$RuH_3(SiCl_2Me)(PPh_3)_3$: A Trihydridosilylruthenium Complex with Three Nonclassical Ru−H···Si Interactions

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The reaction of $RuCl_2(PPh_3)_3$ with $HSiMeCl_2$ in hexanes at 65 °C produced the trihydridosilylruthenium complex $RuH_3(SiMeCl_2)(PPh_3)_3$ (**1**). In the $^1H\{^{31}P\}$ NMR spectrum of **1**, the ruthenium hydrides were observed at −9.76 ppm as a singlet with ^{29}Si satellites (J_{SiH} = 39.7 Hz), indicating the presence of nonclassical Ru···H···Si interactions. These nonclassical interactions were confirmed by a single-crystal X-ray diffraction study of **1**. The silyl and phosphine groups occupy a tetrahedral arrangement around ruthenium, with the hydrides capping the faces defined by the silyl and two phosphines groups. Complex **1** exhibited a short Ru−Si bond (2.2760(4) Å) with three normal Ru−H distances (ca. 1.6 Å) and three long Si···H interactions (ca. 1.9 Å). The Ru−H and Si···H distances are consistent with interligand hypervalent interaction (IHI) theory in which Ru−H electron density is donated to Si−halogen σ^* orbitals, giving rise to Ru−H···Si interactions. Differences between the three Si···H separations in the solid state reflect the asymmetry in the substituent pattern at silicon and are further reinforced by the extent to which the hydride ligands (and one chloride substituent) engage in weak hydrogen bonds with the *ortho* hydrogens of the phenyl groups.

Introduction

Interest in transition-metal silyl complexes and the nature of the metal−silicon bond stems from the intermediacy of these complexes in industrially important catalytic processes such as hydrosilylation and dehydrogenative silylation. The most common and versatile method to prepare transition-metal silyl complexes involves the oxidative-addition of a hydrosilane Si−H bond to a transition-metal center.[1] However, in some cases, the Si−H oxidative-addition to the metal center is incomplete ("arrested").[1−3] These products are described as containing agostic M···H···Si interactions, or as η^2-hydrosilane or σ-complexes.

For a number of years, we have been studying the reaction of ruthenium complexes with hydrosilanes. Ruthenium alkyl complexes $Cp(PR_3)_2RuR'$ (R = Me, R′ = CH_2SiMe_3; R = Ph, R′ = Me) react with hydrosilanes to form ruthenium silyl and ruthenium hydridobis(silyl) complexes.[4,5] Recently, we reported that $RuCl_2(PPh_3)_3$ is a catalytic precursor for the hydrosilylation of phenylacetylene.[6] We have investigated the reaction of $RuCl_2(PPh_3)_3$ with various hydrosilanes to elucidate the possible ruthenium−silicon species involved in the hydrosilylation chemistry. During this study, we isolated the seven-coordinate trihydridosilylruthenium complex $RuH_3(SiCl_2Me)(PPh_3)_3$ (**1**).

A number of group 8 metal complexes containing the trihydridosilyl set of ancillary ligands, $MH_3(SiR_3)L_3$, have been reported. Schubert and co-workers prepared $FeH_3(SiR_3)(CO)(dppe)$[7,8] from the photochemical reaction of $FeH(SiR_3)(CO)_2(dppe)$ with $HSiR_3$ {SiR_3 = $Si(OMe)_3$, $Si(OEt)_3$, $SiMe_3$, $SiMe_2Ph$, $SiPh_3$} and $FeH_3(SiR_3)(PR'Ph_2)_3$ {R′ = Et, Bu; SiR_3 = $SiMe_3$, $SiMe_2Ph$, $SiMePh_2$, $SiPh_3$, $Si(Me_2)OSi(Me_2)H$}[8] from the thermal reaction of $FeH_2(H_2)(PR'Ph_2)_3$ with the appropriate hydrosilane. The ruthenium complexes $RuH_3(SiX_3)(PR_3)_3$ {PR_3 = PPh_3,[9−11] PMe_3,[12] $P(p\text{-}C_6H_4Me)_3$[10]} with alkyl,[9] aryl,[9,10] alkoxy,[9,10] pyrrolyl,[13] or halogen[9,10] substituents on silicon were prepared by the reaction of

