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Steric Crowding in a Rhenium Polyhydride Induced by a Chelating Disilyl Ligand: Synthesis, Characterization, and Reactivity of $ReH_5(disil)(PPh_3)_2$ (disil = 1,2-Bis(dimethylsilyl)benzene and 1,2-Bis(dimethylsilyl)ethane)

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1,2-Bis(dimethylsilyl)benzene ($dmsbH_2$, **2a**) and 1,2-bis(dimethylsilyl)ethane ($dmseH_2$, **2b**) react with $ReH_7(PPh_3)_2$ (**1**) to give the first chelating bis(silyl) polyhydride complexes, $ReH_5(disil)(PPh_3)_2$ (**3a**,**b**). These have been characterized by spectroscopic techniques and, in one case, by single-crystal X-ray diffraction. The structure is not the expected tricapped trigonal prism found for all the other 9-coordinate rhenium polyhydrides. Instead, a dodecahedral structure typical of 8-coordination is adopted. We propose that the compound is $ReH_3(H_2)(disil)(PPh_3)_2$ and contains a stretched η^2-H_2 ligand (where stretched H_2 complexes have $d(H\cdot\cdot H) = 1.1-1.6$ Å). Crystals of $ReH_5(dmsb)(PPh_3)_2$ (**3a**) belong to the space group $P2_1/n$ (No. 14) with lattice parameters $a = 11.063(7)$ Å, $b = 21.016(7)$ Å, $c = 18.490(7)$ Å, $\beta = 106.84(4)°$, $V = 4114(6)$ Å^3, $Z = 4$, and $\varrho_{calc} = 1.463$ g/cm^3. The complexes catalytically dehydrogenate alkanes in the presence of *tert*-butylethylene.

Introduction

Phosphines are important ligands for transition metal complexes largely because their steric and electronic properties can be conveniently varied over a wide range. Silyl groups are much rarer as supporting ligands even though they should be equally flexible in these respects, probably because simple synthetic pathways are not yet well established. We use a simple synthesis of silyl complexes from silanes and metal hydrides to explore the chemistry of the resulting silyl compounds.

Transition metal polyhydrides have interesting structures[1] and reactivities.[2] We hope to examine the possibility of substituting as many hydride ligands as possible with silyl groups. Early examples involve only monodentate silyl dihydride or trihydride complexes,[3] but access to a few silyl polyhydrides became possible with the finding that silanes can react with polyhydrides at ambient temperatures. For example, $ReH_6(SiPh_3)(PPh_3)_2$ (**1a**) is formed when $ReH_5(H\cdot\cdot H)(PPh_3)_2$ (**1**) is treated with excess Ph_3SiH.[4a] In this case, no further substitution proved possible even at elevated temperatures. With other phosphines and silanes, however, double substitution gave a bis(silyl) pentahydride, $ReH_5(PR_3)_2(SiR_3)_2$ (**4**; $PR_3 = PPh^iPr_2$, $PCyp_3$ ($PCyp_3$ = tricyclopentylphosphine); $SiR_3 = SiHPh_2$, SiH_2Ph).[4b] Going from a bis monodentate phosphine to its chelating analog has been a very useful synthetic strategy[5] because the chelated compounds can show very large and useful differences in reactivity from their nonchelated analogs. In particular, the binding constants are greatly enhanced by the chelate effect.

We therefore moved to the potentially chelating disilanes 1,2-bis(dimethylsilyl)benzene ($dmsbH_2$) and 1,2-bis(dimethylsilyl)ethane ($dmseH_2$) and found that $ReH_5(disil)(PPh_3)_2$ (disil = dmsb (**3a**), dmse (**3b**)) is formed by loss of H_2 and consecutive double oxidative addition to give a five-membered chelate ring. The polyhydride complex $ReH_7(PPh_3)_2$ (**1**) was chosen for this study because it has a large number of hydrides and is catalytically active for the dehydrogenation of alkanes.[2] The chelating silane ligands (1,2-bis(dimethylsilyl)benzene, **2a**; 1,2-bis(dimethylsilyl)ethane, **2b**) used here have been previously employed to prepare several low oxidation state metal carbonyl complexes, such as $(disil)M(CO)_4$ (M = Fe, Ru, Os).[6] In one case, for M = Fe and disil = $SiMe_2CH_2CH_2SiMe_2$, metal alkylidenes and disiloxane were formed by reaction of $(disil)M(CO)_4$ with aldehydes in the presence of PR_3.[7] The bis(trialkylsilyl) complex $(CO)_4Fe(SiMe_3)_2$ did not react in the same way, however. The complex $(CO)_4Ru(dmse)$ reacts with cycloheptatriene or cyclooctatetraene with transfer of one or both silicon ligands to the polyolefin.[8]

