Inorg. Chem. **1990**, *29*, 1511–1517 **1511**

Table VI. Positional Parameters for $[(C_5Me_5)Rh(m\text{-}CN\text{-}2,6\text{-xylyl})]_2$

atom	*x*	*y*	*z*
Rh1	0.44175 (4)	0.03882 (4)	0.07860 (4)
N1	0.3333 (5)	0.0869 (5)	−0.1721 (5)
C1	0.4170 (6)	0.1758 (5)	0.1905 (6)
C2	0.4372 (6)	0.0900 (6)	0.2687 (6)
C3	0.3415 (6)	0.0213 (5)	0.2352 (6)
C4	0.2616 (6)	0.0650 (5)	0.1350 (6)
C5	0.3085 (6)	0.1611 (5)	0.1101 (6)
C6	0.4953 (8)	0.2688 (6)	0.2011 (8)
C7	0.5357 (7)	0.0799 (7)	0.3723 (7)
C8	0.3150 (7)	−0.0727 (6)	0.3004 (8)
C9	0.1482 (7)	0.0182 (6)	0.0727 (8)
C10	0.2513 (8)	0.2361 (7)	0.0188 (8)
C11	0.4117 (5)	0.0468 (5)	−0.0982 (5)
C12	0.3161 (6)	0.1263 (5)	−0.2896 (6)
C13	0.2228 (7)	0.0862 (6)	−0.3724 (7)
C14	0.2047 (7)	0.1272 (8)	−0.4878 (7)
C15	0.2756 (8)	0.2041 (8)	−0.5190 (7)
C16	0.3664 (8)	0.2429 (7)	−0.4348 (8)
C17	0.3887 (7)	0.2062 (6)	−0.3194 (6)
C18	0.1456 (8)	0.0028 (7)	−0.3384 (8)
C19	0.4835 (8)	0.2528 (7)	−0.2265 (8)

being refined. Table III contains relevant bond distances and angles, and Table IV contains positional parameters.

X-ray Structural Determination of $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$. Well-formed orange crystals of the compound were prepared by slow evaporation from a CH_2Cl_2 solution. The data collection and reduction were carried out as described above for the rhodium commplex with the parameters given in Table II. Systematic absences uniquely indicated the space group as $P2_1/c$. The structure was solved by using standard heavy-atom methods. Hydrogen atoms were placed in locations based upon peaks in the difference Fourier map but were not varied in the final refinement. Table III contains relevant bond distances and angles, and Table V contains positional parameters.

X-ray Structural Determination of $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$. A small well-formed dark green plate of the compound was prepared by slow evaporation of a hexane solution, mounted to a glass fiber, and coated with epoxy. The sample was cooled to −75 °C in a nitrogen stream, and the lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Initial indexing produced a monoclinic cell. While cell reduction with the program TRACER revealed a centered orthorhombic crystal system (90° ± 0.4°), axial photographs in this setting did not show the required Laue symmetry, but rather were consistent with a monoclinic system. Consequently, data were collected on the crystal in the monoclinic setting in accord with the parameters given in Table II. The space group was assigned as $P2_1/a$ on the basis of the systematic absences. A Patterson map solution showed a Rh atom near a center of symmetry that generated the second half of the dimer, giving a total of two molecules (four halves) per unit cell. Structure expansion with the program DIRDIF revealed all other non-hydrogen atoms. Following isotropic refinement, the program DIFABS was employed to correct for absorption. Full anisotropic refinement with placement of the hydrogen atoms in idealized positions based upon peaks in the difference Fourier map yielded the final structure shown in Figure 3. We thank a reviewer for encouraging us to reexamine the initial orthorhombic cell (which produced an incorrect disordered solution) during review of this manuscript. Table III contains relevant bond distances and angles, and Table VI contains positional parameters.

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Supplementary Material Available: Listings for $(C_5Me_5)Rh(CNMe)Cl_2$, $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$, and $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$ of anisotropic thermal parameters, bond distances and angles, and hydrogen atom parameters (17 pages); listings for all these compounds of calculated and observed structure factors (49 pages). Ordering information is given on any current masthead page.

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Reaction of $ReH_7(PPh_3)_2$ with Silanes: Preparation and Characterization of the First Silyl Polyhydride Complexes, $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$, $SiEt_3$, $SiHEt_2$)

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Reaction of silanes with $ReH_7(PPh_3)_2$ (**1**) gives the novel rhenium silyl hexahydride complexes $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$ (**2a**), $SiEt_3$ (**2b**), $SiHEt_2$ (**2c**)), which have been fully characterized by IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopy and, in the case of **2a**, by single-crystal X-ray crystallography. The spectroscopic and X-ray diffraction data suggest that **2a–c** probably have a classical nine-coordinate tricapped trigonal-prismatic structure with the two phosphine ligands and the silyl group occupying the three equatorial sites and the six hydride ligands occupying the six axial positions. **2a** has been obtained in two crystalline forms, one solvated (CH_2Cl_2) and the other unsolvated, and structures were determined on both. Crystals of the unsolvated **2a** belong to space group $P\bar{1}$ with a = 9.293 (3) Å, b = 13.037 (3) Å, c = 19.152 (2) Å, α = 86.50 (1)°, β = 88.83 (2)°, γ = 88.40 (2)°, V = 2315 (2) Å^3, Z = 2, and ρ_{calcd} = 1.401 (1) g/cm^3. Crystals of **2a**·CH_2Cl_2 belong to space group $P2_1/c$ with a = 10.416 (1) Å, b = 24.065 (5) Å, c = 19.505 (3) Å, β = 100.16 (1)°, V = 4812 (1) Å^3, Z = 4, and ρ_{calcd} = 1.463 (1) g/cm^3. The Re–Si bond lengths, 2.474 (4) Å (**2a**) and 2.475 (4) Å (**2a**·CH_2Cl_2), are shorter than the sum of the covalent radii of the Re and Si atoms (2.65 Å), which is unusual for a transition-metal silyl complex with a formal d^0 configuration.

Introduction

The synthesis and structural characterization of transition-metal polyhydride complexes are of current interest.[1] Many of these complexes undergo a variety of catalytic and stoichiometric reactions, including alkane conversion. This seems to be a result of their ability to generate reactive intermediate species containing vacant coordination sites by elimination of H_2 through thermolysis, photolysis, or acidolysis. Very recently, some polyhydride complexes have been reformulated as having a nonclassical structure containing η^2-H_2 ligands bound in a molecular fashion.[2] The presence of these η^2-H_2 ligands may be related to the facile loss of H_2 found in some cases.

