C_6H_6. The mixture was stirred overnight and detected by gas chromatography (GC)–mass spectroscopy MS ($m/z = 108$, C_8H_{12}). Then C_6H_6 was evaporated to half the volume and 8 cm^3 of pentane was added dropwise. The precipitated cherry-brown solid was collected on a porous-glass filter, washed with a small quantity of pentane and dissolved in C_6D_6.

^{31}P NMR (20°C) shows doublet resonance at $\delta = 57.1$ ppm (J(Rh-P) = 189.1 Hz). ^{1}H NMR (C_6D_6): δ 0.14 (s, –OSiMe$_3$, bridged), 6.9 (m, Ph), 7.7 (m, Ph) ppm.

2.5. Reaction of RhCl(PPh$_3$)$_3$ with NaOSiMe$_3$

Wilkinson complex (0.099 g, 0.11 mmol) in 8 cm^3 of C_6H_6 was added to NaOSiMe$_3$ (0.122 g, 1.09 mmol) in 10 cm^3 of C_6H_6. The mixture was rapidly stirred for 24 h and then filtrated. The solid material on filter appeared to be NaCl (AgNO$_3$ test) and NaOSiMe$_3$. The solution was evaporated under vacuum, resulted oily residue.

^{1}H NMR (C_6D_6): δ 0.14 (s, –OSiMe$_3$, bridged), 6.9, 7.7 (m, Ph), 0.22 (s, NaOSiMe$_3$) ppm. ^{31}P NMR (C_6D_6): δ 57.1 (d, J(Rh–P) = 189.1 Hz), −5.8 (s, PPh$_3$) ppm.

2.6. Titration of [codRh(μ-OSiMe$_3$)]$_2$ with triphenylphosphine

[codRh(μ-OSiMe$_3$)]$_2$ (0.029 g, 0.05 mmol) was dissolved in NMR tube in 0.6 cm^3 of C_6D_6. Triphenylphosphine (0.052 g, 0.20 mmol) was dissolved in 2 cm^3 of C_6D_6 in Schlenk flask equipped with silicon caps. The solution of triphenylphosphine was added to the NMR tube in four portions, each of 52.4 μl (0.013 g, 0.05 mmol of PPh$_3$) every 2 hs and the ^{31}P NMR spectrum was recorded after each portion was added.

^{31}P (C_6D_6): δ [Rh]:[P] = 1:0.5, 24.5 (d, J(Rh–P) = 160.2 Hz); 57.1 (d, J(Rh-P) = 189.1 Hz), 57.5 (d,

J(Rh–P) = 191.8 Hz), 42.7 (d, J(Rh–P) = 204 Hz); [Rh] : [P] = 1 : 1, 24.5 (d, J(Rh–P) = 160.2 Hz), 57.1 (d, J(Rh–P) = 189.1 Hz); [Rh] : [P] = 1.5 : 1, 57.1 (d, J(Rh–P) = 189.1 Hz), −5.8(s); [Rh] : [P] = 1 : 2, 57.1 (d, J(Rh–P) = 189.1 Hz), −5.8 (s) ppm. ^{1}H NMR (C_6D_6): δ 2.10 (s), 5.80 (s) ppm.

2.7. Reaction of [codRh(μ-OSiMe$_3$)]$_2$ with triethylsilane

[codRh(μ-OSiMe$_3$)]$_2$ (0.043 g, 0.072 mmol) was put into an NMR tube and C_6D_6 (0.6 cm^3) was injected. Then, 15.5 μl of HSiEt$_3$ (0.0116 g, 0.143 mmol) was added by a Hamilton chromatography syringe. The solution changed colour from orange–yellow into deep cherry after less than 20 min.

