Table IV. Comparison of the Wavenumbers,[a] cm^{-1}, of ν(C–O) bands, Their Relative Intensities,[b] and Calculated C–M–C Bond Angles[c] for $(C_nH_n)M(CO)_2L$ Species [L = H_2, N_2, and $HSiEt_3$]

$(C_nH_n)M(CO)_2$	H_2	N_2	$HSiEt_3$
$(C_4H_4)Fe(CO)_2$	2023.5 (1.0)	2016.3 (1.0)	2010 (1.0)[d]
	1967.9 (1.22)	1967.0 (1.25)	1950 (1.0)[d]
angle	**95 ± 2.5°**	**96 ± 2.5°**	**90 ± 3°**
$(C_5H_5)Mn(CO)_2$	1992.1 (1.0)	1985.0 (1.0)	1978.3 (1.09)[e]
	1932.7 (1.0)	1934.0 (1.1)	1915.5 (1.0)[e]
angle	**90 ± 2.5°**	**92 ± 2.5°**	**87.5 ± 2.5°**
$(C_6H_6)Cr(CO)_2$	1947.7 (1.7)	1947.3 (1.43)	1921 (1.2)[g]
	1895.7 (1.0)	1905.4 (1.0)	1821 (1.0)[g,h]
angle	**75° (83 ± 5°)**[f]	**80 ± 2.5°**	**85 ± 3°**

[a] Unless otherwise stated the IR data is for scXe at 25 °C from this work, ±0.2 cm^{-1}. [b] Intensity data in parentheses; the values used are the peak absorbance with the weaker of the two bands arbitrarily set to 1.0. In all cases, the symmetric ν(C–O) stretch is the higher wavenumber band. The error in the intensity data is ±10%. [c] For details of calculations see ref 49. [d] Data from ref 8: methylcyclohexane, 100 K, ±2 cm^{-1}. [e] *n*-Heptane solution, 25 °C; as an indication of the solvent shift, the bands of $(C_5H_5)Mn(CO)_3$ are shifted ca. 5 cm^{-1} to lower wavenumber in this solvent than in scXe. [f] These bands have significantly different half-widths; 1947.7 is 3/4 the width of 1895.7. The angle in parentheses is calculated by using (I = absorbance × peak width). [g] Data from ref 8: $HSiEt_3$, 100 K, ±2 cm^{-1}. [h] The wavenumber reported for this band seems anomalously low compared to data from our own work: e.g., $(C_6Me_6)Cr(CO)_2(HSiEt_3)$, 1890 and 1841 cm^{-1}, *n*-heptane −20 °C; $(C_6H_6)Cr(CO)_2(HSiEt_3)$ in *n*-heptane at −40 °C 1931.3 and 1925.1 (two bands, partly resolved, intensity 1.0) and 1872.2 cm^{-1} (intensity 1.2). The two bands have a combined width (FWHM) 1.4 times that of the lower frequency band. Thus, the angle calculated by using (I = absorbance × peak width) is 85.5°.

see Table IV. Although such calculations are difficult to verify in detail, the values for the $HSiEt_3$ compounds of Mn and Cr are similar to the values found in the crystal structures of less labile silane complexes.[51] In addition, the calculations indicate that, for a particular ligand L, the C–M–C angle in $(C_nH_n)M(CO)_2L$ decreases from Fe to Cr. This is consistent with crystallographic studies[52] on the unsubstituted $(C_nH_n)M(CO)_3$ where a similar trend is found. The calculations also suggest that, for a given metal, the η^2-H_2 complex has a larger angle than the $HSiEt_3$ compound. However, the differences are small, and one is probably justified in concluding that steric effects play a relatively minor role in determining the geometry at the metal center in these compounds.

Although the work described in this paper has been carried out in scXe (largely for spectroscopic reasons), less exotic supercritical fluids could also be used as solvents for such reactions. Preliminary experiments[53] indicate that the same compounds can be generated in supercritical CO_2 or ethane. Our experiments have taken advantage of just one specific property of supercritical fluids, their miscibility with H_2 and N_2. Work is now in progress in our laboratory applying some of the other unusual properties of supercritical fluids to organometallic chemistry.

Acknowledgment. We thank the SERC, EEC (Stimulation Contract No. SC1*0007), the BP Venture Research Unit, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and ICI Chemicals and Polymers Ltd for support. M.P. thanks the Nuffield Foundation for a Science Research Fellowship. We are grateful to Professor J. J. Turner, Dr. G. Davidson, M. T. Haward, M. Jobling, Dr. R. Whyman, J. M. Whalley, and D. R. Dye for their help and advice.

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Synthesis and Structural Studies of Some New Rhenium Phosphine Heptahydride Complexes. Evidence for Classical Structures in Solution

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Received July 12, 1989

Abstract: A series of new rhenium phosphine heptahydride complexes ReH_7L_2 (L_2 = a chelating bidentate phosphine) have been synthesized and characterized by IR and ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The hydride resonances of ReH_7(dppf) (**1**, dppf = 1,1′-bis(diphenylphosphino)ferrocene), ReH_7(dppb) (**2**, dppb = 1,4-bis(diphenylphosphino)butane), and ReH_7{(+)-diop} (**3**, (+)-diop = (4*S*,5*S*)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane) undergo decoalescence upon cooling. The low-temperature hydride patterns suggest classical 9-coordinate tricapped trigonal prismatic structures. Consistent with the classical structures, ^{1}H NMR spectra of deuterated ReH_7L_2 complexes show very small and temperature-independent upfield isotope shifts in the hydride region and no change in $^2J_{HP}$. Sequential treatment of **1**, **2**, and **3** with NaH and Me_2SO_4 in the presence of Ph_3SiH leads to $ReH_6(SiPh_3)L_2$ (L_2 = dppf, dppb, (+)-diop). Variable-temperature ^{1}H NMR studies of these silyl derivatives provide further support for the classical formulation of their parent heptahydrides. Theoretical T_1(min) values are calculated for some polyhydrides on the basis of different structural models and are compared with the experimental numbers. Precautions to be taken in interpreting T_1 data are discussed.

Transition-metal dihydrogen complexes[1] have attracted much recent attention. Their structural characterization is a particularly challenging problem for which we have previously developed a solution ^{1}H NMR T_1 method.[2,3] The method is based on the fact that the dipole–dipole mechanism dominates spin–lattice relaxation in small diamagnetic molecules in which the protons are close together (<2 Å). By this mechanism the relaxation rate, i.e. T_1^{-1}, increases with the inverse sixth power of the H···H distance. The T_1 value is dependent on temperature and spectrometer field

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strength. When the temperature dependence of T_1 is examined, a minimum value, T_1(min), which scales with the spectrometer field strength, is often observed. It is only this T_1(min) value that is comparable across a wide range of complexes and provides a useful structural criterion. All the T_1 data below refer to 250 MHz, unless stated otherwise.

