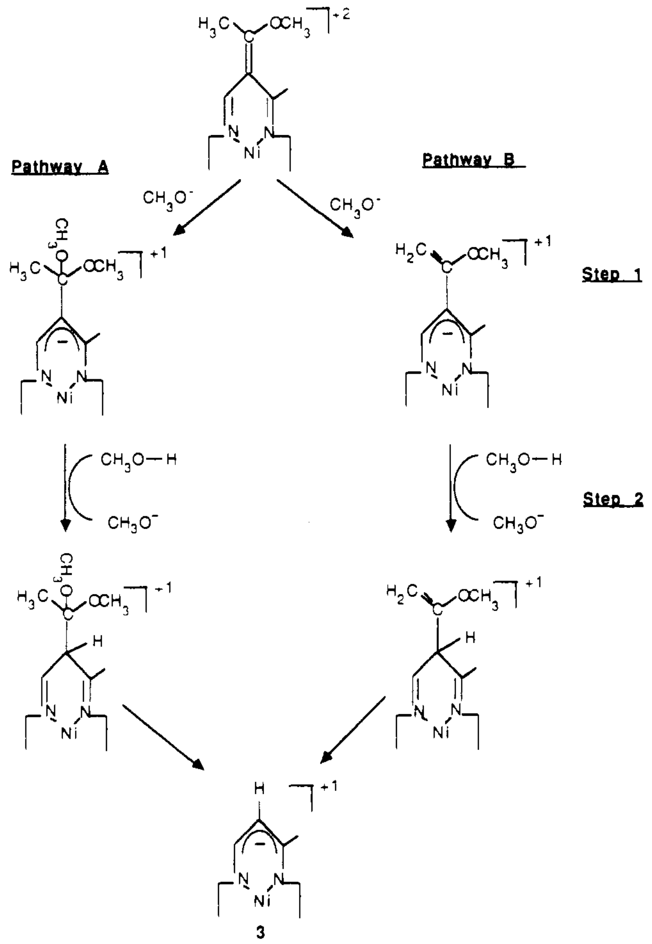
Scheme I



A is commonly observed for vinyl ether groups,[13] while the alternative pathway has the precedence shown in eq 3. Following deprotonation or addition of CH_3O^- to the vinyl ether carbon, the apical position of the macrocycle becomes more basic and deprotonation of methanol occurs (step 2, Scheme I). This reaction accounts for addition of the deuterium label to the apical position on the macrocycle. The basic nature of species like those formed in step 1 has been demonstrated. Loss of the organic fragments acetaldehyde and trimethyl orthoacetate to generate **3** must be a complicated pathway and may involve the methoxide ion produced in step 2. No convincing experimental evidence is available to suggest a pathway for loss of the organic fragments. We do suspect however that some decomposition of the macrocycle occurs that acts to reduce the vinyl ether carbon to an appropriate oxidation state for addition of a proton (deuteron) to form the acetaldehyde. Many extraneous peaks are observed in both the in situ NMR spectrum as well as the mass spectrum.

Since the ^1H NMR spectrum of the cleavage product **3** indicates electronic isolation of the two halves of the molecule, we can only suggest that cleavage of the second vinyl ether group is kinetically limited. The probable cause for this observation is a reduction in the overall electrophilic nature of the macrocyle when the positive charge is lowered from +2 to +1. No doubly cleaved product, which should have an absorption at 561 nm, has been observed spectrophotometrically in the isolated solid, although we cannot discount that some is formed but not detected.

Reactivity of the remaining vinyl ether moiety is evidenced by the metathesis reaction with propylamine and 1-(6-aminohexyl)pyrrole. However, reactivity of the vinyl ether group in **3** is more limited than in **1a**. Since we have as yet been unable to obtain a high-quality single-crystal X-ray structure of **3**, it is not possible to determine if steric effects are important in the reactions of this complex. The reactivity of compound **3** toward selected amines makes it is possible to prepare and evaluate the chemical properties of some interesting asymmetrically substituted macrocycle complexes.

Acknowledgment. We thank Profs. C. Breneman and L. Frye for helpful discussions.

Supplementary Material Available: Figures depicting the structure of 3 and tables of bond distances and angles, crystallographic data, data collection and refinement parameters, and positional parameters (11 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Unusual Stereochemical Rigidity in Seven-Coordination. Synthesis and Structural Characterization of $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn)

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Reaction of $ReH_3(CO)(PMe_2Ph)_3$ (**1**) with Ph_3SiH and Ph_3SnH in refluxing THF leads to the formation of $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si (**2**), Sn (**3**)). The solution spectroscopic data are consistent with the formulation of **2** and **3** as seven-coordinate with no H···H or Si···H interactions, but they are stereochemically rigid on the NMR time scale even at elevated temperatures, which is unusual for seven-coordinate complexes containing only monodentate ligands. Compound **2** has been structurally characterized by single-crystal X-ray crystallography in solvated and unsolvated forms. Crystal data for **2**: monoclinic, space group $P2_1$, $a = 9.958$ (3) Å, $b = 18.268$ (6) Å, $c = 12.175$ (2) Å, $\beta = 112.47$ (2)°, $V = 2047$ (2) Å^3, and $Z = 2$. Crystal data for **2**·THF: monoclinic, space group $P2_1/c$, $a = 15.341$ (2) Å, $b = 15.178$ (2) Å, $c = 19.074$ (1) Å, $\beta = 93.055$ (8)°, $V = 4435.0$ (7) Å^3, and $Z = 4$. Unexpected distortions from standard seven-coordination polyhedra are present in both forms, and possible reasons are discussed.