Results and Discussion

Preparation. We have studied the reaction of **1** with the chelating silane ligands and found that air-stable bis(silyl)

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Scheme 1. Stepwise Synthesis of **3a**

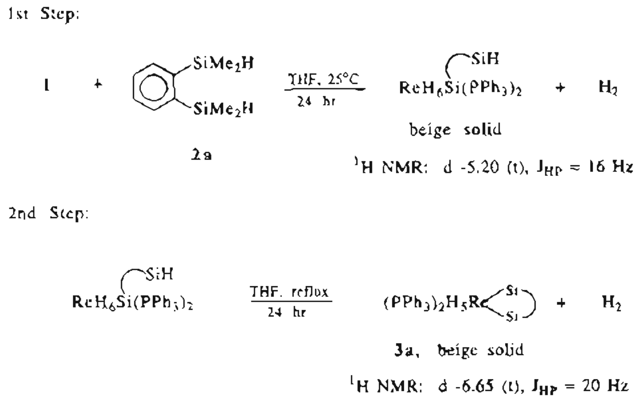


Table 1. Spectral Data for the Complexes

complex	^{1}H NMR[a] MH	^{1}H NMR[a] SiMe$_2$	{^{1}H}^{31}P NMR[b]	IR[c]
ReH$_5$(dmsb)P$_2$	−6.65 (t, 20)	0.45 (s)	26.4 (sextet, 18)	1993 (m), 1861 (m)
ReH$_5$(dmse)P$_2$	−6.98 (t, 20)	0.22 (s)	27.6 (sextet, 19)	1995 (m), 1864 (m)

[a] In CD$_2$Cl$_2$ at 25 °C; reported as position (δ), with the multiplicity and coupling constant (Hz) in parentheses. [b] In CD$_2$Cl$_2$ at 25 °C; relative to external 85% H$_3$PO$_4$. [c] Nujol mull; position in cm^{-1}.

complexes, ReH$_5$(disil)(PPh$_3$)$_2$, can be formed in good yields under mild conditions. Compound **1** reacts with 3−5 equiv of silane in THF, first at room temperature and then under reflux to form the pentahydride complexes ReH$_5$(disil)(PPh$_3$)$_2$ (disil = 1,2-bis(dimethylsilyl)benzene (**3a**), 1,2-bis(dimethylsilyl)ethane (**3b**)). In the case of **3a**, the intermediate complex, with one silicon directly bound to rhenium, was also isolated (Scheme 1).

NMR Spectroscopic Studies. The ^{1}H NMR spectra of **3a** and **3b** in CD$_2$Cl$_2$ show triplet hydride resonances at δ −6.65 ($^2J_{HP}$ = 20 Hz) and δ −6.98 ($^2J_{HP}$ = 20 Hz), respectively (Table 1), showing they are fluxional at room temperature. The selectively hydride-coupled ^{31}P spectra show a binomial sextet at δ 26.4 ($^2J_{HP}$ = 18 Hz) for **3a** and δ 27.6 ($^2J_{HP}$ = 19 Hz) for **3b**, indicating the presence of five hydride ligands. Unlike the previously reported ReH$_6$(SiPh$_3$)(PPh$_3$)$_2$ (**1a**),[4a] **3a** and **3b** are still fluxional down to −90 °C. T_1 data were obtained at 300 MHz as a function of temperature, and a T_1 minimum was found for each complex at −60 °C, where values of 91 and 89 ms were observed for **3a** and **3b**, respectively. These values correspond to 76 (**3a**) and 74 (**3b**) ms at 250 MHz and are in the range reported previously for the classical hexahydride complexes ReH$_6$(SiR$_3$)(PPh$_3$)$_2$ (76−79 ms).[4a] These results rule out the presence of a short H−H distance (<1.1 Å) in the structure. Partial deuteration showed no isotope perturbation effects, suggesting that the heavy isotope distributes equally over all sites.

