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Syntheses and X-ray Diffraction Studies of Half-Sandwich Hydridosilyl Complexes of Ruthenium

Alexander L. Osipov,[†] Sergei M. Gerdov,[†] Lyudmila G. Kuzmina,[‡]
Judith A. K. Howard,[§] and Georgii I. Nikonov*,[†]

*Chemistry Department, Moscow State University, Vorob'evy Gory, 119992 Moscow, Russia,
Institute of General and Inorganic Chemistry RAS, Leninskii Prosp. 31,
119991 Moscow, Russia, and Chemistry Department, University of Durham, South Road,
Durham DH1 3LE, U.K.*

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The reactions of a series of half-sandwich trihydrides of ruthenium, Cp*(R_3P)Ru(H)$_3$ (R_3P = Pr^i_3P, Pr^i_2MeP, Pr^iMe_2P, $PhMe_2P$), with a family of chlorosilanes ($ClSiHMe_2$, Cl_2SiHMe, Cl_3SiH) have been studed with the aim of preparing the dihydridesilyl derivatives Cp*(R_3P)Ru(H)$_2$(SiR_3). The reaction of Cp*(R_3P)Ru(H)$_3$ with $ClSiHMe_2$ occurs at 90 °C and gives two types of products, Cp*(R_3P)Ru(H)$_2$($SiClMe_2$) (**1**) and Cp*(R_3P)Ru(H)$_2$($SiCl_2Me$) (**2**). The yield of complexes **2** increases with the decrease of the size of the phosphine ligand. X-ray structures of Cp*(Pr^i_3P)Ru(H)$_2$($SiClMe_2$) (**1a**) and Cp*(Pr^i_2MeP)Ru(H)$_2$($SiClMe_2$) (**1b**) are consistent with the presence of interligand hypervalent interactions Ru−H···Si−Cl. The compounds Cp*(R_3P)Ru(H)(Cl)($SiCl_2Me$) (**3**) were prepared by the reaction of Cp*(R_3P)Ru(H)$_3$ with Cl_2SiHMe at 60 °C and characterized by NMR and IR spectroscopy. Complex Cp*(Pr^i_3P)Ru(Cl)($SiCl_2Me$)(H) (**3a**) reacts with excess PMe_3 to give the H−Si elimination product Cp*(PMe_3)$_2$RuCl. The reactions of Cp*(R_3P)Ru(H)$_3$ (R_3P = Pr^i_3P, Pr^i_2MeP) with Cl_2SiHMe in the presence of NEt_3 at 90 °C give the dihydridesilyls Cp*(R_3P)Ru(H)$_2$($SiCl_2Me$) (R_3P = Pr^i_3P (**2a**), R_3P = Pr^i_2MeP (**2b**)). X-ray structures of these products may be rationalized as containing a double interligand hypervalent interaction Ru−H_2···Si−Cl_2. NMR reaction between Cp*($MePr^i_2P$)Ru(H)$_3$ and excess Cl_3SiMe at 100 °C resulted in a clean formation of Cp*($MePr^i_2P$)Ru(H)(Cl)($SiCl_2Me$). Complexes Cp*(R_3P)Ru(Cl)($SiCl_3$)(H) (**5**) were prepared by the reaction of Cp*(R_3P)Ru(H)$_3$ with Cl_3SiH at room temperature and characterized by NMR and IR spectroscopy. The reactions of Cp*(R_3P)Ru(H)$_3$ (R_3P = Pr^i_3P, Pr^i_2MeP) with Cl_3SiH in the presence of NEt_3 at 60 °C give the dihydridesilyls Cp*(R_3P)Ru(H)$_2$($SiCl_2H$) (R_3P = Pr^i_3P (**6a**), R_3P = Pr^i_2MeP (**6b**)) along with a mixture of some other compounds, whereas the analogous reactions in the presence of NPr^i_2Et afford the dihydridesilyls Cp*(R_3P)Ru(H)$_2$($SiClH_2$) (R_3P = Pr^i_3P (**7a**), R_3P = Pr^i_2MeP (**7b**)). Complex Cp*(Pr^i_3P)RuH_2(SiH_3) (**8a**), prepared by the reduction of Cp*(Pr^i_3P)Ru(Cl)($SiCl_3$)(H) (**5a**) by $LiAlH_4$, reacts with [$NHMe_2$Ph]Cl to give a mixture of Cp*(Pr^i_3P)Ru(H)$_3$ and Cp*(Pr^i_3P)Ru(H)$_2$($SiClH_2$) (**7a**). The crystal structures of **1a**,**1b**, **2a**, **2c**, **5b**, **5c**, **5d**, and **8a** have been determined by X-ray structure analysis.

Introduction

Orgonosilicon derivatives of ruthenium display a very rich and diverse chemistry in transformations of silicon compounds such as hydrosilylation,[1] dehydrogenative polymerization of silanes,[2] redistribution reactions at silicon atom,[3−5] Si−E (E = C, Si) bond activation and formation,[6,7] and dehydrogenative coupling of silanes to carbosilanes.[8] Apart from this, an impressive abundance of different structural types of silicon-substituted com-

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* To whom correspondence should be addressed. Tel: (095)9391976. Fax: (095)9328846. E-mail: nikonov@org.chem.msu.su.

[†] Moscow State University.

[‡] Institute of General and Inorganic Chemistry RAS.

[§] University of Durham.

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Chart 1. Types of Organosilicon Complexes of Ruthenium

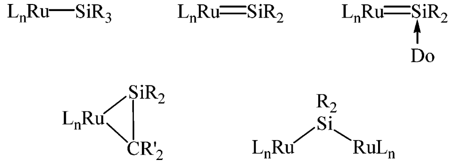


Chart 2. Examples of Ruthenium Complexes with Nonclassical Si−H Interactions

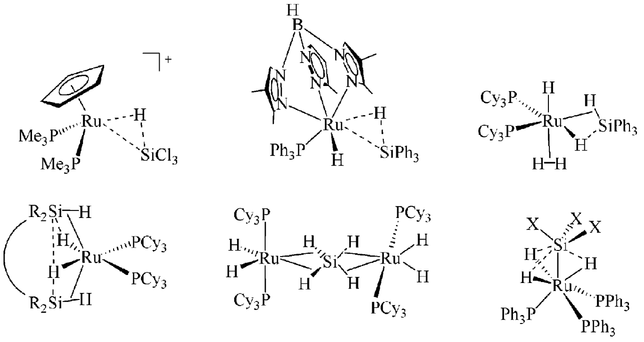
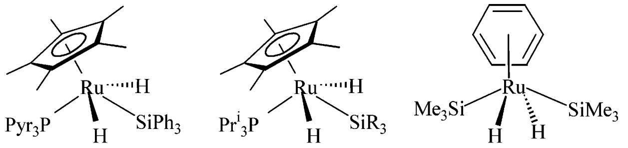


Chart 3. Examples of Classical Silyl Hydride Complexes of Ruthenium



$(Me_3P)_4RuH(SiR_3)$ $(Me_3P)_3RuH_3(SiR_3)$ $(Me_3P)_3RuH_2(SiMe_3)_2$

plexes of ruthenium is found. These include silyl,[9] silylene,[10−12] and silene[13] derivatives (Chart 1) and a range of nonclassical complexes[4,14−26] having nonclassical (secondary) Si−H interactions (Chart 2). The most relevant to the present paper is the class of hydridosilyl complexes of the type $L_nRu(H)_m(SiR_3)_k$ known for different ratios of k and m and different supporting ligands L_n (Chart 3).[11,27−33]

Our interest in the chemistry of the organosilicon complexes of ruthenium stems from our previous studies on the hydridosilyl complexes of early transition metals.[34] We have shown that basic transition metal hydrides having a functionalized silyl group in the cis position to the hydride ligand can have nonclassical interligand hypervalent interactions (IHI) between these groups.[34b−i] This type of interligand bonding has been studied in detail for the metallocene[34d,f−i] and isolobal Cp-imido[34b,c,e] ligand environments (Chart 4). We were

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Chart 4. Examples of Early Transition Metal Complexes with IHI

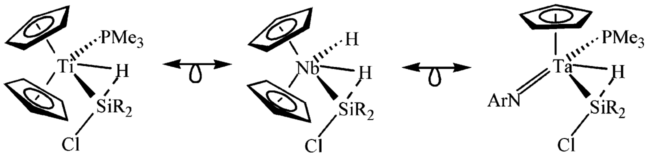
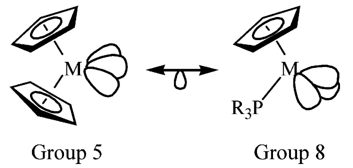


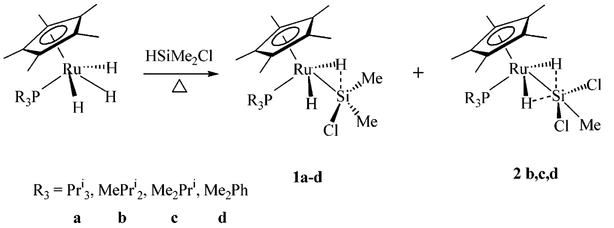
Chart 5. Isolobal Relationship between Group 5 Fragment Cp_2M and Group 8 Fragment $Cp(R_3P)M$



intrigued by the surprising analogy between the group 5 metallocene moiety Cp_2M and group 8 Cp/phosphine fragment $Cp(R_3P)M$. Namely, both fragments have the same number of valence orbitals of identical topological properties and comparable energies[35] and can accommodate up to three substituents. Although, these orbitals lie in one plane in Cp_2M,[35a] which is not the case for $Cp(R_3P)M$,[35b] this discrepancy is not vital for the occurrence of interligand bonding between H and Si atoms. Therefore, the question of whether complexes of the general formula $Cp''(R_3P)Ru(X)(H)(SiR_2Y)$ (Y = halogen; X = any one-electron ligand; Cp″ = Cp or Cp*) can have any interaction between the hydride and silyl groups is appropriate. Taking into account that the ruthenium atom in these complexes has the formal oxidation state (IV), which is good for the formation of silane σ-complexes in many structures,[14−21] this question can be reformulated as whether the donor ability of the Cp/(R_3P) ligand set is sufficient to make the basicity of the hydride ligand high enough to "switch on" IHI of the type Ru−H···Si−Y. The recently determined basicity of the hydrides in $Cp^*(Cy_3P)RuH_3$ (basicity factor $E_j = 0.94$)[36] suggests that this is possible. Some structural features of the compound $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$[29] (Mes = 2,4,6-trimethylphenyl), such as a long Si−Cl bond and short Ru−Si bond, are also indicative of the presence of IHI,[37] whereas the compound $Cp^*(Ph_3P)Ru(H)_2(SiMe_2Cl)$, having a less basic phosphine (and hence less basic hydride), is classical.[37] A few other compounds of the type $Cp''(R_3P)Ru(X)(H)(SiR_2Y)$ are known: ($Cp^*(Pr^i_3P)Ru(H)_2(SiMePh_2)$,[29] $Cp^*(Pr^i_3P)Ru(H)(Cl)(SiR_3)$ (SiR_3 = $SiCl_2Me$, $SiPhH_2$, $SiPhHSiPhH_2$),[28,29] $Cp^*(Me_3P)Ru(H)(SiR_3)_2$ (SiR_3 = $Si(OEt)_3$, $SiClPh_2$, $SiMe_2OEt$),[11a] $Cp^*(PhPr^i_2P)Ru(H)_2(SiR_3)$ (SiR_3 = $Si(OMe)_3$, $SiMe_3$, $SiPh_3$, $SiHPh_2$, $SiPh_2OCH_2CF_3$),[30] $Cp^*((pyrrolyl)_3P)Ru(H)_2(SiMe_2Ph)$,[31] $Cp(R_3P)Ru(H)(SiR'_3)_2$ (R = Me, R′ = Et; R = Ph, R′ = Cl)[32]), but the crucial structural information is very scarce.[31] To get further insight into this problem, we studied the interactions of various trihydrides $Cp^*(R_3P)Ru(H)_3$ with a family of chlorosilanes ($ClSiHMe_2$, Cl_2SiHMe, Cl_3SiH). Our initial goal was to prepare a series of complexes $Cp^*(R_3P)Ru(H)_2(SiR'_{3-n}Cl_n)$ (n = 1−3) and to establish the occurrence and strength of any H−Si interaction as a function of the electronic and steric properties of the substituent R at the phosphorus atom and the number of chlorine groups on the silicon atom. The results of this research are reported here.

Results and Discussion

1. Reactions of Ruthenium Trihydrides with $ClSiHMe_2$. The trihydrides $Cp^*(RPr^i_2P)Ru(H)_3$ (R = Me, Pr^i), containing bulky phosphines Pr^i_3P and $MePr^i_2P$, react with $ClSiHMe_2$ upon heating to 90 °C for 6−10 h to give the target monosilyl dihydride complexes $Cp^*(RPr^i_2P)Ru(H)_2(SiClMe_2)$ (**1a**, R = Pr^i; **1b**, R = Me; eq 1). No reaction occurs at room temperature and only a sluggish one at 60 °C. The optimum temperature for the thermolysis is 90 °C, since raising the temperature over 100 °C results in the formation of impurities. Complexes **1a**,**b** have been characterized by IR and NMR (^1H, ^{13}C, ^{31}P, ^{28}Si) spectroscopy, and their structures have been determined by X-ray diffraction studies. The ^1H NMR spectra of **1a**,**b** show signals of the equivalent methyl groups on silicon atoms (0.98 ppm for **1a** and 1.00 ppm for **1b**) and resonances due to the equivalent hydrides (−12.23 (d, J(P−H) = 28.0 Hz) for **1a** and −12.21 (d, J(P−H) = 28.6 Hz for **1b**)). In addition, the ^1H NMR spectrum of **1b** shows two sets of signals due to the isopropyl groups of the phosphine, consistent with the C_s symmetry of the complex and the central position of the silyl ligand trans to phosphine. No significant (i.e., >20 Hz)[39c,d] silicon−hydride coupling can be seen from the silicon satellites of the hydride signals (J(Si−H) = 11.7 Hz for **1a** and 12.9 Hz for **1b**).



(1)

Analysis of the ^1H NMR spectrum of the NMR tube reaction between $Cp^*(MePr^i_2P)Ru(H)_3$ and $ClSiHMe_2$ showed that the silane redistribution product $Cp^*(MePr^i_2P)Ru(H)_2(SiCl_2Me)$ (**2b**) is also produced in about

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(38) For the related redistribution reactions of silanes on other metals see: (a) Ref 3a. (b) Rahimian, K.; Harrod, J. F. *Inorg. Chim. Acta* **1998**, *270,* 330. (c) Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698. (d) Pestana, D. C.; Koloski, T. S.; Berry, D. H. *Organometallics* **1994**, *13*, 4173.

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5% yield. In contrast, no traces of **2a** can be seen in the NMR tube reaction between Cp*(Pr$^i_3$P)Ru(H)$_3$ and ClSiHMe$_2$. The reaction of the less bulky complex Cp*(Me$_2$Pr^{i}P)Ru(H)$_3$ with ClSiHMe$_2$ is different in that in addition to the expected product Cp*(Me$_2$Pr^{i}P)Ru(H)$_2$(SiClMe$_2$) (**1c**) an equivalent amount of the dichlorosilyl derivative Cp*(Me$_2$Pr^{i}P)Ru(H)$_2$(SiCl$_2$Me) (**2c**) is formed. Like complexes **1a**,**b**, both **1c** and **2c** do not show any significant silicon−hydride coupling constant (both *J*(Si−H) < 13 Hz). The hydride signal of **2c** in the ^{1}H NMR spectrum is shifted to lower field (−11.54 ppm, *J*(P−H) = 29.2 Hz, *J*(Si−H) = 11.0 Hz), compared to the signal of **1c** (−12.13 ppm, *J*(P−H) = 29.4 Hz, *J*(Si−H) = 12.9 Hz). We failed to separate **1c** from **2c** due to their comparable solubility properties. However, an X-ray quality crystal of **2c** was grown by slowly cooling an ether solution of the mixture to −30 °C, and the molecular structure was determined. Analogously, the reaction of Cp*(Me$_2$PhP)Ru(H)$_3$ with HSiClMe$_2$ in toluene in the presence of 15-fold excess silane (5 h, 90 °C) gives a 1:1 mixture of **1d** and Cp*(Me$_2$PhP)Ru(H)$_2$(SiCl$_2$Me) (**2d**) along with another yet unidentified phosphine complex. All attempts to separate these two products failed.