In "pure" dihydrogen complexes $L_nM(\eta^2\text{-}H_2)$, i.e., those containing no classical M–H sites, the exceptionally short H···H distances (<1 Å) of the $\eta^2\text{-}H_2$ ligands give rise to very short T_1(min) values (usually <30 ms). These are much shorter than the T_1(min) values (usually >100 ms) observed for classical dihydrides. Thus, the difference in T_1(min) values expected for classical and nonclassical formulations is so large that there is little chance of error in applying the T_1 criterion. For example, $W(\eta^2\text{-}H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2$ and its classical tautomer show T_1 values of 4 and 1700 ms, respectively, at −80 °C.[4]

In the case of polyhydrides,[5] distinguishing between the classical and nonclassical formulations by the T_1 method is still straightforward if it is possible to freeze out the fluxionality in ^{1}H NMR and to measure directly the ratio and T_1's of the different types of hydrides. For example, $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$ shows T_1 values of 9 ms for the $\eta^2\text{-}H_2$ resonance and 53 ms for the terminal hydride resonance at 193 K.[6]

For polyhydrides that are fluxional at all accessible temperatures, the problem becomes much more complicated. The rapid relaxation of any $\eta^2\text{-}H_2$ ligand present is diluted by exchange with the slowly relaxing terminal hydrides. Equation 1 shows how the observed T_1 ($T_{1,\text{obs}}$) in the complex $MH_n(\eta^2\text{-}H_2)_mL_x$ depends upon both the numbers of protons (n and $2m$) and T_1 values ($T_{1,\text{c}}$ and $T_{1,\text{nc}}$) of classical and nonclassical sites.[3b] Even so, in cases where

$$(n + 2m)/T_{1,\text{obs}} = n/T_{1,\text{c}} + 2m/T_{1,\text{nc}} \qquad (1)$$

the number of classical hydride ligands is not large compared to that of nonclassical ones, the $T_{1,\text{obs}}$ of a nonclassical polyhydride should be significantly shorter than would be expected for a classical structure, and so the data leave little doubt about the structural assignment. For example, T_1(min) values of 24, 38, and 820 ms found for $FeH_2(\eta^2\text{-}H_2)(PEtPh_2)_3$, $RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$, and $OsH_4(P(p\text{-tolyl})_3)_3$, respectively, suggest the assignments shown.[3] A neutron-diffraction study has confirmed our nonclassical assignment in the Fe case.[7]

Rhenium phosphine polyhydrides of the type ReH_7L_2[8] exhibit T_1(min) values in the range 55–67 ms. In our earlier work we questioned the accepted formulation of these compounds as classical d^0 rhenium(VII) heptahydrides and proposed an alternative nonclassical formulation $ReH_5(\eta^2\text{-}H_2)L_2$.[3b] This seemed reasonable at first sight because a number of classical nine-coordinate polyhydrides such as $WH_6(PMe_2Ph)_3$ and $[WH_5(PMePh_2)_4]^+$ give significantly longer T_1(min) values. The d^2 configuration also appeared to be supported by a cyclic voltammetric study,[9] in which the observed oxidation was presumed to be metal based.

The nonclassical formulation for ReH_7L_2 remained controversial, however. We have found low T_1(min) values (76 and 79 ms) for the closely related $ReH_6(SiPh_3)(PPh_3)_2$, which is shown to have a classical nine-coordinate tricapped trigonal prismatic (TTP) structure by variable-temperature ^{1}H NMR and X-ray crystallography.[10] T_1(min) values in the range of 55–80 ms have also been found in a number of other related cases.[11-13] Clearly, T_1(min) values below 100 ms cannot always be associated with nonclassical structures. A recent neutron-diffraction study[14] has shown that ReH_7(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) adopts a classical TTP structure in the solid state. Nevertheless, this does not prove that the classical structure is also adopted in solution because it is known that crystallization of a tautomeric mixture can result in a solid containing only a single tautomer that may not be the major species in solution.[4,15]

In this paper, we report the use of conformationally restrictive phosphines to help freeze out fluxionality in rhenium heptahydrides, which has allowed us to obtain ^{1}H NMR spectroscopic evidence in favor of classical TTP structures in solution. We have calculated theoretical T_1(min) values for ReH_7L_2 and other rhenium polyhydrides based on standard structural models or crystallographic data and compare the values with the experimental ones. Part of this work has been communicated in preliminary form.[16a]

Results and Discussion

Synthesis and Spectroscopic Studies of New Rhenium Phosphine Heptahydride Complexes. Since the fluxionality[17] of all the known rhenium phosphine heptahydrides of the type ReH_7L_2 is the major factor that complicates the ^{1}H NMR T_1 analysis, we looked for examples in which the fluxional processes could be frozen out. It has been reported that the activity and selectivity of a catalyst containing a chelating diphosphine can be greatly affected by variation of the chain linking the two phosphorus atoms, although the reasons are still unknown.[18] Miller and Caulton have found that the barrier of intramolecular rearrangement in trigonal-bipyramidal and octahedral complexes is dependent on the diphosphine chelate ring size.[19] We thought that using a conformationally restrictive chelating diphosphine might slow down the fluxional processes in rhenium heptahydrides.

The reactions of the readily available *trans*-$ReOCl_3(AsPh_3)_2$[20] with 1 equiv of the bidentate phosphines 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,4-bis(diphenylphosphino)butane

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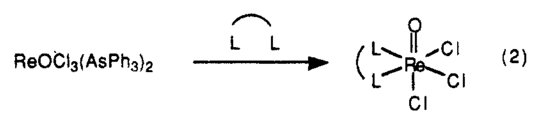
Table I. Selected IR and NMR Data for New ReH_7L_2 Complexes

compd no.	L_2	IR data, ν_{Re-H},[a] cm^{-1}	^1H NMR data, δ_{Ir-H}[b]	$^{31}P\{H\}$ NMR data[c]
1	$Fe(C_5H_4PPh_2)_2$	2008, 1951, 1925	−5.75, t (16.9)	12.9 (16.4[d])
2	$Ph_2P(CH_2)_4PPh_2$	1971, 1943, 1904	−6.18, t (16.2)	11.4
3	(+)-diop	1984, 1953, 1928	−6.11, t (16.2)	0.90
4	cis-$Ph_2PCH{=}CHPPh_2$	1967, 1951, 1891	−6.71, t (13.2)	12.8 (12.8[d])
5	$Ph_2P(CH_2)_3PPh_2$	1961, 1940, 1906	−6.27, t (15.4)	2.1
6	$Ph_2P(CH_2)_5PPh_2$	1972, 1939, 1905	−5.74, t (19.1)	18.6
7	1,2-$(Ph_2P)_2C_6H_4$	1969, 1953, 1898	−6.40, t (13.2)	52.1 (12.9[d])

[a] In Nujol mull. [b] In CD_2Cl_2 at 250 MHz and 298 K. Hydride resonances reported as follows: chemical shift (ppm), intensity, multiplicity (t = triplet) (coupling constant $^2J_{PH}$(Hz)). [c] In CD_2Cl_2 at 202 MHz and 298 K. Chemical shifts given in ppm downfield from external 85% H_3PO_4. [d] $^2J_{HP}$ observed in selectively hydride coupled ^{31}P NMR.