Introduction

The structure and dynamic stereochemistry in seven-coordination has been considered as one of the most complicated subjects in coordination chemistry.[1] Much of the importance of seven-coordinate structures arises from their role as intermediates (or transition states) in the associative or dissociative reactions of six- or eight-coordinate complexes. In this context, synthesis and structural studies of seven-coordinate complexes are beneficial to a thorough understanding of the mechanisms and factors that control these reactions. Stereochemical nonrigidity has been a general observation in seven-coordinate complexes due to facile intramolecular rearrangements.[2]

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Transition-metal polyhydrides[3] show unusual reactivity patterns[4] and structural forms.[5-8] Some adopt classical structures with terminal hydride ligands only, but others have nonclassical structures with one or more η^2-H_2 ligands. We recently reported that $[ReH_4(CO)(PMe_2Ph)_3]^+$ exists as an equilibrium mixture of classical and nonclassical tautomers.[9] In spite of steric and electronic differences, silyl and hydride ligands are isolobal.[10] Transition-metal silyl hydride complexes are known in which short Si···H distances are found by X-ray and neutron diffraction studies.[11-14] This suggests the presence of two-electron three-center $M(\eta^2$-H-$SiR_3)$ interactions,[15] which have also been studied theoretically[16] and by photoelectron spectroscopy.[17]

Some novel silyl polyhydrides of the type $ReH_6(SiR_3)(PPh_3)_2$ have recently been reported.[18a] Although a neutron diffraction study[18b] of the diethylsilyl complex shows a classical structure, X-ray crystallographic data of the triphenylsilyl complex suggest that two hydride ligands are close to the silicon. In order to simplify the problem, we decided to look at a silyl dihydride, where the spectroscopic data might be more readily interpretable but the silicon could still interact with one or two hydride ligands or none at all.

Table I. Crystallographic Data for **2** and **2**·THF

	2	**2**·THF
chem formula	$C_{43}H_{50}OP_3ReSi$	$C_{47}H_{58}O_2P_3ReSi$
fw	890.07	962.18
cryst system	monoclinic	monoclinic
space group	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)
a, Å	9.958 (3)	15.341 (2)
b, Å	18.268 (6)	15.178 (2)
c, Å	12.175 (2)	19.074 (1)
α, deg	90.00	90.00
β, deg	112.47 (2)	93.055 (8)
γ, deg	90.00	90.00
V, Å^3	2047 (2)	4435.0 (7)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.444	1.441
T, °C	25	-50
λ, Å	0.71073 (Mo Kα)	1.54178 (Cu Kα)
μ, cm^{-1}	31.83 (Mo Kα)	67.35 (Cu Kα)
transm coeff	0.76-1.00	0.82-1.53
R, %	3.2	4.1
R_w, %	3.8	5.2

Table II. Selected Positional and Isotropic Thermal Parameters for **2**

atom	x	y	z	B(eq), Å^2
Re	1.251086 (29)	1.2500	−1.069 074 (24)	2.5
P(1)	1.45240 (29)	1.166 17 (16)	1.158 98 (26)	3.3
P(2)	1.41153 (28)	1.361 42 (15)	1.119 25 (22)	2.9
P(3)	1.15246 (27)	1.267 78 (12)	1.222 24 (24)	3.1
Si	1.09439 (28)	1.271 94 (13)	0.860 70 (23)	2.9
C(1)	1.1421 (11)	1.162 87 (56)	1.036 52 (86)	3.4
O	1.08486 (88)	1.106 63 (44)	1.021 18 (80)	5.2
C(2)	0.8881 (11)	1.268 49 (54)	0.829 33 (85)	3.5
C(8)	1.1043 (10)	1.203 21 (54)	0.744 17 (75)	3.2
C(14)	1.1272 (11)	1.362 45 (58)	0.793 79 (86)	3.8
C(20)	1.4465 (16)	1.085 71 (78)	1.065 4 (13)	6.3
C(21)	1.6392 (12)	1.195 43 (75)	1.191 5 (14)	5.7
C(22)	1.4686 (12)	1.119 54 (58)	1.298 2 (10)	4.0
C(28)	1.4979 (14)	1.377 57 (74)	1.012 28 (97)	4.6
C(29)	1.3331 (12)	1.452 23 (56)	1.122 4 (10)	4.0
C(30)	1.5657 (10)	1.365 54 (52)	1.264 80 (80)	5.2
C(36)	0.9756 (13)	1.223 69 (70)	1.183 6 (14)	6.1
C(37)	1.2348 (14)	1.234 59 (73)	1.375 8 (10)	5.3
C(38)	1.1051 (11)	1.362 23 (53)	1.241 96 (84)	3.3