Complexes **2** apparently emerge as a result of a redistribution process at the silicon center. Such a redistribution reaction has many precedents in the organosilicon chemistry of ruthenium.[3−5,32,38] In particular, Lemke et al. have very recently reported that the reaction of RuCl$_2$(PPh$_3$)$_3$ with ClSiHMe$_2$ in benzene produces a mixture of (η^6-C$_6$H$_6$)Ru(PPh$_3$)$_2$(SiClMe$_2$)$_2$, (η^6-C$_6$H$_6$)Ru(PPh$_3$)$_2$(SiClMe$_2$)(SiCl$_2$Me), and (η^6-C$_6$H$_6$)Ru(PPh$_3$)$_2$(SiCl$_2$Me)$_2$; the yield of the more chlorinated silyl derivatives increases when higher temperatures (65 °C) are applied.[5]

The central question of the current study is whether there is any nonclassical Si−H interaction in the (chlorosilyl)hydrido complexes of ruthenium, like **1** and **2**. This question can be answered, in principle, by means of spectroscopic and structural methods. For the silane σ-complexes, such as those shown in Chart 2, the most common criterion of the presence of a Si−H bonding has been the observation of a Si−H coupling constant *J*(Si−H) higher than 20 Hz.[39] It is, however, becoming increasingly clear that this criterion is not generally applicable to all types of nonclassical complexes.[34i,40] For the compounds with IHI, the theory does not require high values of *J*(Si−H) for the presence of Si−H bonding.[34e] In fact, it has been shown for some systems that the Si−H interaction weakens as the absolute value of *J*(Si−H) increases.[34b,i] Therefore, the observation of relatively low values (*J*(Si−H) < 13 Hz) of *J*(Si−H) for **1** and **2c** *does not unequivocally rule out* the presence of Si−H interactions, and structural criteria should be considered. IHI consists in the electron density transfer from the high lying M−H bond orbital to the (Si−X)* antibonding orbital, which results in the elongation of the M−H and Si−X bonds and decrease of the M−Si and Si−H distances.[34b−i] A long Si−Cl bond and short Ru−Si bond are observed in Cp*(Pr$^i_3$P)Ru(H)$_2$(SiHClMes),[29] whereas the compound with the less basic phosphine, Cp*(Ph$_3$P)Ru(H)$_2$(SiMe$_2$Cl), is classical.[37]

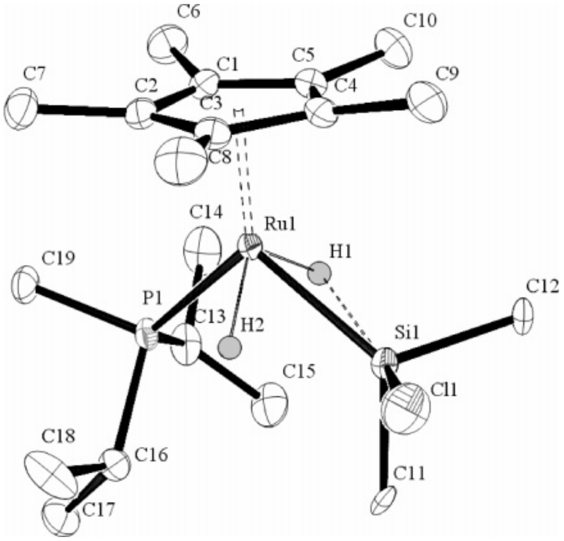

Figure 1. Molecular structure of complex **1b**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms on carbons are omitted for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) for 1a and 1b

	1a	**1b**
Ru(1)−Si(1)	2.332(1)	2.3352(8)
Ru(1)−P(1)	2.3095(9)	2.3079(7)
Ru(1)−H(1)	1.51(4)	1.53(6)
Ru(1)−H(2)	1.53(4)	1.63(6)
Si(1)−H(1)	2.03(4)	2.17(6)
Si(1)−H(2)	2.04(4)	2.03(6)
Si(1)−Cl(1)[a]	2.026(7)	2.170(1)
Si(1)−Cl(1A)[a]	2.118(2)	
Si(1)−C(11)	1.898(3)	1.942(3)
Si(1)−C(12)[a]	1.94(1)	1.913(3)
Si(1)−C(12A)[a]	1.89(5)	
P(1)−Ru(1)−Si(1)	102.69(3)	104.66(3)
H(2)−Ru(1)−H(1)	109(2)	110(3)
Si(1)−Ru(1)−H(1)	59(2)	64(2)
Si(1)−Ru(1)−H(2)	59(1)	58(2)
P(1)−Ru(1)−H(1)	83(2)	79(2)
P(1)−Ru(1)−H(2)	78(2)	79(2)
C(11)−Si(1)−Cl(1)	101.2(2)	100.9(1)
C(11)−Si(1)−Cl(1A)	97.8(1)	
C(12)−Si(1)−C(11)	100.8(4)	102.5(2)
C(12A)−Si(1)−C(11)	99(2)	
C(12)−Si(1)−Cl(1)	101.9(4)	99.3(1)
C(12A)−Si(1)−Cl(1A)	104(2)	
C(11)−Si(1)−Ru(1)	124.0(1)	121.94(9)
C(12)−Si(1)−Ru(1)	115.7(4)	116.6(1)
C(12A)−Si(1)−Ru(1)	112(2)	
Cl(1)−Si(1)−Ru(1)	115.1(1)	
Cl(1A)−Si(1)−Ru(1)	113.19(5)	112.51(5)
Cl(1)−Si(1)−H(1)	153(2)	151(2)
Cl(1)−Si(1)−H(2)	89(2)	83(2)
Cl(1A)−Si(1)−H(1)	84(2)	
Cl(1A)−Si(1)−H(2)	152(2)	

[a] In **1a** the pairs C(12)/C(12A) and Cl(1)/Cl(1A) denote the disordered methyl and chloride groups on Si(1), respectively.

The molecular structure of complex **1b** is shown in Figure 1, and the corresponding figure for **1a** is deposited in the Supporting Information. Some selected molecular parameters for **1a** and **1b** are gathered in Table 1. The analysis of the structure of **1a** is complicated by the disorder of the SiMe$_2$Cl group, which affects the value of the crucial Si−Cl bond length. This problem, however, does not intervene in the Ru−Si bond (2.332(1) Å). Fortunately, the disorder problem does not exist for **1b**, which shows a very similar Ru−Si bond

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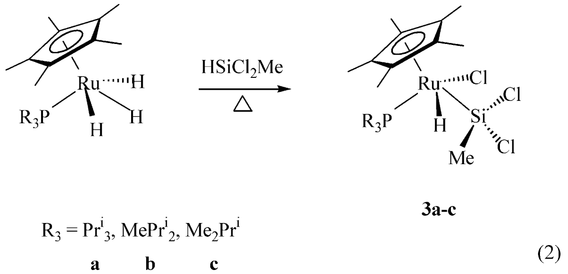
(40) (a) Lichtenberger, D. L. *Organometallics* **2003**, *32*, 1599. (b) Nikonov, G. I. *Organometallics* **2003**, *32*, 1597.

length of 2.3352(8) Å. Both these values are longer than the corresponding parameter in $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ (2.302(3) Å) but are significantly shorter than the Ru−Si bond lengths in the classical compounds $Cp^*(Ph_3P)Ru(H)_2(SiClMe_2)$ (2.364(2) Å) and $Cp^*(pyr_3P)Ru(H)_2(SiPhMe_2)$ (2.4213(7) Å). The difference in the Ru−Si bond lengths in $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ and **1a**,**b** can be accounted for by a combination of steric and electronic factors. Namely, the sum of electronegativities of the H and Mes groups on silicon is somewhat larger than that of two Me groups, thus, in accordance with Bent's rule,[41] leading to a shorter Ru−Si distance. Second and possibly most important, in $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ the smallest group on the silicon atom, the hydrogen atom, is oriented toward the bulky Cp* ligand, whereas in **1a**,**b** this position is occupied by the Me group. Hence, a shorter Ru−Si bond can be accommodated by $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$. Overall, this Ru−Si bond is exeptionally short, taking into account that even the trichlorosilyl complexes $Cp^*(R_3P)Ru(H)(Cl)(SiCl_3)$, discussed below, feature significantly longer bonds (range 2.3107−2.3153(8) Å) in spite of the presence of three electron-withdrawing Cl groups on the silicon atom.

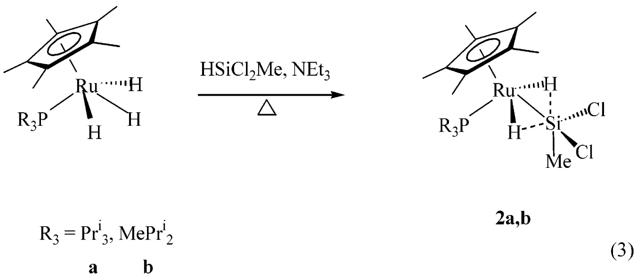
The Si−Cl bond of 2.170(1) Å in **1b** is identical with that in $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ (2.170(4) Å), suggesting that the electronic situation around the silicon center in both compounds is in fact very similar. This value is significantly longer than in the classical silyl complexes bearing the SiR_2Cl group (range 2.094−2.149 Å)[42] but comparable to the elongated Si−Cl bonds in the compounds with IHI (range 2.163−2.222(2) Å).[34] The Si−H distance in **1a**,**b** is a less reliable indicator of the Si−H interaction due to the well-known inaccuracy in finding the hydride in the vicinity of heavy elements. In the complexes $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ and **1a**,**b** one of the hydrides appears to form a short contact to the silicon atom (2.03, 2.04, 2.03 Å, respectively), whereas in $Cp^*(Ph_3P)Ru(H)_2(SiClMe_2)$ both the Si−H distances determined by X-ray study are rather long (2.189 and 2.271 Å). However, in the classical complex $Cp^*(pyr_3P)Ru(H)_2(SiPhMe_2)$ short contacts of 1.95(3) and 2.03(3) Å are also seen. To summarize, the structural trends observed in $Cp^*(Pr^i_3P)Ru(H)_2(SiHClMes)$ and **1a**,**b** are consistent with the presence of interligand hypervalent interaction Ru−H···Si−Cl.

2. Reactions of Ruthenium Trihydrides with $HSiCl_2Me$. The result of the reactions of the trihydrides $Cp^*(R_3P)Ru(H)_3$ ($R_3 = Pr^i_3, MePr^i_2, Me_2Pr^i$) with silane $HSiCl_2Me$ crucially depends on the conditions employed. The reactions are very sluggish (3 weeks for $R_3 = Pr^i_3$) at room temperature and result in the formation of the hydridosilyl complexes $Cp^*(R_3P)Ru(Cl)(SiCl_2Me)(H)$ (**3**, eq 2) and $Cp^*(R_3P)Ru(H)_2(SiClHMe)$ (**4**). At 60 °C the reactions are complete and give complexes **3** in 40−50% isolated yields after 1.5 h. Some other examples of this structural type have been previously prepared by oxidative addition of hydrosilanes to the unsaturated complexes $Cp^*(R_3P)Ru(Cl)$ containing bulky phosphines (PPr^i_3, PCy_3).[28,29] The formation of **3** implies the chlorination of a Ru−H bond under the action of chlorosilanes, which has literature precedents.[25,27] Complexes **3** have been characterized by IR and NMR spectroscopy and by comparison with the previously studied analogues.



(2)

Complexes **4** are the formal silyl-for-hydride exchange products of the reaction of $Cp^*(R_3P)Ru(H)_3$ with $HSiCl_2Me$, and the analogous H/Si exchange has been observed in the related reactions of the compound $Cp(Me_3P)_2Ru(H)$ with chlorosilanes $Cl_{4-k}SiR_k$ ($k = 0, 1, 2$)[43] and in several other systems.[44,45] Lemke et al. reported that the yield of the exchange products $Cp(Me_3P)_2Ru(SiR_kCl_{3-k})$ increases in the presence of amine, since without any added amine an equivalent of $Cp(Me_3P)_2Ru(H)$ is consumed by the HCl released, forming the compound $[Cp(Me_3P)_2Ru(H)_2]Cl$. Given these literature data, we have also studied the reactions of the trihydrides $Cp^*(R_3P)Ru(H)_3$ ($R_3 = Pr^i_3, MePr^i_2$) with $HSiCl_2Me$ in the presence of an amine. Addition of $HSiCl_2Me$ to a mixture of $Cp^*(R_3P)Ru(H)_3$ and NEt_3 at room temperature results in no reaction, consistent with the lower basicity of the hydride ligands in the Ru(IV) compounds $Cp^*(R_3P)Ru(H)_3$ compared to the Ru(II) complex $Cp(Me_3P)_2Ru(H)$.[36b] Unexpected to us, heating the mixture to 90 °C affords the compound $Cp^*(R_3P)Ru(H)_2(SiCl_2Me)$ (**2a**,**b**, eq 3) as the main product contaminated with small amounts of **3** and **4**. An analogous reaction of $Cp^*(PhMe_2P)Ru(H)_3$ gave a mixture of four hydride-containing compounds, comprised in addition to **2d**, **3d**, and **4d** of $Cp^*(PhMe_2P)Ru(H)_2(SiClMe_2)$ (**1d**) and a set of other yet unidentified complexes. Apparently, complex **1d** arises from a redistribution reaction at the silicon center. No reaction occurs at 50 °C between $Cp^*(PhMe_2P)Ru(H)_3$ and the silane Me_2SiCl_2 in the presence of amine $NEtPr^i_2$.



(3)

Addition of 3 equiv of PMe_3 to a toluene-d_8 solution of $Cp^*(Pr^i_3P)Ru(Cl)(SiCl_2Me)(H)$ (**3a**) results in an

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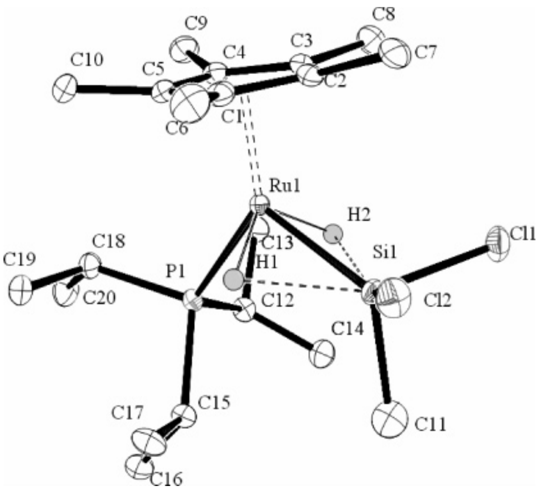

Figure 2. Molecular structure of complex **2a**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms on carbons are omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg) for 2a and 2c

	2a	**2c**
Ru(1)−Si(1)	2.2950(5)	2.3099(9)
Ru(1)−P(1)	2.3237(5)	2.2888(9)
Ru(1)−H(1)	1.56(3)	1.49(5)
Ru(1)−H(2)	1.64(3)	1.68(8)
Si(1)−H(1)	2.11	2.07
Si(1)−H(2)	2.15	1.99
Si(1)−Cl(1)	2.1271(7)	2.109(2)
Si(1)−Cl(2)	2.1170(7)	2.108(2)
Si(1)−C^a	1.944(2)	1.902(3)
P(1)−Ru(1)−Si(1)	102.05(2)	104.08(3)
H(2)−Ru(1)−H(1)	115(2)	102(3)
Si(1)−Ru(1)−H(1)	63(1)	62(2)
Si(1)−Ru(1)−H(2)	64(1)	57(2)
P(1)−Ru(1)−H(1)	80(1)	82(2)
P(1)−Ru(1)−H(2)	77(1)	71(2)
C^a−Si(1)−Cl(1)	98.34(5)	100.6(1)
C^a−Si(1)−Cl(2)	99.43(5)	100.1(2)
Cl(1)−Si(1)−Cl(2)	100.31(3)	99.07(6)
C−Si(1)−Ru(1)	125.98(5)	123.2(1)
Cl(1)−Si(1)−Ru(1)	113.77(3)	115.42(5)
Cl(2)−Si(1)−Ru(1)	114.93(3)	114.74(5)
Cl(1)−Si(1)−H(1)	154(2)	151(3)
Cl(2)−Si(1)−H(2)	154(2)	160(3)

^{a} C stands for C(11) in **2a** and C(16) in **2c**.

instantaneous color change from light green to bright orange-yellow of Cp*$(PMe_3)_2$RuCl and the release of free phosphine Pr^i_3P and an equivalent of the silane $HSiCl_2$-Me characterized by its Si−H signal at 5.22 ppm and Si−Me signal at 0.23 ppm in the ^{1}H NMR spectrum. This suggests that H−Si elimination from **3** is quite facile. In contrast, the compound Cp*$(Pr^i_3P)Ru(H)_2$-(SiHClMes)[29] has been previously reported to arise from the thermal rearrangement of Cp*$(Pr^i_3P)Ru(Cl)(SiH_2$-Mes)(H), which was rationalized in terms of Si−Cl bond elimination and Si−H bond oxidative addition reactions. An analogous Si−Cl elimination was proposed for Cp*-$(Pr^i_3P)Ru(Cl)(SiPh_2Me)(H)$,[13c] whereas the less sterically hindered Cp*$(Pr^i_3P)Ru(Cl)(SiH_2Ph)(H)$ is stable even when heated at 90 °C for several hours.[29] Therefore, the silane H−Si versus Cl−Si elimination from Cp*(R_3P)-Ru(Cl)(SiR′$_3$)(H) is driven by both the sterics and electonegativity of the substituents at the silicon center.

To check the possibility of a direct oxidative addition of the Si−Cl bond to ruthenium,[46] we carried out an NMR study of the reaction between Cp*$(MePr^i_2P)Ru$-$(H)_3$ and excess Cl_3SiMe. No reaction occurs at room temperature, but heating to 100 °C for 2 h results in clean formation of Cp*$(MePr^i_2P)Ru(Cl)(SiCl_2Me)(H)$. The same product is formed when this reaction is carried out in the presence of NEt_3, but no traces of the possible exchange product Cp*$(MePr^i_2P)Ru(H)_2(SiCl_2$-Me) were observed.