IR Studies. The metal−hydride bands are found at 1861 and 1993 cm^{-1} for **3a** and at 1995 and 1864 cm^{-1} for **3b**. No bands were observed in the 2600−2800 cm^{-1} range expected for an unstretched η^2-H$_2$ complex.[1b]

Table 2. Cyclooctane Dehydrogenation Data for **3a** and **3b**

complex	conditions[a]	mmol of catalyst	T, °C	turnover no.
ReH$_5$(dmsb)P$_2$		0.01	180	54
ReH$_5$(dmsb)P$_2$	PPh$_3$	0.01	180	56
ReH$_5$(dmsb)P$_2$	**2a**	0.01	180	60
ReH$_5$(dmsb)P$_2$	air[b]	0.01	180	2.2
ReH$_5$(dmse)P$_2$		0.01	180	17
ReH$_5$(dmse)P$_2$	PPh$_3$	0.01	180	16
ReH$_5$(dmse)P$_2$	**2b**	0.01	180	34
ReH$_7$P$_2$		0.003	175	2.7
ReH$_6$(SiPh$_3$)P$_2$		0.003	175	0.6
ReH$_5$(dmsb)P$_2$		0.003	175	40

[a] All reactions in neat alkane with 76 equiv of tbe for 24 h, except as noted in the table; see also Experimental Section. [b] No tbe present.

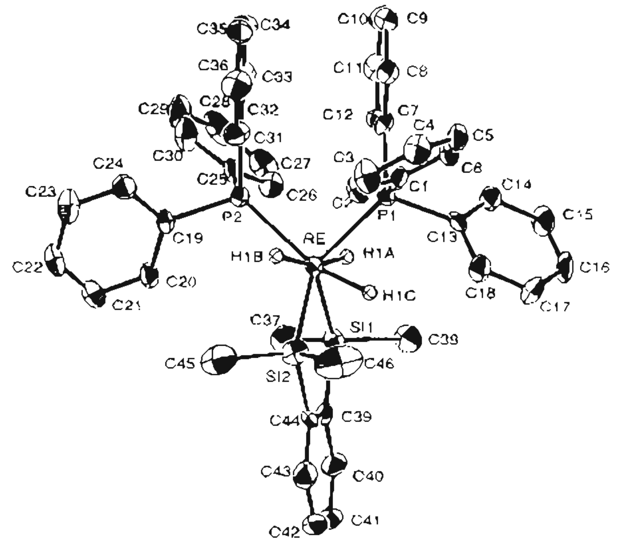


Figure 1. ORTEP diagram of the crystal structure of ReH$_5$(dmsb)(PPh$_3$)$_2$, **3a**, as determined by single-crystal X-ray diffraction. The three terminal hydride positions were tentatively located.

Table 3. Crystallographic Data for **3a**

formula	C$_{46}$H$_{49}$P$_2$Si$_2$Re
fw	906.22
crystal color; size, mm^3	colorless; 0.20 × 0.26 × 0.24
space group	monoclinic: $P2_1/n$ (No. 14)
lattice param (dist, Å; angle, deg)	a = 11.063(7), b = 21.016(7), c = 18.490(7), β = 106.84(4)
V, Å^3	4114(6)
Z	4
ϱ_{calc}, g cm^{-3}	1.463
radiation	Mo Kα (λ = 0.710 69 Å)
μ, cm^{-1}	31.57
T, K	143
F(000)	1832
no. of tot. measd reflns	7890
no. of tot. unique reflns > 3σ(I)	7482
R[a]	0.039
R_w[b]	0.041
max shift/error	0.08

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

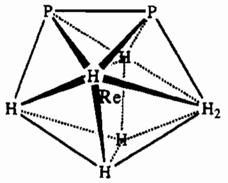
X-ray Structure of 3a. The X-ray structure for **3a**, shown in Figure 1 and described by Tables 3 and 4, differs from that of the silyl hexahydride previously reported (X-ray and neutron diffraction), which has a tricapped trigonal prismatic (TTP) structure, with the six hydrides axial and the heavy atoms equatorial.[4a] Figure 2 shows the coordination geometries for the polyhydrides discussed. In the case of **3a**, the heavy atoms are found in a distorted tetrahedron, inconsistent with a TTP geometry. The bond angles P−Re−P (96.4°) and Si−Re−Si (82.4°) differ from the expected value of 120° for a TTP structure. The bond lengths (Re−Si = 2.49 Å (average) and Re−P = 2.45 Å (average)) are similar to those reported previously for **1a**,[4a] and the bis(silyl) pentahydride complexes.[4b] In a TTP structure, one of the hydrides would have to lie between the two phosphorus or the two silicon atoms but there is not sufficient space for a hydride in either position. The structure of **3a** is also unlike that found by neutron diffraction for ReH$_5$(SiHPh$_2$)$_2$(PPh^{i}Pr$_2$)$_2$ (**4**), which is a monocapped square antiprism.[4b]

