

Rh(I) and Rh(III) silyl PMe_3 complexes. Syntheses, reactions and ^{103}Rh NMR spectroscopy¹

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Abstract

Synthetic approaches to Rh(I) silyls are described. The complexes L_nRhSiR_3 ($\text{L} = \text{PMe}_3$; **6**, $n = 4$, $\text{R}_3 = (\text{OEt})_3$; **7**, $n = 4$, $\text{R}_3 = \text{Me}(\text{OMe})_2$; **21**, $n = 3$, $\text{R}_3 = \text{Ph}_3$) resulted from the reactions of MeRhL_4 (**1**) with the corresponding silanes HSiR_3 . Complex **21** was prepared alternatively from PhRhL_3 (**2**) and HSiPh_3 , while analogous reactions of $\text{HSi}(\text{OEt})_3$, $\text{HSiMe}(\text{OMe})_2$ and $\text{HSi}(\text{OMe})_3$ led to the bis(silyl)hydrides *fac*- $\text{L}_3\text{Rh}(\text{SiR}_3)_2(\text{H})$ (**8**, $\text{R}_3 = (\text{OEt})_3$; **9**, $\text{R}_3 = \text{Me}(\text{OMe})_2$; **13**, $\text{R}_3 = (\text{OMe})_3$). Like in analogous iridium-based systems, the outcome of these reactions largely depends on the nature of substituents at the silicon atom. Synthesis of Rh(I) silyls inaccessible by this route, namely those with *alkyl* substituents at the silicon, L_nRhSiR_3 (**19**, $n = 3$, $\text{R}_3 = \text{PhMe}_2$; **22**, $n = 4$, $\text{R}_3 = \text{Me}_3$), was achieved utilizing nucleophilic attack of the corresponding silyllithiums at $[\text{L}_4\text{Rh}]\text{Cl}$. The solid-state structure of **19** was determined by X-ray crystallography. $\text{C}_{17}\text{H}_{38}\text{P}_3\text{SiRh}$, Fw = 466.38 monoclinic, $\text{C}2/m$, $a = 13.304(3)$ Å, $b = 13.814(2)$ Å, $c = 13.123(4)$ Å, $\beta = 110.66(3)$ deg, $V = 2257(1)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.373$ g cm⁻³, $\mu = 1.019$ mm⁻¹. A series of di(hydrido)silyls *fac*- $\text{L}_3\text{Rh}(\text{H})_2(\text{SiR}_3)$ (**10**, $\text{R}_3 = (\text{OEt})_3$; **15**, $\text{R}_3 = \text{PhMe}_2$; **16**, $\text{R}_3 = \text{Ph}_3$) was synthesized using oxidative additions of HSiR_3 to HRhL_4 (**3**). Complexes **10**, **15**, **16** are thermodynamically stable with respect to H–H and Si–H reductive-elimination reactions at ambient conditions. Complex **8** reductively eliminates $\text{HSi}(\text{OEt})_3$ reversibly at room temperature and complex **13** is capable upon heating of mediating dehydrogenative Si–Si coupling of $\text{HSi}(\text{OMe})_3$ and redistribution of $[(\text{MeO})_3\text{Si}]_2$. ^{103}Rh NMR data obtained for MeRhL_4 (**1**), HRhL_4 (**3**), $\text{L}_3\text{RhSiPhMe}_2$ (**19**), $\text{L}_3\text{RhSiPh}_3$ (**21**) and for the di(hydrido) silyls (**10**, **15**, **16**) allowed to qualitatively evaluate steric and electronic effects of methyl, silyl, and hydride ligands on the ^{103}Rh chemical shift. © 1998 Elsevier Science S.A.

Keywords: Complexes; Silyls; NMR spectroscopy

1. Introduction

The vast majority of mononuclear silyl complexes of rhodium described so far are those of Rh(III) [1–9]. There are a few examples of $\text{Cp}^*\text{Rh}(\text{V})$ silyls [10–15]. Silyl complexes of Rh(I) remain quite rare. In addition to $(\text{PMe}_3)_3\text{RhSiMe}_2\text{Ph}$, which we used in C–F activation reactions of polyfluorobenzenes [8] and which is described in detail here, the following complexes were reported: $\text{Rh}(\text{tripsi})\text{CO}$ and $\text{Rh}(\text{tripsi})\text{PPh}_3$, [4] $(\text{PMe}_3)_3\text{RhSiPh}_3$, [5] $(\text{dtbpm})\text{Rh}(\text{Si}(\text{OEt})_3)(\text{PMe}_3)$, [16]

and $(\text{PMe}_3)_3\text{RhSiMe}_2\text{SiMe}(\text{SiMe}_3)_2$. [17,18] Several reports dealing with catalytic and mechanistic aspects of rhodium-mediated transformations of organosilicon substrates are available [1,2,5,6,8,16–25].

We have been studying synthetic ways to, and reactivity of, silyl complexes of rhodium and iridium because of their possible involvement in useful catalytic reactions of organosilicon compounds. Their isolation and characterization may allow to carry out and study some of the postulated steps of these catalyses. In addition, silyl ligands, which are known for high σ -donicity and trans-influence, when bound to an electron-rich metal center may lead to novel chemistry, like the above mentioned catalytic C–F activation.

Earlier we have investigated competitive reductive eliminations from facial iridium(III) methyl-hydrido-silyl complexes and cyclometalation of the resulting

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iridium(I) silyl intermediates [26–28]. Here we report on synthetic approaches to, spectroscopic characterization and properties of, electron-rich rhodium(I) silyls. A number of related bis(silyl)hydrido- and di(hydrido)silyl-complexes of Rh(III) and their reductive-elimination reactions are described as well. We show in which aspects rhodium-based systems resemble those of iridium and in which these two systems differ from each other. Part of these results was communicated [8,29].

2. Results

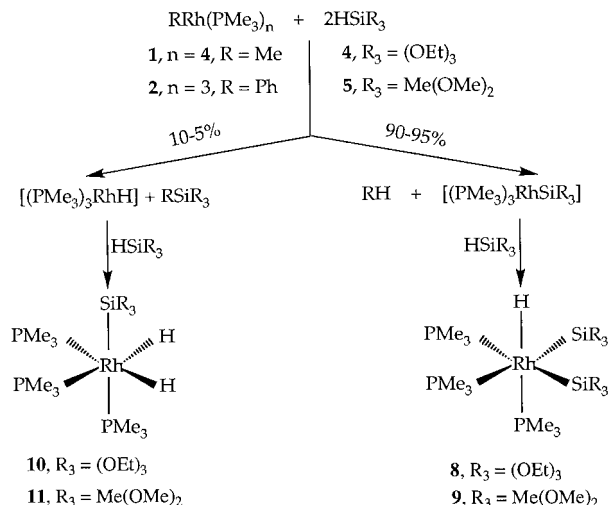
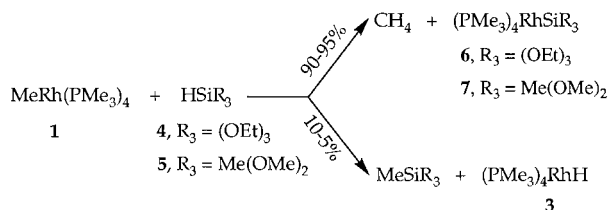
2.1. Reactions of $\text{MeRh}(\text{PMe}_3)_4$ and $\text{PhRh}(\text{PMe}_3)_3$ with silanes

Reaction of RRhL_n (**1**, $\text{R} = \text{Me}$, $n = 4$; **2**, $\text{R} = \text{Ph}$, $n = 3$; $\text{L} = \text{PMe}_3$) with hydrosilanes $\text{R}'_3\text{SiH}$ leads either to C–H or to C–Si coupling, or to both these processes.

2.1.1. Reactivity of alkoxy silanes. Formation of Rh(I) silyls and Rh(III) bis(silyl)hydrides

Rhodium(I) silyl complexes of the general formula L_4RhSiR_3 (**6**, $\text{R}_3 = (\text{OEt})_3$; **7**, $\text{R}_3 = \text{Me}(\text{OMe})_2$) are major products of the reactions between **1** and one equivalent of $\text{HSi}(\text{OEt})_3$ (**4**) or $\text{HSiMe}(\text{OMe})_2$ (**5**) (Scheme 1). In both cases there is some concurrent C–Si coupling leading to the formation of HRhL_4 (**3**), which is produced in ≈ 5 –10% yield at room temperature (or below). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **6** and **7** measured at 20°C are featureless, exhibiting (as does the spectrum of complex **1**) very broad signals in the region of $\delta -22$ to -24 ppm. However, ^1H NMR and low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR (**6**) data allow to unequivocally assign them as tetrakis(phosphine)-rhodium(I) silyls. As expected, **6** adopts at low temperature (-93°C) a trigonal bipyramidal structure, with the silyl group occupying an axial position.