Table III. Selected Positional and Isotropic Thermal Parameters for **2**·THF

atom	x	y	z	B(eq), Å^2
Re	−0.180 450 (21)	0.163 000 (22)	0.177 492 (16)	1.9
P(1)	−0.048 50 (13)	0.153 40 (15)	0.114 62 (10)	2.7
P(2)	−0.245 20 (13)	0.291 53 (14)	0.112 44 (11)	2.6
P(3)	−0.137 64 (14)	0.248 05 (15)	0.282 15 (10)	2.8
Si	−0.297 09 (14)	0.056 17 (14)	0.155 76 (11)	2.3
C(1)	−0.133 99 (50)	0.061 56 (54)	0.224 69 (39)	2.4
O	−0.103 59 (40)	0.000 97 (42)	0.253 05 (29)	3.8
C(2)	−0.338 53 (52)	−0.004 27 (52)	0.235 88 (38)	2.6
C(8)	−0.260 10 (50)	−0.040 44 (53)	0.100 16 (41)	2.7
C(14)	−0.406 01 (50)	0.098 36 (55)	0.116 40 (42)	2.7
C(20)	−0.021 40 (58)	0.040 78 (60)	0.093 41 (45)	3.6
C(21)	−0.047 97 (65)	0.199 64 (69)	0.027 11 (45)	4.1
C(22)	0.055 35 (55)	0.188 68 (64)	0.156 33 (49)	3.8
C(28)	−0.285 03 (59)	0.264 69 (62)	0.024 54 (43)	3.6
C(29)	−0.342 65 (55)	0.337 57 (61)	0.147 30 (48)	3.6
C(30)	−0.180 71 (56)	0.391 03 (56)	0.096 39 (45)	3.2
C(36)	−0.122 93 (71)	0.178 27 (62)	0.360 41 (45)	4.3
C(37)	−0.035 71 (59)	0.311 59 (66)	0.291 04 (50)	4.2
C(38)	−0.218 62 (54)	0.326 56 (55)	0.309 97 (41)	2.9

In this paper, we describe the preparation and structural studies of $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si (**2**), Sn (**3**)). The spectroscopic data for **2** and **3** give no evidence that the solution structures contain either H···H or Si···H interactions. However, these complexes remain stereochemically rigid on the NMR time scale even at elevated temperatures, which is unusual for seven-coordinate complexes with only monodentate ligands. The solid-state structure of **2** has been determined by single-crystal X-ray

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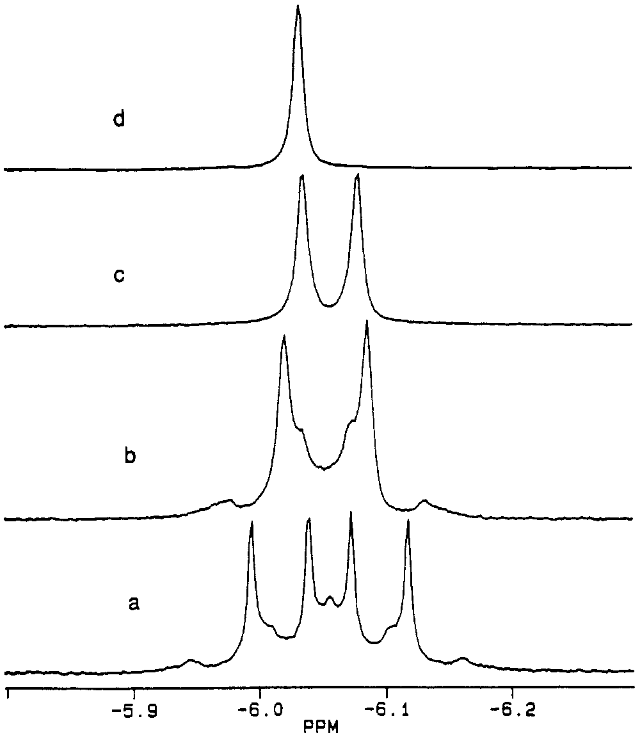

Figure 1. Hydride region of the ^1H NMR spectra (CD_2Cl_2, 298 K, 500 MHz) of $ReH_2(SiPh_3)(CO)(PMe_2Ph)_3$ (**2**): (a) without decoupling of the ^{31}P nuclei; (b) with decoupling of P_A; (c) with decoupling of P_B; (d) with decoupling of both P_A and P_B.

crystallography, with the hope of gaining insight into the origin of the high-energy barriers to the intramolecular rearrangements in these seven-coordinate complexes.

Results

Synthesis. The reaction of $ReH_7(PPh_3)_2$ with hydrosilanes has been used to synthesize silyl hexahydrides of the type $ReH_6(SiR_3)(PPh_3)_2$.[18a] The reaction has been found to proceed via loss of H_2 from the starting heptahydride followed by oxidative addition of the silane. We attempted to prepare a silyl dihydride in this way from $ReH_3(CO)(PMe_2Ph)_3$ (**1**), which is prepared from the reaction of $ReCl_3(CO)(PMe_2Ph)_3$ with $LiAlH_4$.[9]

Reaction of **1** with Ph_3EH (E = Si, Sn) in refluxing THF for 20 min gave new complexes for which the analytical data were consistent with the formulation $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si (**2**), Sn (**3**)) (eq 1). These complexes were isolated in high

$$\underset{\mathbf{1}}{ReH_3(CO)(PMe_2Ph)_3} + Ph_3EH \rightarrow ReH_2(EPh_3)(CO)(PMe_2Ph)_3 + H_2 \quad (1)$$
$$E = Si\ (\mathbf{2}),\ Sn\ (\mathbf{3})$$

yields as off-white or white air-stable solids by partial evaporation of the THF and precipitation with heptane. A mixture of **2** and **2**-d_1 was prepared from the reaction of Ph_3SiH with an isotopomeric mixture of **1**.