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3a**

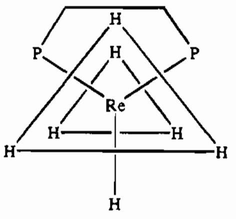
Re−H(1A)	1.60(6)	P(1)−C(13)	1.837(8)
Re−H(1B)	1.52(7)	P(2)−C(19)	1.861(7)
Re−H(1C)	1.52(9)	P(2)−C(25)	1.840(8)
		P(2)−C(31)	1.831(8)
Re−P(1)	2.446(2)		
Re−P(2)	2.451(2)	Si(1)−C(37)	1.888(9)
Re−Si(1)	2.495(2)	Si(1)−C(38)	1.891(8)
Re−Si(2)	2.489(3)	Si(1)−C(39)	1.881(8)
		Si(2)−C(44)	1.887(8)
P(1)−C(1)	1.852(8)	Si(2)−C(45)	1.89(1)
P(1)−C(7)	1.839(8)	Si(2)−C(46)	1.88(1)
P(1)−Re−H(1A)	78(2)	H(1A)−Re−H(1C)	85(4)
P(1)−Re−H(1B)	96(3)	H(1B)−Re−H(1C)	109(4)
P(1)−Re−H(1C)	66(3)		
P(2)−Re−H(1A)	93(2)	P(1)−Re−P(2)	96.43(7)
P(2)−Re−H(1B)	70(3)	P(1)−Re−Si(1)	120.63(7)
P(2)−Re−H(1C)	162(3)	P(1)−Re−Si(2)	122.11(8)
Si(1)−Re−H(1A)	53(2)	P(2)−Re−Si(1)	115.44(7)
Si(1)−Re−H(1B)	141(3)	P(2)−Re−Si(2)	121.97(8)
Si(2)−Re−H(1C)	77(3)	Si(1)−Re−Si(2)	82.37(8)
H(1A)−Re−H(1B)	162(3)		
Nonbonding Hydride Distances			
H(1A)··H(1B)	3.08(9)	H(1B)··H(1C)	2.5(1)
H(1A)··H(1C)	2.1(1)		

The three terminal hydrides were tentatively assigned in the X-ray structure, because electron density maxima were detected in reasonable locations. The Re−H distances are 1.60(6) Å (Re−H(1A)), 1.52(7) Å (Re−H(1B)), and 1.52(9) Å (Re−H(1C)). The nonbonding H··H distances for these three hydrides averaged 2.5 Å, indicating a classical structure. The two remaining hydride ligands most likely occupy the vacant location opposite H(1C). The geometry of **3a** resembles that of an 8-coordinate dodecahedron, with angles of 82.4(1)° for Si(1)−Re−Si(2), 96.4(1)° for P(1)−Re−P(2) (ideal for dodecahedron: 74°), 66(3)° for P(1)−Re−H(1C), and 53(2)° for Si(1)−Re−H(1A) (ideal: 72.5°). The bulk of the P and Si ligands evidently leads to a distortion, which is larger for P because these ligands are not chelating. The dihedral angle of 92(1)° between the H(1B)−Si(2)−Si(1)−H(1A) and P(2)−P(1)−H(1C) planes is close to the ideal value of 90° for a dodecahedron. NMR studies and IR data for **3a** are consistent with either a classical structure or a nonclassical structure containing a stretched (η^2-H_2) ligand.[1] Two hydrogens must occupy the remaining coordination site of the dodecahedron but could not be detected.

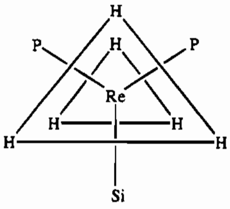
Mercator Map. To look at possible locations for the two remaining hydrides, we have represented the structure in a Mercator projection, which shows the angular extent of the donor atoms (Figure 3). This approach essentially involves considering the cone angles of the atoms in the first coordination sphere. The "North Pole" of the diagram is defined as the midpoint of the two phosphorus groups, and the equator is the locus of points 90° from the North Pole. The ordinate of a Mercator diagram is tan θ, where θ is the latitude or angle between the equator and the point in question. P(1) defines the meridian or line of zero longitude. The abscissa of the diagram shows the longitude of any point in radians. Around each ligand position we have plotted the covalent radius. The only location open to the two remaining hydride ligands is the position marked X on the map. The normal minimum nonbonding H··H distance of 1.65 Å is such that these two hydrogens cannot be mutually nonbonding, but an H··H distance in the range 1.4−1.6 Å would allow these atoms to fit into the available space. A neutron diffraction study is planned. The heavy atom positions in **3a** are appropriate for an 8-coordinate dodecahedral rather than a 9-coordinate TTP arrangement. $ReH_7(dppe)$[9a] is known to have the 9-coordinate TTP structure while $ReH_5(H_2)(P(p\text{-tolyl})_3)_2$[9b] has an 8-coordinate dodecahedral structure, counting the midpoint of the H_2 vector as a coordination position. The T_1 data show that there is no short H−H distance (<1.1 Å) in **3a**. We therefore propose that **3a** is a stretched η^2-H_2 complex.