If in the reactions between **1** and **4** or **5** two equivalents of the silanes are used, one equivalent of PMe_3 is liberated and smooth double additions take place to produce the bis(silyl)hydrides $\text{fac-L}_3\text{Rh}(\text{SiR}_3)_2(\text{H})$ (**8**, $\text{R}_3 = (\text{OEt})_3$; **9**, $\text{R}_3 = \text{Me}(\text{OMe})_2$) in 90–95% yield, the rest being corresponding di(hydrido)silyls fac-



$\text{L}_3\text{Rh}(\text{H})_2(\text{SiR}_3)$ (**10**, $\text{R}_3 = (\text{OEt})_3$; **11**, $\text{R}_3 = \text{Me}(\text{OMe})_2$) (Scheme 2).

Reactions of the phenyl complex **2** with silanes **4** and **5** do not lead to Rh(I) silyls. Instead, the bis(silyls) **8** or **9** are formed even when a 1:1 ratio of the reactants is used, half of **2** remaining unreacted (Scheme 2). The reactions are cleaner when carried out at lower temperatures. The analogous reaction between **2** and $\text{HSi}(\text{OMe})_3$ (**12**) is less selective and produces a 4:1 mixture of $\text{fac-L}_3\text{Rh}(\text{Si}(\text{OMe})_3)_2(\text{H})$ (**13**) and $\text{fac-L}_3\text{Rh}(\text{H})_2(\text{Si}(\text{OMe})_3)$ (**14**) even at -20°C .

Complexes **8**, **9**, **13** are assigned on the basis of their $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR data which are completely analogous. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit doublet-of-doublets and doublet-of-triplets patterns with small coupling constants $^1J_{\text{P-Rh}}$ (≈ 78 and ≈ 100 Hz) indicative of Rh(III). ^1H NMR spectra contain appropriately split and integrated signals due to hydrides and two silyl groups. The facial configuration follows from the aforementioned low values of $^1J_{\text{P-Rh}}$ of the doublet-of-doublets signals³ and from apparent inequivalence of the two sets of methoxy groups of **9** in both proton and carbon NMR spectra. It is further confirmed by the high value of $^2J_{\text{Si-P, trans}} = 183$ Hz observed in the ^{29}Si NMR spectrum of **9**. The dihydridosilyls **10**, **11**, **14** were identified by comparison of their (completely analogous) NMR spectra with those of independently prepared authentic samples of $\text{fac}-(\text{Me}_3\text{P})_3\text{Rh}(\text{H})_2(\text{SiR}_3)$ (**10**, $\text{R}_3 = (\text{OEt})_3$; **15**, $\text{R}_3 = \text{PhMe}_2$; **16**, $\text{R}_3 = \text{Ph}_3$; see Section 5 for details).

³ For PMe_3 complexes of Rh(III) that have meridional arrangement, $^1J_{\text{P-Rh}}$ of the signals due to mutually trans phosphines is expected to have a value of 93–105 Hz. See for example, Refs. [30–32].

2.1.2. Reactivity of alkylsilanes

HSiEt₃ (**17**) reacts with **1** in a benzene solution to produce almost exclusively CH₃SiEt₃ and HRhL₄ (**3**). Only traces of methane are formed. When the reactants are mixed in toluene-d₈ at –78°C and the course of the reaction is monitored by NMR during gradual warming to room temperature, no intermediate is observed.

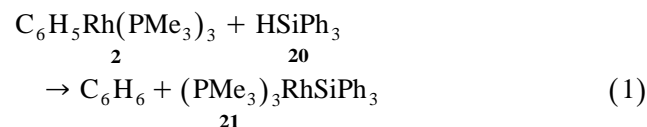
The analogous reaction between **2** and **17** in C₆D₆ leads to complicated mixtures in which the products of both C–H and C–Si coupling, namely C₆H₆ and C₆H₅SiEt₃, are present. Organometallic complexes that could be assigned include HRhL₄, L₃RhSiEt₃, L₃Rh(H)₂(SiEt₃) (the latter two tentatively). At early stages of the 1:1 reaction between **2** and **17**, the analysis is still possible. After 3 h, when about 2/3 of the initial amounts of PhRhL₃ and HSiEt₃ are still present according to ¹H NMR, the L₃RhSiEt₃/C₆H₅SiEt₃ ratio is about 5.6. After 1 day it decreases to approximately 1.5, apparently because of the instability of L₃RhSiEt₃ under these conditions. Unsaturated species such as HRhL₃ and L₃RhSiEt₃, that are initially formed, react further in the presence of free PMe₃, HSiEt₃ and C₆D₆ to form **3** and L₃Rh(H)₂(SiEt₃) in a mixture of fluxional and/or partially deuterated complexes.

Reaction of complex **2** with HSiMe₂Ph (**18**) is also complicated. After 3 h at room temperature according to NMR analysis all silane **18** (about 20% excess with respect to the amount of **2** taken) is consumed. The resulting mixture contains unreacted **2** (≈ 25%), **3** (≈ 7%), L₃Rh(H)₂(SiPhMe₂) (**15**, ≈ 28%), which was identified by NMR and also synthesized independently, and a complex that exhibits in ³¹P{¹H} NMR a doublet δ –17.2 with ¹J_{P–Rh} = 146 Hz (**19**, ≈ 40%, see Sec-

tion 2.1.3). In the ¹H NMR spectrum signals due to C₆H₆ and Me₂SiPh₂ are observed.

2.1.3. Reactivity of HSiPh₃ (**20**)

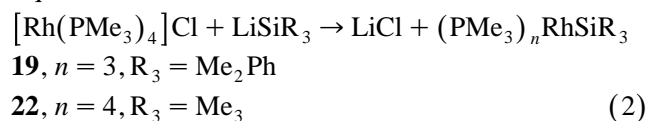
The reaction between **1** and **20**, as reported by Thorn and Harlow, [5] leads to the formation of L₃RhSiPh₃ (**21**) accompanied by the liberation of methane and trimethylphosphine. Similarly, the analogous reaction of complex **2** results in quantitative production of **21** and benzene (Eq. (1)).



Complex **21** was identified by its ¹H NMR spectral data. Its room temperature ³¹P{¹H} NMR spectrum exhibits a very broad doublet at δ –17.6 ppm with apparent ¹J_{P–Rh} ≈ 142 Hz indicative of Rh(I).

2.2. Synthesis of Rh(I) silyls using silyllithium reagents

The cationic complex [RhL₄]Cl reacts with LiSiR₃ (R₃ = PhMe₂; Me₃) to form the Rh(I) silyls L₃RhSiMe₂Ph (**19**) and L₄RhSiMe₃ (**22**) as shown in Eq. (2).



Isolation of **19** and especially **22** is complicated by formation of the undesired HRhL₄ (**3**). Complex **19** can be purified (albeit with significant losses) by recrystallization from cold pentane. Purification of **22** is difficult because of similar solubility to that of HRhL₄, both

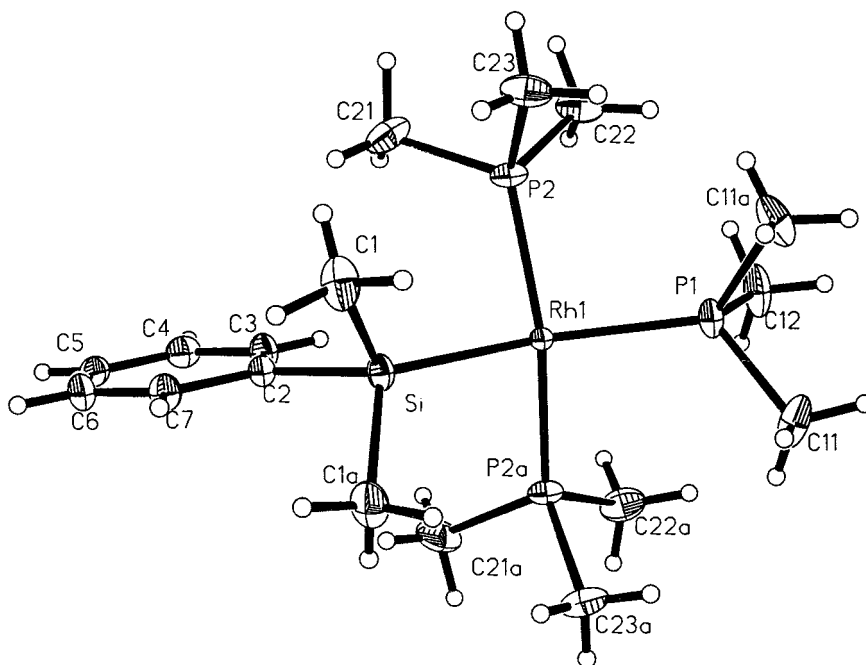


Fig. 1. Perspective view of a molecule of **19**. Hydrogen atoms are omitted for clarity.