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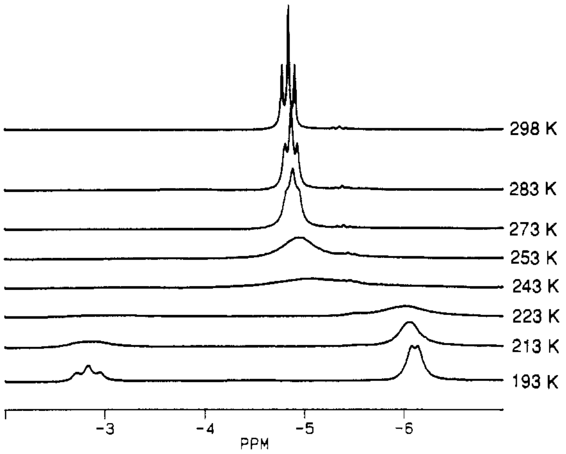

Figure 1. Variable-temperature ^1H NMR spectra of $ReH_6(SiPh_3)(PPh_3)_2$ (**2a**) in CD_2Cl_2 at 250 MHz in the hydride region only.

Transition-metal silyl dihydrides or trihydrides supported by either Cp* or Cp,[3] or by phosphines,[4] are known, but the exact formulations of the compounds are sometimes controversial[4a,b] and only in a few cases[3c–d,4g–h] are crystallographic data available. No examples of metal silyl polyhydrides (i.e., containing more than three hydride ligands) seem to have been reported. In this context, we decided to look at the reactions of transition-metal polyhydride complexes with silanes in the hope that the characterization of these reactions and their products might also throw light on the structure of the parent polyhydrides. We report here the synthesis and characterization of the first silyl polyhydride complexes $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$ (**2a**), $SiEt_3$ (**2b**), $SiHEt_2$, (**2c**)).

Results and Discussion

Preparation. $ReH_7(PPh_3)_2$ (**1**), one of the first polyhydride complexes reported, is unusual in that it undergoes H/D exchange with both D_2 and CH_3OD,[5a] reacts under mild thermal conditions with a variety of 2e ligands to give the corresponding pentahydride complexes,[5] and is capable of catalytic alkane conversions.[6] We have found that **1** reacts slowly (24–36 h) at room temperature with 8–10 mol equiv of R_3SiH in tetrahydrofuran to give the rhenium silyl hexahydride complexes of the type $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$ (**2a**), $SiEt_3$ (**2b**), $SiHEt_2$ (**2c**)) (eq 1). These complexes were isolated in high yields as air-stable beige solids by partial evaporation of the THF and precipitation with hexane or heptane. They were fully characterized on the basis

$$\begin{array}{llll} \underset{\mathbf{1}}{\mathrm{ReH_7(PPh_3)_2}} + \mathrm{R_3SiH} = & \mathrm{ReH_6(SiR_3)(PPh_3)_2} + \mathrm{H_2} & & (1) \\ & \mathbf{2a},\ \mathrm{R_3} = \mathrm{Ph_3} & & \\ & \mathbf{2b},\ \mathrm{R_3} = \mathrm{Et_3} & & \\ & \mathbf{2c},\ \mathrm{R_3} = \mathrm{HEt_2} & & \end{array}$$

of elemental analysis and spectroscopic data and by single-crystal X-ray crystallographic studies in the case of **2a**.

We initially envisaged three possible formulations for **2**: a classical nine-coordinate silyl hexahydride complex $ReH_6(SiR_3)(PPh_3)_2$ (A), a nonclassical eight-coordinate dihydrogen silyl tetrahydride complex $ReH_4(SiR_3)(\eta^2\text{-}H_2)(PPh_3)_2$ (B), or a nonclassical eight-coordinate silane pentahydride complex $ReH_5(\eta^2\text{-}H\text{–}SiR_3)(PPh_3)_2$ (C). As will be discussed below, the spectroscopic and X-ray crystallographic data favor the formulation A, although the crystallographic data seem to indicate that there may be some interaction between two of the six hydrides and the Si.

NMR Spectroscopic Studies. The ^1H NMR spectrum (Figure 1) of **2a** in CD_2Cl_2 at 25 °C shows a triplet hydride resonance at δ -4.82 (J_{HP} = 16.2 Hz), suggesting rapid fluxionality and the presence of two equivalent phosphines. Careful integration of the ^1H NMR spectrum and the observation of a binomial heptet at δ 22.9 (J_{HP} = 15.7 Hz) in the selectively hydride-coupled ^{31}P NMR spectrum demonstrate that six hydrides are present. The ^{13}C NMR spectrum shows the expected eight resonances, four for the two triphenylphosphines and four for the $SiPh_3$ group.

The ^1H NMR spectra of **2b,c** at 25 °C show a similar triplet hydride resonance of intensity 6 at δ -5.91 (J_{HP} = 16.2 Hz) and δ -5.62 (J_{HP} = 16.2 Hz), respectively. Unexpectedly, the ethyl groups in **2b,c** appear as a singlet resonance at δ 0.79 and 0.95, respectively. This is probably due to the fortuitous coincidence of the chemical shifts of the methylene and methyl protons as a result of the diamagnetic anisotropic effect of the ring current of the adjacent phenyl groups of the two PPh_3 ligands. The ^{13}C NMR spectra of **2b,c** are normal and show a triplet and a quartet resonance for the ethyl groups. The selectively hydride-coupled ^{31}P NMR spectra of **2b,c** exhibit a binomial heptet at δ 24.8 (J_{HP} = 15.9 Hz) and 4.9 (J_{HP} = 15.8 Hz), respectively.

Most phosphine polyhydrides such as $ReH_7(PPh_3)_2$ are fluxional on the NMR time scale even at the lowest accessible temperature.[7] Variable-temperature ^1H NMR studies of **2a–c** reveal that replacement of a hydride ligand by a silyl group leads to an increase in the barrier for the fluxional process. Although the six hydrides are equivalent at 25 °C, displaying only a relatively sharp triplet, upon cooling, this triplet broadens and collapses into two separate resonances with an intensity ratio of 2:4, as shown in Figure 1 in the case of **2a**. The triplet at δ–4.82 observed at 298 K changes into a broad feature at 253 K, which is resolved at 193 K into a triplet of intensity 2 at δ -2.83 (J_{HP} = 29.4 Hz) and a doublet of intensity 4 at δ -6.13 (J_{HP} = 16.2 Hz). Homonuclear ^1H-decoupling experiments have shown that HH′ coupling is not important since irradiation of one hydride resonance produced no change in the pattern of the other hydride resonance. A similar decoalescence pattern was observed for **2b**. In the case of **2c**, the barrier of the fluxional process is lower probably because of the smaller size of the $SiHEt_2$ group compared to $SiPh_3$ and $SiEt_3$, and so decoalescence occurs at lower temperature and yields two broad hydride resonances at 183 K with no resolvable H–P coupling. In all cases, there is no significant change in ^{31}P NMR spectra upon cooling, only one resonance being observed at all temperatures.

The 2:4 ratio of the two hydride resonances of **2a–c** at low temperature is most readily interpreted in terms of either of the two classical nine-coordinate tricapped trigonal-prismatic (TTP) structures **3a,b**.[8] In **3a** the phosphines occupy two equatorial positions capping two of the three prism faces, whereas in **3b** they take up two eclipsed prism positions. The expected P–Re–P angles for the two ideal structures are 120° for **3a** and 90° for **3b**.