The molecular structure of complex Cp*$(Pr^i_3P)Ru(H)_2$-$(SiCl_2Me)$ (**2a**) is shown in Figure 2, and selected bond distances and angles are given in Table 2. The Ru−Si bond of 2.2950(5) Å in **2a** is shorter than in the monochlorosilyl complexes discussed above due to Bent's rule effect. Bent's rule states that bonds to the electropositive substituents receive more s-character of the central atom, making these bonds shorter, whereas the p-character goes mainly to the bonds to more electronegative substituents, resulting in their elongation.[41] Thus, the presence of two electron-withdrawing chlorine groups on the silicon atom accounts for the shorter Ru−Si bond in **2a**. The Si−Cl bonds (2.1271(7) and 2.1170(7) Å) are also shorter than in **1a**,**b** because the p-character of silicon is here distributed over two Si−Cl bonds. The known complexes of the type L_nM-$SiRCl_2$ can be classified into two categories: those in which the Si−Cl bond lengths span the range 2.007−2.094 Å,[47] and the complexes with elongated Si−Cl bonds (up to 2.192 Å)[5,25,34b,i,48,49] having either nonclassical interaction between the silyl and hydride ligands[25,34b,i] or a negative hyperconjugation between a metal centered lone-pair and a (Si−Cl)* antibonding orbital.[49] In the compounds $Cp(ArN)Ta(PMe_3)(H)(SiMeCl_2)$[34b] and Cp_2-$Ti(PMe_3)(H)(SiMeCl_2)$[34i] with IHI the longer Si−Cl bond (2.117(2) and 2.192(1) Å, respectively) lies trans to the hydride and participates in IHI, whereas the shorter bond (2.064(3) and 2.134(1) Å, respectively) does not. In **2a** each of the Si−Cl bonds lies approximately trans to one of the hydrides (the bond angles Cl−Si−H are both 154(2)°). This orientation creates the possibility of two weak IHIs of the type $Ru-H_2\cdots Si-Cl_2$, as shown below (structure **A**). It is instructive to compare structure **A** with the related complexes $Cp(Me_3P)_2Ru(SiCl_2R)$ (**B**) studied by Lemke et al.[44,49] In **B** there is a double negative hyperconjugation of the ruthenium-centered orbitals with two Si−Cl bonds. There is a clear analogy between this hyperconjugation and the conjugation of the lower lying Ru−H bond orbitals with two (Si−Cl)* antibonding orbitals in **A**. Because the d orbitals of Ru lie somewhat higher than the Ru−H bond orbitals and the Ru center in $Cp(Me_3P)_2Ru(SiCl_2R)$ has a lower formal oxidation state (II), the effect of the interaction is more pronounced in **B**.

The molecular structure of the complex Cp*$(Me_2$-$Pr^iP)Ru(H)_2(SiCl_2Me)$ (**2c**), obtained according to eq 1, is analogous to that of **2a** and has been deposited in

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(46) For an example of Si−Cl addition to a metal, see: Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049.

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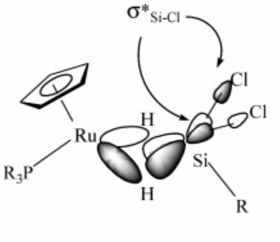

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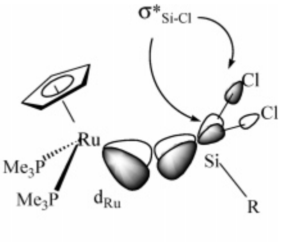
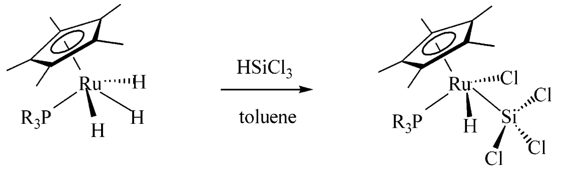


B

the Supporting Information. The selected molecular parameters are given in Table 2. The main difference between **2a** and **2c** is in the values of the Ru−Si and Si−Cl bond lengths. Although **2c** contains a less bulky phosphine and thus is less sterically strained, its Ru−Si bond of 2.3099(9) Å is somewhat longer than in **2a** (2.2950(5) Å). Similtaneously, the Si−Cl bonds are significantly shorter in **2c** (2.108(2) and 2.109(2) Å versus 2.1170(7) and 2.1271(7) Å in **2a**). These trends can be rationalized in terms of decreased IHI in **2c** due to the presence of a less basic phosphine and hence the diminished basicity of the hydride ligand. A shorter Ru−Si bond in **2a** leads to a longer trans Ru−P bond (2.3237(5) versus 2.2888(9) Å in **2c**). However, an alternative explanation of these structural differences is possible, given the fact that the bulky phosphine Pr^i_3P in **2a** suffers from a greater steric repulsion from the Cp* ligand, resulting in a more open P−Ru−X bond angle of 132.8° (where X is the centroid of the Cp* ring; the corresponding value in **2c** is 130.4°) and a longer Ru−P bond length. This and the slightly decreased P−Ru−Si bond angle (102.1° in **2a** versus 101.8° in **2c**) should lead to a weaker phosphine trans-effect in **2a** compared with **2c**. Hence, the former complex can accommodate a shorter Ru−Si bond length, which in turn should lead to longer Si−Cl bond lengths for both steric (to minimize the repulsion from the Cp* ligand) and electronic reasons (Bent's rule effect and the possibility of a stronger IHI with the hydrides). Both electronic effects should result in a greater Si p-character in the Si−Cl bonds, which also has its manifestation in slightly smaller Ru−Si−Cl and Cl−Si−C bond angles and larger Ru−Si−C bond angles in **2a** compared to **2c**. At the moment it is difficult to rationalize which factor (sterically induced diminished phosphine trans effect or increased IHI) in **2a** is the cause and which is the effect of the observed structural differences between **2a** and **2c**.

3. Reactions of Ruthenium Trihydrides with $HSiCl_3$. The reactions of the trihydrides $Cp^*(R_3P)Ru(H)_3$ ($R_3 = Pr^i_3$ (**a**), $MePr^i_2$ (**b**), Me_2Pr^i (**c**), Me_2Ph (**d**)) with the silane $HSiCl_3$ also crucially depend on the conditions employed and in general result in several products. The room-temperature reaction of $Cp^*(R_3P)Ru(H)_3$ with excess $HSiCl_3$ in toluene gives good yields of complexes $Cp^*(R_3P)Ru(Cl)(SiCl_3)(H)$ (**5**, eq 4). These compounds have been characterized by NMR and IR spectroscopy and X-ray studies for **5b**,**c**,**d**. Complex **5a** has been independently prepared by the addition of $HSiCl_3$ to $Cp^*(Pr^i_3P)Ru(Cl)$. The normal value for the P−H coupling constant (range 29.1−34.2 Hz) and the absence of a significant Si−H coupling allows us to rule out an alternative formulation of **5** as silane σ-complexes. In contrast, in the related cationic silane σ-complex $[Cp(Me_3P)_2Ru(\eta^2\text{-H-SiCl}_3)]^+$, having the phopshine ligand in place of chloride in **5**, the decreased $J(P-H) = 11$ Hz and increased $J(Si-H) = 48$ Hz have been observed.[23]



$R_3 = Pr^i_3, MePr^i_2, Me_2Pr^i, Me_2Ph$

a **b** **c** **d**

5a-d

(4)

NMR monitoring of the reaction between $Cp^*(Pr^i_3P)Ru(H)_3$ and excess $HSiCl_3$ (5 equiv) in a thoroughly dried NMR tube in benzene-d_6 at room temperature during one week showed the formation of a 1:1 mixture of **5a** and a new product, $Cp^*(Pr^i_3P)Ru(H)_2(SiHCl_2)$ (**6a**). Prolonged storage of a solution of the mixture of **5** and **6** in the presence of excess silane $HSiCl_3$ results in the conversion of **6** to **5**, probably due to the chlorination of the Si−H and Ru−H bonds. Due to the close solubility properties of **5** and **6**, we failed to isolate **6** in pure form; thus these complexes were characterized by spectroscopic methods only. In the ^1H NMR spectrum compound **6a** exhibits a hydride signal at −11.39 ppm (dd, $J(P-H) = 28.2$ Hz, $J(H-H) = 5.9$ Hz) and the SiH signal at 6.89 ppm (t, $J(H-H) = 5.9$ Hz). Carrying out the reaction of $Cp^*(Pr^i_3P)Ru(H)_3$ under similar conditions at 75 °C for 2 h gives a mixture of **5a**, **6a**, $Cp^*(Pr^i_3P)Ru(H)_2(SiCl_3)$, and $Cp^*(Pr^i_3P)Ru(H)_2(SiH_2Cl)$ (**7a**) in the ratio 2.1:0.7:1:0.25 along with the unreacted $Cp^*(Pr^i_3P)Ru(H)_3$ (42%). The identity of complex **7a** was established on the basis of its Ru−H and Si−H signals in the ^1H NMR spectrum (vide infra).

Carrying out the reactions of $Cp^*(Pr^i_3P)Ru(H)_3$ with $HSiCl_3$ in the presence of an amine increases the yield of the Si−H-containing products. The reaction is slow at room temperature, but heating the reaction mixture with added NEt_3 at 70 °C affords a mixture of complexes **6a** (major product), **5a**, and three minor components, including $Cp^*(Pr^i_3P)Ru(H)_2(SiH_2Cl)$ (**7a**). NMR monitoring of the reaction of $Cp^*(MePr^i_2P)RuH_3$ with $HSiCl_3$ in the presence of NEt_3 in C_6D_6 revealed in addition to **6b** and **7b** another compound, which on the basis of its ^1H NMR data we formulate as an isomer of **6b** having the silyl group cis to phosphine, $Cp^*(Pr^i_2MeP)Ru(H)_2(SiHCl_2)$ (**6b′**). Complex **6b′** exhibits inequivalent hydride signals as broad doublets at −11.04 ($J(P-H) = 25.8$ Hz) and −11.50 ($J(P-H) = 27.7$ Hz) and the Si−H signal at 6.14 ppm (dd, $J(H-H) = 2.5$ Hz, $J(H-H) = 5.0$ Hz) coupled to two inequivalent hydrides. The ratio of **6** and **7** formed in this reaction depends on the conditions used. It appears that increasing the amount of silane favors the formation of **7**.

To avoid any complications arising from the possible complexation of the amine NEt_3 to silane, we have also carried out the reaction of $Cp^*(Pr^i_3P)Ru(H)_3$ with $HSiCl_3$ in the presence of a bulkier amine, $NEtPr^i_2$. To our surprise, this reaction gave selectively the compound **7a** (eq 5).[50] The reaction proceeds smoothly at room

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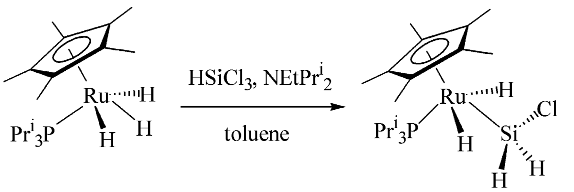
[50] Complexes with the ligand SiH_2Cl are rare. See, for example: (a) Schmitzer, S.; Weis, U.; Käb, H.; Buchner, W.; Malisch, W.; Polzer, T.; Kiefer, W. *Inorg. Chem.* **1993**, *32*, 303. (b) Ref 44. (c) Freeman, S. T. N.; Lofton, L. L.; Lemke, F. R. *Organometallics* **2002**, *21*, 4776.



(5)

7a

temperature too. The Si−H signal of **7a** in the ^{1}H NMR spectrum displays a triplet at 5.88 ppm (t, J(H−H) = 2.4 Hz), and the hydride signal is found at −12.20 ppm (dt, J(P−H) = 27.9 Hz, J(H−H) = 2.4 Hz). The reaction of the trideuteride $Cp^*(Pr^i_3P)Ru(D)_3$ with $HSiCl_3$ in the presence of $NEtPr^i_2$ during 24 h gives a partially deuterated product, $Cp^*(Pr^i_3P)Ru(H)_{1.21}(D)_{0.79}(SiH_{1.48}D_{0.52}Cl)$.

Given the facile preparation of H_2SiCl_2*teeda (teeda = tetraethylethylenediamine) upon reaction of $HSiCl_3$ with teeda,[51] we considered that other amines, NEt_3 and $NEtPr^i_2$, also could cause such a redistribution reaction, affording silanes amenable to give **6** and **7** by Si−H oxidative addition. To check this hypothesis, the room-temperature and thermal reactions of $HSiCl_3$ with NEt_3 and $NEtPr^i_2$ have been studied by NMR. In both cases the formation of some amount of a white amorphous precipitate, presumably the adduct of $HSiCl_3$ with the amine, was observed.[52] No Si−H-containing products apart from the starting $HSiCl_3$ were found in the room-temperature reaction with NEt_3, and only traces of H_2SiCl_2 were observed after heating for 15 h at 65 °C. In contrast, both the room-temperature and thermal reactions (15 h at 65 °C) of $HSiCl_3$ with $NEtPr^i_2$ gave partial conversion to H_2SiCl_2 characterized by its Si−H signal at 4.78 ppm (J(Si−H) = 306 Hz) in the ^{1}H NMR spectrum.[53] In both cases the C_6D_6-soluble part contained about 20% of the redistribution product, suggesting that an equilibrium was reached (due to the formation of a precipitate, the exact yield cannot be determined). Thus, in both cases the silanes amenable to produce **6** and **7** by the Si−H oxidative addition were not present in any significant amount in the reaction mixtures. The reason behind the difference in the chemical behavior of NEt_3 and $NEtPr^i_2$ is not quite clear at the moment, although we noticed that the redistrution of $HSiCl_3$ is caused only by a bulkier diamine such as teeda, whereas tmeda (tmeda = tetramethylethylenediamine) gave only the adduct $HSiCl_3$*tmeda.[51b]

With the aim of independent preparation of compound **7a** we attempted the synthesis of the precursor complex $Cp^*(Pr^i_3P)Ru(H)_2(SiH_3)$ (**8a**).[54] The reaction of a mixture of $Cp^*(Pr^i_3P)Ru(Cl)(SiCl_3)(H)$ (**5a**) and $Cp^*(Pr^i_3P)Ru(H)_2(SiHCl_2)$ (**6a**) with $LiAlH_4$ in ether, followed by a workup, gives $Cp^*(Pr^i_3P)Ru(H)_3$ and complex **8a** in 27% isolated yield. The identity of the latter compound was established by spectroscopic methods, and its connectivity was confirmed by an X-ray study (vide infra). The ^{1}H NMR spectrum of **8a** displays a hydride signal at −12.17 ppm (d, J(P−H) = 28.8 Hz) and a singlet due to the Si−H group at 4.02 ppm. It is noteworthy that the absence of a chlorine substituent at silicon results in the absence of coupling between the hydrides at the Si and Ru centers. This can be attributed to the diminished Si s-contribution in the Ru−Si bond in accordance with Bent's rule. The attempted reaction of **8a** with excess ammonium salt $[HNMe_2Ph]Cl$ in benzene during 24 h gave 20% conversion to **7a** and a significant amount of $Cp^*(Pr^i_3P)RuH_3$ resulting from the protonation of the Ru−Si bond. The lack of selectivity limits the preparative utility of this approach.

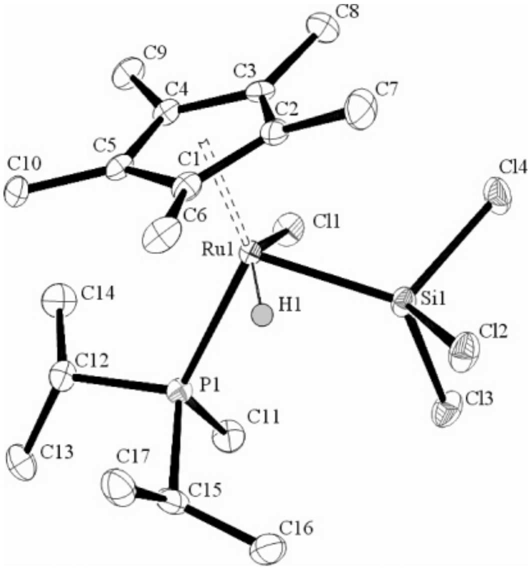


Figure 3. Molecular structure of complex **5b**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms on carbons are omitted for clarity.

The molecular structure of complexe **5b** is shown in Figure 3, and the corresponding figures for **5c** and **5d** are deposited in the Supporting Information. In all the structures, the hydride occupies the position between the two bulkiest non-Cp substituents, the phosphine and silyl groups, to minimize the steric strain. Selected molecular parameters for **5b**, **5c**, and **5d** are gathered in Table 3. The Ru−Si bond lengths of 2.3153(8), 2.3111(5), and 2.3107(7) Å in **5b**, **5c**, and **5d**, respectively, are somewhat shorter than the corresponding bond in the related formally Ru(IV) compound $[Cp(Me_3P)_2Ru(\eta^2\text{-}H\text{-}SiCl_3)]^+$ (2.329(1) Å), rationalized to be a silane σ-complex,[23] but longer than the Ru−Si bond in the Ru(II) compound $Cp(Me_3P)_2Ru(SiCl_3)$ (2.265(5) Å), in which the bond is further contracted due to the negative hyperconjugation Ru→(Si−Cl)*.[23] The related

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(51) (a) Kloos, S. D.; Boudjouk, P. In *Inorganic Synthesis*; Darensbourg, M. Y., Ed.; Wiley: New York, 1998; Vol. 32, p 294. (b) Boudjouk, P.; Kim, P. B.-K.; Kloos, S. D.; Page, M.; Thweatt, D. *J. Chem. Soc., Dalton Trans.* **1998**, 877.