^{1}H NMR (C_6D_6): δ 4.70 (s, cod-olef), 2.20 (d, cod-olef), 1.7 (m, cod-aliph), −11.87 (quint J(Rh-H) = 14.4 Hz) ppm. GC–MS chromatography of C_6D_6 solution: m/z 205, 189, 175 $(CH_3CH_2)_3SiOSi(CH_3)_3$. After the next portion of 15.5 μl of HSiEt$_3$ was added, the spectrum showed changes at the negative range. ^{1}H NMR: δ −13.87 (d, J(Rh-H) = 42 Hz) ppm.

2.8. Reaction of [codRh(μ-OSiMe$_3$)]$_2$ with triethylsilane and triphenylphosphine

[codRh(μ-OSiMe$_3$)]$_2$ (0.036 g, 0.06 mmol) was dissolved in 0.3 cm^3 of C_6D_6 in an NMR tube. Then, PPh$_3$ (0.035 g, 0.13 mmol) in 0.3 cm^3 was added and, after 5 h, 20.6 μl of HSiEt$_3$ (0.016 g, 0.13 mmol) was added. The mixture changed colour from yellow–orange to cherry-brown after 10 min.

^{31}P NMR (C_6D_6): δ 42.7 (d, J(Rh–P) = 204 Hz) ppm. ^{1}H NMR (C_6D_6): δ-11.87 (quint, J(Rh–H) = 14.4 Hz), 2.1 (s, cod-aliph.), 5.8 (s, cod-olef); 3,8 (t, Si–H). GC–MS (C_6D_6 solution): m/z 205 Me$_3$SiOSiEt$_3$. After the next portion of 20.6 μl of HSiEt$_3$ was added, the spectrum showed changes in the negative range. ^{1}H NMR: δ-13.87 (d, J(Rh–H) = 42 Hz) ppm.

3. Results and discussion

3.1. Synthesis of [(diene)Rh(μ-OSiMe$_3$)]$_2$ complexes

Reaction of [(diene)RhCl]$_2$ with sodium trimethylsilanolate has proven to be a general method for the preparation of corresponding siloxy complexes of rhodium:

$$[(\text{diene})\text{RhCl}]_2 + 2\text{Me}_3\text{SiONa} \rightarrow [(\text{diene})\text{Rh}(\mu\text{-OSiMe}_3)]_2 + 2\text{NaCl}$$

where diene≡1,5-cyclooctadiene or norborna-2,5-diene.

A chloro-rhodium complex was dissolved in benzene under an argon atmosphere, and solid sodium trimethylsilanolate was added. After NaCl filtration the solution was evaporated to dryness and the final rhodium siloxy complexes were extracted from pentane as yellow precipitates. They are stable in the absence of air and were characterized by ^{1}H, ^{13}C and ^{29}Si NMR, IR and visible spectroscopy as well as elemental analysis.