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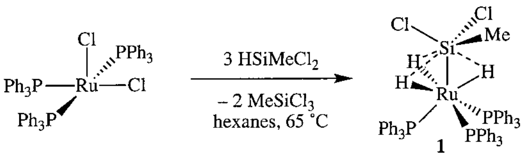
$RuH_2(PR_3)_4$ with the appropriate hydrosilane at elevated temperatures. Similarly, the reaction of $OsH(\eta^2\text{-}H_2BH_2)(CO)(PPr^i_3)_2$[14] or $OsH_4(PPh_3)_3$[13,15] with hydrosilanes produced the osmium complexes $OsH_3(SiR_3)L_3$ {$SiR_3 = SiPh_2H, SiPh_3, SiPh(OMe)_2$; $L_3 = (CO)(PPr^i_3)_2$ and $SiR_3 = SiEt_3, SiPh_3, Si(pyrrolyl)_3, Si(OCH_2CH_2)_3N$; $L_3 = (PPh_3)_3$}. However, few of these complexes have been fully characterized crystallographically.

Herein we report the preparation and structural characterization of $RuH_3(SiCl_2Me)(PPh_3)_3$ (**1**), a seven-coordinate trihydridosilylruthenium complex. Complex **1** is the first trihydridosilylruthenium complex to be structurally characterized in which the hydride ligands have been crystallographically located and contains three nonclassical Ru−H···Si interactions.

Results and Discussion

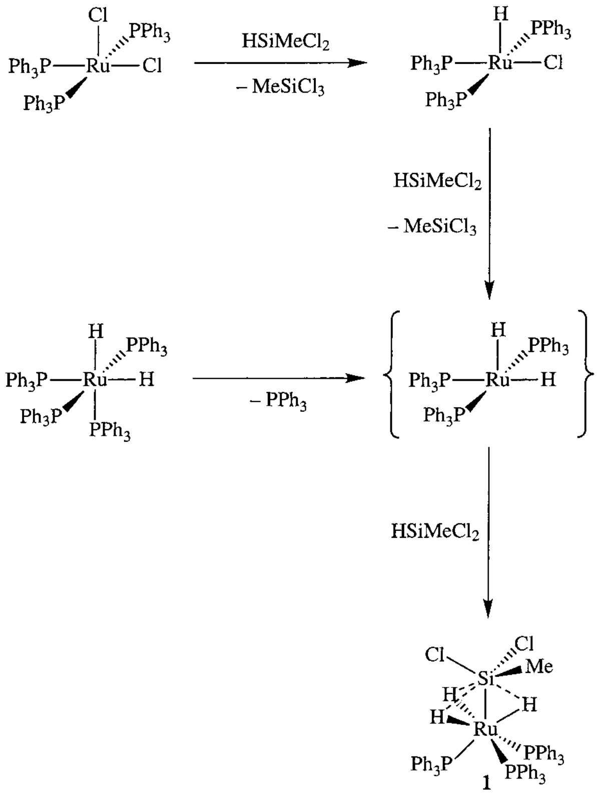
Synthesis of $RuH_3(SiMeCl_2)(PPh_3)_3$. The reaction of $RuCl_2(PPh_3)_3$ with excess $HSiMeCl_2$ in hexanes at 65 °C produced the trihydridosilylruthenium complex $RuH_3(SiMeCl_2)(PPh_3)_3$ (**1**) as a pale white precipitate in good yields (eq 1). ^1H NMR spectroscopy and GC analysis confirmed the formation of $MeSiCl_3$ as a side-product. Complex **1** is air and water sensitive and sparingly soluble in hydrocarbon solvents (benzene, toluene, hexanes) but readily soluble, although unstable, in chlorocarbon solvents (CH_2Cl_2, $CHCl_3$, CCl_4). In the presence of $CHCl_3$ or CCl_4, **1** quantitatively decomposed to $RuHCl(PPh_3)_3$ within 24 h, a reaction previously observed for related trihydridosilylruthenium complexes.[10]



(1)

A proposed mechanism for the formation of **1** is given in Scheme 1. Oxidative-addition of $HSiMeCl_2$ to $RuCl_2(PPh_3)_3$, with or without prior dissociation of PPh_3, followed by reductive-elimination of $MeSiCl_3$ leads to the well-known ruthenium chlorohydride $RuHCl(PPh_3)_3$. Another cycle of $HSiMeCl_2$ oxidative-addition and $MeSiCl_3$ reductive-elimination produced the ruthenium dihydride intermediate {$RuH_2(PPh_3)_3$}, which oxidatively adds another $HSiMeCl_2$ to produce **1**. Complex **1** has also been prepared starting with $RuHCl(PPh_3)_3$ or $RuH_2(PPh_3)_4$ with yields comparable to starting with $RuCl_2(PPh_3)_3$.