being highly soluble in common organic solvents. Identification of **19** and **22** is based on their NMR data and on X-ray structural analysis (**19**). At room temperature both compounds are fluxional on the ^{31}P NMR time scale. Complex **19** exhibits in $^{31}\text{P}\{^1\text{H}\}$ NMR the aforementioned doublet at $\delta -17.2$ ppm with $^1J_{\text{P-Rh}} = 146$ Hz. Upon cooling a toluene solution of **19** to -80°C , it transforms into two broad signals in 1:2 ratio at $\delta -26$ and -12 ppm with apparent $^1J_{\text{P-Rh}} \approx 115$ and 149 Hz respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **22**, which is virtually non-observable at room temperature, converts at -55°C into well-resolved doublet-of-doublets and doublet-of-quartets integrated as 3:1 at $\delta -28.2$ and -15.4 ppm with $^1J_{\text{P-Rh}} = 158$ and 91 Hz. ^1H NMR spectra of **19** and **22** contain signals of appropriate intensity due to PMe_3 and SiR_3 groups in accordance with the proposed formulae.

2.3. X-ray structure of **19**

A ruby-red single crystal of **19** was grown from its concentrated pentane solution at -20°C . A perspective view of a molecule of **19** is presented in Fig. 1 and

Table 1
Crystallographic parameters for the structure of **19**

Empirical formula	$\text{C}_{17}\text{H}_{38}\text{P}_3\text{SiRh}$
Formula mass, amu	466.38
Color and habit	Red prisms
Crystal size, mm	$0.6 \times 0.6 \times 0.6$
Crystal system	monoclinic
Space group	$\text{C}2/m$ (No. 12)
a , Å	13.304 (3)
b , Å	13.814 (2)
c , Å	13.123 (4)
β , deg	110.66 (3)
V , Å ³	2257 (1)
Z	4
Density (calcd), g cm^{-3}	1.373
μ , mm^{-1}	1.019
Diffractionmeter	CAD 4 Enraf–Nonius
Radiation (wavelength, Å)	$\text{Mo K}\alpha$ ($\lambda = 0.71073$)
Monochromator	Graphite
Temperature, K	110
Mode	ω
θ_{max} , deg	26.97
Scan speed, deg min^{-1}	1
Scan width, deg	0.9
Collection range	$-16 \leq h \leq 16$ $-17 \leq k \leq 0$ $-16 \leq l \leq 16$
No. of reflections	
Collected	5129
Independent	2558
$R(\text{int})$	0.0422
Data/restraints/parameters	2553/0/202
Solution	Patterson
Refinement	Full-matrix least-squares on F^2
Final R indices ($I > 2\sigma(I)$)	
$R1$	0.0312
$wR2$	0.0777

Table 2
Selected interatomic bond lengths (Å) in the molecule of **19**

Atoms	Bond length	Atoms	Bond length
Rh(1)–P(1)	2.3094 (9)	P(2)–C(21)	1.827 (3)
Rh(1)–P(2)	2.2708 (6)	P(2)–C(22)	1.833 (3)
Rh(1)–P(2a)	2.2708 (6)	P(2)–C(23)	1.832 (3)
Rh(1)–Si	2.3804 (10)	Si–C(1)	1.903 (3)
P(1)–C(11)	1.831 (3)	Si–C(1a)	1.903 (3)
P(1)–C(11a)	1.831 (3)	Si–C(2)	1.917 (3)
P(1)–C(12)	1.841 (4)		

selected bond distances and angles are presented in Tables 1 and 2. Complex **19** is among the few Rh(I) silyls characterized by X-ray crystallography. Like its closest analog **21**, complex **19** adopts a distorted square planar coordination geometry. However, the distortion of **19** towards tetrahedral structure is less expressed: P(2a)–Rh(1)–P(2) and P(1)–Rh(1)–Si angles in a molecule of **19** are 159.98(3) and 156.43(3) deg compared to 148.21(3) and 143.24(3) reported for **21** [5]. In accordance with the strong trans-influence of silyl ligands the bond P(1)_{trans} to Si–Rh(1) is about 0.04 Å longer than P(2)_{trans} to P–Rh(1). The Rh(1)–Si bond length of 2.3804(10) Å is substantially (by 0.063 Å) longer than that in triphenylsilyl analog **21**. Since this is contrary to steric requirements of the silyl groups in question, electronic factors are likely to be responsible for this. However, the higher deviation of P_{trans} to Si–Rh–Si angle from linearity in **21** may also play a role.

2.4. Reactivity of the bis(silyl)hydrides **8** and **13**

fac- $\text{L}_3\text{Rh}(\text{Si}(\text{OEt})_3)_2(\text{H})$ (**8**) reacts in a benzene solution at room temperature with CO to form mixtures of two carbonyl-containing complexes assigned as *mer*- $\text{L}_3\text{Rh}(\text{CO})(\text{Si}(\text{OEt})_3)$ and $\text{L}_2\text{Rh}(\text{CO})_2(\text{Si}(\text{OEt})_3)$. Depending on the amount of the added CO, mixtures with different ratios of the products are formed that allows to assign the NMR and IR spectra obtained (see Section 5). Both complexes contain only one triethoxysilyl group per rhodium.

Reaction of **8** with 1.3 equivalents of CDCl_3 in benzene at room temperature leads to the formation of *mer*- $\text{L}_3\text{Rh}(\text{Cl})(\text{CDCl}_2)(\text{Si}(\text{OEt})_3)$ in 80% yield over 3 h, indicating (like the reaction with CO above) that **8** is capable of easy loss of triethoxysilane in solution. However, no reductive elimination of hexaethoxydisilane from **8** was observed in any of these experiments.

To test whether Si–Si bond formation can be operative in these systems, we carried out several experiments on thermolysis of *fac*- $\text{L}_3\text{Rh}(\text{Si}(\text{OMe})_3)_2(\text{H})$ (**13**). Heating a benzene solution of **13** at 55°C for 3 days results in its conversion to *fac*- $\text{L}_3\text{Rh}(\text{H})_2(\text{Si}(\text{OMe})_3)$ (**14**) as a major product. Of the organosilicon compounds formed, $(\text{MeO})_3\text{Si-Si}(\text{OMe})_3$ (2% yield) and $(\text{MeO})_4\text{Si}$ (10% yield) were identified by ^1H NMR,

Table 3
 ^{103}Rh NMR chemical shifts (ppm) of $(\text{Me}_3\text{P})_n\text{RhR}$ and $(\text{Me}_3\text{P})_3\text{Rh}(\text{H})_2\text{SiR}_3$ complexes

Compound	$\delta(^{103}\text{Rh})^a$
$(\text{PMe}_3)_3\text{RhSiMe}_2\text{Ph}$, 19	–802
$(\text{PMe}_3)_3\text{RhSiPh}_3$, 21	–735
$(\text{PMe}_3)_3\text{Rh}(\text{H})_2(\text{Si}(\text{OEt})_3)$, 10	–1222
$(\text{PMe}_3)_3\text{Rh}(\text{H})_2(\text{SiMe}_2\text{Ph})$, 15	–1108
$(\text{PMe}_3)_3\text{Rh}(\text{H})_2(\text{SiPh}_3)$, 16	–1091
$(\text{PMe}_3)_4\text{RhH}$, 3	–735
$(\text{PMe}_3)_4\text{RhMe}$, 1	–490 ^b

^aIn ppm towards high frequency, scaled to $\Xi = 3.16$ MHz, $T = 293$ K unless otherwise specified; ^bat 223 K; $\delta(\text{Rh}) = -482$ ppm at 233 K; inaccurate extrapolation gives $\delta(\text{Rh}) = -434$ ppm at 293 K.