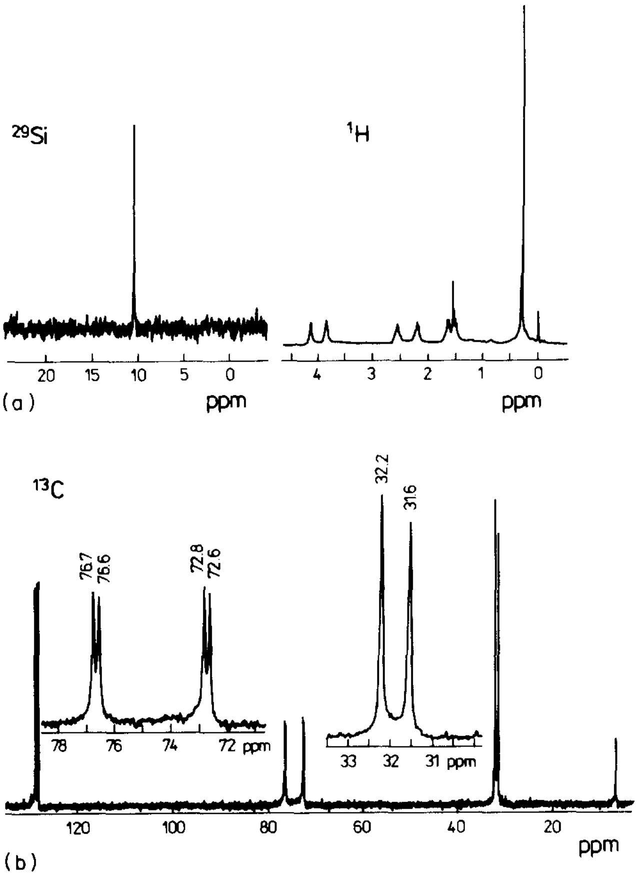


Fig. 1. (a) ^{29}Si, ^{1}H and (b) ^{13}C NMR spectra of [codRh(μ-OSiMe$_3$)]$_2$ recorded in C_6D_6, at T = 20°C.

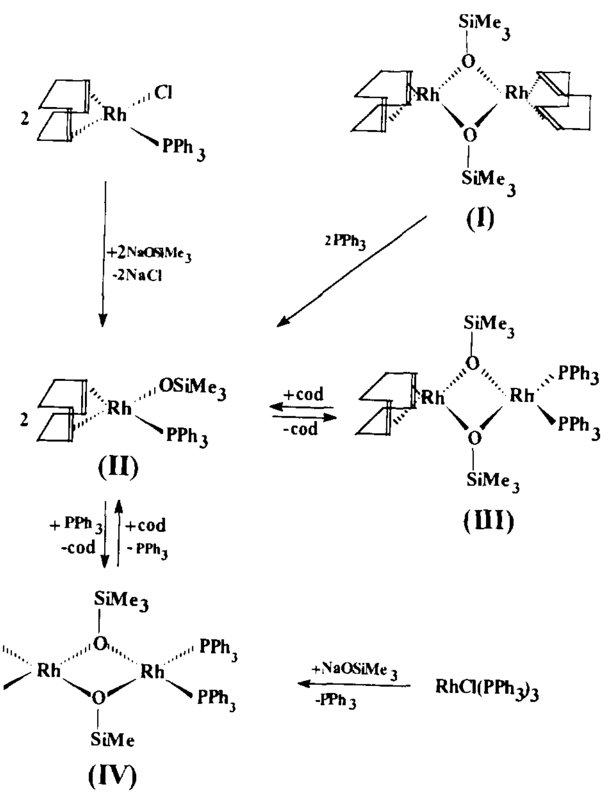
The ^{1}H NMR spectrum of [codRh(μ-OSiMe$_3$)]$_2$ (**I**) shows two chemically inequivalent cod-olefinic resonances which appear as slightly broadened singlets (presumably owing to the unresolved coupling and not to the chemical exchange) at δ = 4.15 and 3.85 ppm (Fig. 1(a)). The rhodium siloxy complex cod-aliphatic resonances are observed as four broadened multiplets at δ = 1.52, 1.65 and 2.20, 2.55 ppm. The Me$_3$Si resonance is a singlet at δ = 0.31 ppm. The rhodium-chloro precursor shows only one type of cod-olefinic resonance at δ = 4.31 ppm and the cod-aliphatic multiplet resonance at δ = 2.14 and 1.30 ppm [26]. The crystal structure of [codRhCl]$_2$ revealed the existence of only one *cis–cis* product [27]. The ^{13}C NMR spectrum of [codRh(μ-OSiMe$_3$)]$_2$ (Fig. 1(b)) is also consistent with a dimeric folded structure, and the cod-olefinic doublet resonance is not equivalent and appears at δ = 76.65 ppm (J(Rh–C) = 13.9 Hz) and 72.70 ppm (J(Rh–C) = 14.4 Hz). The cod-aliphatic resonances appear as two singlets at δ = 31.55 and 32.22 ppm. The Me$_3$Si carbon resonance appears as a singlet at $\delta = 6.51$ ppm. The ^{29}Si NMR spectrum in C_6D_6 shows only a single resonance at $\delta = 10.46$ ppm.