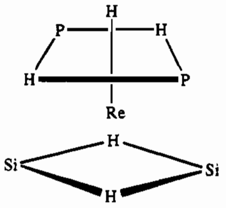
$ReH_7(PR_3)_2$
R = Ph, **1**
R = p-tolyl



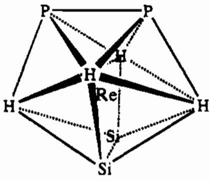
$ReH_7(dppe)$



$ReH_6(SiPh_3)(PPh_3)_2$
1a



$ReH_5(SiHPh_2)_2(PPh^iPr_2)_2$
4



$ReH_5(dmsb)(PPh_3)_2$
3a

Figure 2. Coordination geometries for $ReH_7(PR_3)_2$ (R = Ph (**1**); R = *p*-tolyl (8-coordinate dodecahedron)), $ReH_7(dppe)$ (tricapped trigonal prism), $ReH_6(SiPh_3)(PPh_3)_2$ (**1a**, tricapped trigonal prism), $ReH_5(SiHPh_2)_2(PPh^iPr_2)_2$ (**4**, monocapped antiprism), and $ReH_5(dmsb)(PPh_3)_2$ (**3a**, 8-coordinate dodecahedron).

Steric Compression. $ReH_5(H\cdot\cdot H)(P(p\text{-tolyl})_3)_2$ is a stretched η^2-H_2 complex ($d(H\cdot\cdot H)$ = 1.357 Å (neutron diffraction)),[9b] and NMR data confirm the same is true for $ReH_5(H\cdot\cdot H)(PPh_3)_2$ ($d(H\cdot\cdot H)$ = 1.35 Å (NMR)),[9c] but the substitution of H by SiR_3 in $ReH_6(SiPh_3)(PPh_3)_2$ leads to the formation of a classical polyhydride with no short H··H distances.[4a] This may be a result of the donating character of Si in relation to H, which is expected to encourage back-donation from the metal and so favor the classical d^0 structure over the d^2 nonclassical tautomer. On electronic grounds, the substitution of two H atoms by SiR_3 should lead to a classical hydride. In fact, a stretched η^2-H_2 complex is formed. If we can eliminate an electronic origin, the formation of a stretched η^2-H_2 complex may therefore be the result of a steric effect. We propose that the heavy atom coordination sphere is such that it does not allow all five hydrides to be fully nonbonding, $d(H\cdot\cdot H)$ > 1.65 Å. Rather than having all the H··H distances slightly shorter than 1.65

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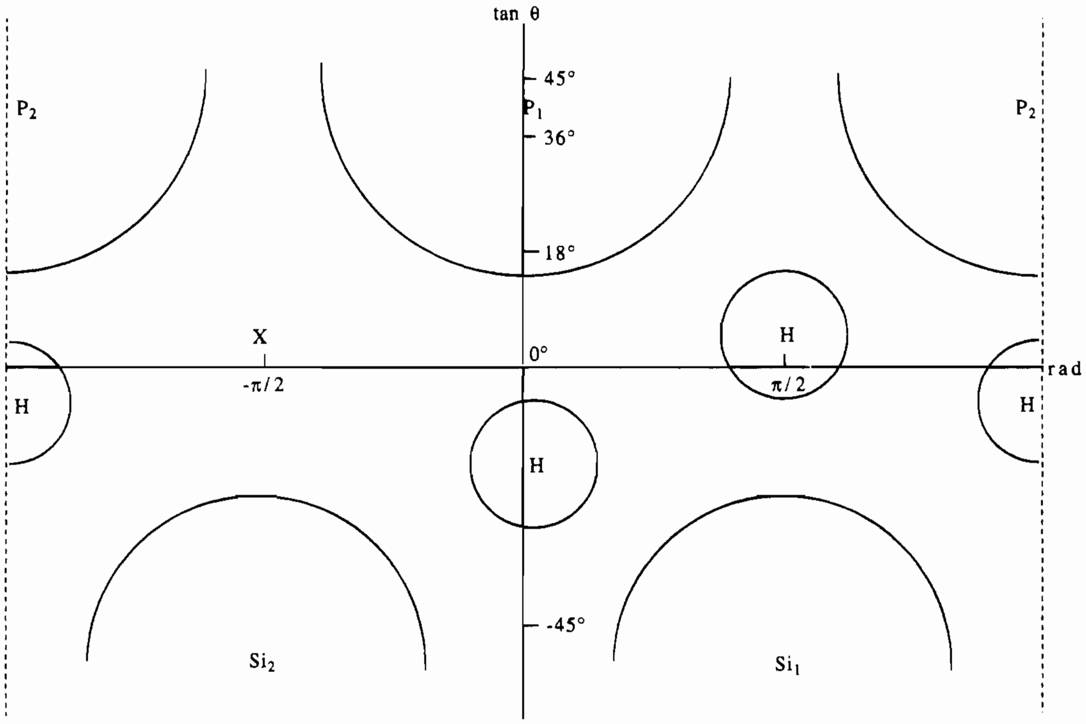