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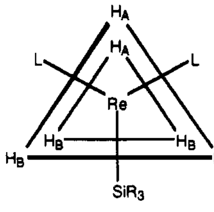
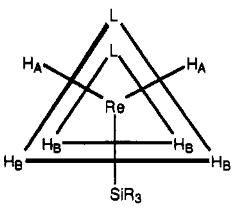
(8) The lines of the two triangular faces in **3a,b** are the edges of the polyhedron and not chemical bonds.



3a

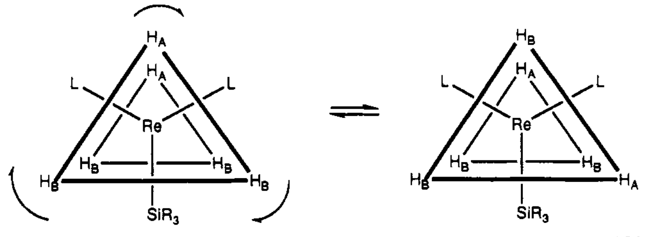


(L = PPh$_3$)

3b

We expect the bulky PPh$_3$ and SiR$_3$ groups to occupy the three equatorial positions of a tricapped trigonal prism and the six hydrides to occupy the axial positions, in order to minimize the steric repulsions. **2a–c** are therefore more likely to adopt the structure **3a**, which has been confirmed by X-ray crystallography in the case of **2a** (vide infra). The structure **3a** is also consistent with the multiplicities of the hydride resonances in the slow-exchange limiting ^{1}H NMR spectra of **2a**,**b**. The two H$_A$'s are cis to two phosphine ligands, and so a triplet with a typical cis $^2J_{HP}$ value is observed. The four H$_B$'s are cis to one phosphine ligand, giving the observed doublet. The second phosphine ligand lies at an angle of ca. 135° to the Re–H$_B$ bond. This particular angle may lead to a near-zero $^2J_{PReH}$ coupling constant, similar to the situation in geminal P–C–H couplings,[9] which show a Karplus-like dependence on the dihedral angle.

Nine-coordinate tricapped trigonal-prismatic structures are known to be highly fluxional due to the very low barriers for pseudorotation.[10] In ReH$_9{}^{2-}$, pseudorotation exchanges H$_{ax}$ (ax = axial) and H$_{eq}$ (eq = equatorial), consistent with the observation of a single hydride resonance at all accessible temperatures. As applied to **3a**, pseudorotation converts it into **3b** with H$_A$'s and H$_B$'s remaining distinct. This means that the exchange of H$_A$ and H$_B$ requires a different mechanism. We cannot distinguish between such possibilities as rotation of one triangular face of the three H$_{ax}$ ligands (eq 2) or rotation of H$_2$ in an intermediate dihydrogen complex.



(2)

To see whether **2a–c** adopt a nonclassical structure containing an η^2-H$_2$ ligand, we carried out variable-temperature ^{1}H NMR T_1 measurements on the hydride resonances of **2a** in CD$_2$Cl$_2$ at 250 MHz. The data are listed in Table I. The minimum T_1 values observed for the resonances at δ −2.83 and −6.13 are 76 and 79 ms, respectively, at 250 MHz and 209 K. These numbers fall into a range that was once[2f] considered typical of nonclassical polyhydrides. However, if one of the two distinct hydride resonances in the slow-exchange-limit spectra of **2a–c** arose from an η^2-H$_2$ ligand, isotopic perturbation of resonance would be expected in the fast-exchange-limit spectra.[11,12] In fact, we found only a very small isotope shift (ca. −0.002 ppm/D) in the ^{31}P-decoupled ^{1}H NMR spectrum of an isotopomeric mixture of **2a**. The small isotope shift probably arises from normal geminal deuterium isotope effects on nuclear magnetic shielding.[13] Therefore, **2a–c** seem unlikely to contain an η^2-H$_2$ ligand.

Table I. Variable-Temperature ^{1}H NMR T_1 Measurement on RH$_6$(SiPh$_3$)(PPh$_3$)$_2$ (**2a**) in CD$_2$Cl$_2$ at 250 MHz

T, K	δ, ppm; intensity; multiplicity; $^2J_{HP}$, Hz	T_1, ms
193	−2.8; 2 H; t; 29	109
	−6.1; 4 H; d; 16	112
203	−2.8; 2 H; t; 29	85
	−6.1; 4 H; d; 16	87
209	−2.8; 2 H; br	76
	−6.1; 4 H; br	79
213	−2.8; 2 H; br	84
	−6.1; 4 H; br	88
253	−4.9; 6 H; br	91
263	−4.8; 6 H; br	102
273	−4.8; 6 H; t; 16	113
283	−4.8; 6 H; t; 16	132
298	−4.8; 6 H; t; 16	187

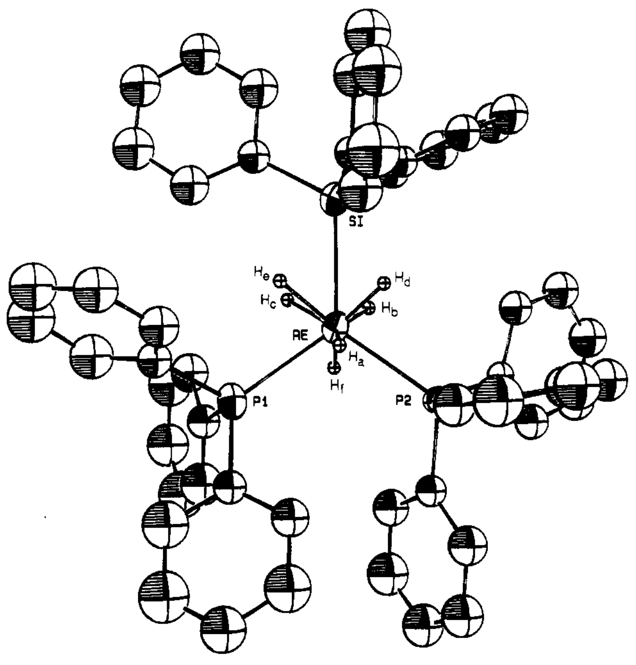


Figure 2. ORTEP diagram of the crystal structure of the unsolvated form of ReH$_6$(SiPh$_3$)(PPh$_3$)$_2$ (**2a**) as determined by single-crystal X-ray diffractometry. The hydride positions shown refer to the observed electron density maxima in the vicinity of the Re atom.