The ^{1}H NMR spectrum of $[(cod)Rh(\mu\text{-}OSiMe_3)]_2$ in $CDCl_3$ shows small differences in the cod-olefinic proton shift compared with C_6D_6 solution; the double resonance is observed as two multiplets at $\delta = 3.96$ and 3.60 ppm. The cod-aliphatic resonance appears at the same range. The ^{13}C NMR spectrum in $CDCl_3$ shows the very same resonance as in C_6D_6. The ^{1}H NMR measurements in C_6D_6 in different temperatures show the covering of cod-aliphatic resonances from $\Delta\delta = 0.13$ ppm for 1.65 and 1.52 ppm at 30°C to $\Delta\delta = 0$ ppm for $\delta = 1.65$ ppm at 70°C. The inequivalency of cod-aliphatic and olefinic resonances recorded in ^{1}H and ^{13}C NMR spectra is apparently due to the isomeric form *cis–trans* presented in the solution.

Contrary to bis(1,5-cyclooctadiene)-di-μ-(trimethylsilyloxy)dirhodium(I), the ^{1}H NMR spectrum of the corresponding (norborna-2,5-diene)-di-μ-(trimethylsilyloxy)-dirhodium(I) shows only one cod-olefinic resonance appears as a single peak at $\delta = 3.64$ ppm as well as one resonance at $\delta = 3.45$ ppm attributed to a bridgehead CH_2 and the nbd aliphatic resonance is observed as a triplet at $\delta = 0.87$ ppm. The IR spectrum in Nujol shows a band characteristic of the Si–O stretching vibrations at 913 cm^{-1} [13].

3.2. Formation of rhodium–silyloxy phosphine complexes

The reaction of $[codRhCl]_2$ with triphenylphosphine in benzene solution leads to a complex in which [Rh] : [P] = 1 : 1 [25,26]. The ^{31}P NMR spectrum shows a doublet resonance at $\delta = 30.8$ ppm, (J(Rh–P) = 152 Hz) [27]. In contrast with the above data, the addition of PPh_3 to **I** leads to the formation of various complexes whose composition and structure depend on the [Rh] : [P] ratio, as in the case of other Rh(I) complexes [28]. The effect of triphenylphosphine noted by the spectroscopic methods can be easily observed by the correlation of ^{31}P NMR spectra (chemical shifts and coupling constant Rh–P) with the [Rh] : [PPh_3] ratio. This spectroscopic method allows us to propose the reaction scheme given in Scheme 1.



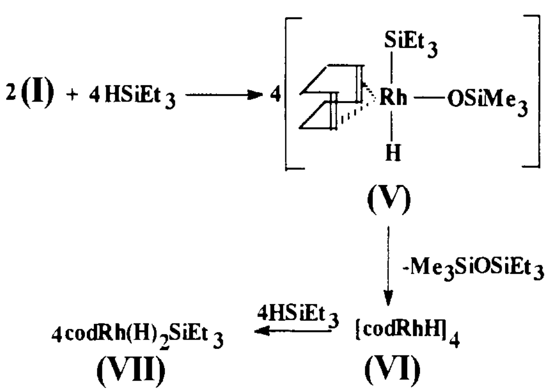
Scheme 1.

^{31}P NMR for tertiary phosphines coordinated to the Rh(I) square planar complex shows a doublet resonance on ^{1}H-decoupled spectra [29]. If the coupling constant J(Rh–P) is between 120 and 160 Hz, then it suggests a monomeric species [30] of square planar as follows from **II** (J(Rh–P) = 160.2 Hz; $\delta = 24.55$ ppm). However, the doublet with J(Rh–P) higher than 160 Hz can be consistent with two isomeric structures of the type **IV** ($\delta = 57.1$ ppm, J(Rh–P) = 189.1 Hz; $\delta = 57.5$ ppm J(Rh–P) = 191.8 Hz). On the contrary, the resonance appearing at $\delta = 42.7$ (d, J(Rh–P) = 204 Hz) ppm (when [P] : [Rh] < 1 : 1) can be the result of the reactions **II** → **III** (although **I** → **III** cannot be ruled out [31]). The disappearance of the doublet resonance at $\delta = 57.5$ ppm (less stable isomer of the dimer) and above all at $\delta = 24.5$ ppm (monomeric square planar complex) and stabilization of the resonance at $\delta = 57.14$ ppm (J(Rh–P) = 189.1 Hz) as well as the appearance of the resonance at $\delta = -5.8$ ppm (s, free phosphine) seem to be very convincing evidence of the transformation **II** → **IV**, as the [P] : [Rh] ratio has increased what can be also confirmed by ^{1}H NMR spectra, showing strong signals from free cod molecule during titration of **I** with PPh_3.