Figure 3. Mercator projection for $ReH_5(dmsb)(PPh_3)_2$. The position marked X on the map is the only location open to the two remaining hydride ligands.

Å, the system seems to prefer to distort in such a way that one pair of hydride ligands are close ($d(H\cdots H) < 1.65$ Å), which would allow all the other H••H distances to be fully nonbonding.

Catalytic Dehydrogenation of Cyclooctane to Cyclooctene by 3a and 3b. The use of transition metal polyhydride complexes for alkane dehydrogenation has been previously studied.[2,10] For example, in the presence of *tert*-butylethylene (tbe) as hydrogen acceptor, complexes such as $ReH_7(PPh_3)_2$,[2] $RuH_4(PR_3)_3$,[11] $IrH_5(PR_3)_2$,[11] and WH_6(triphos) (triphos = $PPh(CH_2CH_2PPh_2)_2$)[5] are active catalysts for the dehydrogenation of cyclooctane to cyclooctene. $ReH_7(PPh_3)_2$ reacts readily with alkenes such as cyclopentene to give cyclopentadienyl complexes and with alkanes in the presence of tbe to give alkenes.[2] Complex **3a** is stable in the presence of cyclopentene or 1,5-cyclooctadiene: no reaction takes place even on refluxing in perfluorodecalin (bp 142 °C) for 2 days, conditions under which $ReH_7(PPh_3)_2$ reacts rapidly.[2] **3a** and **3b** are much more active for cyclooctane dehydrogenation compared to the parent heptahydride $ReH_7(PPh_3)_2$ and to the monosilyl hexahydride complex $ReH_6(SiPh_3)(PPh_3)_2$ (Table 2).

In the case of **3a** (11 mg, 0.01 mmol) with cyclooctane (1.5 mL) and tbe (0.10 mL, 0.78 mmol) at 180 °C, 54 turnovers of cyclooctene in 24 h (turnover frequency = 2.2 turnovers h^{-1}) were obtained as determined by GC. In the case of **3b** (11 mg, 0.01 mmol), 17 turnovers of cyclooctene were obtained (turnover frequency = 0.7 turnover h^{-1}). Under similar conditions, the heptahydride $ReH_7(PPh_3)_2$ (8.4 mg, 0.01 mmol) gives only 1.4 turnovers of cyclooctene in 24 h (turnover frequency = 0.06 turnover h^{-1}). The silyl hexahydride complex $ReH_6(SiPh_3)(PPh_3)_2$ (2.5 mg, 0.003 mmol) gave 0.64 turnover in 24 h. This was compared to the case of **3a** (2.7 mg, 0.003 mmol), which under the same conditions gave 40 turnovers of cyclooctene.

In order to obtain mechanistic information, several control experiments were carried out. In the absence of tbe and under argon, no cyclooctene is formed. In air, however, the same reaction gives 2.2 turnovers of cyclooctene after 24 h. This suggests that air may be a weakly active hydrogen acceptor in this system, although we were not able to detect the water that should have been formed, no doubt because the turnovers were so small. The reaction with **3a** (11 mg, 0.01 mmol) in the presence of excess PPh_3 (4 equiv based on Re) gave slightly higher turnovers (56 in 24 h), which suggests that phosphine dissociation during the reaction is not kinetically significant. In the presence of excess silane (4 equiv based on Re), **3a** gave 60 turnovers of cyclooctene. Likewise, for **3b** in the presence of excess PPh_3, 16 turnovers were obtained but when excess silane was added, the turnovers doubled to 34 in 24 h. This result suggests that the ethylene-bridged disilyl complex **3b** may be less stable than **3a**, having a less rigid structure. The excess silane present may help to regenerate the catalyst after decomposition, thus giving the higher activity. The first step may be loss of H_2, as is the case with $ReH_5(H\cdots H)(PPh_3)_2$,[12] but silane loss cannot be ruled out. Complexes of type **3** are much more stable than **1** and require more severe conditions for catalysis; if H_2 loss is involved, the H_2 in **3** may be more tightly bound, consistent with a more highly stretched H••H distance in **3a**.