(52) (a) Ault, B. S.; Jeng, M. L. H. *Inorg. Chem.* **1990**, *29*, 837. (b) Kummer, D.; Chaudhry, S. C.; Debaerdemaeker, T.; Thewalt, U. *Chem. Ber.* **1990**, *123*, 945. (c) Kummer, D.; Chaudhry, S. C.; Depmeier, W.; Mattern, G. *Chem. Ber.* **1990**, *123*, 2241. (d) Corriu, R. J. P.; Chuit, C.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(53) The ^{1}H NMR signal of H_2SiCl_2 in $CDCl_3$ was reported at 5.40 ppm with J(Si−H) = 288 Hz, but coordination of teeda causes a high-field shift to 4.99 ppm (J(Si−H) = 404 Hz).[51a] Therefore the observed signal of H_2SiCl_2 in C_6D_6 with the somewhat increased J(Si−H) is most likely due to the complexed form $H_2SiCl_2*(NEtPr^i_2)_x$. The simultaneously observed signal of $HSiCl_3$ (5.38 ppm (J(Si−H) = 371 Hz) in C_6D_6 versus 5.42 ppm (J(Si−H) = 370 Hz) was in the normal place.

(54) Complexes with the ligand SiH_3 are rare. (a) See ref 50. (b) Hao, L.; Lebuis, A.-M.; Harrod, J. F. *Chem. Commun.* **1998**, 1089. (c) Wekel, H.-U.; Malisch, W. *J. Organomet. Chem.* **1984**, *264*, C10. (d) Hagen, A. P.; Higgns, C. R.; Russo, P. J. *Inorg. Chem.* **1971**, *10*, 1657. (d) Petri, S. H. A.; Neumann, B.; Stammler, H.-G.; Jutzi, P. *J. Organomet. Chem.* **1998**, *553*, 317. (e) Jiang, Q.; Carrol, P. J.; Bery, D. H. *Organometallics* **1991**, *10*, 3648. (f) Robiette, A. G.; Scheldrick, G. M.; Simpson, R. N. F.; Aylett, B. J.; Campbell, J. A. *J. Organomet. Chem.* **1968**, *14*, 279. (g) Rankin, D. W. H.; Robertson, A. *J. Organomet. Chem.* **1975**, *85*, 225. (g) Rankin, D. W. H.; Robertson, A. *J. Organomet. Chem.* **1976**, *105*, 331.

Table 3. Bond Lengths (Å) and Angles (deg) for 5b, 5c, and 5d

	5b	5c	5d
Ru(1)–Si(1)	2.3152(8)	2.3111(5)	2.3107(7)
Ru(1)–P(1)	2.3694(8)	2.3231(4)	2.3255(6)
Ru(1)–Cl(1)	2.4125(7)	2.4164(4)	2.4234(6)
Cl(2)–Si(1)	2.099(1)	2.0813(7)	2.1017(9)
Cl(3)–Si(1)	2.092(1)	2.0945(7)	2.0800(9)
Cl(4)–Si(1)	2.089(1)	2.1044(7)	2.1018(9)
Ru(1)–H(1)	1.36(2)	1.49(3)	1.62(3)
Si(1)–Ru(1)–P(1)	101.79(3)	106.19(2)	107.11(2)
Si(1)–Ru(1)–Cl(4)	82.26(3)	81.99(2)	83.47(2)
P(1)–Ru(1)–Cl(1)	85.17(3)	82.700(2)	81.38(2)
Cl(2)–Si(1)–Cl(3)	100.01(5)	100.78(3)	101.32(4)
Cl(2)–Si(1)–Cl(4)	100.52(5)	101.13(3)	100.47(4)
Cl(3)–Si(1)–Cl(4)	99.56(5)	100.39(3)	99.68(4)
Cl(2)–Si(1)–Ru(1)	116.74(4)	120.53(3)	114.30(3)
Cl(3)–Si(1)–Ru(1)	121.51(4)	115.96(2)	120.90(4)
Cl(4)–Si(1)–Ru(1)	115.02(4)	114.98(3)	116.96(3)

Ru(II) complex (p-$^{t}Bu_2C_6H_4$)(CO)Ru($SiCl_3$)$_2$, with a π-acceptor ligand, exhibits longer Ru–Si bonds (2.338(1) and 2.340(1) Å).[33c] Surprisingly enough, in apparent violation of Bent's rule, the Ru–Si bond lengths in **5b**, **5c**, and **5d** are between the values observed in **2a** (2.2950(5) Å) and the monochlorosilyl complexes discussed above (range 2.332–2.364(2) Å, with the exception of Cp*(Pr^i_3P)Ru(H)$_2$(SiHClMes), having an even shorter Ru–Si bond of 2.302(3) Å). However, this irregularity can be rationalized if one takes into account the increased steric strain in **5** due to the presence of a bulkier chlorine group on ruthenium in place of hydride in **5b**,**c**,**d**, which is expected to result in the elongation of the Ru–Si bond. This effect might be at least partially compensated for by the contraction of the Ru atomic radius caused by the stronger electron-withdrawing effect of the chlorine group and hence the decrease of the Ru–ligand distances. However, the comparison of the molecular parameters of **2c** with those of **5c** shows that the latter complex indeed has a longer Ru–P bond (2.2888(9) versus 2.3231(4) Å), whereas the Ru–Si bond remains virtually the same (2.3099(9) Å in **2c** and 2.3111(5) Å in **5c**, respectively), in spite of the presence of three Cl atoms on Si in **5c** versus only two Cl atoms in **2c**, and thus the steric factor appears to dominate. The explanation in terms of steric effects is further justified if one compares the rather long Ru–P bond lengths of 2.3694(8), 2.3231(4), and 2.3255(6) Å in **5b**, **5c**, and **5d**, respectively, with the range 2.2050–2.3097(9) Å found for other complexes discussed in this work. The decrease of the Ru–Si bond length along the series **5b**, **5c**, and **5d** is consistent with the diminishing steric strain, as is the decrease of the Ru–P bond lengths on going from **5b** (2.3694(8) Å) to **5c** (2.3231(4) Å), whereas further minor elongation of this bond in **5d** (2.3255(6) Å) may reflect the decreased basicity of the phosphine.

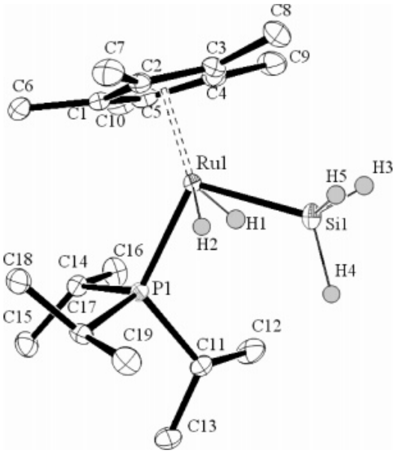


Figure 4. Molecular structure of complex **8a**. Thermal ellipsoids are given at the 50% probability level. Hydrogen atoms on carbons are omitted for clarity.

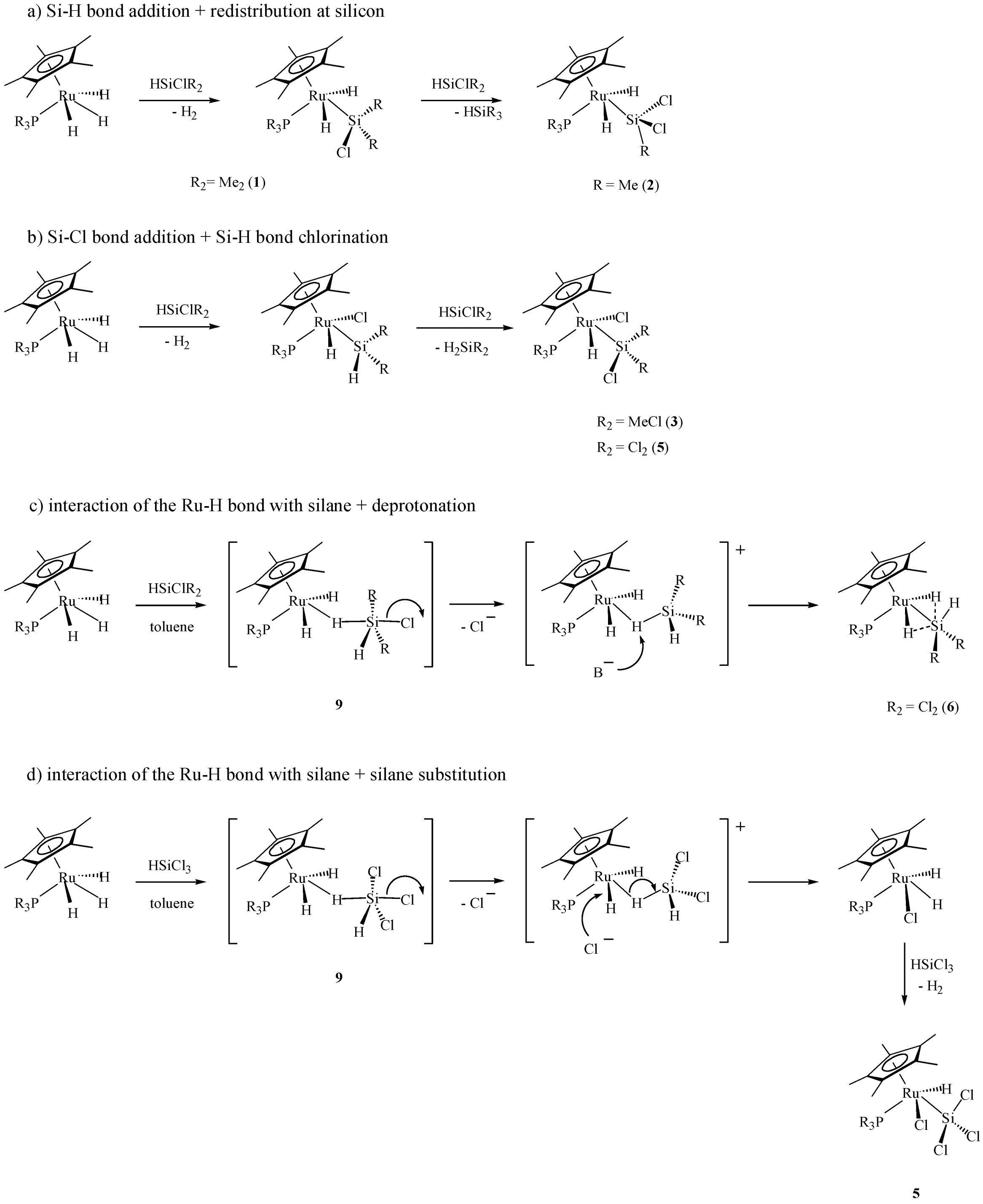
Table 4. Bond Lengths (Å) and Angles (deg) for 8a

Ru(1)–Si(1)	2.3341(6)	Ru(1)–P(2)	2.3064(5)
Ru(1)–H(1)	1.55(3)	Ru(1)–H(2)	1.57(3)
Si(1)–H(3)	1.43(3)	Si(1)–H(4)	1.46(3)
Si(1)–H(5)	1.43(3)		
Si(1)–Ru(1)–P(2)	102.03(2)	H(1)–Ru(1)–H(2)	110(2)
P(1)–Ru(1)–H(1)	74(1)	Si(1)–Ru(1)–H(1)	65(1)
P(1)–Ru(1)–H(2)	74(1)	Si(1)–Ru(1)–H(2)	63(1)
Ru(1)–Si(1)–H(3)	116(1)	Ru(1)–Si(1)–H(4)	119(1)
Ru(1)–Si(1)–H(5)	113(1)	H(3)–Si(1)–H(4)	102(2)
H(3)–Si(1)–H(5)	103(2)	H(4)–Si(1)–H(5)	101(2)

The molecular structure of compound **8a** is presented in Figure 4, and selected molecular parameters are gathered in Table 4. The molecular geometry is very much the same as in complexes **1a** and **1b** discussed above. The Ru–Si bond of 2.3341(6) Å is comparable in length to the corresponding bonds in **1a** and **1b**, suggesting that the electron-accepting ability of three hydrogen atoms in **8** (the sum of Tolman's electronic parameter is 24.9)[44] is of the same magnitude as that of the Me_2Cl set in **1a** and **1b** (the sum of Tolman's electronic parameter is 20.0).[44] The Ru–P bond length (2.3064(5) Å) and the P–Ru–Si bond angle (102.03(2)°) are also very close to the corresponding parameters in **1a** and **1b** (2.3097(9) and 2.3079(7) Å and 102.70(3)° and 104.66(3)°, respectively). The Ru–H bonds (1.55(3) and 1.57(3) Å) and the Si–H bonds (range 1.43–1.46(3) Å) in **8** are normal.

4. Discussion of the Interaction of Ruthenium Trihydrides with Chlorosilanes. It is obvious that the reactions of the trihydrides Cp*(R_3P)Ru(H)$_3$ with chlorosilanes occur in a complex manner and are accompanied by redistribution processes at the silyl center. We have anticipated three reaction pathways for this interaction shown in Scheme 1. The simpliest reaction is based on the thermally induced elimination of dihydrogen from Cp*(R_3P)Ru(H)$_3$ to give a transient complex Cp*(R_3P)RuH amenable to the oxidative addition of the H–Si bond of a silane (path a). This mechanism is the most likely one for the formation of compounds **1**, although the overall cause of the reaction is complicated by a redistribution at the silicon center to give **2**. There is a clear trend that the diminished steric bulkiness of the phosphine ligand facilitates the Me/Cl exchange in the silyl ligand. At the moment we have no working hypothesis how this exchange occurs. It is also noteworthy that the reactions of the silanes $HSiMeCl_2$ and $HSiCl_3$ with the trihydrides Cp*(R_3P)Ru(H)$_3$ proceed at noticeably lower temperatures (60 °C and room temperature, respectively) than the analogous reactions of $HSiMe_2Cl$ (90 °C). Taking into account that any thermally induced elimination of dihydrogen from Cp*(R_3P)Ru(H)$_3$ takes place only at temperatures above 90 °C, these results appear to be rather paradoxal. However, the elimination of dihydrogen from the trihydride can be facilitated by the coordination of a Lewis acidic silane to the Ru–H bond. Such a Lewis acid-

Scheme 1



promoted elimination of dihydrogen has been predicted in a theoretical study.[55]

The second mechanism in Scheme 1 (path b) differs from the first one in that the Si−Cl bond addition happens in preference to the Si−H bond addition. Usually, the stronger and kinetically more inert Si−Cl bond is less prone to oxidative addition than the Si−H bond. However, given the literature precedents[46] and the addition of $MeSiCl_3$ to the compound $Cp^*(MePr^i_2P)Ru(H)_3$ to give $Cp^*(MePr^i_2P)Ru(Cl)(SiMeCl_2)(H)$ (**3b**), such a possibility cannot be a priori ruled out. Therefore route b can, in principle, account for the formation of complexes **3** and **5**, if one assumes that the Si−H bond in the initially formed complexes $Cp^*(MePr^i_2P)Ru(Cl)(SiHRCl)(H)$ (R = Me, Cl) can be chlorinated by excess chlorosilane. An argument against this pathway is based on the more forced conditions (100 °C), required in the reaction of $MeSiCl_3$, than those used in the preparation of complexes **3** and **5** (60 °C and room temperature, respectively).

The last mechanism (paths c and d) in Scheme 1 is based on the *direct interaction* of a chlorosilane with the metal−hydride bond.[44] This reaction is believed[44]

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[55] (a) Camanyes, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *Chem. Eur. J.* **1999**, *5*, 1166. (b) Camanyes, S.; Maseras, F.; Moreno, M.; Lledós, A.; Lluch, J. M.; Bertrán, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 265.

to occur via a hypercoordinate silicon intermediate and, depending on the basicity of the metal−hydride bond and the Lewis acidity of the chlorosilane, leads either to the M−Si[43−45] (route c) or to M−Cl (route d) bond formation.[44] The base used to deprotonate the adduct **9** between the trihydride and a chlorosilane can be just another equivalent of the ruthenium hydride, as it was observed by Lemke et al. for the related reactions of Cp(R_3P)$_2$RuH with chlorosilanes.[43] In this case, the initially formed ruthenium coproduct will be the cationic complex [Cp*(R_3P)Ru(H_2)$_2$]$^+$ (or [Cp*(R_3P)Ru(H_2)(H)$_2$]$^+$),[56] which after the elimination of dihydrogen followed by the coordination of the chloride anion to [Cp*(R_3P)Ru(H_2)]$^+$ will afford the complex Cp*(R_3P)Ru(H)$_2$Cl. The latter compound is known to be unstable,[30] easily eliminating dihydrogen to give the unsaturated species Cp*(R_3P)RuCl amenable to react with the Si−H bond of the silane.[28,29] Thus, this reaction sequence allows for an alternative explanation of the formation of complexes **5** under mild conditions. The room-temperature reaction of Cp*(Pr^i_3P)Ru(H)$_3$ with $HSiCl_3$, affording a 1:1 mixture of **5a** and **6a**, and formation of **4** in the reactions of Cp*(R_3P)Ru(H)$_3$ with $HSiMeCl_2$ support this mechanism. Finally, the reaction pathway (d) differs from (c) in that the chloride anion substitutes the silane in the coordination sphere of ruthenium in [Cp*(R_3P)Ru(H_2)(H-$SiCl_2$H)]$^+$, affording Cp*(R_3P)Ru(H)$_2$Cl and eventually **5** as described above in (c). Apparently, routes (c) and (d) can compete. The observation of a minor amount of complex Cp*(Pr^i_3P)Ru(H)$_2$(SiH_2Cl) (**7a**) along with Cp*(Pr^i_3P)Ru(Cl)($SiCl_3$)(H) (**5a**) and Cp*(Pr^i_3P)Ru(H)$_2$($SiHCl_2$) (**6a**) in the thermal reaction of Cp*(Pr^i_3P)Ru(H)$_3$ with $HSiCl_3$ lends some support to the route (d) since this gives **5a** and the silane H_2SiCl_2, which is a feasible precursor to **7a** according to the route (c) and to **6a** via the Si−H bond oxidative addition.