Scheme 1. Proposed Mechanism for the Formation $RuH_3(SiCl_2Me)(PPh_3)_3$ (1)



NMR Spectra of $RuH_3(SiMeCl_2)(PPh_3)_3$. The $^{31}P\{^1H\}$ NMR spectrum of **1** showed only a singlet at 38.31 ppm which broadens in the proton-coupled ^{31}P NMR spectrum (at 25 and −30 °C), suggesting that the three phosphorus nuclei were equivalent on the NMR time scale. The $^{29}Si\{^1H\}$ DEPT NMR spectrum exhibited a quartet centered at 36.4 ppm ($^2J_{SiP} = 12.8$ Hz); the proton-coupled ^{29}Si NMR spectrum was complicated with no discernible coupling pattern. However, in the room-temperature $^1H-^{29}Si$ HMQC experiment, a $J_{SiH} = 38.4$ Hz was observed, suggesting significant Si···H interaction. In the ^1H NMR spectrum, only one resonance was observed for the three hydride ligands (−9.76 ppm), along with resonances for the three triphenylphosphine and the silicon methyl groups. The hydrides for **1** exhibited a characteristic coupling pattern for $MH_3(SiX_3)(PR_3)_3$ complexes, which has been described as an AA′A″XX′X″ coupling pattern arising from the sum of three phosphorus−hydrogen coupling constants, $|^2J_{HPtrans} + 2\,^2J_{HPcis}|$.[8,13,16] The presence of Ru···H···Si interactions was confirmed in the $^1H\{^{31}P\}$ NMR spectrum, where the complex hydride resonance collapsed to a singlet with ^{29}Si satellites ($J_{SiH} = 39.7$ Hz). Agostic M···H···Si interactions generally exhibit J_{SiH} values of 40−70 Hz.[1] The hydride T_1, spin lattice relaxation time, value for **1** was determined to be 340 ms (223−298 K, 500 MHz), indicating classical ruthenium−hydrogen interactions.[17] The T_1 values of **1** cannot confirm the presence of nonclassical Ru···H···Si interactions, only the absence of nonclassical dihydrogen interactions. Overall, the NMR data for **1** indicate a symmetrical structure of pseudo-C_3 symmetry with the three phosphorus nuclei and the three hydrogen nuclei equivalent on the NMR time scale and the presence of three nonclassical Ru···H···Si interactions.

Structure of $RuH_3(SiMeCl_2)(PPh_3)_3$. The crystal structure of $RuH_3(SiMeCl_2)(PPh_3)_3$ (**1**) has been deter-

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(17) The T_1 values for nonclassical dihydrogen interactions are less than 50 ms, as in the case of $Ru(H_2)H_2(PPh_3)_3$ ($T_1 = 38$ ms).[18] The T_1 value for **1** was also in agreement with other trihydridosilyl complexes: $OsH_3(Si\{OCH_2CH_2\}_3N)(PPh_3)_3$ ($T_1 = 342$ ms, 400 MHz, 298−233 K),[15,16] $RuH_3\{Si(pyr)_3\}(PPh_3)_3$ ($T_1 = 278$ ms, 400 MHz),[13] and $OsH_3\{Si(pyr)_3\}(PPh_3)_3$ ($T_1 = 310$ ms, 400 MHz).[13]