The homogeneity of the system in the case of **3a** was studied by addition of metallic mercury.[13] The solutions remained clear and there was no color change throughout the reaction. The yield of cyclooctane was not affected by the presence of a drop of mercury, which is a known poison for heterogeneous catalysts. Therefore, it is unlikely that metal colloids or metal particles are responsible for the activity found in this system. Traces of free benzene were found after the reaction, which could be due to P–C bond cleavage from the triphenylphosphine ligand.[14] This was previously found to be the deactivation

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pathway for a related catalyst.[14b] A ^1H NMR study of the organometallic residue showed that no hydride ligands were present but the chelating silane was now η^1-bound. The ^{31}P NMR data showed that a metal phosphine complex was present, along with some free PPh_3. A study of the catalyst after the reaction may help us in the future to design better degradation-resistant catalysts. Further studies are needed to fully characterize this product.

Conclusion

The compounds reported here are a new class of chelating bis(silyl) polyhydride complexes, which show enhanced reactivities compared to $ReH_7(PPh_3)_2$ and the silyl hexahydride complex previously reported. Complex **3a** does not adopt the usual 9-coordinate structure expected for this system but has an 8-coordinate dodecahedral structure containing a stretched η^2-H_2 ligand (where stretched η^2-H_2 complexes[1d,e] have $d(H \cdot\cdot H) = 1.1-1.6$ Å), which may result from steric compression of the coordination sphere as a result of the bulky phosphorus and silicon atoms of the phosphine and silyl ligands.

Experimental Section

General Procedures. All experiments were performed under a dry argon atmosphere using standard Schlenk-tube techniques. Tetrahydrofuran and hexanes were distilled from Na/Ph_2CO. ^1H NMR spectra were recorded on a Bruker WM 250 spectrometer; chemical shifts were measured with reference to the residual solvent resonance. ^{13}C and ^{31}P (external 85% H_3PO_4 reference) spectra were recorded on a GE Omega 300 spectrometer. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Atlantic Microlabs. The disilanes were purchased from Fluka and Huls and were used as received. $ReH_7(PPh_3)_2$ was prepared according to the literature method.[2f]

Pentahydrido[1,2-benzenediylbis(dimethylsilyl)]bis(triphenylphosphine)rhenium(VII) (3a). A solution of $ReH_7(PPh_3)_2$ (102 mg, 0.142 mmol) in 10 mL of THF was subjected to three freeze–pump–thaw cycles, and the silane (0.10 mL, 0.46 mmol) was added. The solution was stirred at room temperature for 24 h. Every 8 h the flask was evacuated and refilled with argon to remove any H_2 formed during the reaction. The solution was then refluxed for 24 h. The volume of the solution was reduced to about 1 mL under vacuum, and hexanes (20 mL) were added to precipitate a tan solid. The product was filtered off, washed with hexanes (2 × 10 mL), and dried in vacuo. Yield: 81 mg, 62%. Anal. Calc for $C_{46}H_{51}P_2ReSi_2$: C, 60.83; H, 5.66. Found: C, 59.74; H, 5.87. IR (Nujol): ν_{Re-H} 1993, 1861 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.6 (c, 34 H, Ph), 0.45 (s, 12 H, Me), −6.65 (t, $^2J_{HP} = 20$ Hz, 5 H, ReH). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 26.4 (sextet, $^2J_{HP} = 18$ Hz). Off-resonance ^1H-decoupled ^{13}C NMR (CD_2Cl_2, 298 K): δ 138.6 (s, C_1 of dmsb), 134.3 (s, C_1 of PPh_3), 134.2 (s, C_2 of PPh_3), 131.0 (s, C_2 of dmsb), 129.9 (s, C_4 of PPh_3), 128.2 (s, C_3 of PPh_3), 126.9 (s, C_3 of dmsb), 13.9 (s, Si–*Me* of dmsb), 13.6 (s, Si–*Me* of dmsb).