Unexpected results were observed when amines were used to consume the HCl released.[44] The first important observation is that addition of NEt_3 completely stops the formation of a Ru−Cl bond in the case of $HSiMeCl_2$ and significantly diminishes the formation of complexes **5** in the reactions with $HSiCl_3$. However, in both cases only weak signals in the ^{1}H NMR spectra attributable to the H/Si exchange products Cp*(R_3P)Ru(H)$_2$(SiHRCl) (R = Me, Cl, respectively) were observed. Second, the reaction requires higher temperatures, and finally, a formal Si−H addition product is formed in eq 3. These observations can be explained in the following way. The addition of an amine to the mixture of Cp*(R_3P)Ru(H)$_3$ and $HSiCl_2Me$ decreases the effective acidity of the silane, due to the reversible complexation of the amine to silane to give an adduct $Et_3N\rightarrow SiR_3Cl$.[52] Since the Ru−H bond in the Ru(IV) complex Cp*(R_3P)Ru(H)$_3$ is less basic than that in the Ru(II) complex Cp(Me_3P)$_2$Ru(H) studied by Lemke et al.,[44] it cannot effectively compete with the amine for the silicon center to give adduct **9** in Scheme 1, so that for $HSiMeCl_2$ both the direct H/Si and H/Cl exchange reactions are suppressed and the usual sequence of dihydrogen elimination from Cp*(R_3P)Ru(H)$_3$ and the silane Si−H bond addition to the intermediate Cp*(R_3P)Ru(H) becomes favorable (route (a) in Scheme 1). Thus, the addition of an amine suppresses the interaction of $HSiMeCl_2$ with the Ru−H bond, which otherwise leads to the formation of a Ru−Cl bond in **3**. For the more acidic silane $HSiCl_3$, all three reactions (H−Si addition, H/Si, and H/Cl exchanges) compete under these conditions and lead to the observed products Cp*(R_3P)Ru(H)$_2$($SiCl_3$), Cp*(R_3P)Ru(H)$_2$($SiHCl_2$) (**6**), and Cp*(R_3P)Ru(Cl)($SiCl_3$)(H) (**5**), respectively.

Another unexpected feature of the reactions with amine is their surprising sensitivity to the nature of the amine employed. The difference in product composition of the reactions in the presence of NEt_3 versus $NEtPr^i_2$ remained a puzzle to us until we found that the latter amine easily promotes the formation of H_2SiCl_2 from $HSiCl_3$ at room temperature whereas NEt_3 does not. Lemke et al. showed that the H/Si exchange is very sensitive to steric hindrance of the silane, so one can expect that the reaction of Cp*(Pr^i_3P)Ru(H)$_3$ with $HSiCl_3$ to give **6a** and **6a′** is slower than its reaction with H_2SiCl_2 to give Cp*(Pr^i_3P)Ru(H)$_2$(SiH_2Cl) (**7a**). The facile room-temperature reaction of Cp*(Pr^i_3P)Ru(H)$_3$ with $HSiCl_3$ in the presence of a weakly coordinating amine $NEtPr^i_2$ to give **7a** (eq 5) provides further support to the H/Si exchange mechanism (route c), as neither the H−Si addition nor H/Cl exchange products are formed. The lack of reaction between $HSiCl_3$ and NEt_3, but formation of H_2SiCl_2 in the analogous reaction with $NEtPr^i_2$, showed that the silane precursors H_xSiCl_{4-x} to **6** and **7** through the Si−H oxidative addition reactions (H_2SiCl_2 and H_3SiCl, respectively) are absent in the reaction mixtures. However, these products could be formed from the trihydrides by the H/Si exchange with $HSiCl_3$ and H_2SiCl_2, respectively.

Conclusions

The initial goal of this study was to prepare a series of half-sandwich silyl hydride complexes of ruthenium and to study the occurrence and strength of any H−Si interaction in these compounds, as a function of the electronic and steric properties of the substituent at phosphorus and silicon atoms. The reactions of ruthenium trihydrides Cp*(R_3P)RuH$_3$ with chlorosilanes occur in a complex manner and generally result in several products. Even for the least Lewis acidic silane used, $HSiClMe_2$, an unexpected redistribution process at the silicon center was observed, which led to the formation of complexes Cp*(R_3P)RuH$_2$($SiCl_2Me$) (**2**) in addition to the Si−H addition products Cp*(R_3P)RuH$_2$($SiClMe_2$) (**1**). The decrease of the steric bulk of the phosphine ligand from Pr^i_3P to Pr^iMe_2P and $PhMe_2P$ appears to be the dominating factor that facilitates such an exchange reaction, but its precise mechanism still remains unknown. With more acidic silanes, $HSiCl_2Me$ and $HSiCl_3$, the formation of the Ru−Cl bond becomes one of the major reaction routes. An unexpected feature of the reactions of Cp*(R_3P)RuH$_3$ with these silanes is that they crucially depend on the presence and nature of added amine. The amines (NEt_3 and $NEtPr^i_2$) are believed to play a multiple role in this reaction. First, they reduce the Lewis acidity of silanes, thus either stopping (in the case of $HSiCl_2Me$) the interaction of the silane with the Ru−H bond or increasing its selectivity (in the case of $HSiCl_3$). Second, they serve as external Lewis bases to consume the HCl released during the H/Si exchange. And finally, $NEtPr^i_2$ was found to cause

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(56) Grundemann, S.; Ulrich, S.; Limbach, H.-H.; Golubev, N. S.; Denisov, G. S.; Epstein, L. M.; Sabo-Etienne, S.; Chaudret, B. *Inorg. Chem.* **1999**, *38*, 2550.

a redistribution reaction of the starting silane $HSiCl_3$ to give H_2SiCl_2.

To probe the occurrence of H−Si interactions in the silyl hydride derivatives prepared in this work, X-ray structures of several representatives with different numbers of chlorine substituents at silicon and different bulk and basicity of phosphines have been established. Although, some structural trends in the monocloro- and dichloro-substituted silyl derivatives are consisent with the presence of interligand hypervalent interaction (M−H···Si−Cl in **1a** and **1b** and double interaction $M{-}H_2{\cdots}Si{-}Cl_2$ in **2a** and **2b**), conclusive evidence is absent. The measurement of NMR Si−H coupling constants showed values less than 14 Hz in all compounds, which is better in accord with a classical description of these complexes, although our recent studies showed that there is no strict correlation between the magnitude of *J*(Si−H) and the strength of interligand interaction.[34b,i,40] In conclusion, although there is still a potential that the $Cp^*(R_3P)$ fragment can support the occurrence of H−Si interaction in its silyl hydride derivatives, a thorough theoretical study is required to clear up this problem.

Experimental Section

All manipulations were carried out using conventional high-vacuum or argon-line Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl and either kept under argon or distilled into the reaction vessel by high-vacuum gas-phase transfer. NMR spectra were recorded on Bruker (^{1}H, 300 MHz; ^{13}C, 75.4 MHz, ^{29}Si 59.6 MHz) and Varian (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{31}P, 161.9 MHz) spectrometers. The positions of the ^{29}Si NMR signals of complexes containing the SiMe groups were determined by ^{1}H−^{29}Si gHMQC experiments. IR spectra were obtained as Nujol mulls with a FTIR Perkin-Elmer 1600 series spectrometer. $RuCl_3$*(aq) and silanes were obtained from Sigma-Aldrich. Complexes $Cp^*(R_3P)RuH_3$[57] and phosphines were prepared according to the literature methods.

Preparation of $Cp^*(Pr^i_3P)RuH_2SiClMe_2$ (1a). To 0.400 g (1 mmol) of $Cp^*Ru(PPr^i_3)H_3$ in 20 mL of toluene was added 1 mL (9 mmol) of $HSiMe_2Cl$. The reaction mixture was heated to 90 °C during 4 h. The volatiles were removed in a vacuum to afford a maroon amorphous product. This compound was dissolved in 20 mL of ether, and the solution was filtered and slowly (5 days) concentrated to 1 mL at room temperature to give colorless crystals. The solution was decanted, and crystals were washed by 5 mL of cold hexane. Yield: 0.150 g (30%). The X-ray quality crystals were obtained by cooling a dilute ether solution to −30 °C. IR (Nujol): ν(Ru−H) 1998.0 and 2026.0 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.79 (s, 15, $C_5(CH_3)_5$), 1.81 (dsept, *J*(H−H) = 7.4 Hz, *J*(P−H) = 15.9 Hz 3, $PCH(CH_3)_2$), 0.99 (dd, *J*(H−H) = 7.4 Hz, *J*(P−H) = 13.2 Hz, 18, $PCH(CH_3)_2$), 0.98 (s, 6, $Si(CH_3)$), −12.23 (d, *J*(P−H) = 28.0 Hz + *J*(Si−H) = 11.7 Hz, 2, RuH_2). ^{13}C NMR (C_6D_6): δ 95.8 (s, $C_5(CH_3)_5$), 27.9 (br s, P $CH(CH_3)_2$), 19.5 (s, $PCH(CH_3)_2$), 17.8 (s, Si(CH)), 11.4 ($C_5(CH_3)_5$). ^{31}P NMR (C_6D_6): 83.1 (s). ^{29}Si NMR (C_6D_6): δ 63.3. Anal. Calcd for $C_{21}H_{44}ClPRuSi$: C 51.25; H 9.01. Found: C 51.21; H 8.95.

Preparation of $Cp^*(MePr^i_2P)RuH_2SiMe_2Cl$ (1b). To 0.370 g (1 mmol) of $Cp^*(MePr^i_2P)RuH_3$ in 20 mL of toluene was added 1 mL (9 mmol) of $HSiMe_2Cl$. The reaction mixture was heated to 90 °C during 6 h. The volatiles were removed in a vacuum to afford a dark red solid. This material was dissolved in 20 mL of hexane, and the solution was filtered and slowly (1 week) concentrated to 1 mL at room temperature to give orange crystals. The solution was decanted, and crystals were washed by 5 mL of cold hexane. Yield: 0.200 g (43%) of a light yellow compound. The X-ray quality crystals were obtained by cooling a dilute hexane solution to −30 °C. IR (Nujol): ν(Ru−H) 1952.0, 2026.0 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.81 (d, *J*(P−H) = 1.3 Hz, 15, $C_5(CH_3)_5$), 1.55 (sept, *J*(H−H) = 7.0 Hz, 2, $PCH(CH_3)_2$), 1.00 (s, 6, $SiCH_3$), 0.91 (dd, *J*(H−H) = 7.2 Hz, *J*(P−H) = 16.2 Hz, 6, $PCH(CH_3)_2$), 0.85 (d, *J*(P−H) = 7.4 Hz, 3, PCH_3), 0.72 (dd, *J*(H−H) = 6.9 Hz, *J*(P−H) = 13.8 Hz, 6, $PCH(CH_3)_2$), −12.21 (d, *J*(P−H) = 28.6 Hz + *J*(Si−H) = 12.9 Hz, 2, RuH_2). ^{13}C NMR (C_6D_6): δ 95.7 (d, *J*(P−C) = 1.7 Hz, $C_5(CH_3)_5$), 28.5 (d, *J*(P−C) = 27.2 Hz, $PCH(CH_3)_2$), 18.2 (broad s, $PCH(CH_3)_2$ and PCH_3), 16.7 (s, $SiCH_3$), 11.5 (d, *J*(P−C) = 1.7 Hz, $C_5(CH_3)_5$). ^{31}P NMR (C_6D_6): δ 60.0 (s). ^{29}Si NMR (C_6D_6): δ 61.5. Anal. Calcd for $C_{19}H_{40}ClPRuSi$: C 49.17; H 8.69. Found: C 49.21; H 8.65.

Reaction of $Cp^*(Me_2Pr^iP)RuH_3$ with $HSiMe_2Cl$ to Give $Cp^*(Me_2Pr^iP)RuH_2SiMe_2Cl$ (1c) and $Cp^*(Me_2Pr^iP)RuH_2SiMeCl_2$ (2c). To 0.150 g (0.37 mmol) of $Cp^*(Me_2Pr^iP)RuH_3$ in 20 mL of toluene was added 0.2 mL (1.85 mmol) of $HSiMe_2Cl$. The reaction mixture was heated to 90 °C during 3.5 h. The volatiles were removed in a vacuum to afford a dark red solid. This material was dissolved in 20 mL of ether, and the dark red-violet solution was filtered from the red-brown residue and slowly concentrated to 1 mL at room temperature to give white crystals. The viscous red-violet solution was decanted, and the crystals were washed by 2 mL of cold ether. Yield: 0.060 g of white compound. The NMR check showed formation of a 1:1 mixture of $Cp^*(Me_2Pr^iP)RuH_2SiMe_2Cl$ and $Cp^*(Me_2Pr^iP)RuH_2SiMeCl_2$. An X-ray quality crystal of $Cp^*(Me_2Pr^iP)RuH_2SiMeCl_2$ was obtained from the ether solution of the mixture. IR (Nujol): ν(Ru−H) 1968.0 cm^{-1}.

$Cp^*(Me_2Pr^iP)RuH_2SiMe_2Cl$ (1c). ^{1}H NMR (C_6D_6): δ 1.80 (s, 15, $C_5(CH_3)_5$), 1.33 (sept, *J*(H−H) = 7.5 Hz, 1, $PCH(CH_3)_2$), 1.01 (s, 6, $SiCH_3$), 0.98 (d, *J*(P−H) = 8.7 Hz, 6, PCH_3), 0.78 (dd, *J*(H−H) = 7.5 Hz, *J*(P−H) = 16.2 Hz, 6, $PCH(CH_3)$), −12.13 (d, *J*(P−H) = 29.4 Hz + *J*(Si−H) = 12.9 Hz, 2, RuH_2). ^{13}C NMR (C_6D_6): δ 95.7 (d, *J*(P−C) = 1.8 Hz, $C_5(CH_3)_5$), 32.4 (d, *J*(P−C) = 31.1 Hz, $PCH(CH_3)$), 19.0 (d, *J*(P−C) = 20.0 Hz, PCH_3), 18.2 (s, $SiCH_3$), 17.3 (s, $PCH(CH_3)$), 11.4 (s, $C_5(CH_3)_5$). ^{31}P NMR (C_6D_6): δ 35.6 (s). ^{1}H−^{29}Si gHMQC (C_6D_6): 61.9.

$Cp^*(Me_2Pr^iP)RuH_2SiMeCl_2$ (2c). ^{1}H NMR (C_6D_6): δ 1.77 (s, 15, $C_5(CH_3)_5$), 1.35 (sept, *J*(H−H) = 7.5 Hz, 1, $PCH(CH_3)_2$), 1.28 (s, 3, $SiCH_3$), 0.93 (d, *J*(P−H) = 9.0 Hz, 6, PCH_3), 0.72 (dd, *J*(H−H) = 7.5 Hz, *J*(P−H) = 15.3 Hz, 6, $PCH(CH_3)$), −11.54 (d, *J*(P−H) = 29.2 Hz + *J*(Si−H) = 11.0 Hz, 2, H). ^{13}C NMR (C_6D_6): δ 96.9 (s, $C_5(CH_3)_5$), 31.9 (d, *J*(P−C) = 32.3 Hz, $PCH(CH_3)$), 23.8 (s, $SiCH_3$), 19.2 (d, *J*(P−C) = 29.3 Hz, PCH_3), 17.2 (s, $PCH(CH_3)$), 11.1 (s, $C_5(CH_3)_5$). ^{31}P NMR (C_6D_6): δ 33.3 (s). ^{29}Si NMR (C_6D_6): δ 68.2.

Reaction of $Cp^*(Me_2PhP)RuH_3$ with $HSiMe_2Cl$. To 0.210 g (0.56 mmol) of $Cp^*(Me_2PhP)RuH_3$ in 20 mL of toluene was added 0.3 mL (2.70 mmol) of $HSiMe_2Cl$. The reaction mixture was heated to 90 °C during 5 h. A specimen was taken form the toluene solution. The NMR check showed the formation of a mixture of 1:1:1 $Cp^*(Me_2PhP)RuH_2SiMe_2Cl$ (**1d**), $Cp^*(Me_2PhP)RuH_2SiMeCl_2$ (**2d**), and another yet unidentified phosphine complex.

$Cp^*(Me_2PhP)RuH_2SiMe_2Cl$ (**1d**). ^{1}H NMR (C_6D_6): δ 1.63 (d, *J*(P−H) = 1.5, 15, $C_5(CH_3)_5$), 1.26 (d, *J*(P−H) = 9.1 Hz, 6, PCH_3), 1.01 (s, 6, $SiCH_3$) −12.11 (d, *J*(P−H) = 29.5 Hz, 2, RuH_2). ^{31}P NMR (C_6D_6): δ 18.4 (s).