²⁹Si-INEPT NMR and GC-MS. Similar thermolyses carried out in the presence of an excess of $\text{HSi}(\text{OMe})_3$ result in higher yields of these products. Heating phosphine-deficient bis(trimethoxysilyl) complexes of rhodium (obtained by partial oxidation of the PMe_3 groups of **13**) allows to get in the presence of 100 equivalents of $\text{HSi}(\text{OMe})_3$ 97% and 250% yields of $(\text{MeO})_3\text{Si-Si}(\text{OMe})_3$ and $(\text{MeO})_4\text{Si}$ respectively (see Section 5 for details).

2.5. Rh NMR chemical shifts data

^{103}Rh NMR chemical shifts obtained for 4-coordinate Rh(I) silyls **19** and **21**, 6-coordinate Rh(III) di(hydrido)silyls **10**, **15**, **16** and 5-coordinate Rh(I) hydride and methyl complexes **3** and **1** are compiled in Table 4.

3. Discussion

3.1. Rhodium(I) silyls

As described, Rh(I) silyl complexes with alkoxy, alkyl, aryl and mixed substituents at silicon can be formed in solution and some of them can be isolated. The synthetic pathways involve either reactions of methyl or phenyl rhodium complexes with the corresponding hydrosilanes (A), or nucleophilic attack of silyl anions at the cationic rhodium center (B). Both pathways have their limitations: route B is limited mainly by the accessibility of silyllithium reagents, while route A is applicable for alkoxy- and arylsilanes, that is, for those bearing electronegative substituents at the silicon, and not to trialkylsilanes.

Both the 16-e L_3RhSiR_3 and the 18-e L_4RhSiR_3 complexes were found to be non-rigid at room temperature on the NMR time scale, giving rise to broad signals in $^{31}\text{P}\{^1\text{H}\}$ NMR. Whereas fluxionality is quite common for 5-coordinate monovalent d^8 complexes, it is rare for their 4-coordinate counterparts. The well-known strong

trans-influence of silyl ligands [27,33,34] may facilitate phosphine dissociation, resulting in intermolecular exchange of the phosphine ligands in the 16-e complexes.

It is worthy of note that for sterically non-demanding silyl groups, such as $(\text{EtO})_3\text{Si}$, $(\text{Me})(\text{OMe})_2\text{Si}$ and Me_3Si , saturated 5-coordinate L_4RhSiR_3 complexes are formed, while with the bulkier Ph_3Si and PhMe_2Si ligands 4-coordinate L_3RhSiR_3 are produced. Another important observation is the fact that in the reaction between PhRhL_3 , **2**, with the small reactive alkoxy-silanes $\text{HSi}(\text{OEt})_3$ or $\text{HSiMe}(\text{OMe})_2$, the initially formed transient L_3RhSiR_3 species are substantially more reactive towards Si–H oxidative addition than the starting phenylrhodium complex. This results in the fast double addition and the formation of bis(silyls) *fac*- $\text{L}_3\text{Rh}(\text{H})(\text{SiR}_3)_2$ **8** and **9** even when a 1:1 ratio of the reactants is used. For comparison, when one starts with the saturated methyl complex **1**, the intermediate L_3RhSiR_3 species are captured with the extra phosphine present, thus allowing to isolate the saturated L_4RhSiR_3 complexes **6** and **7**.

As expected, all the Rh(I) silyls are highly air and moisture sensitive. Upon exposure to air these compounds are quickly oxidized and/or hydrolyzed.⁴

3.2. Rhodium(III) bis(silyl)hydrides and di(hydrido)silyls

As expected, Rh(III) complexes are readily formed in these electron-rich systems. Starting with sterically non-demanding reactive alkoxy-silanes one can easily synthesize bis(silyl) complexes $\text{L}_3\text{Rh}(\text{H})(\text{SiR}_3)_2$ **8**, **9**, **13** and di(hydrido)silyls $\text{L}_3\text{Rh}(\text{H})_2(\text{SiR}_3)$ **10**, **11**, **14**. The latter species can be obtained using bulkier arylsilanes as well (**15**, **16**). All of these complexes have a facial arrangement of ligands with the strong trans-directing hydrides and silyls in mutually *cis* positions. Formation of the di(hydrido)silyls of rhodium(III) from HRhL_4 (**3**) and HSiR_3 is a facile straightforward reaction, which takes place at room temperature with quantitative yields indicating that under these conditions such species are thermodynamically quite stable with respect to Si–H or H–H reductive eliminations. A few Rh(III) bis(silyl)hydrides are known, [7,16] and one of them, namely *fac*- $(\text{PMe}_3)_3\text{Rh}(\eta^2\text{-SiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{H})$, was crystallographically characterized [7]. An iridium analog *fac*- $(\text{PMe}_3)_3\text{Ir}(\text{H})(\text{Si}(\text{OEt})_3)_2$ was observed in solution [27]. However, no reactivity of these com-

⁴In general, these reactions result in decomposition to mixtures due to easy oxidation of PMe_3 and Rh(I) center and due to high affinity of silicon for oxygen. However, upon careful hydrolysis of **6** in the absence of oxygen, the silyl ligand is lost and the cationic *cis*- $[\text{L}_4\text{RhH}_2]^+$ is produced cleanly. It was identified by its ^{31}P NMR, see Ref. [35].

plexes, e.g., Si–Si bond formation, was reported.^{5, 6} Our findings demonstrate that H–Si reductive elimination from **8** is a facile reversible process that takes place at room temperature. This is exemplified by trapping of the transient $[L_3RhSi(OEt)_3]$ species with CO (as Rh(I) silyls) and with $CDCl_3$ (in a form of an oxidative-addition product). Reductive elimination of Si–Si bonds^{7, 8} from **13** is likely to be thermodynamically less favorable [45] than that of Si–H bonds. Nevertheless, using an excess of $HSi(OMe)_3$, reductive elimination of $(MeO)_3SiSi(OMe)_3$ can be induced, albeit the outcome is complicated by the formation of $(MeO)_4Si$ by redistribution processes.⁹ The Si–Si reductive elimination becomes more pronounced under phosphine-deficient conditions.¹⁰

3.3. Comparison of Rh and Ir systems

In contrast to methyl- and phenyliridium, [26,27] both methyl- and phenylrhodium PMe_3 complexes **1** and **2**, when reacted with hydrosilanes, do not lead to stable primary oxidative-addition adducts. Moreover, even monitoring the reaction between **1** and $HSiEt_3$ at low-temperature did not allow to spectroscopically detect the product of Si–H oxidative addition. This is not unexpected, since rhodium(III) complexes have a higher propensity to reductively eliminate C–H [46] bonds than do their isostructural iridium(III) analogs. Significantly, C–Si bond formation at the rhodium centers, like in the iridium systems, is substantially more expressed for alkylsilyl ligands. Thus, the selectivity of the reaction between $MeRhL_4$ and $HSiEt_3$ is completely shifted to C–Si coupling, contrary to that of alkoxy- and phenylsilylanes for which C–H bond formation prevails. As discussed previously [26,27] the reasons are both thermodynamic, i.e. strengthening of M–Si bonds for silyls that bear electronegative substituents at the silicon, and kinetic, i.e. low directionality of the silicon-centered orbitals that are involved in M–Si bonding. The described phenomenon, being common for iridium and rhodium, has important mechanistic and synthetic impli-

cations. First, it implies that the product-forming steps and even the mechanisms of catalytic reactions involving organosilicon compounds may depend on the nature of the substrate used. Second, it renders alkylsilylrhodium(I) complexes inaccessible via the reactions of methyl- or arylrhodium complexes with alkylsilylanes. Importantly, however, we have shown here that this approach allows to generate rhodium(I) alkoxy- and phenylsilyls, such as **6**, **7**, **19** and **21**, which are isolable, but are highly unstable to air and moisture. It should be noted that their electron-rich iridium analogs are not available because of facile cyclometalation reactions [17,18,26–28,47,48]. Similarly, while nucleophilic attack of $PhMe_2SiLi$ and Me_3SiLi at $[RhL_4]Cl$ leads to the formation of Rh(I) dimethylphenyl- and trimethylsilyl complexes **19** and **22**, respectively, the reaction of $[IrL_4]Cl$ with $PhMe_2SiLi$ leads to the orthometalated Ir(III) complex [28]. We have not observed formation of rhodasilacycles in these systems, which is, again, in line with the relatively lower propensity of rhodium to undergo oxidative-addition reactions.