Spectroscopic Characterization. The Nujol mull IR spectra of **2** and **3** show bands characteristic of terminal hydride and carbonyl stretching frequencies. The ^1H, ^{31}P, and ^{13}C NMR spectra of **2** and **3** are very similar and show no temperature dependence in the range 193–298 K. The $^{31}P\{^1H\}$ NMR spectrum shows an AB_2 pattern. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet of triplets for the CO group. The ^1H NMR spectrum shows three doublets for the methyl groups of the phosphine ligands. These three doublets do not coalesce up to 338 K in toluene-d_8 when the compound starts to decompose.

The hydride region of the ^1H NMR spectrum of **2** (Figure 1) shows a complex AA'XX'Y pattern centered at δ −6.06 that can be simplified by decoupling ^{31}P. An AA'XX' pattern is observed upon decoupling P_A, an A_2Y pattern ($^2J_{HP_A}$ = 21.8 Hz) is seen upon decoupling P_B, and finally, upon decoupling of both P_A and P_B, a singlet is observed with no observable ^{29}Si satellite peaks.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **2** and **2**·THF

	2	**2**·THF
	Bond Distances	
Re–C(1)	1.88 (1)	1.903 (9)
Re–Si	2.451 (3)	2.434 (2)
Re–P(1)	2.426 (3)	2.412 (2)
Re–P(2)	2.514 (3)	2.490 (2)
Re–P(3)	2.439 (3)	2.438 (2)
C(1)–O	1.16 (1)	1.153 (9)
	Bond Angles	
Si–Re–P(1)	131.28 (1)	120.26 (7)
Si–Re–P(2)	102.31 (9)	99.61 (7)
Si–Re–P(3)	119.12 (9)	130.98 (7)
Si–Re–C(1)	80.4 (3)	78.2 (2)
P(1)–Re–P(2)	93.6 (1)	97.05 (7)
P(1)–Re–P(3)	104.12 (9)	104.04 (7)
P(1)–Re–C(1)	82.6 (3)	83.3 (2)
P(2)–Re–P(3)	96.35 (8)	94.36 (7)
P(2)–Re–C(1)	176.2 (3)	177.6 (2)
P(3)–Re–C(1)	84.6 (3)	87.9 (2)
C(2)–Si–C(8)	100.5 (4)	101.3 (4)
C(2)–Si–C(14)	106.4 (5)	98.8 (4)
C(8)–Si–C(14)	100.6 (4)	108.6 (4)

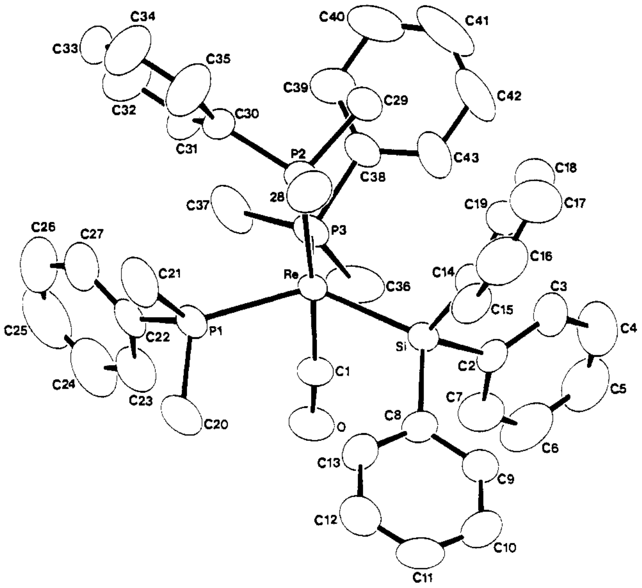

Figure 2. ORTEP diagram of the X-ray crystal structure of the unsolvated form of $ReH_2(SiPh_3)(CO)(PMe_2Ph)_3$ (**2**).

The hydride region of the $^1H\{^{31}P\}$ NMR spectrum of a mixture of **2** and **2**-d_1 shows an upfield isotope shift of −0.0072 ppm/D. Variable temperature T_1 measurements (CD_2Cl_2, 250 MHz) gave minimum values of 133 and 137 ms for **2** and **3**, respectively.

Solid-State Structure of 2. The complex **2** was obtained in two crystalline forms from the same THF/heptane solution, one solvated (THF), the other unsolvated. The X-ray crystal structures were determined for both forms. The crystallographic data appear in Tables I–IV, and ORTEP diagrams are shown in Figures 2 and 3.