$Cp^*(Me_2PhP)RuH_2SiMeCl_2$ (2d). ^{1}H NMR (C_6D_6): δ 1.59 (d, *J*(P−H) = 1.8 Hz, $C_5(CH_3)_5$), 1.36 (s, 3, $SiCH_3$), 1.19 (d, *J*(P−H) = 9.7 Hz, 6, PCH_3), −11.55 (d, *J*(P−H) = 28.8 Hz, 2, RuH_2).

Preparation of $Cp^*(Pr^i_3P)RuH_2SiMeCl_2$ (2a). To the solution of the compound $Cp^*(Pr^i_3P)RuH_3$ (0.400 g, 1.0 mmol) in 20 mL of toluene were added NEt_3 (0.5 mL, 6.9 mmol) and $HSiMeCl_2$ (0.82 mL,10 mmol). The reaction mixture was heated during 14 h to 90 °C to give a misty orange solution.

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NMR test showed the completion of the reaction and formation of only the final complex. The volatiles were removed in a vacuum to give an orange-red oil. The product was washed with 5 × 20 mL of hexane, and the hexane solutions were decanted, combined, and dried in vacuo to give a red oil. To this oil was added 10 mL of hexane, and the solution was decanted and cooled to −30 °C. A greenish-white powder was formed. The cold solution was decanted to the flask with the red oil, the mixture was warmed to room temperature, the oil was stirred in hexane, and the extraction was repeated in this way six times. This procedure gave 90 mg of light green crystalline compound. Yield: 18%. The crystals for the X-ray study were obtained by very slow concentration of a hexane solution of the product. The complex decomposes in ether solution. IR (Nujol): ν(Ru–H) 2010.0, 2081.0 cm^{-1}. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.81 (dsept, J(P–H) = 7.2 Hz, J(H–H) = 7.0 Hz, 3, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.78 (s, 15, $\mathrm{C_5}(\mathrm{C}H_3)_5$), 1.22 (s, 3, $\mathrm{SiC}H_3$), 0.93 (dd, J(P–H) = 13.2 Hz, J(H–H) = 7.0 Hz, 18, $\mathrm{PCH}(\mathrm{C}H_3)_2$), −11.55 (d, J(P–H) = 27.9 Hz, 2, $\mathrm{Ru}H_2$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 97.1 (d, J(P–C) = 1.8 Hz, $C_5(\mathrm{CH_3})_5$), 27.9 (d, J(P–C) = 22.0 Hz, $\mathrm{P}C\mathrm{H}(\mathrm{CH_3})$), 22.8 (s, $\mathrm{Si}C\mathrm{H_3}$), 19.4 (s, $\mathrm{PCH}(C\mathrm{H_3})_2$), 11.1 (s, $\mathrm{C_5}(C\mathrm{H_3})_5$)). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 82.0 (s). ^{29}Si NMR ($\mathrm{C_6D_6}$): δ 69.9. Anal. Calcd for $\mathrm{C_{20}H_{41}Cl_2PRuSi}$: C 46.86; H 8.06. Found: C 46.98; H 8.01.

Decomposition of $\mathrm{Cp^*(Pr^i_3P)RuH_2SiMeCl_2}$ in Ether. The crude compound prepared as above in toluene was dissolved in 20 mL of ether. The resulting deep blue solution was cooled to −30 °C to give white crystals. The cold solution was decanted, and the white crystals were dried in a vacuum. The NMR test showed the formation of a mixture of $\mathrm{Cp^*(Pr^i_3P)RuH_2SiMeCl_2}$ and another yet unidentified compound. Attempted recrystallization of this material in ether revealed a steady decrease of solubility and increasing formation of the second product, which is poorly soluble in ether, contaminated by some other impurities. The ^{1}H NMR spectrum in $\mathrm{C_6D_6}$ of this product shows a broad signal integrated as 15 and tentatively assigned to the Cp* ligand and two sets of signals corresponding to two coordinated phopshine ligands $\mathrm{Pr^i_3P}$. No hydride signals were observed up to −16 ppm. Please note that $\mathrm{Cp^*(Pr^i_3P)_2RuCl}$ is not formed upon addition of $\mathrm{Pr^i_3P}$ to $\mathrm{Cp^*(Pr^i_3P)RuCl}$.[28]

The Second Product $\mathrm{Cp^*(Pr^i_3P)RuX}$ (X = unspecified one-electron ligand, X ≠ H, Cl). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 2.24 (m, J(H–H) = 7.2, J(P–H) = 11.7 Hz, 6, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.94 (v br s, 15), 0.97 (dd, J(H–H) = 7.2 Hz, J(P–H) = 16.4 Hz, 32, $\mathrm{PCH}(\mathrm{C}H_3)_2$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 20.1 (d, J(P–C) = 31.6 Hz, $\mathrm{P}(C\mathrm{H}(\mathrm{CH_3})_2)_3$), 18.4 (s, $\mathrm{P}(\mathrm{CH}(C\mathrm{H_3})_2)_3$), 10.6 (br s). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 32.6 (br s).

Preparation of $\mathrm{Cp^*(MePr^i_2P)RuH_2SiMeCl_2}$ (2b). To 20 mL of a toluene solution of complex $\mathrm{Cp^*(MePr^i_2P)RuH_3}$ (330 mg, 0.89 mmol) were added $\mathrm{NEt_3}$ (0.43 mL, 4.45 mmol) and $\mathrm{HSiMeCl_2}$ (0.73 mL, 8.9 mmol). The reaction mixture was heated during 12 h to 90 °C to give a misty orange solution. The NMR test showed formation of a mixture of complexes $\mathrm{Cp^*(MePr^i_2P)RuH_2SiMeCl_2}$ (major product), $\mathrm{Cp^*(MePr^i_2P)RuH(Cl)SiMe_2}$, and one more yet unidentified compound. The solution was filtered off from a white precipitate and stripped of volatiles. The resultant material was extracted by 10 mL of hexane heated to 40 °C, and the solution was decanted from the oil. Cooling to −30 °C gave a yellow powder. The cold solution was transferred to the previous flask with oil, the mixture was heated to 40 °C, and the oil was thoroughly stirred. The extraction was repeated in this way 10 times to give 0.240 g of a yellow product. Since the NMR test showed that $\mathrm{Cp^*(MePr^i_2P)RuH_2SiMeCl_2}$ was still contaminated with some imputities, the product was dissolved in 50 mL of ether and filtered and the solution was slowly concentrated to 5 mL. This procedure gave a colorless powder and a viscous solution. The solution was decanted and the residue washed by 5 mL of cold ether. The yield of colorless crystalline product was 0.150 g (36%). IR (Nujol): ν(Ru–H) 1952.0, 1981.0 cm $^{-1}$. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 1.78 (d, J(P–H) = 1.3 Hz, 15, $\mathrm{C_5}(\mathrm{C}H_3)_5$), 1.51 (sept, J(H–H) = 7.0 Hz, 2, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.27 (s, 3, $\mathrm{SiC}H_3$), 0.90 (dd, J(H–H) = 7.0 Hz, J(P–H) = 9.1 Hz, 6, $\mathrm{PCH}(\mathrm{C}H_3)_2$), 0.79 (d, J(P–H) = 7.9 Hz, 3, $\mathrm{PC}H_3$), 0.68 (dd, J(H–H) = 7.0 Hz, J(P–H) = 7.4 Hz, 6, $\mathrm{PCH}(\mathrm{C}H_3)_2$), −11.58 (d, J(P–H) = 27.6 Hz, 2, $\mathrm{Ru}H_2$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 96.7 (d, J(P–C) = 1.7 Hz, $C_5(\mathrm{CH_3})_5$), 28.0 (d, J(P–C) = 30.1 Hz, $\mathrm{P}C\mathrm{H}(\mathrm{CH_3})_2$), 23.1 (s, $\mathrm{Si}C\mathrm{H_3}$), 17.8 (br s, $\mathrm{PCH}(C\mathrm{H_3})_2$ and $\mathrm{P}C\mathrm{H_3}$), 16.3 (s, $\mathrm{PCH}(C\mathrm{H_3})_2$), 10.8 (s, $\mathrm{C_5}(C\mathrm{H_3})_5$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 58.5 (s). Anal. Calcd for $\mathrm{C_{18}H_{37}Cl_2PRuSi}$: C 44.62; H 7.70. Found: C 44.71; H 7.68.

Reaction of $\mathrm{Cp^*(Me_2PhP)RuH_3}$ with $\mathrm{HSiMeCl_2}$ to Give $\mathrm{Cp^*(Me_2PhP)RuH_2SiMeCl_2}$ (2d). To 20 mL of a toluene solution of complex $\mathrm{Cp^*(PhMe_2P)RuH_3}$ (0.100 g, 0.26 mmol) were added $\mathrm{NEt_3}$ (0.2 mL, 2.6 mmol) and $\mathrm{HSiMeCl_2}$ (0.2 mL, 2.6 mmol). The reaction mixture was heated under stirring during 4 h to 90 °C. All volatiles were removed in vacuo, and the residue was extracted by 15 mL of ether. An NMR spectrum showed formation of a mixture of products: $\mathrm{Cp^*(Me_2PhP)RuH_2SiMeCl_2}$, $\mathrm{Cp^*(Me_2PhP)RuH_2SiMeHCl}$ along with a smaller amount of $\mathrm{Cp^*(Me_2PhP)Ru(Cl)(SiMeCl_2)(H)}$, $\mathrm{Cp^*(Me_2PhP)RuH_2SiCl_3}$, and the starting $\mathrm{Cp^*(Me_2PhP)RuH_3}$. Ether was removed in vacuo, and the mixture was redissolved in 20 mL of toluene. $\mathrm{HSiMeCl_2}$ was added (1 mL, 13 mmol), and the reaction mixture was heated for a further 20 h to 90 °C. This procedure resulted in major decomposition; the only hydride compounds left were $\mathrm{Cp^*(Me_2PhP)Ru(Cl)(SiMeCl_2)(H)}$ and $\mathrm{Cp^*(Me_2PhP)RuH_2SiMeCl_2}$.

$\mathrm{Cp^*(Me_2PhP)RuH_2SiMeHCl}$ (4d). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.45 (mult, $J(\mathrm{H_{SiMe}}$–H) = 3.4 Hz, 1, $\mathrm{Si}H\mathrm{MeCl}$), 1.60 (d, J(P–H) = 1.2 Hz, $\mathrm{C_5}(\mathrm{C}H_3)_5$), 1.21 (d, J(P–H) = 9.7 Hz, 6, $\mathrm{PC}H_3$), 1.15 (d, $J(\mathrm{H_{SiH}}$–H) = 3.4 Hz, 3, $\mathrm{SiC}H_3$), −11.92 (br d, J(P–H) = 29.6, 1, $\mathrm{Ru}H^{\mathrm{a}}$), −12.10 (br d, J(P–H) = 296, 1, $\mathrm{Ru}H^{\mathrm{b}}$).

Preparation of $\mathrm{Cp^*(Pr^i_3P)Ru(Cl)(SiMeCl_2)(H)}$ (3a). To 20 mL of a toluene solution of complex $\mathrm{Cp^*(Pr^i_3P)RuH_3}$ (0.390 g, 0.97 mmol) was added $\mathrm{HSiMeCl_2}$ (1 mL, 12 mmol). The reaction mixture was heated during 1.5 h to 60 °C with periodical removal of the gas evolved. An NMR test showed formation of a mixture of complexes $\mathrm{Cp^*(Pr^i_3P)Ru(Cl)(SiMeCl_2)(H)}$ (major) and $\mathrm{Cp^*(Pr^i_3P)RuH_2(SiClHMe)}$ (**4a**) (minor). The volatiles were removed in vacuo to give a red-orange oil. The product was dissolved in 20 mL of ether, and to this solution was added 1.5 mL of $\mathrm{HSiMeCl_2}$. The orange solution was slowly concentrated to 5 mL to afford a yellow tiny crystalline precipitate. The solution was decanted, and the precipitate was sequentially washed by 5 mL of ether and 5 mL of hexane. The product was dried in vacuo to give 0.250 g of a light yellow crystalline product. The yield was 47%. An alternative preparation of this compound has been reported.[29]

$\mathrm{Cp^*(Pr^i_3P)Ru(Cl)(SiMeCl_2)(H)}$ (3a). IR (Nujol): ν(Ru–H) 2096.0 cm $^{-1}$. ^{1}H NMR (toluene-d_8): δ 2.22 (d sept, J(P–H) = 14.1 Hz, J(H–H) = 6.9 Hz, 3, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.51 (s, 15, $\mathrm{C_5}(\mathrm{C}H_3)_5$), 1.33 (s, 3, $\mathrm{Si}(\mathrm{C}H_3)$), 1.14 (dd, J(P–H) = 13.5 Hz, J(H–H) = 6.9 Hz, 9, $\mathrm{PCH}(\mathrm{C}H_3)_2$), 1.02 (br dd, J(P–H) = 12.2 Hz, J(H–H) = 6.9 Hz, 9, $\mathrm{PCH}(\mathrm{C}H_3)_2$), − 9.51 (d, J(P–H) = 33.6 Hz, 1, $\mathrm{Ru}H$). ^{13}C NMR (toluene-d_8): δ 100.1 (s, $C_5(\mathrm{CH_3})_5$), 30.2 (br s, $\mathrm{P}C\mathrm{H}(\mathrm{CH_3})_2$) 27.4 (s, 30.2, $\mathrm{PCH}(C\mathrm{H_3})_2$)), 27.2 (s, $\mathrm{PCH}(C\mathrm{H_3})_2$), 17.0 (s, $\mathrm{Si}(C\mathrm{H_3})$)), 10.3 (s, $\mathrm{C_5}(C\mathrm{H_3})_5$). ^{31}P NMR (toluene-$d_8$): δ 53.6 (s). ^{29}Si (toluene-d_8): δ 61.0. Anal. Calcd for $\mathrm{C_{20}H_{40}Cl_3PRuSi}$: C 43.91; H 7.37; Cl 19.44. Found: C 43.54; H 7.10; Cl 19.13.

$\mathrm{Cp^*(PPr^i_3)RuH_2(SiMeHCl)}$ (4a). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 6.09 (dpent, $J(\mathrm{H_{SiMe}}$–H) = 3.4 Hz, $J(\mathrm{H_{RuHa}}$–H) = 3.2 Hz, $J(\mathrm{H_{RuHb}}$–H) = 4.9 Hz, J(Si–H) = 204.6 Hz, 1, $\mathrm{Si}H\mathrm{MeCl}$), 1.79 (sept d, J(H–H) = 7.2 Hz, 3, $\mathrm{PC}H(\mathrm{CH_3})_2$), 1.79 (d, J(P–H) = 1.3 Hz, 15, $\mathrm{C_5}(\mathrm{C}H_3)_5$), 1.14 (d, $J(\mathrm{H_{SiH}}$–H) = 3.4 Hz, 3, $\mathrm{SiC}H_3$), 1.08 (dd, J(H–H) = 7.2, J(P–H) = 13.3 Hz, 9, $\mathrm{PCH}(\mathrm{C}H_3)_2$), −11.58 (dd, $J(\mathrm{H_{SiH}}$–H) = 4.9, J(P–H) = 28.6, 1, $\mathrm{Ru}H^{\mathrm{b}}$), −12.39 (br d, J(P–H) = 28.6, 1, $\mathrm{Ru}H^{\mathrm{a}}$). ^{31}P NMR ($\mathrm{C_6D_6}$): δ 82.6 (s).

NMR Tube Reaction of $\mathrm{Cp^*(Pr^i_3P)Ru(Cl)(SiMeCl_2)(H)}$ (3a) with $\mathrm{PMe_3}$. To a NMR tube with a solution of **3a** in toluene-d_8 (0.6 mL) was added 3 equiv of $\mathrm{PMe_3}$. The color instantaneously changed from light green to bright orange-yellow. The NMR check showed the formation of Cp*(PMe$_3$)$_2$RuCl and the release of free Pr$^i_3$P and an equivalent of the silane HSiCl$_2$Me characterized by its Si−H signal at 5.22 ppm (q, *J*(H−H) = 2.1 Hz) and the SiMe signal at 1.50 (d, *J*(H−H) = 2.1 Hz). ^{1}H NMR (toluene-*d*$_8$): 1.56 (s, 15, C$_5$(C*H*$_3$)$_5$), 1.25 (vt, *J*(P−H) = 7.8 Hz, 18, PMe$_3$). ^{13}C NMR (toluene-*d*$_8$): 87.8 (s, *C*$_5$(CH$_3$)$_5$), 20.4 (m, P*C*H$_3$), 11.0 (d, *J*(P−C) = 4.6 Hz, C$_5$(*C*H$_3$)$_5$). ^{31}P NMR (toluene-*d*$_8$): 3.64 (s).