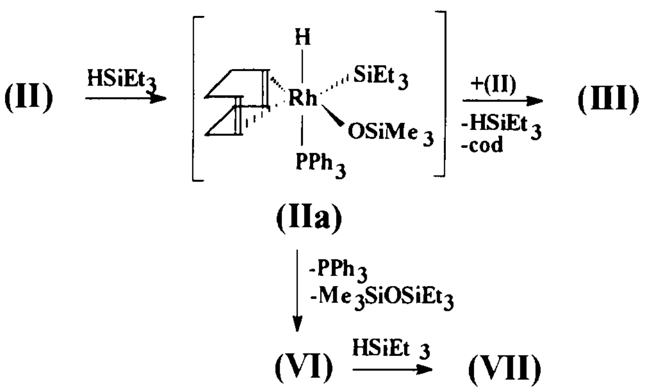
Complex **IV** can also be synthesized by the reaction of the Wilkinson complex $RhCl(PPh_3)_3$ with sodium trimethylsilanolate after prior elimination of the PPh_3 ligand. Moreover, this synthesis is further evidence of the proposed structure **IV**. In ^{31}P NMR spectra, the resonance at $\delta = 25.1$ ppm appears as a single resonance due to the free $O{=}PPh_3$ released when traces of oxygen are present in solution. Details of ^{1}H NMR and ^{13}C NMR for phosphine–rhodium complexes are given in Section 2.

3.3. Reactions of $[(cod)Rh(\mu\text{-}OSiMe_3)]_2$ with triethylsilane

The direct reaction of **I** with triethylsilane occurs at a twofold excess of hydrosilane as in Scheme 2. The



Scheme 2.



Scheme 3.

intermediate **V** imediately undergoes the reaction, giving finally triethyltrimethyldisiloxane measured by GC–MS, and **VI** which was identified by ^{1}H NMR (Fig. 2).

Compound **VI** shows resonance at $\delta = -11.87$ ppm (quint, J(Rh–H) = 14.4 Hz). This complex was previously synthesized by thermal decomposition of the [(μ-C_2H_5)Rh(cod)]$_2$ dimer (obtained in the reaction of [codRhCl]$_2$ in diethyl ether at −80°C) through a series of β-hydride elimination and dissociation steps [32]. Fast elimination of disiloxanes $Et_3SiOSiMe_3$ recorded by GC–MS of the reaction mixture can be a very important pathway for generating Rh(I) hydride intermediates active in hydrosilylation, hydrogenation, metathesis and other reactions. With excess of triethylsilane, **VI** and **VII** are recorded by ^{1}H NMR. A doublet resonance at −13.85 ppm (J(Rh–H) = 42Hz) is due to the dihydride monomeric complex **VII**.