Discussion

The large $^2J_{HP}$ coupling constants observed for **2** and **3** exclude the presence of an η^2-H_2 ligand, which normally shows much smaller $^2J_{HP}$ values (<5 Hz). The T_1 data are also consistent with a classical structure. The small upfield isotope shift for partially deuterated **2** is consistent with a geminal deuterium isotope effect and therefore with a classical structure.[9,18a,19] The spectroscopic data suggest the formulation of **2** and **3** as stereochemically rigid

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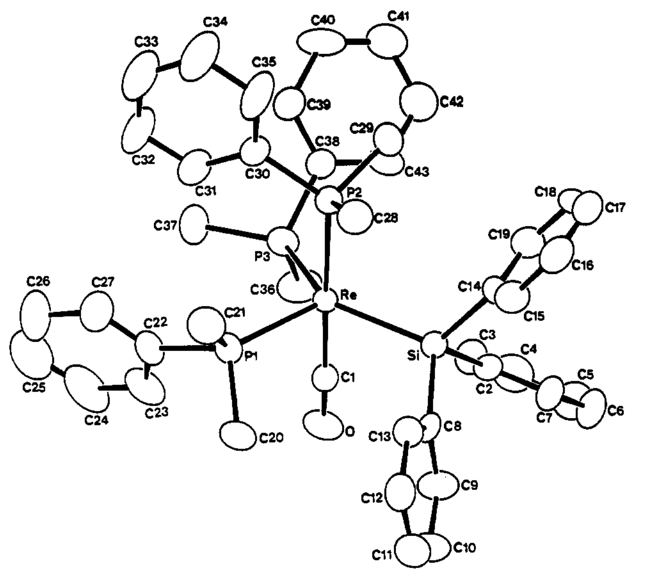
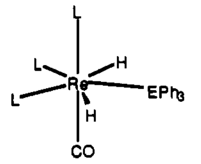
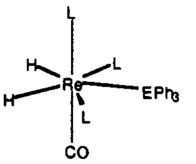


Figure 3. ORTEP diagram of the X-ray crystal structure of ReH$_2$(SiPh$_3$)(CO)(PMe$_2$Ph)$_3$·THF (**2**·THF). The disordered lattice THF is not shown.

seven-coordinate complexes. The most likely structure is one of the pentagonal bipyramids A and B.



A

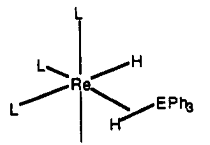


B

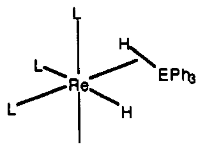
Structure B, where the three bulky ligands are close together in the pentagonal plane, is less likely for steric reasons. In both structures, the plane of symmetry contains the axial but not the equatorial phosphines. The latter therefore have diastereotopic methyl groups. The appearance of three methyl resonances even at elevated temperatures means that the axial and equatorial phosphines do not exchange on the NMR time scale. The AA′XX′ hydride pattern observed upon decoupling P$_A$ clearly indicates that neither the two equatorial phosphines nor the two hydrides exchange.

Molecular orbital calculations[1a] have shown that different polytopal forms[20] of seven-coordination have very similar energy and intramolecular rearrangements have very low energy barriers. Stereochemical nonrigidity is therefore commonly observed for seven-coordinate complexes.[21] Occasionally, the fluxionality can be frozen out at low temperature. Rarer still are examples in which intramolecular rearrangements are slow on the NMR time scale at room temperature.[22-26] However, all these rigid complexes contain chelating polydentate ligands that presumably cause substantial constraints in the structures, and the majority of them[23-26] also contain η^5-C$_5$H$_5$, which was taken as a pseudomonodentate ligand. To our knowledge, **2** and **3** are the first examples of seven-coordinate complexes containing only monodentate ligands that are stereochemically rigid at and above room temperature.

Since six-coordinate complexes are usually stereochemically rigid, one might speculate that **2** and **3** are actually six-coordinate, adopting structure C with an η^2-H–EPh$_3$ ligand.[15] There are three



C



C′

arguments against structure C, however. First, the observed chemical equivalence of the two hydride ligands and the two equatorial L ligands requires that the EPh$_3$ group rapidly shuttle between the two hydride ligands (C $\rightleftharpoons$ C′) so as to generate a time-averaged plane of symmetry, but the hydride ligands cannot exchange because they remain magnetically inequivalent as observed; this seems unlikely because facile exchange of dihydrogen and hydride ligands is generally observed in nonclassical polyhydrides. Second, it is often possible to observe the IPR (isotopic perturbation of resonance)[27] effect as a result of isotope fractionation within a fluxional structure such as C if one of the sites is chemically different from the others. This leads to a temperature-dependent shift of the averaged resonances for the d$_n$ isotopomers compared to the d$_0$ isotopomer. We did not observe any IPR shift but only a small geminal isotope shift for **2**. Third, while the known complexes containing η^2-H–SiR$_3$ ligands show J_{SiH} coupling constants in the range 30–70 Hz, we did not observe ^{29}Si, ^{117}Sn, and ^{119}Sn satellites in the hydride region of the ^{1}H{^{31}P} NMR spectra of **2** and **3**, suggesting the absence of direct Si···H and Sn···H interactions. All the spectroscopic data are therefore most consistent with **2** and **3** being rare examples of stereochemically rigid seven-coordinate complexes in solution.

The crystal structures of **2** and **2**·THF were determined by X-ray crystallography to try to find out the causes of the unusual stereochemical rigidity. The two hydride ligands could not be located in the difference Fourier maps because of the usual difficulties of detecting hydrogen atoms in the presence of heavy atoms,[28] nor can their positions be readily deduced from those of the heavy donor atoms around the Re. The C(1)–Re–P(2) angles are 176.2 (**2**) and 177.6° (**2**·THF), indicating that CO is essentially trans to P(2). However, no simple ideal seven-coordinate polyhedron easily accounts for the observed bond angles

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in the equator of the molecule. For example, the P(1)–Re–P(3) angles, 104.1° in **2** and 104.0° in **2**·THF, are far from the ideal values of 72° for A and 142° for B. Other typical seven-coordinate polyhedra, such as the monocapped octahedron, also fail to explain the bond angles.