These results have led us to undertake a reinvestigation of the structures of ReH$_7$P$_2$ complexes. We[14a] have found that the hydride resonances of ReH$_7$(dppb) (dppb = 1,4-bis(diphenylphosphino)butane) and ReH$_7$(dppf)(dppf = 1,1′-bis(diphenylphosphino)ferrocene) decoalesce at low temperature. The low-temperature hydride patterns, T_1, and deuterium isotope effect data indicate a classical TTP structure, as have been observed for ReH$_7$(dppe) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) by neutron diffraction.[15] Clearly, the lower limit of the range of T_1(min) values previously assigned to nonclassical structures is too high. We will

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Table II. Crystallographic Data for **2a** and **2a**·CH_2Cl_2

	unsolvated complex	solvated complex
formula	$ReP_2SiC_{54}H_{51}$	$ReCl_2P_2SiC_{55}H_{53}$
mol wt	976.24	1061.18
cryst color; size, μm	colorless; 300 × 150 × 100	colorless; 450 × 300 × 200
space group	triclinic: $P\bar{1}$	monoclinic: $P2_1/c$
cell dimens (dist, Å; angle, deg)	$a = 9.293$ (3), $b = 13.037$ (2), $c = 19.152$ (2), $\alpha = 86.50$ (1), $\beta = 88.83$ (2), $\gamma = 88.40$ (1)	$a = 10.416$ (1), $b = 24.065$ (5), $c = 19.505$ (3), $\beta = 100.16$ (1)
V, Å^3	2315	4812
Z	2	4
ρ_{calcd}, g cm^{-3}	1.401 (1)	1.465 (1)
λ(Mo Kα), Å	0.71073	0.71073
T, K	295	295
linear abs coeff, mm^{-1}	2.787	2.796
F(000)	988	2144
abs: min, max	0.912, 1.118	0.809, 1.160
θ limits, deg	1, 20	1, 20
k: min, max	−8, 8	−10, 10
k: min, max	−12, 12	0, 23
k: min, max	0, 18	0, 18
decay: %; t, h	−6.4; in 64	−13; in 68
no. of tot. measd reflns	4477	4797
no. of tot. unique reflns > $3\sigma(I)$	2921	2829
no. of tot. indep params	251	241
weights	unity	unity
final $R(F)$	0.043	0.045
final $R_w(F_2)$	0.055	0.057
max shift/error	0.030	0.05

discuss this problem more fully in another paper.[14b]

Mechanism of the Reaction of $ReH_7(PPh_3)_2$ with Silanes. From a detailed kinetic study of the reaction of $ReH_7(PCy_3)_2$ with a variety of nucleophiles, Caulton has concluded that $ReH_5(PCy_3)_2$ is the reactive intermediate formed by thermal loss of H_2 from $ReH_7(PCy_3)_2$.[16] The reaction of eq 1 likely proceeds in the same way via $ReH_5(PPh_3)_2$ in view of the ease with which **1** loses dihydrogen in solution under mild thermal conditions to yield the dimer $Re_2H_8(PPh_3)_4$.[5a,17] Consistent with this mechanism, we found that the presence of H_2 slows down the reaction and that ReH_7(dppe), which is much more stable toward loss of H_2 than **1**,[5a] fails to react with silanes even in refluxing THF. A concerted four-center mechanism, which is analogous to that commonly proposed in the hydrogenolysis of metal–carbon σ bonds in d^0 systems, seems much less likely.[18]

The reaction of $ReD_7(PPh_3)_2$ (**1**-d_7) with Et_2SiH_2 gave $ReHD_5(SiHEt_2)(PPh_3)_2$ as the only product identified by ^1H and ^2H NMR spectroscopy. The product did not undergo H/D exchange with H_2 or excess Et_2SiH_2, nor did it undergo intramolecular H/D exchange between the Si–H and Re–D sites. These results shows that D_2 is first lost from **1**-d_7 to form $ReD_5(PPh_3)_2$, which then undergoes oxidative addition with Et_2SiH_2 to form the observed product. The concerted four-center mechanism is ruled out, since it would give $ReD_6(SiHEt_2)(PPh_3)_2$ as the product.

X-ray Crystallographic Studies on 2a. We determined the structure of an unsolvated form of **2a** as well as that of the CH_2Cl_2 solvate by single-crystal X-ray crystallography. The crystallographic data for **2a** and **2a**·CH_2Cl_2 appear in Tables II–IV, and an ORTEP diagram of the unsolvated form of **2a** is shown in Figure 2. The key feature of both structures is the nearly coplanar arrangement of Re, Si, and two P atoms. The structures resemble the neutron diffraction structure[19] of ReH_9^{2-} with the three equatorial hydrides replaced by the $SiPh_3$ group and two PPh_3 ligands in **2a**. The Re atom lies only 0.138 (1) and 0.028 (1) Å out of the P_2Si plane in the solvated and unsolvated compounds, respectively. Since the unsolvated compound gave the best refinement, we discuss this structure in detail below.

The bond angles P–Re–P (109.9°) and P–Re–Si (average 124.6°) differ from 120° expected for a nine-coordinate tricapped trigonal-prismatic structure with these atoms in the equatorial positions (**3a**), but relatively little structural work has been done in this coordination geometry, and such distortions may prove not to be unusual. Alternatively, the phosphines may be described as being in eclipsed axial positions (ideal P–Re–P = 90°) with the silyl group as the capping ligand on the opposite face (ideal Si–Re–P = 135°).

Muir[20a] first pointed out that d^0 group 4 metal–silyl bonds are long. Surprisingly, the Re–Si bond lengths, 2.474 (4) Å (**2a**) and 2.475 (4) Å (**2a**·CH_2Cl_2), are shorter than the sum of the covalent radii of the Re and Si atoms (2.65 Å). This is unusual for a transition-metal silyl complex with a formal d^0 configuration where M(d$_\pi$) to Si(d$_\pi$) back-donation is unlikely, although a short Ti–Si bond has been reported in a bridging silylene Ti(d^0) complex $Cp_2Ti(\mu\text{-}SiH_2)_2TiCp_2$.[20b] In fact, the Re–Si bonds in **2a** and **2a**·CH_2Cl_2 seem to be shorter than any previously reported Re–Si bond in any crystallographically characterized rhenium silyl complex in the literature. Tilley et al. have shown that the long and relatively weak M(d^0)–Si bonds in group 4 and 5 transition-metal silyl complexes undergo facile insertion reactions with a variety of substrates.[21] In contrast, the short Re–Si bond of **2a** does not undergo insertion reactions with CO and ^{t}BuNC, although this may be because no labile coordination site is available.

Six electron density maxima were observed and persisted after the absorption correction has been applied. These were tentatively identified with the hydride ligands and refined as such. In both structures they form a trigonal prism, as expected on the basis of a tricapped trigonal-prismatic structure with the P- and Si-donor ligands in the equatorial plane. The hydride positions are shown for the unsolvated complex in Figure 2. Crystals suitable for neutron diffraction have not yet been obtained, and so the hydride positions shown in Figure 2 are only a working hypothesis. The general pattern of a trigonal prism as expected from the model

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shown as **3a** is found, but, surprisingly, two of the hydrides appear to be close to the Si atoms. The $Si\cdots H_d$ and $Si\cdots H_e$ distances are 1.76 and 1.92 Å, respectively. These are longer than the normal Si–H covalent bond length (1.48 Å) but are much shorter than the sum of the van der Waals radii of the two atoms (3.1 Å). The two hydrides may therefore be interacting with silicon.