(dppb), (4*S*,5*S*)-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxolane ((+)-diop), 1,3-bis(diphenylphosphino)propane (dppp), *cis*-1,2-bis(diphenylphosphino)ethylene (dppe′), 1,5-bis(diphenylphosphino)pentane (dppt), and 1,2-bis(diphenylphosphino)benzene (dpbz) at room temperature in CH_2Cl_2 led to the formation of the substitution products of the type *cis*-$ReOCl_3L_2$, where L_2 represents a chelating bidentate phosphine ligand (eq 2). All the *cis*-$ReOCl_3L_2$ complexes were isolated as



(2)

green or blue products in nearly quantitative yields. The IR spectra show strong sharp bands at 960–990 cm^{-1}, characteristic of Re=O stretching frequencies.[21] The stereochemistry of *cis*-$ReOCl_3L_2$ complexes shown in eq 2 follows from the equivalence of the two phosphorus nuclei in ^{31}P NMR for all the complexes except *cis*-$ReOCl_3\{(+)\text{-diop}\}$, which shows an AB pattern ($^2J_{PP'}$ = 11.5 Hz) due to the lower symmetry (C_1). Similar cis structures have been reported for $ReOCl_3$(bp) (bp = bis(pyrazolyl)methane)[11] and $ReOCl_3(PEt_3)_2$.[22]

Treatment of *cis*-$ReOCl_3L_2$ with excess $LiAlH_4$ in Et_2O gave the new heptahydride complexes ReH_7L_2 (L_2 = dppf (**1**), dppb (**2**), (+)-diop (**3**), dppe′ (**4**), dppp (**5**), dppt (**6**), dpbz (**7**)), which were isolated as white or pale-yellow solids and characterized spectroscopically and by elemental analyses. Selected IR and NMR data are given in Table I. All the new heptahydrides show a triplet hydride resonance integrating as seven protons in the ^1H NMR spectrum at 298 K, indicating rapid fluxionality. The $^{31}P\{^1H\}$ NMR spectrum displays a singlet resonance at all accessible temperatures for the two equivalent ^{31}P nuclei. In the cases of **1**, **4**, and **7**, where all the protons of the diphosphine ligand resonate in a relatively narrow region, the selectively hydride-coupled ^{31}P NMR spectrum shows a binomial octet, confirming the presence of seven hydride ligands. **1**–**7** resemble ReH_7(dppe) (**8**)[8a,10] in that they are resistant to hydrogen loss and do not react with pyridine, PPh_3, and silanes even in refluxing THF. In contrast, rhenium heptahydrides containing monodentate phosphines, such as $ReH_7(PPh_3)_2$ (**9**) and $ReH_7(PCy_3)_2$ (**10**), lose H_2 easily and undergo a variety of reactions including C–H activation.[8a–d,23]

Ferrocenylphosphines are known to give bimetallic complexes with interesting structures and reactivities,[24] but up to now, no example of a polyhydride complex of this type of ligand has been reported. The P–M–P bite angles of dppf are in the range 95–103°,[24] somehwat larger than those observed for analogous complexes of common bidentate phosphines such as dppm, dppe, and dppp. We wondered whether the conformational constraints imposed by the chelating dppf ligand would allow the fluxionality of **1** to be frozen out at low temperatures.

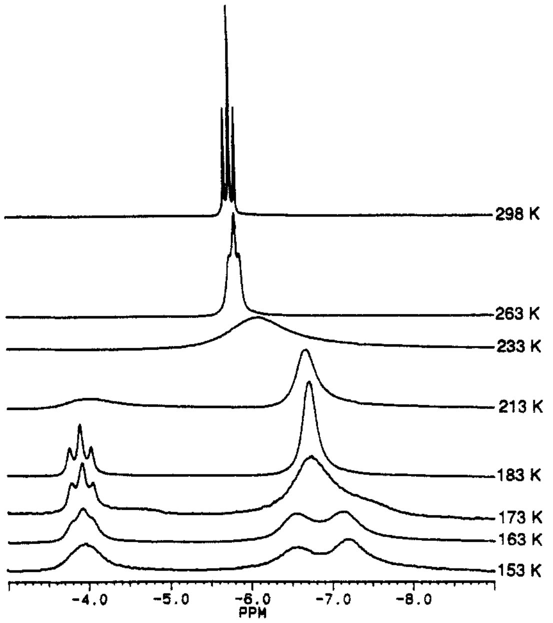


Figure 1. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of ReH_7(dppf) (**1**) in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

Figure 1 shows the variable-temperature ^1H NMR spectra of **1** in $CD_2Cl_2/CFCl_3$ (3:2 v/v) at 250 MHz in the hydride region. The seven hydrides are equivalent at 298 K, giving a triplet resonance (δ −5.75, $^2J_{PH}$ = 16.9 Hz). Upon cooling to 233 K, this changes into a broad feature, which is then resolved at 183 K into a triplet (δ −3.89, $^2J_{PH}$ = 32 Hz) integrating as two protons and a broad resonance (δ −6.70) integrating as five protons. The resonance at δ −3.89 must arise from classical hydrides, because the $^2J_{PH}$ value is much larger than reported for any η^2-H_2 ligand.[1] Upon further cooling to 153 K, while the triplet at δ −3.89 remains unchanged, the resonance at δ −6.70 due to five hydrides collapses into two broad peaks, the one of lower intensity at δ −6.57 and the other of higher intensity at δ −7.19. It is difficult to measure accurately the intensity ratio of the two resonances by integration because they are broad and overlap with each other. However, the ratio must be either 1:4 or 2:3 since the total intensity is five. Cutting and weighing the peaks gave a ratio closer to 2:3 than to 1:4. Interestingly, the resonances of the cyclopentadienyl (Cp) ring protons of the dppf ligand also vary with temperature. Each of the two resonances observed at 298 K decoalesces into a pair of resonances at 153 K. There is no apparent change in $^{31}P\{^1H\}$ NMR with temperature.