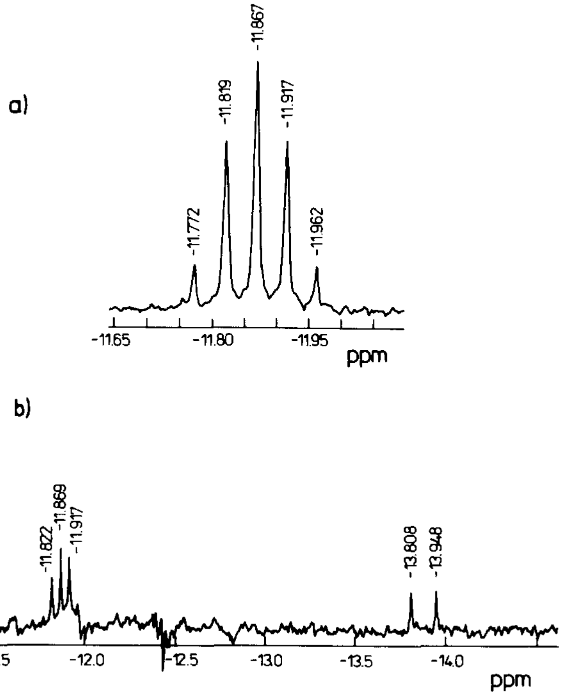


Fig. 2. ^{1}H NMR spectra (negative range; C_6D_6; $T = 20$°C) of products of $HSiEt_3$ addition to [codRh(μ-$OSiMe_3$)]$_2$ at (a) 1 : 1 and (b) 1 : 2 Rh : $HSiEt_3$ molar ratios.

3.4. *Reactions of [(cod)Rh(μ-OSiMe$_3$)]$_2$ with triphenylphosphine and triethylsilane*

^{1}H and ^{31}P NMR spectra of the products formed in the reactions of **I** with PPh_3 and $HSiEt_3$ ([Rh] : [P] = 1 : 1) and GC–MS of the reaction mixture suggest the sequence of the competitive reactions given in Scheme 3.

Oxidative addition of silicon hydride to **II** gives presumably the labile octahedral complex **IIa** from which trimethyltriethyldisiloxane can be predominantly eliminated forming cluster **VI** with simultaneously release of the PPh_3 ligand. On the contrary, cod (observed by ^{1}H NMR and GC–MS) can be competitively eliminated from **IIa**, giving the H($SiEt_3$)Rh($OSiMe_3$)-PPh_3 square planar complex which reacts subsequently with excess of **II** yielding finally **III** with elimination of initiated triethylsilane (observed by ^{1}H NMR). The latter pathway explains the role of triethylsilane in producing **III** which is not observed in the absence of silicon hydride (when [Rh] : [P] = 1 : 1). Elimination of phosphine from RhCl(cod)PPh_3 under hydrosilylation conditions, i.e. in the presence of trisubstituted silanes, was previously observed by a spectrophotometric method [33,34]. In the presence of trisubstituted silanes, no **IV** is formed. A separate study on the reaction of Wilkinson complex RhCl(PPh_3)$_3$ in the presence of sodium trimethylsilanolate allowed us to synthesize **IV**, but no reaction of **IV** with triethylsilane under the conditions examined was observed.

Acknowledgement

This work was supported by funds from the Committee of Scientific Research, under Project 206819101.

References

[1] F. Schindler and H. Schmidbaur, *Angew. Chem., 79* (1967) 697.

[2] H. Schmidbaur, *Angew. Chem., 77* (1965) 206.

[3] I. Shiihara, W.T. Schwartz and H.W. Post, *Chem. Rev., 61* (1961) 1.

[4] D.C. Bradley and R.C. Mehrotra, Metal Alkoxides, Academic Press, New York, 1978.

[5] A.G. Williams and L.V. Interrante, *Better Ceramics Through Chemistry, Materials Research Society Symp. Proc.*, Vol. 32, Elsevier, New York, 1984, p. 151.

[6] R.C. Mehrotra, *J. Non-Cryst. Solids, 100* (1988) 1.

[7] J.H. Wengrovius, M.F. Garbauskas, E.A. Wiliams, R.C. Going, P.E. Donahue and J.F. Smith, *J. Am. Chem. Soc., 108* (1986) 982.

[8] F.J. Feher, *J. Am. Chem. Soc., 108* (1986) 3850.

[9] A.K. McMullen, T.D. Tilley, A.L. Rheingold and S.J. Geib, *Inorg. Chem., 29* (1990) 2228.