3.4. Rhodium-103 NMR data

The nuclear shielding of transition metal nuclei like ¹⁰³Rh is mainly determined by the paramagnetic contribution σ^p to the overall shielding, which may according to the Ramsey Eq. (3) be described by changes in the average excitation energy, ΔE_{av} , the d-orbital radius, $\langle r_d^{-3} \rangle$, and the angular imbalance of charge, ΣQ_N .

$$\sigma = \sigma^d - \sigma^p = A - c \cdot (\Delta E_{av})^{-1} \cdot \langle r_d^{-3} \rangle \cdot \Sigma Q_N \quad (3)$$

The ¹⁰³Rh NMR shifts for **1**, **3**, **10**, **15**, **16**, **19**, **21** (see Table 4) fall within the range expected for Rh(I) and Rh(III) compounds containing ligands of intermediate to strong ligand field strength for the respective coordination geometries [49]. As the ligand field splitting term ΔE_{av} is large for the 4- and 5- as well as for the currently described 6-coordinate compounds,¹¹ small changes in their structure will be clearly reflected in the Rh chemical shift. The ΔE_{av} term will in fact govern the magnitude of σ^p and hence it may for qualitative purposes be invoked for comparison within this series.

Comparing the shifts for **19** and **21**, the increase of $\delta(Rh)$ with increasing bulk of the SiR_3 group is readily

⁵ Mitchell et al. reported NMR evidence for a degenerate reversible Si–Si reductive-elimination process from two analogous unsaturated Rh(III) silyl complexes. See Ref. [17].

⁶ Hofmann et al. prepared a $(EtO)_3Si$ analog of **6** and **7** with one PMe_3 and a chelating $(^tBu_2P)_2CH_2$ ligand (dtbpm). According to their data no Si–Si coupling could be induced from this complex. See Ref. [16].

⁷ Examples of stoichiometric Si–Si reductive elimination from isolated complexes are rare. See Refs. [36–38].⁵

⁸ For dehydrogenative coupling of hydrosilanes, catalysed by platinum metals, see Refs. [39–44].

⁹ Facilitation of C–H reductive elimination by loss of phosphine ligands is known. See Ref. [46].

¹⁰ We did not identify other redistribution products of these reactions.

¹¹ As discussed by Mann, [49] although most 6-coordinate compounds have much higher shifts (due the presence of small, weak-field donor ligands which leads to smaller ΔE) compared to square planar ones, the advent of compounds having larger, strong-field ligands has extended the range of shifts of 6-coordinate compounds to very low values indeed.

explained by the larger deviation from the square planar geometry for **21**, as inferred from the P–Rh–P and P–Rh–Si angles for **19** and **21** (see above). [5] This structural feature is accompanied by a diminished overlap between the $d_{x^2-y^2}$ orbital and ligand orbitals, causing a smaller ligand field splitting and hence larger $(\Delta E_{av})^{-1}$ term, resulting in the higher $\delta(\text{Rh})$ for **21**.

The compounds **10**, **15**, **16** have rather low ^{103}Rh chemical shifts for 6-coordinate compounds, which is readily accounted for by the presence of six strong-field ligands. Their shifts are at higher frequencies compared to the related $\text{HRh}(\text{Cp}^*)(\text{SiR}_3)_2\text{L}$ and $\text{H}_2\text{Rh}(\text{Cp}^*)(\text{SiR}_3)_2$, [14] in agreement with the smaller ligand field splitting by PMe_3 ligands in **10**, **15**, **16** compared to Cp^* in $\text{H}_m\text{Rh}(\text{Cp}^*)(\text{SiR}_3)_n$. Within the series **10**, **15**, **16** a steady increase in $\delta(\text{Rh})$ is observed, reflecting the increase in relative steric bulk of the SiR_3 group. A similar argumentation as in the case of **19** versus **21**, i.e. an increasing perturbation of the quasi-octahedral environment when going from the $\text{Si}(\text{OEt})_3$ to SiMe_2Ph and SiPh_3 analogue, pertains in this case. We note a similar trend in the ^{103}Rh NMR data for compounds $\text{HRh}(\text{Cp}^*)(\text{SiR}_3)_2\text{L}$ ($\text{L} = \text{CO}, \eta^2\text{-C}_2\text{H}_4$) obtained by Ruiz et al. [14] which was not discussed by these authors. The notion of increasing deviation from octahedral geometry in the series **10**, **15**, **16** is, albeit circumstantially, corroborated by X-ray data on a series of similar iridium compounds [50]. The trend of diminishing $\text{P}_{\text{trans-Si}}\text{-Rh-Si}$ angles (and other relevant angles) in $(\text{PMe}_3)_3\text{IrH}_2(\text{SiR}_3)$ reflects a more perturbed quasi-octahedral geometry in case of the more bulky SiR_3 group.¹²

For 5-coordinate compounds the ligand field splitting will be slightly smaller than for 4-coordinate square planar systems. [51] The energy of the $d_{x^2-y^2}$ orbital and hence ΔE are mainly determined by the ligands in the basal plane of 5-coordinate compounds, [52] but the energy of the d_z^2 orbital will be influenced by the apical ligand. It is therefore expected that the ^{103}Rh shifts for **3** and **1** will be close to but higher than those of **19** and **21**, as is indeed observed. The low frequency shift of **3** relative to **1** is in qualitative agreement with the higher σ -donor capacity of H compared to CH_3 .

4. Conclusions

We have reported two synthetic ways to Rh(I) silyl complexes, namely: (i) reactions of tertiary silanes with MeRhL_4 or PhRhL_3 and (ii) nucleophilic attack of silyl anions at $[\text{RhL}_4]\text{Cl}$. We have described the scope and limitations of these two strategies, demonstrated that

both 4-coordinate 16-e and 5-coordinate 18-e Rh(I) silyls can be prepared, and determined the X-ray structure for one of them, namely $\text{L}_3\text{RhSiMe}_2\text{Ph}$. We have also described syntheses of a series of rhodium(III) bis(silyl)hydrides and di(hydrido)silyls. Whereas the latter are thermodynamically stable at room temperature with respect to H–H and H–Si reductive-elimination reactions, the former are prone to Si–H and on moderate heating to Si–Si reductive eliminations.

Comparison with related iridium silyl systems demonstrated that, along with the expected differences in reactivities of second and third row metals, there exists an important common factor of major importance, that is, the effect of the substituents at the silicon atom on reductive-elimination reactivity.

^{103}Rh NMR spectra of selected Rh(I)- and Rh(III)-silyl compounds have been measured and a qualitative understanding of the ^{103}Rh chemical shifts as a function of their structural features has been established.

5. Experimental

5.1. General

The compounds described herein are air and moisture sensitive and were handled as reported in detail elsewhere [27]. HSiPh_3 , HSiPhMe_2 , and $\text{HSi}(\text{OEt})_3$ were purchased from Aldrich; HSiEt_3 was purchased from Petrarch System $\text{HSiMe}(\text{OMe})_2$ was synthesized from HSiMeCl_2 and $\text{HC}(\text{OMe})_3$ [53]. Liquid silanes were degassed by purging with dry N_2 before use. $\text{MeRh}(\text{PMe}_3)_4$, [54,55] $\text{PhRh}(\text{PMe}_3)_4$, [56] $\text{HRh}(\text{PMe}_3)_4$, [54] $[(\text{PMe}_3)_4\text{Rh}]\text{Cl}$, [35] LiSiMe_2Ph , [57,58] and $\text{Hg}(\text{SiMe}_3)_2$ [59] were synthesized according to published procedures. ^{31}P , ^1H , ^{13}C NMR spectra were measured in C_6D_6 as a solvent unless otherwise specified and were referenced as described elsewhere. [27] Variable-temperature NMR spectra obtained in toluene- d_8 were referenced to external 85% H_3PO_4 (0.0 ppm, $^{31}\text{P}\{^1\text{H}\}$ NMR) and to the residual signals of $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ (2.10 ppm, ^1H NMR). ^{29}Si NMR spectra were recorded using an inverse $^1\text{H}\text{-}^{29}\text{Si}$ method and were referenced to the external Me_3SiCl at $\delta + 29.9$ ppm. All NMR spectra except for those of the ^{103}Rh nucleus (see Section 5.2) were obtained using Bruker AMX400 spectrometer.