If the two hydrides are ignored, the overall geometry of the ReP_3CSi core is that of a distorted trigonal bipyramid. It is known that, in some hydride complexes with bulky ligands, the hydride ligands are not stereochemically active. For example, $RhH(PPh_3)_4$ and $FeH_2\{PPh(OEt)_2\}_4$ both have an approximately regular tetrahedral MP_4 core, with one and two capping hydride ligands, respectively.[29] As suggested by a reviewer, the two hydride ligands of **2** may be capping the C(1)P(1)Si and C(1)P(3)Si faces of the ReP_3CSi core. In this way, the hydrides are chemically, but not magnetically, equivalent. This structure is also consistent with the small $^2J_{HP}$ values. The capping hydrides probably prevent the ReP_3CSi core from undergoing Berry pseudorotation. For steric reasons, it is probably unfavorable for the hydrides to cap the P(1)P(2)P(3), P(1)P(2)Si, and P(2)P(3)Si faces, which contain three bulky ligands. Nevertheless, it is not obvious why the P(1)P(3)C(1) face is unfavorable, and so electronic reasons may also apply in the site preference of the hydride ligands.

Both **2** and **2**·THF have a somewhat noncoplanar arrangement of the Re, Si, P(1), and P(3) atoms, with the Re atom deviating from the Si–P(1)–P(3) plane by 0.32 and 0.30 Å, respectively. The P(1)–Re–P(2), P(3)–Re–P(2), and Si–Re–P(2) bond angles are larger than 90° so that the two equatorial PMe_2Ph ligands and the $SiPh_3$ group are bent away from the third axial PMe_2Ph toward the smaller axial CO group, presumably as a result of steric effects.

The Si is not symmetrically disposed in the equator of the molecule with respect to P(1) and P(3); the Si–Re–P(1) and Si–Re–P(3) angles differ by 12.2° in **2** and 10.7° in **2**·THF. This distortion is not just a packing effect because it is found in both crystalline forms. A similar distortion has been observed in *eq*-$M(CO)_4(SbPh_3)$ (M = Ru, Os) and attributed to the differential interactions between the equatorial carbonyls and one of the phenyl rings, which lies in the equatorial plane.[30] However, none of the $SiPh_3$ phenyl groups are so oriented in **2** and **2**·THF.

To account for the distortion in the equatorial plane in **2**, it is tempting to postulate that it may adopt a solid-state structure such as C in which one or both of the two hydrides are bridging between the Re and Si atoms. Although the solution spectroscopic data appear to disfavor any structure containing a Si···H interaction, the possibility exists that the solution and solid-state structures are not the same. In both **2** and **2**·THF, the bond angles around the Si seem to be consistent with a tetracoordinate silicon. Nevertheless, this is not strong evidence against a Si···H interaction, because Corriu et al.[31] have found that the approximate tetrahedral geometry of a silicon atom can be retained upon formation of a six-coordinate silicon species with a bicapped tetrahedral geometry[32] at Si. An X-ray crystallographic study[18a] of $ReH_6(SiPh_3)(PPh_3)_2$ suggests that two of the hydride ligands may interact with the silicon atom.

The Re–Si bond distances, 2.451 (2) and 2.434 Å (**2**·THF), are significantly shorter than the sum of the covalent radii of the Re and Si atoms (2.65 Å), which is expected for a transition-metal silyl complex with a non-d^0 configuration where $M(d_\pi)$ to Si–R-(σ^*) back-donation can occur.[33] The Re–P(2) bond length in both **2** and **2**·THF is significantly longer than the Re–P(1) and Re–P(3) bond lengths, which can be attributed to the high trans influence of the CO ligand. The C(1)–Re–Si angles, 80.4 (**2**) and 78.2° (**2**·THF), are smaller than 90°. As a result, the C(1)···Si distances, 2.83 (**2**) and 2.77 Å (**2**·THF), are about 1.0 Å shorter than the sum of the van der Waals radii of the two atoms (3.75 Å). Although the C(1)–Si distances are still 0.8–0.9 Å longer than the sum of the covalent radii (1.95 Å), they may indicate a weak attractive interaction between the CO and $SiPh_3$ group.

Conclusion

$ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si (**2**), Sn (**3**)) can be prepared by reaction of $ReH_3(CO)(PMe_3)_2$ with Ph_3EH. The solution spectroscopic data are consistent with the formulation of **2** and **3** as classical seven-coordinate complexes containing neither H···H nor Si···H interactions. Unexpectedly, unlike other known seven-coordinate complexes, **2** and **3** show stereochemical rigidity on the NMR time scale even at elevated temperatures. The X-ray crystal structures of the solvated and unsolvated forms of **2** show distortions that are very difficult to understand on any of the ideal polyhedra usually invoked.