[10] H. Schmidbaur and J. Adlkofer, *Chem. Ber., 107* (1974) 3680.

[11] G.A. Sigel, R.A. Bartlett, O. Decker, M.M. Olmsted and P.P. Power, *Inorg. Chem., 26* (1987) 1773.

[12] S. Komiya, R.S. Srivatsava, A. Yamamoto and T. Yamamoto, *Organometallics, 4* (1985) 1504.

[13] L. Marko and A.J. Vizi-Orosz, *Trans. Met. Chem., 7* (1982) 216.

[14] G. Palyi, C. Zucchi, R. Ugo, R. Psaro, A. Sironi and A.J. Vizi-Orosz, *J. Mol. Catal., 74* (1992) 51.

[15] P. Shapley, Hoon-Sik Kim and S.R. Wilson, *Organometallics, 7* (1988) 928.

[16] G.C. Bruce and S.R. Stobart, *Inorg. Chem., 27* (1988) 3879.

[17] J.P. Poulton, K. Folting, W.E. Streib and K.G. Caulton, *Inorg. Chem., 31* (1992) 3190.

[18] A. Choplin, B. Besson, L. D'Orneles, R. Sanchez-Delgado and J.M. Basset, *J. Am. Chem. Soc., 110* (1988) 2783.

[19] J. Puga, F. Fehlner, B.C., Gates, D. Braga and F. Grepioni, *Inorg. Chem., 29* (1990) 2376.

[20] P. Braunstein, M. Knorr, M. Strampfer, A. DeCian and J. Fischer, *J. Chem. Soc. Dalton Trans.,* (1994) 117.

[21] M.M. Levitsky, O. Shchegolikhina, A.A. Zhdanov, V.E. Igonin, V.E. Ovchinnikov, V.E. Shklover and Yu.T. Struchkov, *J. Organomet. Chem., 401* (1991) 199.

[22] G. Gavioli, M. Borsari, C. Zucchi, G. Palyi, R. Psaro, R. Ugo, O. Shchegolikhina and A.A. Zhdanov, *J. Organomet. Chem., 467* (1994) 165.

[23] J. Chatt and L.M. Venanzi, *J. Chem. Soc.,* (1957) 4735.

[24] G. Giordano and R.H. Crabtree, *Inorg. Synth., 19* (1979) 218.

[25] E.W. Abel, M.A. Bennet and G. Wilkinson, *J. Chem. Soc.,* (1959) 3178.

[26] M.A. Kulzick, R.T. Price, R.A. Andersen and E.L. Muetterties, *J. Organomet. Chem., 333* (1987) 105.

[27] J.C.A. Boyens, L.S. Denner, W. Orchard, I. Rencken and B.S. Rose, *S. Afr. J. Chem., 39* (1986) 229.

[28] M. Li Wu, J. Desmond and R.S. Drago, *Inorg. Chem., 18* (1979) 679.

[29] P.E. Garrou, *Chem. Rev., 85* (1985) 171.

[30] P.E. Garrou and G.E. Hartwell, *Inorg. Chem., 15* (1976) 646.

[31] D.W. Meek, P.E. Kreter and G.G. Christoph, *J. Organomet. Chem, 231* (1982) C53.

[32] M.A. Kulzick, R.T. Price, E.L. Muetterties and V.E. Day, *Organometallics, 1* (1982) 1256.

[33] W. Duczmal, B. Marciniec and W. Urbaniak, *J. Organomet. Chem., 327* (1987) 295.

[34] B. Marciniec, W. Duczmal, W. Urbaniak and E. Śliwińska, *J. Organomet. Chem., 385* (1990) 319.

Note added in proof

Synthesis by other method and characterization of (cod)Rh(μ-OSiMe$_3$) has recently appeared: A. Vizi-Orasz, R. Ugo, R. Psaro, A. Sironi, M. Moret, C. Zucchi, F. Ghelfi and G. Pàlyi, *Inorg. Chem., 33* (1994) 4600.