5.2. Rh NMR measurements

The instrumentation and procedures used to obtain inverse two-dimensional $^{31}\text{P}\{^1\text{H}\}\text{-}^{103}\text{Rh}$ [60,61] and $^1\text{H}\text{-}^{103}\text{Rh}$ NMR [62,63] spectra were described in detail elsewhere. [61,63] The spectral resolution in the ^{103}Rh domain was better than 3 Hz (1 ppm). All measurements, except that of $\text{MeRh}(\text{PMe}_3)_4$ (**1**), were carried

¹² In $(\text{PMe}_3)_3\text{IrH}_2(\text{SiR}_3)$ the $\text{P}_{\text{trans-Si}}\text{-Rh-Si} = 157.3(1)^\circ$ (average) for SiHPh_2 , $146.4(1)^\circ$ for SiPh_3 and $141.8(1)^\circ$ for SiClBu_2 .

out at 293 K in C_6D_6 . The data for **1** were obtained at two temperatures (223 and 233 K) in toluene- d_8 and were extrapolated to 293 K. Chemical shifts are reported relative to $\Xi = 3.16$ MHz. Signals at higher frequencies are taken as positive.

5.3. $(Me_3P)_4RhSi(OEt)_3$ (**10**)

To a solution of 21 mg (0.05 mmol) of **1** in 1 ml of C_6D_6 was added by a microsyringe 8 mg (0.049 mmol) of $HSi(OEt)_3$ (**4**). NMR analysis after 2 h showed formation of **6** in $\approx 92\%$ yield, the rest being $HRh(PMe_3)_4$ (**3**).

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -23.4 very broad signal with a shoulder at -22.8. $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, $-93^\circ C$): δ -25.9 dd ($^1J_{P-Rh} = 151.9$ Hz, $^2J_{P-P} = 50.7$ Hz), 3P_{eq}; -11.7 dq ($^1J_{P-Rh} \approx 101$ Hz, $^2J_{P-P} \approx 51$ Hz), 1P_{ax} *trans* to Si. 1H NMR (C_6D_6): δ 1.31 t ($^3J_{H-H} = 6.9$ Hz), 9H, $Si(OCH_2CH_3)_3$; 1.37 br s, 36H, 4P(CH_3)₃; 4.03 q ($^3J_{H-H} = 6.9$ Hz), 6H, $Si(OC_2H_5)_3$.

5.4. $(Me_3P)_4RhSiMe(OMe)_2$ (**7**)

A solution of 21 mg (0.05 mmol) of **1** in 4 ml of toluene was cooled to $-20^\circ C$ in a drybox freezer and to it was added in four portions over 2 h a similarly precooled solution of 1.05 equivalents of $HSiMe(OMe)_2$ (**5**) in 1 ml of toluene. After the addition was complete, the reaction mixture was allowed to warm up to room temperature and was left overnight. Then the solvent was removed under vacuum and the oily residue was dissolved in C_6D_6 . The $^{31}P\{^1H\}$ NMR analysis indicated the presence in the solution of $\approx 75\%$ of **7**, $\approx 17.5\%$ of $HRh(PMe_3)_4$, and $\approx 7.5\%$ of the double addition product **9**.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -24 very br. 1H NMR (C_6D_6): δ 0.61 s, 3H, $SiCH_3$; 1.30 br s, 36H 4P(CH_3)₃; 3.62 s, 6H, $Si(OC_2H_5)_2$.

5.5. $Fac-(Me_3P)_3Rh(Si(OEt)_3)_2(H)$ (**8**)

This complex was prepared by adding two equivalents of **4** to 1 ml of a benzene solution of **1** (21 mg, 0.05 mmol) at room temperature over 15 min. **8** was isolated after removal of the volatile components of the reaction mixture as a brownish oil in $\approx 95\%$ purity, di(hydrido)silyl **10** (see Section 5.8) being the side product. Alternatively, **8** can be prepared from **2** and two equivalents of **4** in toluene at $-20^\circ C$ (see the procedure for **13** in Section 5.7). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -26.0 dd ($^1J_{P-Rh} = 77.7$ Hz, $^2J_{P-P} = 29.3$ Hz), 2P *trans* to Si; -19.4 dt ($^1J_{P-Rh} = 99.3$ Hz, $^2J_{P-P} = 29.3$ Hz), 1P *trans* to H. 1H NMR (C_6D_6): δ -10.76 d of pseudo q ($^2J_{H-P, trans} = 124.4$ Hz, $J_q = 18.5$ Hz), 1H, Rh-H; 1.29 2nd order symm. 3-line m (outer lines' separation $\Delta = 6.2$ Hz), 18H, 2P(CH_3)₃

trans to Si; 1.44 d ($^2J_{H-P} = 7.8$ Hz), 9H, P(CH_3)₃ *trans* to H; 1.36 t ($^3J_{H-H} = 7.0$ Hz), 18H, 2Si(OCH_2CH_3)₃; 4.10 symm. m ($^3J_{H-H} = 7.0$ Hz), 12H, 2Si(OC_2H_5)₃.

5.6. $Fac-(Me_3P)_3Rh(SiMe(OMe)_2)_2(H)$ (**9**)

This complex was prepared from **1** or **2** analogously to **8** using **5** instead of **4**. As in the case of **8**, complex **9** is produced contaminated with the corresponding di(hydrido)silyl **11** ($\approx 10\%$).

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -26.7 dd ($^1J_{P-Rh} = 77.7$ Hz, $^2J_{P-P} = 29.0$ Hz), 2P *trans* to Si; -19.4 dt ($^1J_{P-Rh} = 103.0$ Hz, $^2J_{P-P} = 29.0$ Hz), 1P *trans* to H. 1H NMR (C_6D_6): δ -10.63 d of pseudo q ($^2J_{H-P, trans} = 122.0$ Hz, $J_q \approx 17$ Hz), 1H, Rh-H; 0.68 s, 6H 2Si(CH_3)₃; 1.21 2nd order symm. 3-line m (outer lines' separation $\Delta = 6.0$ Hz), 18H, 2P(CH_3)₃ *trans* to Si; 1.28 d ($^2J_{H-P} = 7.4$ Hz), 9H, P(CH_3)₃ *trans* to H; 3.57 s and 3.59 s, 6H each, 2Si(OC_2H_5)₂. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 7.34 app tdd ($J_t = 9.8$ Hz, $J_{d1} = 4.2$ Hz, $J_{d2} = 1.9$ Hz), 2Si(CH_3); 24.11 dtd ($^1J_{C-P} = 21.6$ Hz, $^3J_{C-P, cis} = 6.4$ Hz, $^2J_{C-Rh} \approx 1.3$ Hz), P(CH_3)₃ *trans* to H; 24.94 m, 2P(CH_3)₃ *trans* to Si; 50.10 br s and 50.39 br s, 2Si(OCH_3)₂. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 36.8 dm ($^2J_{Si-P, trans} = 183$ Hz).

5.7. $Fac-(Me_3P)_3Rh(Si(OMe)_3)_2(H)$ (**13**) and $fac-(Me_3P)_3Rh(H)_2(Si(OMe)_3)$ (**14**)

61 mg (0.15 mmol) of **2** and 30 mg (0.30 mmol) of $HSi(OMe)_3$ (**12**) were each dissolved in 2 ml of toluene, cooled to $-20^\circ C$ in a drybox freezer and combined. After 24 h at $-20^\circ C$ the reaction mixture was allowed to warm to room temperature and all volatile components were removed under vacuum. The yellow oily residue was dissolved in C_6D_6 . The NMR analysis indicated the presence of 80% of **13**, the rest being **14**.

5.7.1. Characterization of **13**

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -26.1 dd ($^1J_{P-Rh} = 78.3$ Hz, $^2J_{P-P} = 29.8$ Hz), 2P *trans* to Si; -18.8 dt ($^1J_{P-Rh} = 99.0$ Hz, $^2J_{P-P} = 29.8$ Hz), 1P *trans* to H. 1H NMR (C_6D_6): δ -10.79 d of pseudo q ($^2J_{H-P, trans} = 122.0$ Hz, $J_q = 16.0$ Hz), 1H, Rh-H; 1.23 2nd order symm. 3-line m (outer lines' separation $\Delta = 6.4$ Hz), 18H, 2P(CH_3)₃ *trans* to Si; 1.38 d ($^2J_{H-P} = 7.9$ Hz), 9H, P(CH_3)₃ *trans* to H; 3.76 s, 18H, 2Si(OC_2H_5)₃.