The dynamic behavior of the ^1H NMR hydride and Cp ring proton resonances is most readily interpreted in terms of either of the two classical 9-coordinate TTP structures A or B,[25] shown below. At 153 K the dppf ligand adopts a frozen staggered

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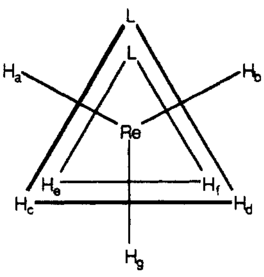
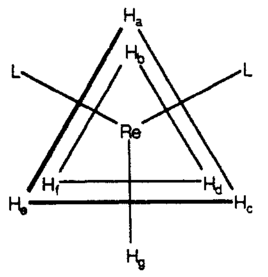


A



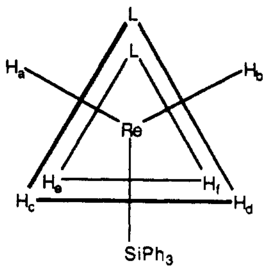
B

conformation that has been observed for other dppf complexes in the solid state.[24] As a result, the sole symmetry element of A or B is a C_2 axis coincidental with the Re–H_g bond, and so the seven hydride ligands can be divided into four chemically inequivalent sets: H_a, H_b; H_c, H_f; H_d, H_e; and H_g. Both structures are expected to show four resonances for the Cp ring protons and a 2:2:2:1 hydride ratio in the slow-exchange limit. Experimentally, we observed a 2:2:3 hydride ratio probably due to the accidental degeneracy of the chemical shifts of two of the four sets of hydrides.

The diphosphine takes up two eclipsed prism positions in structure A, whereas it occupies two equatorial positions capping two of the three prism faces in structure B. The expected P–Re–P angles in the two ideal structures are 90° for A and 120° for B. Since the bite angles of dppf are generally smaller than 100°,[24] structure A is more likely to be adopted. A neutron-diffraction study has shown that $ReH_7(dppe)$ adopts structure A.[14]

To confirm the conclusions outlined above, we decided to study $ReH_6(SiPh_3)(dppf)$. Complexes of the type $ReH_6(SiR_3)(PPh_3)_2$,[10] prepared from reaction of **9** with R_3SiH, exhibit a 2:4 hydride ratio in low-temperature ^1H NMR, indicating a TTP structure as was observed by X-ray crystallography. In the previous work, attempted preparation of $ReH_6(SiR_3)L_2$ (L_2 = a chelating diphosphine) from ReH_7L_2 and R_3SiH failed. Ephritikhine and Felkin et al. found that **8** can be activated to react with dienes by deprotonation with $KOBu^t$ to give $[ReH_6(dppe)]^-$, which is then methylated with Me_2SO_4.[26] In a similar manner, we have successfully synthesized $ReH_6(SiPh_3)(dppf)$ by sequential treatment of **1** with NaH and Me_2SO_4 in the presence of Ph_3SiH.

If the above analysis of the variable-temperature ^1H NMR of **1** is correct, we would predict that its silyl derivative, formed formally by replacement of the H_g in **1** with a $SiPh_3$ group as shown in structure C, should show a 2:2:2 hydride ratio in the slow-exchange limit. Figure 2 depicts the variable-temperature ^1H NMR spectra. At 298 K, the hydride region displays a slightly broadened triplet (δ −5.11, $^2J_{PH}$ = 16.2 Hz, 6 H). Upon cooling to 263 K, the resonance becomes a broad feature. At 213 K, two well-resolved resonances appear, a triplet (δ −3.33, $^2J_{PH}$ = 31.2 Hz) integrating as two protons and a doublet (δ −6.25, $^2J_{PH}$ = 15.4 Hz) integrating as four protons. Upon further cooling, the doublet broadens and decoalesces at 173 K into two separate broad singlets (δ −6.20 and δ −6.50) of equal intensity. The region of the Cp ring protons shows dynamic behavior similar to that observed for **1**. The 2:2:2 hydride pattern in the final low-temperature spectrum conforms to the prediction and supports our interpretation of the ^1H NMR data of **1**.



C

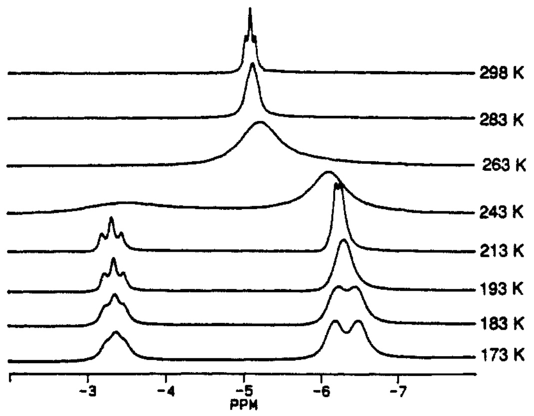


Figure 2. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of $ReH_6(SiPh_3)(dppf)$ in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

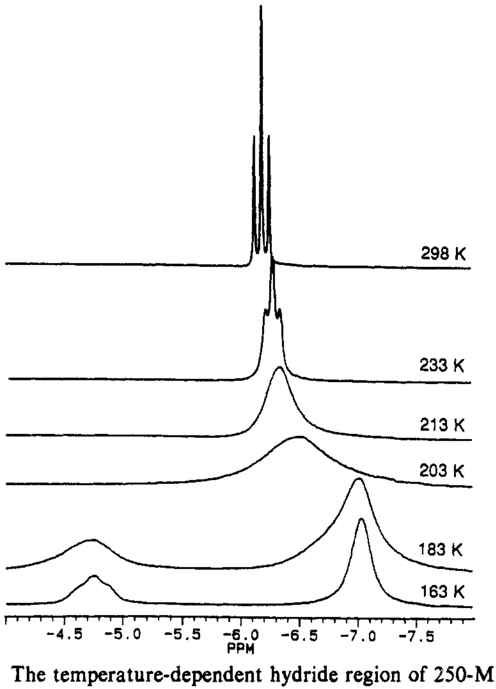


Figure 3. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of $ReH_7(dppb)$ (**2**) in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

The variable-temperature ^1H NMR spectra of $ReH_7(dppb)$ (**2**) are given in Figure 3. The spectrum at 298 K shows a triplet hydride resonance at δ −6.18 ($^2J_{PH}$ = 16.2 Hz), which becomes a broad feature at 203 K and is subsequently resolved at 163 K into a broad triplet at δ −4.73 ($^2J_{PH}$ = 32 Hz) and a broad singlet at δ −7.02 in an intensity ratio of 2:5. **2** is apparently more fluxional than **1**, and only the first decoalescence can be reached upon cooling to the lowest accessible temperature. The low-temperature hydride pattern of **2** is therefore consistent with classical structures A and B, with A being more likely in view of the bite angle of dppb.[27]