Two-electron three-center $Si—H\cdots M$ interactions have been observed in compounds of the type $CpMn(CO)LHSiR_3$ (L = phosphine or CO) both by X-ray and neutron diffraction methods[22–24] and supported by theoretical calculations.[25] A related type of interaction has been suggested to be involved in the catalysis of silane alcoholysis.[26] An $M(\eta^2\text{-}H\text{-}SiR_3)$ arrangement would be reasonable in view of the high formal oxidation state of the metal center in **2**. An $M(\eta^3\text{-}H_2SiR_3)$ arrangement is unprecedented, but not unreasonable since it can be viewed as an $M(\eta^3\text{-}H_3)$ analogue. The current interest in $\eta^2\text{-}H_2$ complexes has lead to speculation and theoretical studies concerning the possibility of $\eta^3\text{-}H_3$ complexes.[27] On the basis of the unusually large HH′ couplings in $CpIrLH_3^+$ [28] and $(C_5H_{5-n}R_n)_2NbH_3$,[29] $M(\eta^3\text{-}H_3)$ structures have been suggested. However, more recent NMR studies[30] show that proton–proton exchange couplings are responsible for the anomalous NMR behavior and a neutron diffraction study[31] on $Cp^*Ir(PMe_3)H_3$ reveals that a classical structure is adopted in the solid state.

We have attempted to obtain spectroscopic evidence for a bridging structure of **2a**. The small isotope shift in the hydride resonance, mentioned above, rules out a structure containing a coordinated $\eta^2\text{-}H_2$ but is probably only weak evidence against an Si–H–Re bridge, because the M–H stretching frequencies are not expected to differ greatly on bridge formation. The IR spectra of both the solvated and unsolvated forms of **2a** in different solvents and in the solid state show no unusual features that could be associated with bridging hydrides. The ^{31}P-decoupled ^1H NMR spectra show no satellite hydride peaks due to coupling to ^{29}Si either at 298 K or at low temperature, but even if a bridging structure were adopted, the fluxionality could result in a very small H–Si coupling that might not be observable experimentally. The X-ray crystal structure of **2a** shows no special distortion of the $SiPh_3$ group, such as might be seen if Re–H–Si bridges were present in the solid state.

On the other hand, two lines of evidence tend to favor the $Re(\eta^3\text{-}H_2SiR_3)$ structure. First, the Re–Si distance is unusually short for a d^0 silyl complex, which may be caused by the two hydrides bridging between the Re and Si atoms. Second, the tricapped trigonal prism **3a** should have P–Re–P and P–Re–Si angles close to 120° since $SiPh_3$ and PPh_3 groups are essentially isosteric. The observed angles are significantly different: P–Re–P, 109.9°; P–Re–Si, average 124.6°. The presence of $Re(\mu\text{-}H)_2Si$ bridges would naturally lead to an opening of the P–Re–Si angles. Alternatively, it may be useful to recall that if the phosphines are better described as being in the eclipsed axial positions (ideal P–Re–P = 90°) with the silyl group as the capping ligand on the opposite face (ideal Si–Re–P = 135°), as shown in **3b**, then the nonsymmetrical angles could arise without needing to postulate distortions due to bridging hydrides. We hope to test some of these ideas in future neutron diffraction work.

Conclusion

We have synthesized and characterized the first silyl polyhydrides, $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$ (**2a**), $SiEt_3$ (**2b**), $SiHEt_2$ (**2c**)). The replacement of a hydride in $ReH_7(PPh_3)_2$ by a silyl group allows the fluxionality to be frozen out in the ^1H NMR spectrum at low temperatures. The results from the variable-temperature ^1H NMR studies suggest that **2a–c** adopt a classical nine-coordinate tricapped trigonal-prismatic structure, all the hydrides being axial. Pseudorotation does not exchange the two types of hydride ligands in the structure, and so we propose that rotation of one triangular face of the tricapped trigonal prism or rotation of H_2 in an intermediate dihydrogen complex is responsible. Single-crystal X-ray crystallographic studies of **2a** and **2a**·CH_2Cl_2 confirm the classical nine-coordinate structure postulated from the NMR data. The Re–Si bonds in **2a** and **2a**·CH_2Cl_2 are unusually short. The possibility exists that two hydride ligands may bridge between the Re and Si atoms to form a $Re(\eta^3\text{-}H_2SiR_3)$ species.

Experimental Section

General Information. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. ^1H, ^2H, and ^{13}C NMR spectra were recorded on a Bruker WM 250 or WM 500 spectrometer; chemical shifts are measured with reference to the residual solvent resonance. ^{31}P NMR spectra were recorded on a Bruker WM 500 spectrometer; chemical shifts are given in ppm downfield from external 85% H_3PO_4. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Desert Analytic Co. Reagents were purchased from Aldrich Chemical Co. Tetrahydrofuran, hexane, and heptane were distilled from Na/Ph_2CO; dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over 4-Å molecular sieves. $ReH_7(PPh_3)_2$ was prepared according to the literature method.[32]

Hexahydrido(triphenylsilyl)bis(triphenylphosphine)rhenium(VII) (2a). A solution of $ReH_7(PPh_3)_2$ (250 mg, 0.10 mmol) and Ph_3SiH (500 mg, 1.0 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 24 h. About every 8 h, the vapor phase was pumped away to remove the H_2 formed in the reaction and the flask refilled with nitrogen. The volume of the solution was then reduced to 1 mL in vacuo, and hexane (30 mL) was added to precipitate **2a** as a beige solid. The product was filtered out, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 220 mg, 75%. Anal. Calcd for $C_{54}H_{51}P_2ReSi$: C, 66.44; H, 5.27. Found: C, 65.15; H, 5.58. IR (Nujol): ν_{Re-H} 1992, 1950, 1929 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.4 (c, 45 H, Ph), −4.82 (t, $^2J_{HP}$ = 16.2 Hz, 6 H, Re–H). ^1H NMR (CD_2Cl_2, 193 K): δ 7.2–7.4 (c, 45 H, Ph), −2.83 (t, $^2J_{HP}$ = 29.4 Hz, 2 H, Re–H_A), −6.13 (d, $^2J_{HP}$ = 16.2 Hz, 4 H, Re–H_B). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 22.9 (heptet, $^2J_{HP}$ = 15.7 Hz). Off-resonance ^1H-decoupled ^{13}C, NMR (CD_2Cl_2, 298 K): δ 138.0 (c, 6 C, C_1 of PPh_3), 134.2 (dt, $^2J_{PC}$ = 5.4 Hz, 12 C, C_2 of PPh_3), 129.8 (s, 6 C, C_4 of PPh_3), 128.1 (dt, $^3J_{PC}$ = 4.8 Hz, 12 C, C_3 of PPh_3), 149.2 (s, 3 C, C_1 of $SiPh_3$), 136.4 (d, 6 C, C_2 of $SiPh_3$), 127.3 (d, 3 C, C_4 of $SiPh_3$), 127.0 (d, 6 C, C_3 of $SiPh_3$).