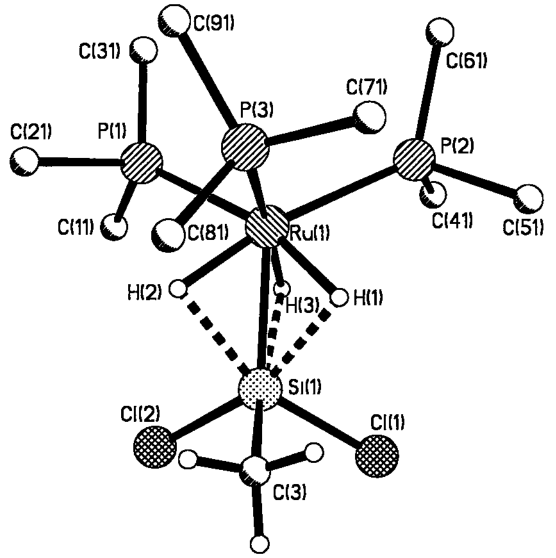

Figure 1. View of $RuH_3(SiCl_2Me)(PPh_3)_3$ (**1**), highlighting the ruthenium coordination geometry. Phenyl groups are omitted except for *ipso* carbons. Only the major contributors to the disordered chloride, Cl(2), and methyl group, C(3), sites are shown. Selected bond distances (Å): Ru(1)−Si(1) 2.2760(4), Ru(1)−H(1) 1.68(3), Ru(1)−H(2) 1.54(2), Ru(1)−H(3) 1.59(2), Si(1)−H(1) 1.94(3), Si(1)−H(2) 1.86(2), Si(1)−H(3) 1.94(2), Si(1)−Cl(1) 2.130(1), Si(1)−Cl(2) 2.075(1), Si(1)−C(3) 2.012(1). Selected angles (deg): Ru(1)−H(1)−Si(1) 77.5(10), Ru(1)−H(2)−Si(1) 83.7(11), Ru(1)−H(3)−Si(1) 79.6(11), Si(1)−Ru(1)−H(1) 56.2(9), Si(1)−Ru(1)−H(2) 54.2(9), Si(1)−Ru(1)−H(3) 56.9(9).

mined by X-ray diffraction at 183 K. The molecular structure of **1** (Figure 1) can be considered to consist of a seven-coordinate ruthenium center with facially disposed phosphines and hydrides approximately occupying the vertexes of an octahedron with the silyl group capping the face of the octahedron delimited by the three hydrides. Alternatively, the structure could be viewed as a distorted tetrahedral arrangement of the phosphine and silyl ligands about the ruthenium center [Si−Ru−P 113.6° (av) and P−Ru−P 104.9° (av)], with the hydrides capping three faces of the tetrahedron, each defined by two phosphines and the silyl ligand. The substituents of the silyl group are eclipsed with the phosphine ligands as viewed about the Ru−Si bond [P(2)−Ru(1)−Si(1)−Cl(1) −6.1°, P(1)−Ru(1)−Si(1)−Cl(2) 2.2°, P(3)−Ru(1)−Si(1)−C(3) −7.5°]. The Ru−Si distance of 2.276 Å is consistent with a single bond and is short compared to the range (2.29−2.55 Å) observed for other d^4 ruthenium silyl complexes.[19] The Ru−P distances (ca. 2.42 Å) are long due to the *trans* influence of the hydride ligands.

Of greater interest, however, is the fact that while the Ru−H distances (ca. 1.6 Å) are characteristic of terminal ruthenium hydrides,[20,21] the hydrides lie only ca. 1.9 Å from the silicon atom, suggesting a significant Si···H interaction. Bridging M−H−Si interactions have been well studied both by crystallographic and spectroscopic methods, especially NMR.[1−3] Such interactions can be considered to represent an arrested oxidative-addition of the Si−H bond to a transition-metal center. More commonly, such interactions are representative of an early part of the oxidative-addition reaction coordinate, i.e., M···H−Si, whereas in the current structure, the Si−H bond can be thought of being almost fully cleaved, i.e., M−H···Si.

We are aware of six compounds of the type $MH_3(SiX_3)L_3$ that are closely related to **1** for which crystal structures have been reported: $FeH_3\{Si(OEt)_3\}(CO)(dppe)$ (**2a**),[7] $RuH_2(\mu\text{-}H{-}SiPh_3)(\eta^2\text{-}H_2)(PCy_3)_2$ (**2b**),[22] $OsH_3\{Si(NC_4H_4)_3\}(PPh_3)_3$ (**2c**),[13] $OsH_3(SiHPh_2)(CO)(P^iPr_3)_2$ (**2d**),[14] $OsH_3(SiMe_3)(CO)(PPh_3)_2$ (**2e**),[16] and $OsH_3\{Si(OCH_2CH_2)_3N\}(PPh_3)_3$ (**2f**).[15] In all but one case, the set of three ligands, L, comprises either phosphines or CO. The exception is **2b**, where one of the three ligands is dihydrogen (η^2-H_2). In only three of the structures (**2b**, **2e**, and **2f**) were the hydride ligands located and refined by X-ray crystallography (see Table 1). In addition, the hydride geometry has been determined by ab initio calculations for a model system derived from **2c** and by DFT calculations for **2b** and **2d**. The latter, **2d**, is shown to exhibit a different overall geometry from that of **1** and is thus not considered further. In **1**, **2c**, and **2f**, the three hydride ligands appear to interact with the silicon center, whereas in **2b** there are two shorter H···Si separations, suggesting stronger interactions, and one longer H···Si separation indicative of no H···Si interaction in the solid state. The structure of **2e** might also be interpreted in terms of two H···Si interactions being stronger than the third.