5.7.2. Characterization of **14**

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -24.6 dt ($^1J_{P-Rh} = 85.6$ Hz, $^2J_{P-P} = 26.8$ Hz), 1P *trans* to Si; -14.0 dd ($^1J_{P-Rh} = 97.5$ Hz, $^2J_{P-P} = 26.8$ Hz), 2P *trans* to H. 1H NMR (C_6D_6): δ -10.51 d of pseudo t ($^2J_{H-P, trans} = 120.0$ Hz, $J_t = 20.0$ Hz), 2H, Rh-H; 1.09 d ($^2J_{H-P} = 6.1$ Hz), 9H, P(CH_3)₃ *trans* to Si; 1.25 d ($^2J_{H-P} = 7.0$ Hz), 18H, 2P(CH_3)₃ *trans* to H; 3.82 s, 6H, Si(OC_2H_5)₃.

5.8. *Fac*-(Me_3P)₃Rh(H)₂(Si(OEt)₃) (**10**)

The synthetic procedure and the yield were the same as for the dimethylphenylsilyl analog **15** (see Section 5.9), except that 18 mg (0.110 mmol) of HSi(OEt)₃ was used.

³¹P{¹H} NMR (C₆D₆): δ -24.5 dt with ²⁹Si satellites (¹J_{P-Rh} = 85.2 Hz, ²J_{P-P} = 26.5 Hz, ²J_{P-Si, trans} ≈ 229 Hz), 1P *trans* to Si; -13.7 dd (¹J_{P-Rh} = 98.7 Hz, ²J_{P-P} = 26.5 Hz), 2P *trans* to H. ¹H NMR (C₆D₆): δ -10.53 d of pseudo t (²J_{H-P, trans} = 118.2 Hz, J_t = 19.4 Hz), 2H, Rh-H; 1.10 d (²J_{H-P} = 6.0 Hz), 9H, P(CH₃)₃ *trans* to Si; 1.29 d (²J_{H-P} = 7.0 Hz), 18H, 2P(CH₃)₃ *trans* to H; 1.39 t (³J_{H-H} = 7.0 Hz), 9H, Si(OCH₂CH₃)₃; 4.13 q (³J_{H-H} = 7.0 Hz), 6H, Si(OC₂H₅)₃.

5.9. *Fac*-(Me_3P)₃Rh(H)₂(SiMe₂Ph) (**15**)

To a solution of HRh(PMe₃)₄ (45 mg, 0.110 mmol) in C₆H₆ (3 ml) was added 19 mg (0.140 mmol) of HSiMe₂Ph. After 15 min the solvent and the excess silane were removed under vacuum to leave 50 mg (97%) of an analytically pure yellow-white solid.

³¹P{¹H} NMR (C₆D₆): δ -24.4 dt with ²⁹Si satellites (¹J_{P-Rh} = 85.4 Hz, ²J_{P-P} = 24.3 Hz, ²J_{P-Si, trans} ≈ 146 Hz), 1P *trans* to Si; -16.0 dd (¹J_{P-Rh} = 100.0 Hz, ²J_{P-P} = 24.3 Hz), 2P *trans* to H. ¹H NMR (C₆D₆): δ -10.12 d of pseudo t (²J_{H-P, trans} = 121.8 Hz, J_t = 19.0 Hz), 2H, Rh-H; 0.89 br s, 6H, Si(CH₃)₂; 0.98 d (²J_{H-P} = 6.0 Hz), 18H, 2P(CH₃)₃ *trans* to H; 1.09 d (²J_{H-P} = 6.0 Hz), 9H, P(CH₃)₃ *trans* to Si; [8.03 m, 2H; 7.35 t (7.4 Hz), 2H; 7.19 m, 1H], SiC₆H₅.

5.10. *Fac*-(Me_3P)₃Rh(H)₂(SiPh₃) (**16**)

This compound was prepared earlier and was fully characterized [5]. In the present work it was synthesized completely analogously to the above described di(hydrido)silyls, using equimolar amounts of reactants, and was isolated in 95% yield. ³¹P{¹H} NMR (C₆D₆): δ -25.0 dt with ²⁹Si satellites (¹J_{P-Rh} = 89.2 Hz, ²J_{P-P} = 21.7 Hz, ²J_{P-Si, trans} ≈ 154 Hz), 1P *trans* to Si; -17.6 dd (¹J_{P-Rh} = 102.1 Hz, ²J_{P-P} = 21.7 Hz), 2P *trans* to H. ¹H NMR (C₆D₆): as reported [5].

5.11. (Me_3P)₃RhSiMe₂Ph (**19**)

To a suspension of [Rh(PMe₃)₄]Cl (150 mg, 0.339 mmol) in THF (10 ml), 0.8 ml of a 0.53 M solution of LiSiMe₂Ph (1.25 equiv.) in THF was added upon stirring. The reaction mixture gradually turned brown-red. After 40 min stirring, the mixture was evacuated and the dry residue formed was extracted with pentane (two portions of 3 ml each). After filtration, the extract was evacuated to yield 88 mg of a red oily material. This

was recrystallized from pentane at -20°C to yield a dark red solid, pure enough for further experiments. The yield at best was 42%. The analytical sample and red single crystals, suitable for X-ray analysis, were obtained by slow evaporation of the solvent from a concentrated pentane solution of **19** at -30°C.

³¹P{¹H} NMR (C₆D₆): δ -17.2 d (J = 146 Hz). ³¹P{¹H} NMR (C₆D₅CD₃, -80°C): δ -26, very br d (¹J_{P-Rh} ≈ 115 Hz), 1P *trans* to Si; -12 br d (¹J_{P-Rh} ≈ 149 Hz), mutually *trans* 2P. ¹H NMR (C₆D₆): δ 0.79 br s, 6H, Si(CH₃)₂; 1.08 br s, 27H, 3P(CH₃)₃; [7.91 m, 2H; 7.31 t (7.4 Hz), 2H; 7.19 m, 1H], SiC₆H₅.

5.12. Reaction of [Rh(PMe₃)₄]Cl with LiSiMe₃. Formation of (Me₃P)₄RhSiMe₃ (**22**)

A solution of LiSiMe₃ was generated from 350 mg Hg(SiMe₃)₂ and 30 mg Li sand in 1 ml of THF over 1 day. After removing excess Li and free Hg, that was formed, the resulting brown solution was immediately used in the next step. To 76 mg (0.170 mmol) of [Rh(PMe₃)₄]Cl suspended in 5 ml of THF approximately 2-fold excess of LiSiMe₃ was added dropwise upon stirring. After 30 min all [Rh(PMe₃)₄]Cl dissolved and the dark yellow-brown solution was formed. The solvent was removed under vacuum to leave a sticky brown solid. This was extracted with pentane (2 × 3 ml) and the extract was evaporated to dryness to yield 40 mg of orange-brown powder, which was shown by ¹H and ³¹P{¹H} NMR to consist of **22** and **3** in ≈ 3:2 ratio. Complex **22** exhibited the following spectral data.

³¹P{¹H} NMR (C₆D₆): extremely broad signal between δ -17 and -30 ppm. ³¹P{¹H} NMR (C₆D₅CD₃, -55°C): δ -28.2 dd (¹J_{P-Rh} = 158.1 Hz, ²J_{P-P} = 50.3 Hz), 3P_{eq}; -15.4 dq (¹J_{P-Rh} = 91.1 Hz, ²J_{P-P} = 50.3 Hz), 1P_{ax} *trans* to Si. ¹H NMR (C₆D₆): δ 0.68 s, 9H, Si(CH₃)₃; 1.19 br s, 36H, 4P(CH₃)₃. ¹H NMR (C₆D₅CD₃, -55°C): δ 0.83 br s, 9H, Si(CH₃)₃; 1.09 d (²J_{H-P} = 5.1 Hz), 9H, P(CH₃)₃ unique; 1.25 br s, 27H 3P(CH₃)₃.

5.13. Reactivity of *fac*-(Me_3P)₃Rh(Si(OEt)₃)₂(H) (**8**)

5.13.1. Reaction with CO

A solution of 10 mg (0.015 mmol) of **8** in 4 ml of C₆H₆ was transferred to a Fischer-Porter pressure flask and was pressurized with 10 psi of CO. After 3 h of stirring at room temperature the solvent was removed under vacuum. ³¹P{¹H}, ¹H NMR and IR analyses of the yellow oil indicated the formation of 67% of L₂(CO)₂Rh(Si(OEt)₃) and 33% of L₃(CO)Rh(Si(OEt)₃).

10 mg (0.015 mmol) of **8** were dissolved in 1 ml (C₆D₆) under a nitrogen atmosphere and transferred to a NMR tube equipped with a rubber septum. The gas room of the NMR tube was flushed three times with CO. Every time the solution was shaken well which led

to a gradual loss of the yellow color. NMR and IR analyses indicated a product ratio of 20% of $L_2(CO)_2Rh(Si(OEt)_3)$ and 80% of $L_3(CO)Rh(Si(OEt)_3)$.