The isotopomeric mixture of **2a**–d_{0-6} was similarly prepared by reaction of the mixture of $ReH_{7-x}D_x(PPh_3)_2$ (x = 0–7) with Ph_3SiH.

Hexahydrido(triethylsilyl)bis(triphenylphosphine)rhenium(VII) (2b). A solution of $ReH_7(PPh_3)_2$ (250 mg, 0.10 mmol) and Et_3SiH (200 μL, 1.0 mmol) in 15 mL of tetrahydrofuran was stirred at room temperature for 36 h, as described above. The solution was then concentrated to ca. 1 mL in vacuo. Addition of heptane (30 mL) led to precipitation of **2b** as a beige solid. The product was filtered out, washed with heptane (4 × 5 mL), and dried in vacuo. Yield: 220 mg, 65%. Anal. Calcd for $C_{42}H_{51}P_2ReSi$: C, 60.62; H, 6.18. Found: C, 58.87; H, 6.01. IR (Nujol): ν_{Re-H} 1990, 1973, 1944 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.4 (c, 30 H, Ph), 0.79 (br s, 15 H, Et), −5.91 (t, $^2J_{HP}$ = 16.2 Hz, 6 H, Re–H). ^1H NMR (CD_2Cl_2, 193 K): δ 7.2–7.4 (c, 30 H, Ph), 0.78

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Table III. Positional and Thermal Parameters with Esd's for **2a** and **2a**·CH_2Cl_2[a,b]