Another interesting aspect of the ^1H NMR of **2** is the fluxionality of the chelate ring. Each of the two methylene resonances observed at 298 K decoalesces into a pair of resonances at 163 K. Since only a single resonance is observed in $^{31}P\{^1H\}$ NMR at all temperatures, this is unlikely to be due to conformational isomerism of the chelate ring at low temperature[28] and is better

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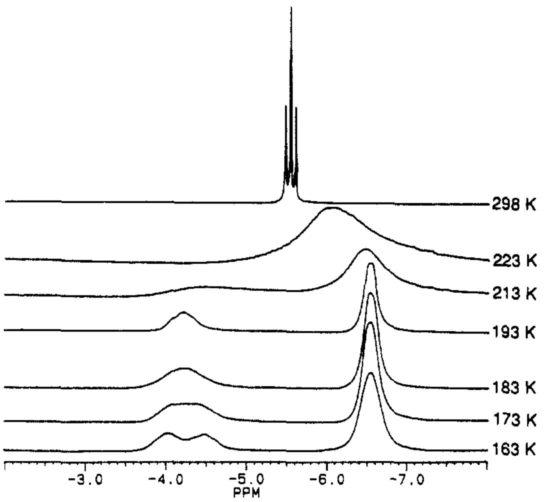

Figure 4. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of $ReH_6(SiPh_3)(dppb)$ in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

attributed to the inequivalence of the geminal protons by freezing the chelate ring conformation due to the bulky PPh_2 and ReH_7 groups. Seven-membered rings are generally puckered to minimize Pitzer strain.[29] Conformational analysis of cycloheptane has revealed that the potential energies of the four possible conformations increase in the order twist-chair (C_2) < chair (C_s) < twist-boat (C_2) < boat (C_s),[29d-g] with the symmetry given in parentheses. All four conformations have been found in X-ray crystallographic studies of diphosphine complexes.[27,30] The decoalescence of the hydride resonances of **2** is not complete at the lowest accessible temperature presumably due to the very similar chemical shifts of the inequivalent sets of hydrides. As a result, we cannot determine whether the chelate ring has C_2 symmetry or C_s symmetry. The former should give a 2:2:2:1 hydride ratio in the slow-exchange limit as in the case of **1**, while the latter should show a 1:1:2:2:1 ratio (i.e., H_a; H_b; H_c, H_e; H_d, H_f; H_g).

To confirm the above analysis, the triphenylsilyl derivative of **2**, $ReH_6(SiPh_3)(dppb)$, was synthesized by the method used for the dppf analogue. This compound should show either a 2:2:2 or a 1:1:2:2 hydride ratio in the slow-exchange limit, depending on the symmetry (C_2 or C_s) of the chelate ring. The variable-temperature ^1H NMR spectra are shown in Figure 4. The triplet hydride resonance (δ -5.57, $^2J_{PH}$ = 16.2 Hz, 6 H) observed at 298 K decoalesces into a broad triplet (δ -4.21, $^2J_{PH}$ = 30 Hz, 2 H) and a doublet (δ -6.52, $^2J_{PH}$ = 14 Hz, 4 H) at 193 K. Upon further cooling to 163 K, the triplet collapses into two broad triplets (δ -4.02, $^2J_{PH}$ = 28 Hz, 1 H and δ -4.49, $^2J_{PH}$ = 32 Hz, 1 H), while the doublet broadens into a featureless lump. The 1:1:4 hydride ratio in the low-temperature spectrum is in favor of C_s symmetry with a mirror plane containing the H_a, H_b, and Si atoms in structure C. The broadening of the doublet resonance at δ -6.50 below 193 K suggests the presence of two inequivalent sets of hydrides (H_c, H_e and H_d, H_f) with very similar chemical shifts. The methylene proton region shows a dynamic process similar to that observed for **2**.

$ReH_7\{(+)\text{-diop}\}$ (**3**) is the first example of a polyhydride complex containing a chiral diphosphine. The triplet hydride resonance (δ -6.11, $^2J_{PH}$ = 16.2 Hz) observed at 298 K collapses into two broad resonances (δ -4.60 and -6.97) in an intensity ratio of 2:5 at 153 K (Figure 5). $ReH_6(SiPh_3)\{(+)\text{-diop}\}$, the silyl derivative of **3**, shows variable-temperature ^1H NMR spectra (Figure 6) analogous to those of $ReH_6(SiPh_3)(dppf)$. The triplet hydride resonance (δ -5.52, $^2J_{PH}$ = 16.2 Hz, 6 H) observed at 298 K is resolved into a triplet (δ -4.08, $^2J_{PH}$ = 30 Hz, 2 H) and a broad singlet (δ -6.57, 4 H) at 183 K. The latter collapses into two resonances (δ -6.52 and -6.65) of equal intensity at 163 K. The 2:2:2 hydride pattern in the low-temperature limit suggests that the chelate ring has C_2 symmetry. Indeed, in most diop complexes that have been studied crystallographically, the chelate ring shows the twist-chair conformation (C_2 symmetry) in the solid state.[30]

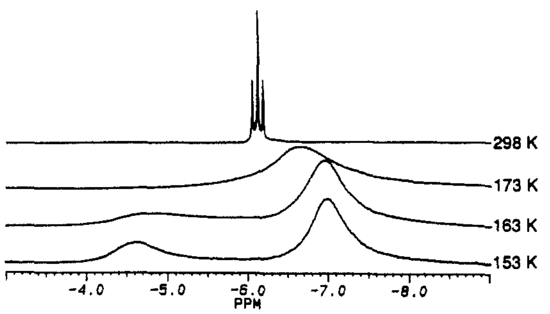

Figure 5. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of $ReH_7\{(+)\text{-diop}\}$ (**3**) in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

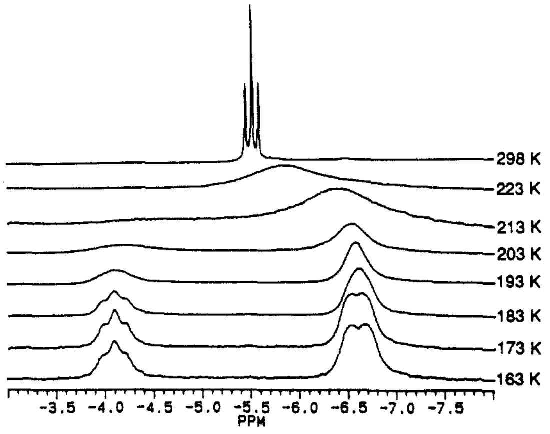

Figure 6. The temperature-dependent hydride region of 250-MHz ^1H NMR spectra of $ReH_6(SiPh_3)\{(+)\text{-diop}\}$ in $CD_2Cl_2/CFCl_3$ (3:2 v/v).