The nature of these H···Si interactions is of considerable interest, not least of which as it pertains to an understanding of Si−H bond activation by transition-metal centers.[1] The interligand hypervalent interaction (IHI) theory proposed by Nikonov and co-workers[23−25] provides an explanation of the Ru−H···Si bonding in **1**. The IHI arises from the donation of Ru−H electron density into Si−halogen σ^* orbitals and gives rise to Ru−H···Si−halogen multicenter interactions (Figure 2a). (The short Ru−H and long Si···H distances observed in **1** (vide supra) are consistent with IHI.) Short Ru−Si distances arise from silicon substituent inductive effects and “rehybridization” of the silicon center. Electronegative substituents (X) on silicon require more Si p-character in the Si−X bond, thus leaving more Si s-character for Ru−Si bonding (Bent’s rule).[26] Also, the hypervalent coordination around silicon causes a “rehybridization” of silicon to give more Si p-character in the Si−X bonds resulting in more Si s-character for Ru−Si bonding. The higher s-character then leads to a shortened Ru−Si bond. Calculations by Hübler, Roper, and co-workers on $OsH_3(SiR_3)(PH_3)_3$ (R = H, NH_2,

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Table 1. Structural and Spectroscopic Data on M−H···Si Interactions in $MH_3SiX_3L_3$ Compounds

	M−Si (Å)	M−H (Å)	Si···H (Å)	$J(^{29}Si-^{1}H)$ (Hz)
1 (Ru)	2.2760(4)	1.54(2), 1.59(2), 1.68(3)	1.86(2), 1.94(2), 1.94(3)	39.7
2b (Ru)[22]	2.385(2)	1.49(4), 1.54(4), 1.66(2)	1.72(3), 1.83(3), 2.40(4)	
2c (Os)[13]	2.293(3)			29.2
	2.313[a]	1.646[a]	2.100[a]	(47.4)[b]
2e (Os)[16]	2.4533(8)	1.58(9), 1.55(9), 1.45(10)	1.980, 2.062, 2.211	
2f (Os)[15]	2.3442(8)	1.52(3), 1.57(3), 1.66(3)	1.96(3), 2.00(4), 2.06(4)	c

[a] From ab initio calculations on $OsH_3\{Si(NC_4H_4)_3\}(PH_3)_3$ model system. [b] For the ruthenium derivative $RuH_3\{Si(NC_4H_4)_3\}(PPh_3)_3$.[13] [c] Hydride signal in the $^{1}H\{^{31}P\}$ NMR spectrum reported as a singlet.

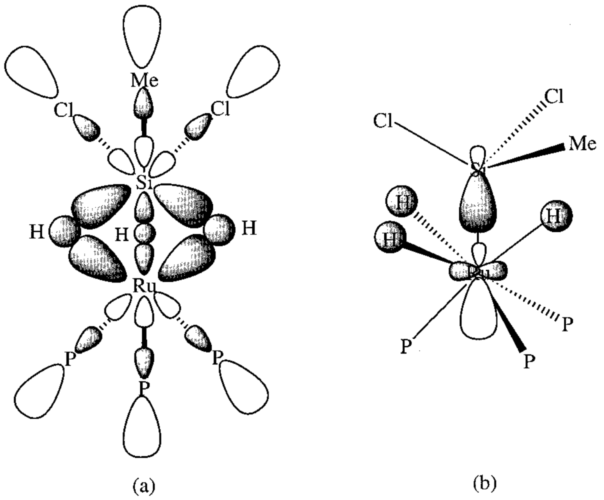

Figure 2. Orbital representation of Ru−H···Si bonding showing (a) the interaction of filled Ru−H σ orbitals with Si−X σ* orbitals and (b) the interaction of filled Ru−H σ orbitals with the Ru−Si σ* orbital (adapted from ref 13).

pyrrolyl) systems provided a similar view of the Ru−H···Si interactions in **1**. However, their calculations suggested an additional bonding interaction involving the M−H bonds and the M−Si σ* orbitals (Figure 2b) which shortens the M−Si bond as in **2c**.[13] They also noted that electron-withdrawing groups at silicon accentuate both of the orbital interactions described in Figure 2.