Experimental Section

General Procedures. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WM 250 or WM 500 spectrometer with CD_2Cl_2 as the solvent; ^1H and ^{13}C chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. 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, diethyl ether, hexane, and heptane were distilled from Na/Ph_2CO and stored under N_2 over 4-Å molecular sieves. $ReH_3(CO)(PMe_2Ph)_3$ was prepared from $ReCl_3(CO)(PMe_2Ph)_3$ by a method previously described.[9]

Dihydrido(triphenylsilyl)carbonyltris(dimethylphenylphosphine)rhenium(III) (2). A solution of $ReH_3(CO)(PMe_2Ph)_2$ (**1**) (0.57 g, 0.60 mmol) and Ph_3SiH (0.70 g, 2.7 mmol) in 15 mL of tetrahydrofuran was heated at reflux for 20 min. The resulting orange solution was then concentrated to 1 mL in vacuo, and heptane (30 mL) was added to precipitate **2** and **2**·THF as an off-white solid. The product was filtered out, washed with heptane (3 × 10 mL), and desolvated by drying in vacuo at 25 °C for 1 day. Yield: 0.71 g (76%). The product was analytically and spectroscopically pure without further purification. Anal. Calcd for $C_{43}H_{50}OP_3ReSi$: C, 58.03; H, 5.66. Found: C, 57.73; H, 5.66. IR (Nujol): ν_{Re-H} 1915, 1880 cm^{-1}; ν_{CO} 1838 cm^{-1}. ^1H NMR (298 K): δ 7.1–7.7 (c, 30 H, Ph), 1.72 (d, 7.4 Hz, 6 H, Me), 1.56 (d, 6.6 Hz, 6 H, Me), 0.82 (d, 6.6 Hz, 6 H, Me), −6.06 (c, 2 H, Re–H). $^{31}P\{^1H\}$ NMR (298 K): δ −30.4 (t, $^2J_{PP}$ = 30.7 Hz, 1 P, P_A), −32.1 (d, $^2J_{PP}$ = 30.7 Hz, 2 P, P_B). $^{13}C\{^1H\}$ NMR (298 K): δ 201.2 (dt, $^2J_{PC}$ = 45.1, 10.6 Hz, CO), 149.9 (s, C_1 of $SiPh_3$), 144.3 (t, $^1J_{PC}$ = 37.2 Hz, C_1 of $P_BMe_2\textit{Ph}$), 139.9 (d, $^1J_{PC}$ = 31.9 Hz, C_1 of $P_AMe_2\textit{Ph}$), 137.2 (s, C_2 of $SiPh_3$), 131.8 (d, $^2J_{PC}$ = 11.1 Hz, C_2 of $P_AMe_2\textit{Ph}$), 130.1 (t, $^2J_{PC}$ = 5.9 Hz, C_2 of $P_BMe_2\textit{Ph}$), 129.6 (s, C_4 of $P_AMe_2\textit{Ph}$), 129.0 (s, C_4 of $P_BMe_2\textit{Ph}$), 128.5 (t, $^3J_{PC}$ = 10.4 Hz, C_3 of $P_BMe_2\textit{Ph}$), 128.1 (d, $^3J_{PC}$ = 9.3 Hz, C_3 of $P_AMe_2\textit{Ph}$), 127.0 (s, C_4 of $SiPh_3$), 126.7 (s, C_3 of $SiPh_3$), 23.5 (t, $^1J_{PC}$ = 31.4 Hz, $P_B\textit{Me}_2Ph$), 21.9 (d, $^1J_{PC}$ = 27.8 Hz, $P_A\textit{Me}_2Ph$), 21.6 (t, $^1J_{PC}$ = 33.3 Hz, $P_B\textit{Me}_2Ph$).

A mixture of **2**-d_1 and **2**-d_2 was prepared similarly by reaction of Ph_3SiH with an isotopomeric mixture of **1**-d_{0-3}.

Dihydrido(triphenylstannyl)carbonyltris(dimethylphenylphosphine)-rhenium(III) (3). This compound was similarly prepared as a white solid by the above method but by substituting Ph_3SnH for Ph_3SiH. Yield: 80%. Anal. Calcd for $C_{43}H_{50}OP_3ReSn$: C, 52.67; H, 5.14. Found: C, 52.53; H, 5.19. IR (Nujol): ν_{Re-H} 1950 cm^{-1}; ν_{CO} 1838 cm^{-1}. ^1H NMR (298 K): δ 7.1–7.7 (c, 30 H, Ph), 1.82 (t, 6.0 Hz, 6 H, Me), 1.70 (t, 6.0 Hz, 6 H, Me), 0.96 (d, 5.9 Hz, 6 H, Me), −6.39 (c, 2 H, Re–H). $^{31}P\{^1H\}$ NMR (298 K): δ −30.8 (t, $^2J_{PP}$ = 27.7 Hz, 1 P, P_A), −31.6 (d, $^2J_{PP}$ =