Pentahydrido[1,2-ethanediylbis(dimethylsilyl)]bis(triphenylphosphine)rhenium(VII) (3b). A solution of $ReH_7(PPh_3)_2$ (99 mg, 0.14 mmol) in 10 mL of THF was subjected to three freeze–pump–thaw cycles before addition of silane (0.15 mL, 0.92 mmol). This mixture was stirred at room temperature and then refluxed as described above. The solution was concentrated to ca. 1 mL in vacuo, and hexanes (20 mL) were added to precipitate an off-white solid. The product was filtered off, washed with hexanes (2 × 10 mL), and dried in vacuo. Yield: 36 mg, 31%. Anal. Calc for $C_{42}H_{51}P_2ReSi_2$: C, 58.65; H, 5.98. Found: C, 58.00; H, 6.03. IR (Nujol): ν_{Re-H} 1995, 1864 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.1–7.2 (c, 30 H, Ph), 0.22 (s, 12 H, Me), −6.98 (t, $^2J_{HP} = 20$ Hz, ReH). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ 27.6 (sextet, $^2J_{HP} = 19$ Hz). Off-resonance ^1H-decoupled ^{13}C NMR (CD_2Cl_2, 298 K): δ 134.4 (s, C_1 of PPh_3), 134.2 (s, C_2 of PPh_3), 129.7 (s, C_4 of PPh_3), 128.1 (s, C_3 of PPh_3), 23.4 (s, C_1 of dmse), 12.8 (s, Si–*Me* of dmse), 12.3 (s, Si–*Me* of dmse).

Dehydrogenation of Cyclooctane with 3a and 3b. In a typical experiment, **3a** (11 mg, 0.01 mmol), cyclooctane (1.5 mL, 11.15 mmol), and *tert*-butylethylene (0.10 mL, 0.78 mmol) were placed in a resealable triple-thickness 10 mL glass vessel equipped with a Teflon stopcock. This was degassed with six freeze–pump–thaw cycles. The vessel was then filled with argon and heated for 24 h with magnetic stirring at 180 °C in a thermostated oil bath. After cooling, the brown solution was distilled in vacuo and the organic phase was analyzed by GC. The involatile organometallic residue was dissolved in CD_2Cl_2 and analyzed by ^1H and ^{31}P NMR.

The catalytic system for **3a** was tested for homogeneity using the mercury test.[13] The reaction was run as described above, except that one drop of mercury (5 g) was initially added.

X-ray Crystallographic Analysis of 3a. Suitable crystals of **3a** were grown from THF/heptane at low temperature. A colorless plate crystal of **3a** was cut to approximate dimensions 0.20 × 0.26 × 0.24 mm^3 and mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation. The unit cell constants (Table 3) and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $12.69° < 2\theta < 15.24°$. The data were collected at −130 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50.2°. ω scans of several intense reflections made prior to data collection had an average width at half-height of 0.23° with a takeoff angle of 6.0°. Scans of $(1.26 + 0.30 \tan \theta)°$ were made at a speed of 6.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans), and the counts were accumulated to ensure good counting statistics. H(1A), H(1B), and H(1C) were located in the difference map following a low angle ($\theta < 15°$) least-squares refinement. The electron density peaks were of intensity greater than 0.6 e/Å^3. They were subsequently introduced into the final refinements and refined isotropically. Stationary-background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 285.0 mm.

Of the 7890 reflections collected, 7482 were unique ($R_{int} = 0.127$). The intensities of three representative reflections measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 31.6 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of Patterson and direct methods.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions, and in the case of the methyl groups, one hydrogen atom was located in the difference maps for each methyl group and included in an idealized location to set the orientation of the other two hydrogens. The final cycle of full-matrix least-squares refinement[16] was based on 4720 observed reflections ($I > 3.00\sigma(I)$) and 472 variable parameters and converged (largest parameter shift was 0.08 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.039$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2} = 0.041$.

The standard deviation of an observation of unit weight[17] was 1.67. The weighting scheme was based on counting statistics and included a factor ($p = 0.02$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$ reflection order in data collection $(\sin \theta)/\lambda$

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(17) Standard deviation of an observed unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.

and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.09 and -1.67 e/Å^3, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[18] Anomalous dispersion effects were included in F_c;[19] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[20] All calculations were performed using the TEXSAN[21] crystallographic software package of the Molecular Structure Corp.

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Supplementary Material Available: An X-ray structure report and tables of X-ray experimental data, positional and thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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