unsolvated complex					solvated complex				
atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
Re	0.17371 (8)	0.27915 (5)	0.25682 (4)	2.68 (1)*	Re	0.17693 (6)	0.10367 (3)	0.25514 (3)	2.15 (1)*
P(1)	0.2332 (4)	0.1851 (3)	0.1522 (2)	3.13 (9)*	P(1)	0.1565 (6)	0.1656 (3)	0.3525 (3)	1.9 (2)
P(2)	0.1083 (4)	0.1583 (3)	0.3542 (2)	2.8 (1)*	P(2)	0.1876 (6)	0.1609 (3)	0.1513 (3)	2.8 (2)
Si	0.1398 (5)	0.4680 (3)	0.2577 (2)	2.9 (1)*	Si	0.1783 (7)	0.0007 (3)	0.2567 (4)	3.2 (2)
C(1)	0.151 (2)	0.063 (1)	0.1373 (7)	3.2 (3)	C(1)	0.021 (1)	0.2155 (7)	0.3447 (8)	2.5 (3)
C(2)	0.064 (2)	0.015 (1)	0.1865 (8)	4.0 (3)	C(2)	−0.043 (2)	0.2320 (7)	0.2823 (9)	3.4 (4)
C(3)	0.001 (2)	−0.078 (1)	0.173 (1)	5.9 (4)	C(3)	−0.145 (2)	0.2706 (7)	0.2750 (9)	3.9 (4)
C(4)	0.021 (2)	−0.124 (1)	0.1115 (8)	5.5 (4)	C(4)	−0.180 (2)	0.2942 (7)	0.3326 (9)	3.3 (4)
C(5)	0.104 (2)	−0.076 (2)	0.063 (1)	7.1 (5)	C(5)	−0.118 (2)	0.2773 (8)	0.396 (1)	4.0 (4)
C(6)	0.169 (2)	0.020 (1)	0.073 (1)	6.3 (5)	C(6)	−0.016 (2)	0.2381 (7)	0.4045 (9)	3.5 (4)
C(7)	0.188 (2)	0.256 (1)	0.0700 (8)	3.5 (3)	C(7)	0.132 (1)	0.1290 (6)	0.4328 (8)	2.3 (3)
C(8)	0.284 (2)	0.271 (1)	0.0145 (9)	5.7 (4)	C(8)	0.024 (2)	0.0970 (8)	0.4297 (9)	4.0 (4)
C(9)	0.243 (2)	0.333 (1)	−0.046 (1)	6.6 (5)	C(9)	−0.004 (2)	0.0695 (8)	0.4882 (9)	4.3 (4)
C(10)	0.110 (2)	0.372 (1)	−0.051 (1)	6.0 (5)	C(10)	0.083 (2)	0.0772 (8)	0.551 (1)	4.2 (4)
C(11)	0.012 (2)	0.357 (1)	0.0020 (9)	5.2 (4)	C(11)	0.190 (2)	0.1104 (8)	0.5549 (9)	4.3 (4)
C(12)	0.050 (2)	0.300 (1)	0.0640 (8)	4.4 (4)	C(12)	0.217 (2)	0.1365 (7)	0.4961 (8)	3.2 (4)
C(13)	0.424 (2)	0.156 (1)	0.1410 (8)	3.6 (3)	C(13)	0.299 (1)	0.2091 (7)	0.3838 (8)	2.5 (3)
C(14)	0.519 (2)	0.234 (1)	0.1371 (9)	4.9 (4)	C(14)	0.290 (2)	0.2657 (7)	0.3951 (8)	2.7 (3)
C(15)	0.668 (2)	0.218 (2)	0.128 (1)	6.9 (5)	C(15)	0.403 (2)	0.2970 (7)	0.4185 (8)	3.2 (4)
C(16)	0.715 (2)	0.119 (1)	0.127 (1)	6.7 (5)	C(16)	0.521 (2)	0.2733 (7)	0.4272 (9)	3.6 (4)
C(17)	0.634 (2)	0.038 (2)	0.133 (1)	7.8 (6)	C(17)	0.535 (2)	0.2170 (8)	0.4176 (9)	4.0 (4)
C(18)	0.481 (2)	0.058 (1)	0.141 (1)	6.1 (5)	C(18)	0.425 (2)	0.1853 (8)	0.3959 (9)	3.5 (4)
C(19)	0.158 (2)	0.023 (1)	0.3491 (7)	3.0 (3)	C(19)	0.040 (2)	0.2010 (7)	0.1176 (8)	2.8 (3)
C(20)	0.067 (2)	−0.057 (1)	0.3701 (8)	4.6 (4)	C(20)	0.043 (2)	0.2583 (7)	0.1050 (8)	3.3 (4)
C(21)	0.110 (2)	−0.161 (1)	0.3684 (9)	5.3 (4)	C(21)	−0.073 (2)	0.2872 (9)	0.085 (1)	4.5 (4)
C(22)	0.243 (2)	−0.181 (1)	0.3472 (9)	5.6 (4)	C(22)	−0.192 (2)	0.2606 (8)	0.0739 (9)	4.2 (4)
C(23)	0.339 (2)	−0.107 (1)	0.3255 (9)	5.8 (4)	C(23)	−0.196 (2)	0.2030 (8)	0.0840 (9)	3.8 (4)
C(24)	0.294 (2)	−0.003 (1)	0.3255 (8)	4.3 (4)	C(24)	−0.081 (2)	0.1733 (8)	0.1061 (8)	3.4 (4)
C(25)	0.188 (1)	0.184 (1)	0.4375 (7)	2.4 (3)	C(25)	0.214 (1)	0.1217 (6)	0.0729 (8)	2.8 (3)
C(26)	0.191 (2)	0.284 (1)	0.4596 (8)	3.6 (3)	C(26)	0.329 (2)	0.0870 (8)	0.083 (1)	4.7 (4)
C(27)	0.245 (2)	0.306 (1)	0.5239 (8)	4.5 (4)	C(27)	0.356 (2)	0.060 (1)	0.023 (1)	6.1 (5)
C(28)	0.306 (2)	0.228 (1)	0.5664 (9)	5.2 (4)	C(28)	0.276 (2)	0.0638 (9)	−0.037 (1)	5.9 (5)
C(29)	0.302 (2)	0.131 (1)	0.5467 (9)	5.2 (4)	C(29)	0.168 (2)	0.0950 (9)	−0.048 (1)	5.5 (5)
C(30)	0.245 (2)	0.107 (1)	0.4821 (8)	3.9 (3)	C(30)	0.131 (2)	0.1279 (8)	0.009 (1)	5.0 (5)
C(31)	−0.085 (2)	0.157 (1)	0.3747 (7)	3.3 (3)	C(31)	0.314 (1)	0.2128 (6)	0.5167 (7)	1.8 (3)
C(32)	−0.141 (2)	0.163 (1)	0.4417 (9)	4.5 (4)	C(32)	0.354 (2)	0.2425 (7)	0.2184 (8)	3.1 (3)
C(33)	−0.287 (2)	0.169 (1)	0.4542 (9)	4.4 (4)	C(33)	0.443 (2)	0.2843 (8)	0.222 (1)	4.2 (4)
C(34)	−0.383 (2)	0.167 (1)	0.4029 (9)	5.3 (4)	C(34)	0.495 (2)	0.3009 (8)	0.163 (1)	4.7 (4)
C(35)	−0.334 (2)	0.157 (1)	0.336 (1)	6.3 (5)	C(35)	0.458 (2)	0.2722 (8)	0.1032 (9)	4.2 (4)
C(36)	−0.185 (2)	0.154 (1)	0.3196 (9)	4.6 (4)	C(36)	0.368 (2)	0.2287 (7)	0.0988 (9)	3.3 (4)
C(37)	0.242 (2)	0.547 (1)	0.1869 (8)	3.3 (3)	C(37)	0.013 (2)	−0.0334 (6)	0.2541 (8)	2.6 (3)
C(38)	0.282 (2)	0.513 (1)	0.1221 (9)	4.7 (4)	C(38)	−0.101 (2)	−0.0070 (7)	0.2581 (8)	3.4 (4)
C(39)	0.344 (2)	0.579 (1)	0.070 (1)	5.6 (4)	C(39)	−0.221 (2)	−0.0342 (8)	0.254 (1)	5.0 (5)
C(40)	0.363 (2)	0.676 (1)	0.0814 (9)	5.5 (4)	C(40)	−0.223 (2)	−0.0922 (8)	0.2481 (9)	5.0 (5)
C(41)	0.327 (2)	0.716 (1)	0.1435 (9)	5.2 (4)	C(41)	−0.109 (2)	0.1206 (9)	0.247 (1)	5.3 (5)
C(42)	0.262 (2)	0.651 (1)	0.1975 (9)	4.8 (4)	C(42)	0.009 (2)	−0.0923 (8)	0.2480 (9)	4.8 (4)
C(43)	−0.050 (2)	0.518 (1)	0.2491 (7)	3.0 (3)	C(43)	0.291 (1)	−0.0277 (7)	0.3367 (8)	2.8 (3)
C(44)	0.166 (2)	0.457 (1)	0.2399 (9)	5.2 (4)	C(44)	0.417 (2)	−0.0131 (8)	0.350 (1)	4.5 (4)
C(45)	−0.309 (2)	0.496 (2)	0.232 (1)	7.0 (5)	C(45)	0.503 (2)	−0.0331 (9)	0.410 (1)	5.9 (5)
C(46)	−0.337 (2)	0.597 (1)	0.2346 (9)	5.9 (4)	C(46)	0.453 (2)	−0.0700 (9)	0.454 (1)	6.1 (5)
C(47)	−0.228 (2)	0.661 (1)	0.2446 (9)	5.5 (4)	C(47)	0.329 (2)	−0.085 (1)	0.443 (1)	6.8 (6)
C(48)	−0.085 (2)	0.623 (1)	0.2510 (9)	4.8 (4)	C(48)	0.246 (2)	−0.0647 (8)	0.3823 (9)	4.4 (4)
C(49)	0.203 (2)	0.522 (1)	0.3428 (7)	3.0 (3)	C(49)	0.234 (2)	−0.0333 (7)	0.1786 (8)	2.8 (3)
C(50)	0.108 (2)	0.552 (1)	0.3953 (8)	4.0 (3)	C(50)	0.152 (2)	−0.0346 (8)	0.1156 (9)	4.2 (4)
C(51)	0.164 (2)	0.582 (1)	0.4581 (9)	5.0 (4)	C(51)	0.193 (2)	−0.0603 (9)	0.057 (1)	5.9 (5)
C(52)	0.305 (2)	0.584 (1)	0.467 (1)	5.6 (4)	C(52)	0.319 (2)	−0.0808 (9)	0.063 (1)	6.0 (5)
C(53)	0.400 (2)	0.554 (1)	0.4189 (9)	5.3 (4)	C(53)	0.397 (2)	−0.080 (1)	0.124 (1)	7.1 (6)
C(54)	0.350 (2)	0.521 (1)	0.3545 (8)	4.0 (3)	C(54)	0.359 (2)	−0.0567 (8)	0.183 (1)	4.5 (4)
Re–H Hydride Positions									
H_a	0.03 (2)	0.25 (1)	0.240 (8)	3.0	H_a	0.17 (2)	0.052 (8)	0.219 (9)	3.0
H_b	0.31 (2)	0.33 (1)	0.225 (7)	3.0	H_b	0.05 (2)	0.125 (7)	0.247 (9)	3.0
H_c	0.28 (2)	0.31 (1)	0.309 (7)	3.0	H_c	0.27 (2)	0.150 (8)	0.266 (9)	3.0
H_d	0.13 (2)	0.35 (1)	0.195 (7)	3.0	H_d	0.26 (2)	0.079 (7)	0.327 (9)	3.0
H_e	0.07 (2)	0.34 (1)	0.296 (7)	3.0	H_e	0.34 (2)	0.082 (7)	0.220 (9)	3.0
H_f	0.32 (2)	0.22 (1)	0.273 (7)	3.0	H_f	0.06 (2)	0.051 (8)	0.305 (9)	3.0
Solvent of Crystallization									
					CO(12)	0.3416 (8)	0.6449 (4)	0.2284 (4)	10.10 (2)**
					Cl(1)	0.321	0.600	0.154	10.1**
					Cl(2)	0.350	0.608	0.305	10.1**
					CO(34)	0.320 (2)	0.6388 (7)	0.2865 (9)	9.5 (4)**
					Cl(3)	0.317	0.619	0.198	9.5**
					Cl(4)	0.347	0.585	0.346	9.5**