Preparation of Cp*(MePr$^i_2$P)Ru(Cl)(SiMeCl$_2$)(H) (3b). To 20 mL of a toluene solution of complex Cp*(MePr$^i_2$P)RuH$_3$ (0.370 g, 0.97 mmol) was added HSiMeCl$_2$ (1 mL, 12 mmol). The reaction mixture was heated during 1.5 h to 60 °C with periodical removal of the gas evolved. The volatiles were removed in vacuo to give a red-orange oil. The product was dissolved in 20 mL of ether, and to this solution was added 1.5 mL of HSiMeCl$_2$. The solution was slowly concentrated to 5 mL to afford an orange solution and a yellow tiny crystalline precipitate. The solution was decanted, and the precipitate was sequentially washed by 5 mL of ether and 5 mL of hexane. The product was dried in vacuo to give 0.220 g of light yellow crystalline product. The yield was 42%. IR (Nujol): ν(Ru−H) 2076.0 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 1.87 (d sept, *J*(H−H) = 6.9 Hz, *J*(P−H) = 18.4 Hz 2, PC*H*(CH$_3$)$_2$), 1.52 (s, 15, C$_5$(C*H*$_3$)$_5$), 1.36 (s, 3, Si(C*H*$_3$)), 1.16 (d, *J*(P−H) = 9.9 Hz, 3, PC*H*$_3$), 1.07 (dd, *J*(P−H) = 16.0 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 1.03 (dd, *J*(P−H) = 14.5 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 0.69 (dd, *J*(P−H) = 11.4 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 0.57 (dd, *J*(P−H) = 16.0 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), −9.86 (d, *J*(P−H) = 33.6 Hz, 1, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 100.1 (s, *C*$_5$(CH$_3$)$_5$), 28.4 (d, *J*(P−C) = 31.7 Hz, P*C*H(CH$_3$)$_2$), 25.6 (d, *J*(P−C) = 19.3 Hz, P*C*H(CH$_3$)$_2$), 19.0 (s, PCH(*C*H$_3$)), 18.3 (s, PCH(*C*H$_3$)), 17.7 (s, PCH(*C*H$_3$)), 17.3 (s, PCH(*C*H$_3$)), 16.8 (d, *J*(P−C) = 7.3 Hz, Si*C*H$_3$), 10.2 (s, C$_5$(*C*H$_3$)$_5$), 4.7 (d, *J*(P−C) = 29.0 Hz, P*C*H$_3$). ^{31}P NMR (C$_6$D$_6$): δ 45.8 (s). ^{29}Si NMR (toluene-*d*$_8$): δ 61.5. Anal. Calcd for C$_{18}$H$_{36}$Cl$_3$PRuSi: C 41.66; H 6.99; Cl 20.49. Found: C 41.59; H 6.94; Cl 19.89.

Preparation of Cp*(Me$_2$Pr^{i}P)Ru(Cl)(SiMeCl$_2$)(H) (3c). To 20 mL of a toluene solution of complex Cp*(Me$_2$Pr^{i}P)RuH$_3$ (0.160 g, 0.47 mmol) was added HSiMeCl$_2$ (0.38 mL, 4.6 mmol). The reaction mixture was heated during 1.5 h to 60 °C with periodical removal of the gas evolved. The volatiles were removed in vacuo to give a red-orange oil. Then 50 mL of ether and 1.0 mL of HSiMeCl$_2$ were added to this product. The oil was thoroughly stirred, and the orange solution was decanted and slowly concentrated to 10 mL and cooled to −30 °C. Dark red crystals were formed in a few days. The cold supernatant solution was decanted, and the precipitate was washed by 5 mL of cold ether. The product was dried in vacuo to give 0.120 g of a dark red crystalline product. The yield was 52%. IR (Nujol): ν(Ru−H) 2042.0 cm^{-1} and a shoulder at 1962.0 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 1.48 (d, *J*(P−H) = 1.9 Hz, 15, C$_5$(C*H*$_3$)$_5$), 1.40 (s, 3, SiC*H*$_3$), 1.29 (sept, *J*(H−H) = 7.0 Hz, 1, PC*H*(CH$_3$)), 1.07 (d, *J*(P−H) = 10.5 Hz, 3, PC*H*$_3$), 1.03 (d, *J*(H−H) = 9.6 Hz, 3, PC*H*$_3$), 0.85 (dd, *J*(H−H)= 7.1 Hz, *J*(P−H) = 17.4 Hz, 3, PCH(C*H*$_3$)), 0.66 (dd, *J*(H−H) = 7.1 Hz, *J*(P−H) = 12.9 Hz, 3, PCH(C*H*$_3$)), −9.93 (d, *J*(P−H) = 30.5 Hz + *J*(Si−H) = 20.7 Hz, 1, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 95.7 (d, *J*(P−C) = 1.8 Hz, *C*$_5$(CH$_3$)$_5$), 27.4 (d, *J*(P−C) = 33.4 Hz, P*C*H(CH$_3$)), 17.6 (d, *J*(P−C) = 2.0 Hz, PCH(*C*H$_3$)), 17.5 (s, Si*C*H$_3$), 16.6 (d, *J*(P−C) = 5.4 Hz, PCH(*C*H$_3$)), 12.4 (d, *J*(P−C) = 25.7 Hz, P*C*H$_3$), 9.7 (s, C$_5$(*C*H$_3$)$_5$)) 9.4 (d, *J*(P−C) = 37.0 Hz, P*C*H$_3$). ^{31}P NMR (C$_6$D$_6$): δ 36.8. ^{29}Si (toluene-*d*$_8$): 63.0. Anal. Calcd for C$_{16}$H$_{32}$Cl$_3$PRuSi: C 39.15; H 6.57. Found: C 39.28; H 6.59.

Preparation of Cp*(Pr$^i_3$P)Ru(Cl)(SiCl$_3$)(H) (5a). (a) To 30 mL of a toluene solution of the complex Cp*(Pr$^i_3$P)RuH$_3$ (0.230 g, 0.58 mmol) was added at room temperature HSiCl$_3$ (0.6 mL, 5.9 mmol). In a few minutes gas evolution started. The reaction mixture was left overnight at room temperature. The volatiles were removed in vacuo to give a red oil. This product was dissolved in 20 mL of a 1:1 mixture of benzene and hexane. In a few days red crystals precipitated. The solution was decanted, and the crystals were washed by 10 mL of cold toluene and dried. Yield: 0.160 g (49%).

(b) To 30 mL of a toluene solution of the complex Cp*(Pr$^i_3$P)RuH$_3$ (0.30 g, 0.75 mmol) was added HSiCl$_3$ (1.0 mL, 1.0 mmol). The reaction mixture was heated for 4 h at 90 °C to give an orange solution. The volatiles were removed in vacuo to give a red-orange oil. The produt was dissolved in 20 mL of toluene, and the solution was filtered, slowly concentrated to 5 mL, and cooled to −30 °C. Red-orange crystals precipitated from the solution during a few days. The cold solution was decanted and the residue dried in vacuo. Yield: 0.150 g (35%).

(c) A solution of Cp*(Pr$^i_3$P)RuCl in 0.6 mL of C$_6$D$_6$ was treated by a slight excess of HSiCl$_3$. An immediate color change from blue to orange occurred. The NMR spectrum showed quantitative formation of Cp*(Pr$^i_3$P)Ru(Cl)(SiCl$_3$)(H) (**5a**). IR (Nujol): ν(Ru−H) = 2120.0 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 2.35 (v br s, 3, PC*H*(CH$_3$)), 1.46 (d, *J*(P−H) = 1.2 Hz, 15, C$_5$(C*H*$_3$)$_5$), 1.13 (br dd, *J*(P−H) = 14.4 Hz, *J*(H−H) = 7.2 Hz, 9, PCH(C*H*$_3$)), 0.98 (br dd, *J*(P−H) = 12.3 Hz, *J*(H−H) = 6.9 Hz, 9, PCH(C*H*$_3$)), −9.47 (d, *J*(P−H) = 34.2 Hz, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 101.5 (d, *J*(P−C) = 1.7 Hz, *C*$_5$(CH$_3$)$_5$), 26.9 (d, *J*(P−C) = 21.6 Hz, P*C*H(CH$_3$)), 21.1 (s, PCH(*C*H$_3$)), 20.0 (br s, PCH(*C*H$_3$)), 10.1 (s, C$_5$(*C*H$_3$)$_5$). ^{31}P NMR (C$_6$D$_6$): δ 51.0. Anal. Calcd for C$_{19}$H$_{37}$Cl$_4$PRuSi: C 40.22; H 6.57; Cl 24.99. Found: C 40.64; H 6.48; Cl 22.46.

NMR Tube Reaction of Cp*(Pr$^i_3$P)RuH$_3$ with HSiCl$_3$ in C$_6$D$_6$. (a) In a thoroughly dried NMR tube was prepared a solution of Cp*(Pr$^i_3$P)RuH$_3$ in C$_6$D$_6$, and then HSiCl$_3$ (5 equiv) was added. In 24 h the NMR spectrum was recorded, which showed formation of a mixture of Cp*(Pr$^i_3$P)RuH$_3$ and minor amounts of Cp*(Pr$^i_3$P)RuH(Cl)SiCl$_3$ and Cp*(Pr$^i_3$P)RuH$_2$SiHCl$_2$. After 1 week at room temperature a mixture of Cp*(Pr$^i_3$P)Ru(Cl)(SiCl$_3$)(H) and Cp*(Pr$^i_3$P)RuH$_2$SiHCl$_2$ (1:1) was formed.

(b) An NMR sample was prepared as above with the ratio Cp*(Pr$^i_3$P)RuH$_3$:HSiCl$_3$ = 1:10. The NMR tube was heated to 75 °C during 2 h; 58% of the starting trihydride reacted, the products being Cp*(Pr$^i_3$P)Ru(Cl)(SiCl$_3$)(H) (**5a**, 30%) Cp*(Pr$^i_3$P)RuH$_2$(SiCl$_3$) (14%), Cp*(Pr$^i_3$P)RuH$_2$SiHCl$_2$ (**6a**, 10.5%), and Cp*(Pr$^i_3$P)RuH$_2$SiH$_2$Cl (**7a**, 3.5%).

Cp*(Pr$^i_3$P)RuH$_2$(SiCl$_3$). ^{1}H NMR (C$_6$D$_6$): δ 1.71 (d, *J*(P−H) = 1.2 Hz, 15, C$_5$(C*H*$_3$)$_5$), −10.73 (d, *J*(P−H) = 27.3 Hz, 2, Ru*H*$_2$).

Cp*(Pr$^i_3$P)RuH$_2$SiHCl$_2$ (6a). ^{1}H NMR (C$_6$D$_6$): δ 6.89 (td, *J*(H−H) = 5.9 Hz, *J*(P−H) = 1.4 Hz, 1, Si*H*Cl$_2$), 1.78 (d, *J*(P−H) = 1.2 Hz, 15, C$_5$(C*H*$_3$)$_5$), −11.39 (dd, *J*(P−H) = 28.2 Hz, *J*(H−H) = 5.9 Hz, 2, Ru*H*$_2$).

Cp*(Pr$^i_3$P)RuH$_2$SiH$_2$Cl (7a). ^{1}H NMR (C$_6$D$_6$): δ 5.88 (t, *J*(H−H) = 2.4 Hz + *J*(Si−H) = 204 Hz, 2, Si*H*$_2$Cl), 1.77 (s, 15, C$_5$(C*H*$_3$)$_5$), −12.20 (dt, *J*(P−H) = 27.9 Hz, *J*(H−H) = 2.4 Hz, 2, Ru*H*$_2$).

Preparation of Cp*(MePr$^i_2$P)Ru(Cl)SiCl$_3$(H) (5b). To 20 mL of a toluene solution of the complex Cp*(MePr$^i_2$P)RuH$_3$ (0.39 g, 1.05 mmol) was added at room temperature HSiCl$_3$ (1.0 mL, 10.5 mmol). In a few minutes a weak gas evolution was noticed. The reaction mixture was stirred overnight, affording a yellow solution. The solution was concentrated to give an orange oil. To the oil was added slowly 20 mL of ether, which resulted in the precipitation of a yellow compound. The solution was decanted, and the residue was washed by 10 mL of toluene and dried in a vacuum. Yield: 0.240 g (42%). X-ray quality crystals were obtained by slow diffusion of hexane vapor into a THF solution of the product. IR (Nujol): ν(Ru−H) 2078.0 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 2.25 (sept, *J*(H−H) = 6.9 Hz, 2, PC*H*(CH$_3$)$_2$), 1.47 (d, *J*(P−H) = 0.9 Hz 15, C$_5$(C*H*$_3$)$_5$), 1.35 (d, *J*(P−H) = 10.2 Hz, 3, PC*H*$_3$), 1.13 (dd, *J*(P−H) = 16.2 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 0.97 (dd, *J*(P−H) = 14.7 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 0.61 (dd, *J*(P−H) = 12.0 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), 0.57 (dd, *J*(P−H) = 16.2 Hz, *J*(H−H) = 6.9 Hz, 3, PCH(C*H*$_3$)), −9.76 (d, *J*(P−H) = 34.2

Hz, 1, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 101.4 (s, *C*$_5$(CH$_3$)$_5$), 28.4 (d, *J*(P–C) = 33.7 Hz, P*C*H(CH$_3$)$_2$), 25.6 (d, *J*(P–C) = 19.3 Hz, P*C*H(CH$_3$)$_2$), 19.1 (s, PCH(*C*H$_3$)), 18.2 (s, PCH(*C*H$_3$)), 17.5 (s, PCH(*C*H$_3$)), 17.3 (s, PCH(*C*H$_3$)), 10.0 (s, C$_5$(*C*H$_3$)$_5$), 4.2 (d, *J*(P–C) = 30.3 Hz, P*C*H$_3$). ^{31}P NMR (C$_6$D$_6$): δ 44.0. ^{1}H–^{29}Si gHMQC (C$_6$D$_6$): ^{29}Si signal coupled to hydride at −9.76: 35.8. Anal. Calcd for C$_{17}$H$_{33}$Cl$_4$PRuSi: C 37.85; H 6.17; Cl 26.29. Found: C 37.95; H 6.19; Cl 26.29.

Preparation of Cp*(Me$_2$Pr^{i}P)Ru(Cl)(SiCl$_3$)(H) (5c). To 20 mL of a toluene solution of the complex Cp*(Me$_2$Pr^{i}P)RuH$_3$ (0.11 g, 0.32 mmol) was added at room temperature HSiCl$_3$ (0.32 mL, 3.2 mmol). In a few minutes a weak gas evolution was noticed. The reaction mixture was stirred overnight, affording a yellow solution. The solution was dried in vacuo and the residue dissolved in 5 mL of THF. Then slowly, trying to avoid any stirring, was added 0.5 mL of HSiCl$_3$ followed by 10 mL of hexane. The system was cooled to −30 °C, trying not to mix the layers. In a few days dark orange crystals were formed. The solution was decanted and the residue washed by 5 mL of toluene and dried in vacuo. The yield of red crystalline substance: 0.100 g (61%). X-ray quality crystals were obtained by slow diffusion of hexane vapor into a THF solution of the product. IR (Nujol): ν(Ru–H) 2056.0 cm $^{-1}$. ^{1}H NMR (C$_6$D$_6$): δ 1.41 (d, *J*(P–H) = 1.9 Hz, 15, C$_5$(C*H*$_3$)$_5$), 1.27 (d, *J*(P–H) = 10.8 Hz, 3, PC*H*$_3$), 1.23 (sept, *J*(H–H) = 6.9 Hz, 1, PC*H*(CH$_3$)), 0.95 (d, *J*(H–H) = 9.9 Hz, 3, PC*H*$_3$), 0.85 (dd, *J*(H–H) = 6.9 Hz, *J*(P–H) = 17.3 Hz, 3, PCH(C*H*$_3$)), 0.63 (dd, *J*(H–H) = 6.9 Hz, *J*(P–H) = 13.5 Hz, 3, PCH(C*H*$_3$)), −9.74 (d, *J*(P–H) = 30.9 Hz, 1, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 100.7 (s, *C*$_5$(CH$_3$)$_5$), 27.7 (d, *J*(P–C) = 33.9 Hz, P*C*H(CH$_3$)), 17.6 (s, PCH(*C*H$_3$)), 16.6 (d, *J*(P–C) = 1.4 Hz, PCH(*C*H$_3$)), 12.4 (d, *J*(P–C) = 25.7 Hz, P*C*H$_3$), 9.6 (s, C$_5$(*C*H$_3$)$_5$)) 9.2 (d, *J*(P–C) = 33.9 Hz, P*C*H$_3$). ^{31}P NMR (C$_6$D$_6$): δ 35.3. ^{1}H–^{29}Si gHMQC (C$_6$D$_6$): ^{29}Si signal coupled to H signal at −9.74 ppm is 33.3 ppm. Anal. Calcd for C$_{15}$H$_{29}$Cl$_4$PRuSi: C 35.23; H 5.72; Cl 27.73. Found: C 35.30; H 5.74; Cl 27.71.

Preparation of Cp*(Me$_2$PhP)Ru(Cl)(SiCl$_3$)(H) (5d). To 40 mL of a 1:1 mixture of toluene/hexane solution of Cp*(Me$_2$PhP)RuH$_3$ (0.300 g, 0.81 mmol) was added 1 mL of HSiCl$_3$, resulting in the precipitation of a white voluminous compound and intensive gas evolution. In 10–15 min the precipitate dissolved, and a yellow solution and red oil were formed. The reaction mixture was left overnight. The yellow solution was decanted from the oil and cooled to −50 °C. In 1 h a yellow-green microcrystalline precipitate was formed. The cold solution was decanted and added to the oil formed at the previous stage. The oil was stirred under the solution and allowed to stay for 1 h at room temperature.Then the solution was added to the yellow-green precipitate, and the mixture was cooled to −50 °C. In 1 h the cold solution was decanted and the produt dried in vacuo. Yield: 0.280 g (63%). The X-ray quality crystals were obtained by slow diffusion of hexane vapor into a dilute THF solution of the product. IR (Nujol): ν(Ru–H) 2018.0 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 7.32 (m, 2, o-Ph), 6.96 (m, 3, m, p-Ph), 1.50 (d, *J*(P–H) = 10.8 Hz, 3, PC*H*$_3$), 1.42 (d, *J*(P–H) = 10.5 Hz, 3, PC*H*$_3$), 1.25 (s, 15, C$_5$(C*H*$_3$)$_5$), −9.57 (d, *J*(P–H) = 29.1 Hz, 1, Ru*H*). ^{13}C NMR (C$_6$D$_6$): δ 130.8 (d, *J*(P–C) = 9.6 Hz, i-PhP) 130.0 (s, o-Ph), 100.6 (s, *C*$_5$(CH$_3$)), 20.7 (d, *J*(P–C) = 36.3 Hz, P(*C*H$_3$)), 12.9 (d, *J*(P–C) = 31.7 Hz, P(*C*H$_3$)), 9.1 (s, C$_5$(*C*H$_3$)). ^{31}P NMR (C$_6$D$_6$): δ 23.2 (s). Anal. Calcd for C$_{18}$H$_{27}$Cl$_4$PRuSi: C 39.64; H 4.99; Cl 26.00. Found: C 39.46; H 4.99; Cl 25.49.