The other new ReH_7L_2 complexes **4**–**7** are more fluxional than **1**–**3**, and we were not able to observe decoalescence for any of them. Their hydride resonances become broad features at 173 K without resolvable coupling to ^{31}P, suggesting that decoalescence may be imminent. It is interesting to note the irregular trend of the energy barrier for the fluxional process in $ReH_7(Ph_2P(CH_2)_nPPh_2)$ with the chelate ring size. As indicated by variable-temperature ^1H NMR studies, the barrier increases from n = 2 to 4 and then decreases from n = 4 to 5. We do not yet understand the reasons for this trend.

Variable-temperature ^1H NMR T_1 measurements were carried out for the hydride resonances of **1**–**7** in CD_2Cl_2 at 250 MHz. The T_1(min) values (Table II) are in the range 54–68 ms. These are similar to those reported for the known complexes **8**–**10** that were previously[3b] formulated as nonclassical. The similarity of the T_1 data for **1**–**10** suggest that they all adopt classical structures in solution, but the evidence is definitive only for **1**–**3**.

Like **1**–**3**, **4**–**8** probably adopt structure A because of the small P-Re-P bite angles imposed by chelation. The monodentate phosphine complexes, such as **9**–**10**, are generally fluxional at all accessible temperatures, and so NMR spectroscopy cannot tell which positions the phosphine ligands occupy in a TPP structure. X-ray crystallographic studies on $ReH_7(PMe_2Ph)_2$[8e] and ReH_7-

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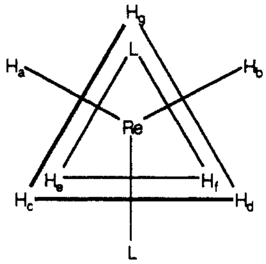
Table II. ^{1}H NMR T_1 and Isotope Shift Data for ReH_7L_2 Complexes[a]

compd	L_2	temp, K	δ_{Ir-H}[b]	T_1,[c] ms	IS,[d] ppm/D
1	$Fe(C_5H_4PPh_2)_2$	153	−3.93, 2 H, br	351	−0.002[e]
			−6.57, 2 H,[f] br	301[g]	
			−7.19, 3 H,[f] br	301[g]	
		183	−3.89, 2 H, t (32)	112	
			−6.70, 5 H, br	95	
		213	−3.95, 2 H, br	62	
			−6.70, 5 H, br	58	
		233	−5.98, 7 H, br	**54**	
		243	−5.94, 7 H, br	75	
		298	−5.75, 7 H, t (16.9)	132	
2	$Ph_2P(CH_2)_4PPh_2$	163	−4.73, 2 H, t (32)	211	−0.0062[e]
			−7.02, 5 H, br	186	
		183	−4.71, 2 H, br	154	
			−6.99, 5 H, br	134	
		219	−6.30, 7 H, br	**56**	
		243	−6.30, 7 H, br t (16)	88	
		298	−6.18, 7 H, t (16.2)	125	
3	(+)-diop	153	−4.73, 2 H, br	202	−0.0071[e]
			−7.02, 5 H, br	198	
		183	−6.31, 7 H, br	141	
		213	−6.30, 7 H, br t (16)	**59**	
		243	−6.30, 7 H, t (16.2)	90	
		298	−6.18, 7 H, t (16.2)	128	
4	cis-$Ph_2PCH{=}CHPPh_2$	206	−6.86, 7 H, t (13)	**68**	−0.002[h]
5	$Ph_2P(CH_2)_3PPh_2$	209	−6.42, 7 H, t (15)	**58**	−0.0069[h]
6	$Ph_2P(CH_2)_5PPh_2$	213	−6.89, 7 H, t (15)	**58**	−0.0081[h]
7	1,2-$(Ph_2P)_2C_6H_4$	216	−6.43, 7 H, t (13)	**63**	−0.0073[h]
8	$Ph_2P(CH_2)_2PPh_2$	222	−6.79, 7 H, t (13)	**67**[i]	−0.0075[h]
9	$(PPh_3)_2$	193	−5.12, 7 H, t (19)	**55**[i]	−0.0088[h]
10	$(PCy_3)_2$	200	−7.07, 7 H, t (19)	**60**[i]	−0.0083[h]

[a] All NMR studies were carried out at 250 MHz in either CD_2Cl_2 or, for measurements carried out below 183 K, $CFCl_3/CD_2Cl_2$ (ca. 2:3 v/v) as solvent. [b] Hydride resonances reported as follows: chemical shift (ppm), intensity, multiplicity (t = triplet, br = broad singlet) (coupling constant $^2J_{PH}$(Hz)). [c] T_1(min) values observed are given in bold type. For a complex that does not undergo decoalescence, only the T_1(min) value is listed. [d] The isotope shift (ppm/D) is defined as IS = $\delta_{ReH_{6-x}D_{x+1}} - \delta_{ReH_{7-x}D_x}$, an upfield isotope shift given a negative sign. [e] In the range 273–298 K. [f] The intensity cannot be accurately measured because the two resonances at δ −6.54 and −7.19 overlap. [g] The T_1 value measured for the combination of the resonances at δ −6.52 and −7.12. [h] In the range 253–298 K. [i] From ref 5b.

$(P\text{-}i\text{-}Pr_2Ph)_2$[31] revealed large P–Re–P angles in the range of 141–148°, which suggests structure D in which the two phosphines occupy the opposing axial and equatorial sites in order to minimize the steric repulsions.



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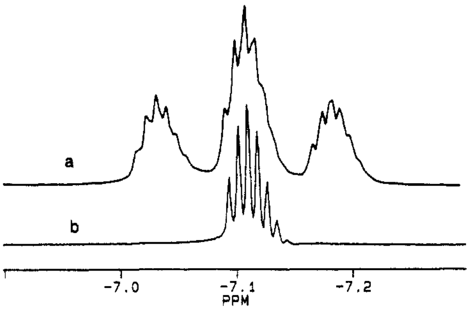

Figure 7. The hydride region of ^{1}H NMR spectra of an isotopomeric mixture of $ReH_{7-x}D_x(PCy_3)_2$ (x = 0–7) in CD_2Cl_2 at 298 K: (a) at 250 MHz without ^{31}P decoupling; (b) at 500 MHz with ^{31}P decoupling.