[a] Single asterisks indicate atoms were refined anisotropically: isotropic equivalent displacement parameters are given by $^4/_3\sum_{ij}\vec{\mathbf{a}}_i\vec{\mathbf{a}}_j\beta_{ij}$. [b] Double asterisks indicate disordered C and Cl atoms were given 0.5 occupancy factors.

Table IV. Selected Comparative Bond Lengths (Å) and Angles (deg) for **2a** and **2a**·CH_2Cl_2

	unsolvated complex	solvated complex
Re–P(1)	2.457 (4)	2.453 (4)
Re–P(2)	2.445 (4)	2.462 (4)
Re–Si	2.474 (4)	2.475 (4)
P(1)–C(1)	1.82 (2)	1.84 (2)
P(1)–C(7)	1.83 (1)	1.86 (2)
P(1)–C(13)	1.82 (2)	1.83 (2)
P(2)–C(19)	1.81 (1)	1.84 (2)
P(2)–C(25)	1.83 (1)	1.85 (2)
P(2)–C(31)	1.83 (1)	1.81 (1)
Si–C(37)	1.90 (1)	1.90 (2)
Si–C(43)	1.87 (1)	1.91 (2)
Si–C(49)	1.92 (1)	1.91 (2)
mean C–C (phenyl)	1.38 (2)	1.39 (2)
P(1)–Re–Si	124.8 (2)	126.9 (1)
P(2)–Re–Si	124.4 (2)	124.3 (1)
P(1)–Re–P(2)	109.9 (1)	108.7 (1)
mean C–C–C (phenyl)	120 (2)	120 (2)

(br s, 15 H, Et), −3.69 (t, $^2J_{HP}$ = 29.4 Hz, 2 H, Re–H_A), −7.31 (d, $^2J_{HP}$ = 14.0 Hz, 4 H, Re–H_B). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 24.8 (heptet, $^2J_{HP}$ = 15.9 Hz). Off-resonance ^{1}H-decoupled ^{13}C NMR (CD_2Cl_2, 298 K): δ 138.9 (c, 6 C, C_1 of PPh_3), 134.2 (dt, $^2J_{PC}$ = 5.3 Hz, 12 C, C_2 of PPh_3), 129.6 (d, 6 C, C_4 of PPh_3), 127.9 (dt, $^3J_{PC}$ = 4.3 Hz, 12 C, C_3 of PPh_3), 18.3 (t, 3 C, CH_2 of $SiEt_3$), 9.2 (q, 3 C, CH_3 of $SiEt_3$).

Hexahydrido(diethylsilyl)bis(triphenylphosphine)rhenium(VII) (2c). This compound was prepared as an off-white product by a method similar to that for **2b**. Yield: 62%. Anal. Calcd for $C_{40}H_{47}P_2ReSi$: C, 59.76; H, 5.89. Found: C, 58.71; H, 5.77. IR (Nujol): ν_{Re-H} 1990, 1961, 1942 cm^{-1}; ν_{Si-H} 2026 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.2–7.4 (c, 30 H, Ph), 5.04 (s, 1 H, Si–H), 0.95 (br s, 10 H, Et), −5.62 (t, $^2J_{HP}$ = 16.2 Hz, 6 H, Re–H). ^{1}H NMR (CD_2Cl_2, 183 K): δ 7.2–7.4 (c, 30 H, Ph), 5.01 (s, 1 H, Si–H), 0.94 (br s, 10 H, Et), −3.47 (br, 2 H, Re–H_A), −6.99 (br, 4 H, Re–H_B). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 4.9 (heptet, $^2J_{HP}$ = 15.5 Hz). Off-resonance ^{1}H-decoupled ^{13}C NMR (CD_2Cl_2, 298 K): 138.7 (c, 6 C, C_1 of PPh_3), 134.2 (dt, $^2J_{PC}$ = 5.0 Hz, 12 C, C_2 of PPh_3), 129.8 (d, 6 C, C_4 of PPh_3, 128.0 (dt, $^3J_{PC}$ = 4.1 Hz, 12 C, C_3 of PPh_3), 17.5 (t, 2 C, CH_2 of $SiHEt_2$), 10.7 (q, 2 C, CH_3 of $SiHEt_2$).

X-ray Crystallographic Analysis of 2a. Crystals of **2a**, solvated and unsolvated, suitable for X-ray diffraction measurements were grown from acetone/dichloromethane or from pure acetone. Selected crystals were sealed in a thin-walled Lindemann glass capillary and mounted on an Enraf-Nonius CAD-4 fully automated diffractometer, equipped with a graphite monochromator. The unit cells (Table II) were determined from the setting angles of 25 randomly selected reflections (16° < 2θ < 24°). Three standard reflections were monitored every hour of data collection and used to correct for crystal decomposition. The data were also corrected for Lorentz and polarization effects, and an absorption correction was applied by using the empirical DIFABS method.[33] Atomic scattering factors and anomalous dispersion terms were taken from the literature.[34] The "Structure Determination Package" program[35] was used on a Microvax II.

All atoms except Re (and P and Si for the unsolvated compound) were refined isotropically. Hydrogen atoms of the phenyl groups were introduced into the ideal geometry, constrained to ride on their carbon atom, and given a thermal parameter B_H of $1.3B_C$. Hydride hydrogens in the vicinity of the Re atom were associated with electron density peaks of intensity 0.5–0.8 e/Å^3 in the difference map, following a least-squares refinement limited to low θ (15°), and were introduced into the ultimate refinement with their thermal parameters fixed at 3 Å^2. In the solvated complex, the CH_2Cl_2 was located as disordered in two positions of equal occupancy, in each of which the solvent had a reasonable geometry.

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Supplementary Material Available: A fully labeled ORTEP diagram of **2a** and tables of H atom positions, bond distances and angles, and anisotropic displacement parameters for **2a** and **2a**·CH_2Cl_2 (10 pages); tables of F_o and F_c values for **2a** and **2a**·$CHCl_2$ (22 pages). Ordering information is given on any current masthead page.

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