Generation of Cp*(Pr$^i{}_3$P)RuH$_2$SiHCl$_2$ (6a). To 20 mL of a toluene solution of Cp*(Pr$^i{}_3$P)RuH$_3$ (0.400 g, 1 mmol) was added first 0.05 mL of NEt$_3$ (0.37 mmol) and then 1 mL of HSiCl$_3$ (10 mmol). The reaction mixture was heated at 70 °C for 6 h in a sealed ampule. NMR monitoring showed formation of a mixture of three compounds: Cp*(Pr$^i{}_3$P)RuH$_2$SiHCl$_2$, Cp*(Pr$^i{}_3$P)Ru(H)(Cl)SiCl$_3$, and Cp*(Pr$^i{}_3$P)RuH$_2$SiH$_2$Cl (δ −12.20 (dt, *J*(P–H) = 27.9 Hz, *J*(H–H) = 2.4 Hz, 2, RuH$_2$). Although Cp*(Pr$^i{}_3$P)RuH$_2$SiHCl$_2$ was the main product, all attempts to separate it from the mixture by crystallization failed.

Cp*Ru(P^{i}Pr$_3$)H$_2$SiHCl$_2$ (6a). ^{1}H NMR (C$_6$D$_6$): δ 6.89 (td, *J*(H–H) = 5.9 Hz, *J*(P–H) = 1.4 Hz +*J*(Si–H) = 254.6 Hz, 1, Si*H*Cl$_2$), 1.79 (sept d, *J*(H–H) = 7.0 Hz, 3, PC*H*(CH$_3$)$_2$), 1.78 (d, *J*(P–H) = 1.2 Hz, 15, C$_5$(C*H*$_3$)$_5$), 0.93 (dd, *J*(H–H) = 7.0 Hz, *J*(P–H) = 13.5 Hz, 18, PCH(C*H*$_3$)$_2$), −11.39 (dd, *J*(P–H) = 28.2 Hz, *J*(H–H) = 5.9 Hz, 2, Ru*H*$_2$]. ^{31}P NMR (C$_6$D$_6$): δ 81.5.

Generation of Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (6b). To 5 mL of a toluene solution of Cp*(MePr$^i{}_2$P)RuH$_3$ (0.330 g, 0.89 mmol) was added first 0.1 mL of NEt$_3$ (0.98 mmol) and then 0.88 mL of HSiCl$_3$ (8.9 mmol). The reaction mixture was heated to 65 °C for 2.5 h in a sealed ampule to afford a misty orange solution. NMR spectra revealed a mixture of Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (**6b′**), Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (**6b**) (major product), and Cp*(MePr$^i{}_2$P)RuH$_2$SiH$_2$Cl (**7b**). Although Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (**6b**) was the main product, all attempts to separate the mixture by crystallization failed.

Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (6b). IR (Nujol): ν(Si–H) 2248.0 and ν(Ru–H) = 1990.0 cm $^{-1}$. ^{1}H NMR (C$_6$D$_6$): δ 7.09 (td, *J*(H–H) = 5.6 Hz, *J*(P–H) = 1.0 Hz, Si*H*Cl$_2$), 1.78 (d, *J*(P–H) = 1.5 Hz, 15, C$_5$(C*H*$_3$)$_5$), 1.79 (sept, *J*(H–H) = 7.0 Hz, 2, PC*H*(CH$_3$)$_2$), 0.84 (dd, *J*(H–H) = 7.0 Hz, *J*(P–H) = 16.1 Hz, 6, PCH(C*H*$_3$)$_2$), 0.79 (d, *J*(P–H) = 8.3 Hz, 3, PC*H*$_3$), 0.65 (dd, *J*(H–H) = 7.0 Hz, *J*(P–H) = 14.2 Hz, 6, PCH(C*H*$_3$)$_2$), −11.39 (dd, *J*(P–H) = 28.2 Hz, *J*(H–H) = 5.6 Hz, 2, Ru*H*$_2$). ^{31}P NMR (C$_6$D$_6$): δ 57.6 (s).

Cp*(MePr$^i{}_2$P)RuH$_2$SiHCl$_2$ (6b′). ^{1}H NMR (C$_6$D$_6$): δ 6.14 (dd, *J*(H–H) = 2.5 Hz, *J*(H–H) = 5.0 Hz, 1, Si*H*), 1.77 (s, 15, C$_5$(C*H*$_3$)$_5$), −11.04 (br d, *J*(P–H) = 25.8 Hz, 1, Ru*H*), −11.50 (br d, *J*(P–H) = 27.7 Hz, 1, Ru*H*), other signals are obscured. ^{31}P NMR (C$_6$D$_6$): δ 56.2.

Cp*(MePr$^i{}_2$P)RuH$_2$SiH$_2$Cl (7b). ^{1}H NMR (C$_6$D$_6$): δ 6.12 (t, *J*(H–H) = 2.5 Hz, Si*H*$_2$Cl), 1.75 (s, 15, C$_5$(CH$_3$)$_5$), −12.13 (d, *J*(P–H) = 29.00 Hz, 2, Ru*H*$_2$), other signals are obscured by the signals of other compounds. ^{31}P NMR (C$_6$D$_6$): δ 59.7.

Preparation of Cp*(Pr$^i{}_3$P)RuH$_2$SiH$_2$Cl (7a). To a solution of complex Cp*(Pr$^i{}_3$P)RuH$_3$ (0.310 g, 0.78 mmol) in 20 mL of toluene was added first NEtPr$^i{}_2$ (2.00 g, 15.0 mmol) and then HSiCl$_3$ (1.73 mL, 17.5 mmol). The reaction mixture was heated during 4 h to 60 °C. The solution was filtered, and the crystalline residue was washed by 10 mL of toluene. Volatiles were removed in vacuo from the combined fractions, and the material thus obtained was extracted twice by 10 mL of hexane. The solution was filtered and dried in vacuo to give 0.320 g of a gray crustalline product. Yield: 62%. IR (Nujol): ν(Si–H) 2095, 2074 cm^{-1}; ν(Ru–H) 1994, 1968 cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ 5.88 (t, *J*(H–H) = 2.4 Hz + *J*(Si–H) = 204 Hz, 2, Si*H*$_2$Cl), 1.86 (sept. d, *J*(H–H) = 7.4 Hz, 3, P(C*H*(CH$_3$)$_2$)$_3$), 1.77 (s, 15, C$_5$(C*H*$_3$)$_5$), 0.97 (dd, *J*(H–H) = 7.4 Hz, *J*(P–H) = 13.5 Hz, 18, P(CH(C*H*$_3$)$_2$)$_3$), −12.20 (dt, *J*(P–H) = 27.9 Hz, *J*(H–H) = 2.4 Hz, 2, Ru*H*$_2$). ^{13}C NMR (C$_6$D$_6$): δ 92.5 (s, *C*$_5$(CH$_3$)$_5$), 27.7 (br s, P(*C*H(CH$_3$)$_2$)$_3$), 14.9 (s, P(CH(*C*H$_3$)$_2$)$_3$), 9.1 (C$_5$(*C*H$_3$)$_5$). ^{31}P NMR (C$_6$D$_6$): δ 83.9. Anal. Calcd for C$_{19}$H$_{40}$ClPRuSi: C 49.17; H 8.69. Found: C 49.31; H 8.73.

NMR Reaction of Cp*(Me^{i}Pr$_2$P)RuH$_3$ with HSiCl$_3$ in the Presence of NEt$_3$. To a solution of Cp*(Me^{i}Pr$_2$P)RuH$_3$ in C$_6$D$_6$ were sequentially added NEt$_3$ and HSiCl$_3$. Only insignificant reaction occurs at room temperature (4%). The mixture was then heated at 60 °C until the starting trihydride was consumed, giving a mixture of Cp*(Me^{i}Pr$_2$P)RuH$_2$SiHCl$_2$ (**6b** and its cis isomer **6b′**) and Cp*(Me^{i}Pr$_2$P)RuH$_2$SiH$_2$Cl (**7b**) with the ratio **6b**:**6b′**:**7b** = 2.3:1.34:1.

NMR Reaction of Cp*(Pr$^i{}_3$P)RuH$_3$ with HSiCl$_3$ in the Presence of EtN^{i}Pr$_2$. (a) To a solution of Cp*(Pr$^i{}_3$P)RuH$_3$ in C$_6$D$_6$ were added EtN^{i}Pr$_2$ and HSiCl$_3$ (about 5-fold excess each), and the mixture was heated to 50 °C during 1 h. The ^{1}H NMR spectrum showed that Cp*(Pr$^i{}_3$P)RuH$_2$SiH$_2$Cl was formed in 45% yield. Further heating to 50 °C for 3 h gives 90% convertion to Cp*(Pr$^i{}_3$P)RuH$_2$SiH$_2$Cl. No other silyl products were observed.

(b) To a solution of $Cp^*(Pr^i_3P)RuD_3$ in C_6D_6 were added $EtN{}^iPr_2$ and $HSiCl_3$. The tube was sealed and kept for 24 h at room temperature. The ^1H NMR spectrum showed clean formation of $Cp^*(Pr^i_3P)RuH_xD_ySiH_zD_kCl$ ($x + y = z + k = 2$). No changes were observed after the mixture had been heated to 70 °C for 2.5 h or kept at room temperature for 3 weeks.

Preparation of $Cp^*(Pr^i_3P)RuH_2SiH_3$ (8a). (a) A mixture of $Cp^*(Pr^i_3P)Ru(Cl)(SiCl_3)(H)$, $Cp^*(Pr^i_3P)RuH_2SiCl_3$, $Cp^*(Pr^i_3P)RuH_2SiHCl_2$, and $Cp^*(Pr^i_3P)RuH_2SiH_2Cl$ (obtained by the reaction of $Cp^*(Pr^i_3P)RuH_3$ with $HSiCl_3$ in the presence of NEt_3 and containing about 1.0 mmol of ruthenium compounds) was suspended in 20 mL of ether. The mixture was cooled to −50 °C, and a precooled solution of $LiAlH_4$ (0.110 g, 2.9 mmol) and NEt_3 (0.3 mL, 4 mmol) in 20 mL of ether was added under stirring. The reaction mixture was slowly warmed to room temperature and further stirred for 30 min. Then 10 mL of toluene was added, and all volatiles were removed in vacuo (the addition of NEt_3 and toluene in this protocol improves the properties of the residue formed after the removal of the volatiles). The product thus formed was extracted by 3 × 10 mL of hexane, and the resultant light red solution was filtered. Degassed water was slowly added to the solution until the evolution of gas finished. The solution was filtered and hexane was removed in vacuo to give an oil, from which in few days coloress crystals were formed. The crystals were quickly washed by cold ether and dried in vacuo. Yield: 0.120 g (0.27 mmol, about 27%).

(b) The compound was prepared as above by treating $Cp^*(Pr^i_3P)RuH_2SiH_2Cl$ (0.07 g, 0.15 mmol) by $LiAlH_4$ (0.01 g, 0.26 mmol) in 10 mL of ether at room temperature. Yield: 0.059 g (0.14 mmol, 93%). X-ray quality crystals were grown from ether by slow evaporation of the solution at room temperature. IR (Nujol): ν(Si−H) 2074, 2036 cm^{-1}; ν(Ru−H) 1994 cm^{-1}. ^1H NMR (C_6D_6): δ 4.01 (s, 3, SiH_3), 1.88 (sept, J(H−H) = 7.3 Hz, 3, P(CH(CH$_3$)$_2$)$_3$), 1.79 (s, 15, $C_5(CH_3)_5$), 1.00 (dd, J(H−H) = 7.3 Hz, J(P−H) = 13.1 Hz, 18, PCH(CH_3)$_2$), −12.20 (d, J(P−H) = 27.9 Hz, 2, RuH_2). ^{13}C NMR (C_6D_6): δ 94.8 (s, $C_5(CH_3)_5$), 27.0 (d, J(P−C) = 22.65 PCH(CH$_3$)$_2$), 19.3 (s, PCH(CH_3)$_2$), 11.8 ($C_5(CH_3)_5$). ^{31}P NMR (C_6D_6): δ 86.1 (s). Anal. Calcd for $C_{19}H_{41}PRuSi$: C 53.11; H 9.62. Found: C 53.44; H 9.78.

NMR Tube Reaction of $Cp^*(Pr^i_3P)RuH_2SiH_3$ with $(PhMe_2NH)^+Cl^-$ in C_6D_6. To a solution of $Cp^*(Pr^i_3P)RuH_2SiH_3$ in C_6D_6 was added $(PhMe_2NH)^+Cl^-$. The mixture was left at room temperature for 10 h to give a mixture of $Cp^*(Pr^i_3P)RuH_3$, $Cp^*(Pr^i_3P)RuH_2SiH_3$, and $Cp^*(Pr^i_3P)RuH_2SiH_2Cl$.

NMR Tube Reaction of $Cp^*(MePr^i_2P)RuH_3$ with $MeSiCl_3$ in C_6D_6. A 1:6 mixture of $Cp^*(MePr^i_2P)RuH_3$ and $MeSiCl_3$ was prepared in 0.6 mL of C_6D_6. The course of the reaction was monitored by ^1H NMR spectroscopy. No reaction occurs at room temperature, whereas heating to 70 °C for 1 h causes only insignificant formation of $Cp^*(MePr^i_2P)Ru(Cl)(SiMeCl_2)(H)$. Further heating to 100 °C for 2 h results in a complete reaction and formation of $Cp^*(MePr^i_2P)Ru(Cl)(SiMeCl_2)(H)$.

NMR Tube Reaction of $Cp^*(MePr^i_2P)RuH_3$ with $MeSiCl_3$ in the Presence of NEt_3 in C_6D_6. A mixture of $Cp^*(MePr^i_2P)RuH_3/MeSiCl_3/NEt_3$ in the ratio 1:6:2.5 was prepared in 0.6 mL of C_6D_6. The sample was heated to 100 °C during 2 h to give an intensely colored violet solution. The reaction is complete and the product is $Cp^*(MePr^i_2P)RuH(Cl)SiMeCl_2$. No traces of other silyl products are seen.

NMR Tube Reaction of $Cp^*(Pr^i_3P)RuCl$ with $MeSiCl_3$ in C_6D_6. To a solution of $Cp^*(Pr^i_3P)RuH_3$ in C_6D_6 was added $[Me_2PhNH]^+Cl^-$, and the NMR tube was heated to 50 °C during 30 min, which resulted in an intensive evolution of dihydrogen and formation of a violet solution of $Cp^*(Pr^i_3P)RuCl$ identified by ^1H NMR. $MeSiCl_3$ was added to the mixture, and the solution was further heated to 50 °C for 30 min. According to the ^1H NMR spectrum the reaction does not occur.

Crystal Structure Determinations. Crystals of **1a**,**b**, **2a**,**c**, **5b**,**c**,**d**, and **8a** were covered by polyperfluoro oil and mounted directly to the Bruker Smart three-circle diffractometer with CCD area detector at 120 K. The crystallographic data and characteristics of structure solution and refinement are given in Table 9 included in the Supporting Information. The structure factor amplitudes for all independent reflections were obtained after Lorentz and polarization corrections. The Bruker SAINT program[58] was used for data reduction. An absorption correction based on the SADABS program was applied. The structures were solved by direct methods[59] and refined by full-matrix least-squares procedures, using $w(|F_o^2| - |F_c^2|)^2$ as the refined function. All hydrogen atoms were found from the difference maps. All the non-hydrogen atoms were refined with anisotropic thermal parameters. For **2b** all hydrogen atoms were refined isotropically. For the other structures non-hydride hydrogen atoms were refined using the "riding" model and the hydride atoms were refined isotropically.

Structure **1a** displays a disorder on the Cl atom and one of two Me groups, $C(12)H_3$, at the silicon atom, with the site occupation factors being 0.74 and 0.26. This disorder resulted in a reduction of the final accuracy of the structure determination.

Structure **2c** represents a racemic twin with an approximately equal population of individual phases.

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Supporting Information Available: A table with crystal and structure refinement data and figures of **1a**, **2c**, **5c**, and **5d** are included in the Supporting Information. Crystallographic information files (CIF) are available free of charge via the Internet at http://pubs.acs.org.

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[58] *SAINT*, Version 6.02A; Bruker AXS Inc.: Madison, WI, 2001.

[59] *SHELXTL-Plus*, Release 5.10; Bruker AXS Inc.: Madison, WI, 1997.