It is particularly noteworthy that compound **1** exhibits the shortest M−Si distance to date of the crystallographically characterized $MH_3(SiX_3)L_3$ (M = Ru, Os) systems (see Table 1) and shorter H···Si separations than all but the asymmetric system, **2b**. This is consistent with the presence of electron-withdrawing chloro substituents on the silyl ligand, which make the silicon center more electron-deficient, thus promoting electron donation from the hydrides. Indeed the shortest H···Si interaction involves H(2), which lies *trans* (at Si) to Cl(1), the most electron-withdrawing substituent. Hydrides H(1) and H(3) lie *trans* to a site that is ca. 2:1 or 1:2 Cl:Me, respectively. This points to the importance of the H···Si bonding interaction depicted in Figure 2a.[27]

Conclusion

$RuH_3(SiCl_2Me)(PPh_3)_3$ (**1**), formed from the reaction of $RuCl_2(PPh_3)_3$ with excess $HSiCl_2Me$, is the first ruthenium derivative of the type $MH_3(SiX_3)L_3$ to be structurally characterized in which the hydride ligands were crystallographically located and their positions refined. The structure of **1** shows three nonclassical Ru−H···Si interactions with short Ru−H and long Si···H distances. These interactions are not adequately described as electron-deficient three-center−two-electron (agostic Ru···H−Si) bonding in which a Si−H σ-bond donates electron density to the ruthenium center with concomitant metal-to-Si−H σ* orbital back-bonding. Rather, the ruthenium−hydrogen−silicon bonding in **1** is best described as electron-rich nonclassical Ru−H···Si−E (E = Cl or C) multicenter interactions arising from the donation of electron density from the Ru−H bonds to Si−E (E = Cl or C) σ* orbitals.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using either standard vacuum line or drybox techniques.[28] Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR-8900 spectrometer in CH_2Cl_2 solutions between CsF plates. ^{1}H NMR spectra were collected using Bruker AC-250 (250.13 MHz), Varian Unity Plus (299.95 MHz), and Bruker ARX-500 (500.13 MHz) spectrometers and were referenced to the residual proton peak of the solvent. ^{31}P NMR (101.26 MHz) spectra were obtained using a Bruker AC-250 spectrometer and externally referenced to 85% H_3PO_4. ^{29}Si DEPT spectra were recorded on Varian VXR 400s (79.5 MHz) and Bruker ARX-500 (99.37 MHz) spectrometers and externally referenced to $SiMe_4$.

Materials. $RuCl_2(PPh_3)_3$ was prepared by the published method[29] or used as received from Pressure Chemical (Lot #026588001). Hexanes (Fisher) were deolefinated with concentrated H_2SO_4 followed by distillation from potassium/benzophenone. Distilled hexanes and anhydrous diethyl ether were stored over $[Cp_2TiCl_2]_2ZnCl_2$.[30] Dichloromethane was distilled from and stored over CaH_2 and degassed prior to use. Dichloromethane-d_2 (Cambridge Isotopes) was stored over CaH_2. $HSiCl_2Me$ (Gelest) was dried and stored over CaH_2 and vacuum transferred prior to use.

$Ru(SiCl_2Me)H_3(PPh_3)_3$ (1). A 10 mL Kjeldahl flask fitted with a Teflon stopcock valve was charged with $RuCl_2(PPh_3)_3$ (530 mg, 0.55 mmol) and hexanes (3 mL) in the glovebox. Excess $HSiCl_2Me$, ca. 40 equiv, was added to the reaction flask using vacuum transfer techniques. The brown suspension was heated in a 65 °C oil-bath for 12 h. Upon completion, the unreacted hydrosilane and ~50% of the solution volume were removed under vacuum to initiate precipitation. The precipitate was collected, washed with hexanes, and dried under vacuum to afford **1** (460 mg, 83%) as a near colorless solid. ^{1}H NMR (CD_2Cl_2): δ −9.76 (m, 3H, RuH), 0.48 (s, 3H, $SiCl_2Me$), 6.98−7.23 (m, ca. 45H, PPh_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 128.11, 129.54, 134.45 (Ph). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 38.31

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[27] This bonding description is reinforced upon examination of hydrogen-bonding interactions also present in **1** (see Supporting Information).