^{1}H NMR Deuterium Isotope Effects in Rhenium Phosphine Heptahydrides. As a test of the classical formulation of ReH_7L_2, we studied the deuterium isotope effects on the ^{1}H NMR hydride resonances of **1**–**10**. Geminal substitution of H by D in second-row main group elements can cause upfield isotope shifts of −0.01 to −0.03 ppm/D in ^{1}H NMR,[32,33] but no data on deuterium isotope shifts of hydride resonances in polyhydrides had been available[34] until our recent work on N-donor polyhydrides.[11]

The isotopomeric mixtures of **1**–**10**, i.e., $ReH_{7-x}D_xL_2$ (x = 0–7), were prepared by treatment of $ReOCl_3L_2$ with $LiAlD_4$ followed by hydrolysis with H_2O/D_2O. ^{13}C NMR showed that no deuterium was incorporated into the phosphine ligand. Figure 7 shows the ^{1}H NMR spectra of an isotopomeric mixture of $ReH_7(PCy_3)_2$ both with and without ^{31}P decoupling. The isotope shifts (ppm per deuterium substitution) of the hydride resonances, defined as IS = $\delta_{ReH_{6-x}D_{x+1}} - \delta_{ReH_{7-x}D_x}$, are listed in Table II. All the heptahydride complexes studied show small and temperature-independent isotope shifts ranging from −0.002 to −0.009 ppm/D. The isotope shifts upon successive deuterium substitution are the same within experimental error, and so seven evenly spaced singlets assignable to $ReH_{7-x}D_xL_2$ (x = 0–6) are observed with ^{31}P decoupling (Figure 7). No HD coupling can be observed at all temperatures.

1, **2**, and **3** show several distinct hydride resonances in the low-temperature spectra (Figures 1, 3, and 5). If one of the resonances arose from the η^2-H_2 ligand, large and temperature-dependent IPR (isotopic perturbation of resonance)[35,36] shifts due

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(34) (a) In a six-coordinate complexes containing two or three hydride ligands, the isotope shift for D cis to H is usually less than −0.02 ppm (upfield), whereas the value for D trans to H can be as large as 0.05–0.1 ppm (downfield)[34b,c] due to the relatively large differential isotopic trans effects of H vs D.[34d] (b) Harrod, J. F.; Hamer, G.; Yorke, W. *J. Am. Chem. Soc.* **1979**, *101*, 3989. (c) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527. (d) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698.

Table III. T_1(min) Values (250 MHz) Calculated for Polyhydrides with Standard Polyhedra or, for **9**, the Neutron-Diffraction Coordinates

compd	model	T_1(min), ms
ReH_9^{2-}	TTP	68
ReH_8L^-	TTP[a]	85
ReH_7L_2	TTP (A)	94
ReH_7L_2	TTP (B)	107
ReH_7L_2	TTP (D)	101
$TpReH_6$	TTP[b]	103
ReH_7(dppe)	neutron-diffraction data[c]	77
$Re(\eta^2\text{-}H_2)H_5L_2$	r(H–H) = 0.8 Å	20[d]
$Re(\eta^2\text{-}H_2)H_5L_2$	r(H–H) = 1 Å	55[d]

[a] L occupies one equatorial site. [b] The three N-donor atoms of the tris(pyrazolyl)borate (Tp) ligand occupy two eclipsed axial sites and one adjacent equatorial site. [c] From ref 14. [d] The C factor (see text) is taken as 0.79.

to the isotopic fractionation between the classical Re–H sites and the nonclassical $Re(\eta^2\text{-}H_2)$ sites would be observed in the fast-exchange limit for the isotopomeric mixtures of **1**–**3**. The isotopic fractionation has been observed in an unambiguously nonclassical rhenium polyhydride $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$, with a substantial preference for deuterium to occupy the nonclassical site.[6b] The small temperature-independent isotope shifts for **1**–**10** are therefore very unlikely to be due to the isotopic fractionation in nonclassical structures, but instead can be ascribed to geminal deuterium isotope effects.[32–34]

In addition, we observed geminal deuterium isotope effects on ^{31}P shielding for $ReH_{7-x}D_xL_2$. For example, the $^{31}P\{^1H\}$ NMR of an isotopomeric mixture of **10** shows a downfield deuterium isotope shift of ca. 0.03 ppm/D. Similar isotope shifts have previously been observed by us and other workers.[37]

A large and temperature-dependent variation of $^1J_{CH}$ upon deuteration has been reported in agostic M···H–C systems.[36] Similar behavior would be expected for $^2J_{HP}$ in nonclassical phosphine polyhydrides, each isotopomer showing a different $^2J_{HP}$. The $^2J_{HP}$ values observed for different isotopomers of **1**–**10** are the same within experimental error (Figure 7), which disfavors nonclassical structures. Since $^2J_{HD}$ coupling is unchanged on deuteration of XH_n (X = C, N) groups,[33] it is no surprise that the isotopomers of a ReH_7L_2 complex give the same $^2J_{HP}$ if the complex has a classical structure.

Theoretical Calculation of T_1(min) Values in Rhenium Polyhydrides. The T_1(min) values of **1**–**10** are among the shortest ever reported for classical polyhydride. To try to find the origin of the fast T_1 relaxation, we have carried out some theoretical calculations. For a given polyhydride, we first choose reasonable structural models from which the H···H distances can be derived. The rate of dipole–dipole relaxation R(DD) (s^{-1}) at 250 MHz is calculated from eq 3,[2,3,38] where r is the internuclear distance

$$R(\mathrm{DD}) = T_1(\mathrm{DD})^{-1} = 157.2r^{-6} \qquad (3)$$

(Å) between the hydride being relaxed and a neighboring hydride responsible for the relaxation. On the basis of arguments developed by Woessner[39] and Noggle and Schirmer[40] for fast methyl group rotation, Morris et al.[41] have shown that rotation of the $\eta^2\text{-}H_2$ ligand around the $M\text{–}H_2$ axis reduces the relaxation rate, which requires us to multiply the right-hand side of eq 3 by C^6, where C is 0.79 for a fast-rotating $\eta^2\text{-}H_2$ ligand and is 1.0 for a slow-rotating $\eta^2\text{-}H_2$ ligand. The overall relaxation rates for each hydride are obtained by summing the pairwise contributions from every other hydride and then averaged to give the observed relaxation rate, $T_1(\min)^{-1}$, for a fluxional polyhydride as a whole. The results of the calculations are listed in Table III.