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27.7 Hz, 2 P, P_B). $^{13}C\{^1H\}$ NMR (298 K): δ 197.9 (dt, $^2J_{PC}$ = 48.1, 8.5 Hz, CO), 149.5 (s, C_1 of $SnPh_3$), 144.4 (t, $^1J_{PC}$ = 40.6 Hz, C_1 of P_BMe_2*Ph*), 140.2 (d, $^1J_{PC}$ = 39.4 Hz, C_1 of P_AMe_2*Ph*), 137.6 (s, C_2 of $SnPh_3$), 131.8 (d, $^2J_{PC}$ = 11.1 Hz, C_2 of P_AMe_2*Ph*), 130.0 (t, $^2J_{PC}$ = 9.2 Hz, C_2 of P_BMe_2*Ph*), 129.6 (s, C_4 of P_AMe_2*Ph*), 129.1 (s, C_4 of P_BMe_2*Ph*), 128.5 (t, $^3J_{PC}$ = 8.1 Hz, C_3 of P_BMe_2*Ph*), 128.1 (d, $^3J_{PC}$ = 7.4 Hz, C_3 of P_AMe_2*Ph*), 127.8 (s, C_4 of $SnPh_3$), 127.6 (s, C_3 of $SnPh_3$), 24.0 (t, $^1J_{PC}$ = 35.1 Hz, P_B*Me*$_2$Ph), 23.6 (d, $^1J_{PC}$ = 24.1 Hz, P_A*Me*$_2$Ph), 22.6 (t, $^1J_{PC}$ = 33.3 Hz, P_B*Me*$_2$Ph).

Single-Crystal X-ray Crystallographic Studies. Colorless single crystals of **2** and **2**·THF suitable for X-ray diffraction measurements were grown from THF/heptane at −4 °C.

Crystallography of 2. A parallelpiped crystal of **2** with dimensions 0.25 × 0.23 × 0.20 mm was selected and mounted in a random orientation in a thin-walled glass capillary. Diffraction measurements were made on a κ-geometry Enraf-Nonius CAD-4 fully automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The unit cell (Table I) was determined and refined from a high-angle cell of 25 carefully centered reflections. The space group, on the basis of the systematic absences of $0k0$, $k \neq 2n$, and the successful solution and refinement of the structure, was assigned as $P2_1$ (No 4), with one molecule of $C_{43}H_{50}OP_3ReSi$ forming the asymmetric unit.

There were 3917 reflections collected with $2\theta \leq 50°$. Of those reflections, 3693 were unique (R_{int} = 0.004), and 3243 (88%) with $I \geq 3\sigma(I)$ were adjudged observed. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient for Mo Kα was 31.83 cm^{-1}. An empirical absorption correction using ψ scans[34] was applied, which resulted in transmission coefficients ranging from 0.76 to 1.00.

The structure was solved by a combination of Patterson and difference Fourier syntheses.[35] The position of the Re atom was obtained from the Patterson synthesis. The remaining non-hydrogen atoms were obtained by iterative use of the WFOURIER option in DIRDIF.[36] All hydrogen atoms of the PMe_2Ph and $SiPh_3$ ligands were calculated and input at their idealized positions with isotropic thermal parameters that were 20% greater than the equivalent value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 3243 observed reflections with $I \geq 3\sigma(I)$ and 441 variables. This resulted in convergence of the following conventional crystallographic reliability factors: $R = \sum(F_o - F_c)/F_o = 0.032$, and $R_w = [\sum w(F_o - F_c)^2/\sum wF_f^2]^{1/2} = 0.038$. The structure of the other enantiomer was also refined, which resulted in $R = 0.039$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.050$.

Crystallography of 2·THF. A pyramidal crystal of **2**·THF of dimensions 0.37 × 0.25 × 0.18 mm was selected and mounted in a random orientation in a thin-walled glass capillary. Diffraction measurements were made on a four-circle Rigaku AFC5S fully automated diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Due to crystal instability at room temperature, the data were collected at −50 °C. The unit cells (Table I) were determined and refined from a high-angle cell of 25 carefully centered reflections. The space group, on the basis of the systematic absences of $h0l$, $1 \neq 2n$, and $0k0$, $k \neq 2n$, and the successful solution and refinement of the structure, was assigned as $P2_1/c$ (No. 14), with one molecule of $C_{47}H_{58}O_2P_3ReSi$ forming the asymmetric unit.

There were 7538 reflections collected with $2\theta \leq 120°$. Of those reflections, 6896 were unique (R_{int} = 0.082), and 4648 (67%) with $I \geq 3\sigma(I)$ were adjudged observed. Scans of $(1.10 \pm 0.30 \tan\theta)°$ were made at a speed of 8.0°/min. The weak reflections ($I \leq 10.0\sigma(I)$) were rescanned (a maximum of three rescans) and the counts were accumulated to ensure good counting statistics. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient for Cu Kα is 67.35 cm^{-1}. An empirical absorption correction using the DIFABS method[37] was applied, which resulted in transmission factors ranging from 0.82 to 1.53.

The structures was solved in a way similar to that for **2**. The final cycle of full-matrix least-squares refinement was based on 4648 observed reflections with $I \geq 3\sigma(I)$ and 495 variables. This resulted in convergence of the following conventional crystallographic reliability factors: $R = \sum(F_o - F_c)/F_o = 0.041$, and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0.052$. There is disorder about the lattice THF, which accounts for the high thermal parameters.

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Supplementary Material Available: For **2** and **2**·THF, X-ray experimental data, additional positional parameters, isotropic and anisotropic thermal parameters, bond distances and angles, and torsion and conformation angles (Tables S-1–S-5, S-7–S-11, S-13, and S-14) (28 pages); F_o vs F_c values (Tables S-6 and S-12) (54 pages). Ordering information is given on any current masthead page.

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