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Table 2. Data Collection, Structure Solution, and Refinement Parameters for $RuH_3(SiMeCl_2)(PPh_3)_3$ (1)

cryst syst	orthorhombic
space group, Z	$Pna2_1$, 4
a (Å)	23.7603(4)
b (Å)	14.6024(3)
c (Å)	13.9643(3)
V (Å^3)	4845.0(2)
density (g/cm^{-3})	1.378
temp (K)	183(5)
X-ray wavelength (Å)	0.71073
$\mu_{(\text{Mo K}\alpha)}$ (mm^{-1})	1.258
θ range	1.64−30.61
no. of reflns collected	84 251
no. of ind reflns (R_{int})	14 197 (0.036)
no. of obsd reflns ($I > 2\sigma(I)$)	13 399
least squares params	570
$R(F)$, $I > 2\sigma(I)$	0.024
$wR(F^2)$, all data	0.065
$S(F^2)$, all data	0.997

(s). $^{29}Si\{^1H\}$ DEPT NMR (CD_2Cl_2): δ 34.6 (q, $J_{SiP} = 12.8$ Hz). IR (CH_2Cl_2): ν(Ru−H−Si) 1933 (br) cm^{-1}. IR (KBr): ν(Ru−H−Si) 1961.5 (br) cm^{-1}. Anal. Calcd for $C_{55}H_{51}Cl_2P_3RuSi$: C, 65.73; H, 5.11. Found: C, 65.23; H, 4.69.

X-ray Crystal Structure Determination of $Ru(SiCl_2Me)H_3(PPh_3)_3$ (1). Crystals of **1** suitable for X-ray diffraction analysis were grown by vapor diffusion of Et_2O into a CH_2Cl_2 solution of **1** at room temperature in the glovebox. X-ray diffraction data for **1** were obtained using a Bruker SMART CCD diffractometer. Data were corrected for absorption by empirical methods (SADABS).[31,32] The structure was solved by direct methods and refined to convergence by full-matrix least-squares using the SHELXTL suite of programs.[33] All non-hydrogen atoms were refined anisotropically. Phenyl hydrogen atoms were included in calculated positions and refined using a riding model with fixed isotropic displacement parameters. The hydride ligands were located from the difference map and refined with no positional constraints and a common isotropic displacement parameter. The $SiMeCl_2$ group was orientationally disordered such that two of the three substituent positions on silicon were partially occupied by a chloride and partially occupied by a methyl group. After trying a number of refinement models, a model was chosen whereby the disordered chlorine and carbon atoms occupied common sites (67:33 and 33:67 occupancy), but were permitted independent displacement parameters.[34] Hydrogen atoms were added and refined using a riding model on the methyl group of major occupancy. Experimental crystallographic details are provided in Table 2.

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Supporting Information Available: Tables of crystal data, data collection and refinement parameters, positional and anisotropic displacement parameters, and interatomic distances and angles, descripton of C−H···H−Ru and C−H···Cl−Si hydrogen bonds, and ^1H NMR spectra for $RuH_3(SiMeCl_2)(PPh_3)_3$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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[31] Sheldrick, G. *SADABS*, Empirical Absorption Correction Program; University of Göttingen, 1995, based on the method of Blessing.[32]

[32] Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

[33] *SHELXTL PLUS Software Package for the Determination of Crystal Structures, Version 5.0*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1994.

[34] It should be noted that the crystallographic model does not distinguish between the possibilities of orientational disorder of the $SiMeCl_2$ group as reported and an alternative involving a 1:1 solid solution of $RuH_3(SiMeCl_2)(PPh_3)_3$ and $RuH_3(SiMe_2Cl)(PPh_3)_3$. However, a ^1H NMR spectrum (CD_2Cl_2) of this set of crystals indicated only the presence of **1**, δ(SiMe) = 0.48, with no detectable amount of $RuH_3(SiMe_2Cl)(PPh_3)_3$, δ(SiMe) = 0.27.