5.13.1.1. Characterization of $L_2(CO)_2Rh(Si(OEt)_3)$.
 $^{31}P\{^1H\}$ NMR (C_6D_6): δ -25.5 d ($^1J_{Rh-P} = 110.5$ Hz).
 1H NMR (C_6D_6): δ 1.13 vt ($J = 3.8$ Hz), 18H, $2P(CH_3)_3$; 1.40 t, ($^3J_{H-H} = 7.0$ Hz), 9H, $Si(OCH_2CH_3)_3$; 4.42 q ($^3J_{H-H} = 7.0$ Hz), 6H, $Si(OC_2H_5)_3$. IR(Film): $\nu_{CO} = 1975$ (s), 1925(vs).

5.13.1.2. Characterization of $L_3(CO)Rh(Si(OEt)_3)$.
 $^{31}P\{^1H\}$ NMR (C_6D_6): δ -26.0 d ($^1J_{Rh-P} = 112.0$ Hz).
 1H NMR (C_6D_6): δ 1.23 br d ($^2J_{P-H} = 5.4$ Hz), 27H, $3P(CH_3)_3$; 1.38 t ($^3J_{H-H} = 7.0$ Hz), 9H, $Si(OCH_2CH_3)_3$; 4.41 q ($^3J_{H-H} = 7.0$ Hz), 6H, $Si(OC_2H_5)_3$. IR(Film): $\nu_{CO} = 1948$ (s), 1900(s).

5.13.2. Reaction with $CDCl_3$

To a solution of 16 mg (0.025 mmol) of **8** in 2 ml of C_6H_6 , a solution of 4 mg $CDCl_3$ in 1 ml of C_6H_6 was added upon stirring. After 3 h of stirring at room temperature all volatile components were removed under vacuum. $^{31}P\{^1H\}$ and 1H NMR analyses showed the formation of 80% of a product identified as *mer*- $L_3Rh(Cl)(CDCl_2)(Si(OEt)_3)$.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -8.2 dd ($^1J_{Rh-P} = 95.0$ Hz, $^2J_{P-P} = 30.0$ Hz), 2P; 3.7 dt ($^1J_{Rh-P} = 128.7$ Hz, $^2J_{P-P} = 30.0$ Hz), 1P. 1H NMR (C_6D_6): δ 1.10 t ($^3J_{H-H} = 7.0$ Hz), 9H, $Si(OCH_2CH_3)_3$; 1.35 d ($^2J_{P-H} = 10.5$ Hz), 9H, $P(CH_3)_3$; 1.58 t ($^2J_{P-H} = 3.5$ Hz), 18H, $2P(CH_3)_3$; 3.90 q ($^3J_{H-H} = 7.0$ Hz), 6H, $Si(OC_2H_5)_3$.

5.14. Thermolyses of *fac*- $(Me_3P)_3Rh(Si(OMe)_3)_2(H)$ (**13**)

All following thermolyses were carried out in screw-capped NMR tubes. The inner surface of the NMR tubes was silylated with Me_3SiCl prior to the experiments. The yields are reported with regard to the used amount of **13**.

(a) A solution of 23 mg (0.04 mmol) of **13** in 1.5 ml of (C_6D_6) was warmed up to 55°C. After 72 h the ^{31}P NMR follow-up of the reaction showed a complete transformation of **13** to **14** and an unknown decomposition product. 1H NMR and GC-MS indicated the presence of 2% $[(MeO)_3Si]_2$ and 10% $(MeO)_4Si$. $[(MeO)_3Si]_2$: 1H NMR (C_6D_6): δ 3.52 s (coincidental with the signal due to added authentic sample of $[(MeO)_3Si]_2$). $(MeO)_4Si$: 1H NMR (C_6D_6): δ 3.43 s.

(b) A 6-fold excess (15 mg, 0.12 mmol) of $HSi(OMe)_3$ was added to a solution of 12 mg (0.02 mmol) of **13** in 1.5 ml C_6D_6 . The solution was treated as in (a). $^{31}P\{^1H\}$, 1H and GC-MS were measured, showing the signals of **14** and the formation of 4% of $[(MeO)_3Si]_2$ and 10% of $(MeO)_4Si$.

(c) A solution of 12 mg (0.02 mmol) of **13** and 244 mg (2.00 mmol) $HSi(OMe)_3$ in 1.5 ml C_6D_6 was warmed up to 55°C. The reaction progress was followed by periodical measurement of $^{31}P\{^1H\}$ NMR of the solution. After 40 h **13** had completely converted to **14** and the sample was cooled to room temperature. NMR analysis indicated a yield of 10% of $[(MeO)_3Si]_2$ and 40% of $(MeO)_4Si$, as quantified by addition of an internal standard ($HSiMe_2Ph$).

(d) To a solution of 12 mg (0.02 mmol) of **13** in 1.5 ml of C_6D_6 244 mg (2.00 mmol) of $HSi(OMe)_3$ was added. About 10% of the PMe_3 -groups were oxidised to Me_3PO by treatment of the sample with a small amount of air. Warming up of the reaction mixture to 55°C over 40 h resulted in the formation of 97% of $[(MeO)_3Si]_2$ and 250% of $(MeO)_4Si$, as quantified by addition of an internal standard ($HSiMe_2Ph$). $^{31}P\{^1H\}$ NMR of the sample showed 20% of **14**, the rest being decomposition products. ^{29}Si -INEPT-NMR (C_6D_6): δ -51.7 ($[(MeO)_3Si]_2$); -78.8 ($(MeO)_4Si$).

(e) 12 mg (0.02 mmol) of **13** and 10 mg (0.02 mmol) of $[(MeO)_3Si]_2$ were dissolved in 1.5 ml of C_6D_6 and transferred to a screw capped NMR tube. The reaction progress was monitored by $^{31}P\{^1H\}$ NMR. After 40 h at 55°C the reaction mixture contained 53% of **14** as a major organometallic product. 1H NMR showed the disappearance of 50% of $[(MeO)_3Si]_2$ and the appearance of significant amounts of $(MeO)_4Si$.

5.15. X-ray crystallography

From the batch of crystals obtained from a concentrated pentane solution of **19**, a red prismatic crystal of dimensions $0.6 \times 0.6 \times 0.6$ mm was chosen for the analysis. The data were collected using a CAD4 Enraf-Nonius diffractometer, equipped with a graphite monochromator ($Mo K\alpha$, $\lambda = 0.71073$ Å). Unit cell dimensions were determined from 25 reflections. Details of crystal parameters and data collection are given in Table 3. Three standards were collected 50 times each with no changes in intensities and 11% changes in azimuthal scan. The data were corrected for absorption based on a psi scan. The structure was solved by automated Patterson analysis (SHELXS-86) [64] and Fourier method (SHELXL-93), [65] refined using full-matrix least-squares refinement based on F^2 . Hydro-

Table 4
Selected bond angles (deg) in the molecule of **19**

Atoms	Bond angle	Atoms	Bond angle
P(2a)-Rh(1)-P(2)	159.98 (3)	C(23)-P(2)-C(22)	100.36 (13)
P(2a)-Rh(1)-P(1)	94.04 (2)	C(11a)-P(1)-C(11)	96.1 (2)
P(2a)-Rh(1)-Si	89.94 (2)	C(11a)-P(1)-C(12)	100.63 (12)
P(1)-Rh(1)-Si	156.43 (3)	C(1)-Si-C(1a)	97.7 (2)
C(21)-P(2)-C(23)	101.37 (14)	C(1)-Si-C(2)	101.38 (10)
C(21)-P(2)-C(22)	97.12 (14)		

gens were found from the difference Fourier map and refined in a free mode with individual temperature factors. Scattering factors, including anomalous terms for Rh, Si and P, were taken from the literature. [66] For 202 parameters the following final discrepancy factors were obtained: R_1 (based on F) = 0.0312 and wR_2 (based on F^2) = 0.077 ($I > 2\sigma(I)$); R'_1 = 0.0344, wR'_2 = 0.04389 (all data). GOF (on F^2) = 1.180, largest electron density 1.473 eÅ⁻³. Selected interatomic bond lengths and angles are listed in Tables 1 and 2. The molecule is occupying a mirror plane of symmetry with atoms C12, P1, Rh1, Si, C2, C3, C4, C5, C6, and C7 lying precisely on this plane.

Complete lists of bond lengths and angles, and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

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