For 9-coordinate classical polyhydrides of the type ReH_xL_{9-x}, we generally choose standard TTP structures, with $Re\text{–}H_{ax}$ vectors inclined at 45° to the 3-fold axis of the trigonal prism and with Re–H bond distances of 1.65 Å. ReH_9^{2-} has the lowest calculated T_1(min) value (68 ms) because it has the highest number of hydride ligands and therefore the highest number of H···H interactions. A minimum cannot be observed experimentally due to the very low moment of inertia. The calculated values for ReH_7L_2 depend only slightly on which of the three different ideal TTP structures A (94 ms), B (107 ms), and D (101 ms) is adopted. The calculated T_1(min) values are significantly longer than the observed values (54–68 ms) for **1**–**10** because the phosphine ligands tend to distort the coordination polyhedra from the ideal ones in such a way as to make the H···H nonbonding contacts, and therefore the T_1, shorter.

The T_1(min) value of 77 ms of **8** calculated from the neutron-diffraction coordinates[14] is 10 ms longer than the observed value of 67 ms, perhaps because the calculation ignores several sources of additional relaxation. Probably the most important are thermal excursions of the hydride ligands from their equilibrium positions, which leads to instantaneous shorter H···H distances than given by the neutron-diffraction structure. Because of the r^{-6} dependence of dipole–dipole relaxation, these shorter H···H distances will contribute a disproportionately large amount to the overall relaxation. In addition, relaxation due to the solvent, ligand protons, and phosphorus nuclei is also ignored in the calculation.

The calculation for the hypothetical $Re(\eta^2\text{-}H_2)H_5L_2$ is complicated by the fact that there are several possible 8-coordinate polyhedra, and several possible arrangements of the ligands for each. Representative structures tend to show relaxation rates close to 10 s^{-1} (i.e., $T_{1,c}$ = 100 ms) for the classical M–H sites. If the H–H distance in the H_2 ligand is 0.80 Å and C is 0.79, the T_{1nc} will be 6.9 ms. The $T_{1,obs}$ calculated from eq 1 will be 20 ms. Such a short value would be easily distinguishable from the longer values expected for the classical structures. On the other hand, for an H–H distance as long as 1.0 Å, the $T_{1,nc}$ will be 26.2 ms and the calculated $T_{1,obs}$ of 55 ms will approach the range expected for the classical structures.

Precautions in the Interpretation of T_1 Data. The calculations show that classical polyhydrides can give low T_1(min) values (<100 ms at 250 MHz) because all the ligands are brought closer together as the coordination number increases, and the sum of the contributions from several close nonbonding H···H contacts results in the low T_1(min) values.

In the case of fluxional nonclassical polyhydrides, the validity of the T_1 method is also contingent on the H–H distance of the $\eta^2\text{-}H_2$ ligand being short. If the H–H distance is longer than 1.0 Å and the number of classical hydride ligands is large, the relaxation of the $\eta^2\text{-}H_2$ ligand may only make a modest contribution to the overall relaxation. In addition, the rotation of the $\eta^2\text{-}H_2$ ligand reduces the relaxation rate. A combination of these effects may make the $T_{1,obs}$ value of a genuinely nonclassical polyhydride so high as to be indistinguishable from the value expected for a classical structure. Under these circumstances, the T_1 method cannot detect the presence of the $\eta^2\text{-}H_2$ ligand in nonclassical polyhydrides.

It is clearly not valid simply to measure T_1(min) values and apply an arbitrary cutoff of 100 ms as the boundary between the classical and nonclassical structures in polyhydrides of high co-

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ordination number. In formulating a given polyhydride, it is better to calculate the T_1(min) values expected on the basis of plausible classical and nonclassical models and to compare these with the experimental value; only if a significant difference exists will the T_1 method be able to make a distinction between the classical and nonclassical structures.

Do Non Dipole–Dipole Relaxation Mechanisms Contribute? A commonly encountered objection to our work is that the T_1 of rhenium polyhydrides can be affected by the quadrupolar Re. While quadrupolar effects on T_2 are common, T_1 is only affected if ω_X, the Larmor frequency of the quadrupolar nucleus X, happens to be close to ω_A, the Larmor frequency of the observed nucleus A. This follows from the $(\omega_X - \omega_A)^2$ term in the theoretical expression[38c] for the T_1 contribution from the scalar relaxation mechanism shown in eq 4 where J_{AX} is the A–X coupling, I is the nuclear spin, and τ_{sc} is the correlation time for scalar relaxation.

$$\{T_1(\mathrm{SC})\}^{-1} = (8/3)\pi^2(J_{AX})^2 I_X(I_X + 1)\tau_{sc}\{1 + (\omega_X - \omega_A)^2\tau_{sc}^2\}^{-1} \quad (4)$$

For the situation considered here (scalar relaxation of the second kind), τ_{sc} is $\{T_1\}^{-1}$ for the quadrupolar nucleus. The frequencies in question are the following: ^{1}H, $I = {}^{1}/_{2}$, 99.98%, 100 MHz; ^{185}Re, $I = {}^{5}/_{2}$, 37%, 22.72 MHz; ^{187}Re, $I = {}^{5}/_{2}$, 63%, 22.94 MHz. Significant scalar contributions to T_1 have only been seen when the two Larmor frequencies are very close, e.g., ^{13}C, $I = {}^{1}/_{2}$, 1.1%, 25.145 MHz and ^{79}Br, $I = {}^{3}/_{2}$, 50.5%, 25.130 MHz.[38c] This mechanism is therefore insignificant in our case.

Of the remaining mechanisms, only spin rotation (SR) can be plausibly considered as a significant contributor. Since SR relaxation shows a monotonic dependence on temperature, its presence would skew the usual V-shaped ln T_1 vs $1/T$ curve arising from DD relaxation. It cannot be a large contributor in the cases we have studied.

Conclusion

We have synthesized and characterized a series of new rhenium phosphine heptahydrides of the type ReH_7L_2. Using conformationally restrictive diphosphines allows us to freeze out the fluxionality on cooling. Rather than the previously[3b] proposed nonclassical formulation, the variable-temperature ^{1}H NMR studies, T_1 measurements, and deuterium isotope effect data are more consistent with classical nine-coordinate TTP structures for all the ReH_7L_2 complexes. The classical structure is definitively established only for **1–3**, where decoalescence is observed. If an H_2 ligand is present in any of **4–10**, the H···H distance would have to be long (>1 Å). As shown by the calculations, the interpretation of T_1 data of fluxional polyhydride complexes is complicated by several factors. T_1(min) values in the range 55–100 ms at 250 MHz cannot always be taken as an indication of the presence of an η^2-H_2 ligand. Several close nonbonding H···H contacts resulting from the high coordination number can also give low T_1(min) values. On the other hand, the calculations show that a genuinely nonclassical polyhydride may give a T_1(min) value that is indistinguishable from the value expected for a classical structure if the η^2-H_2 ligand undergoes fast rotation and has a long H–H distance. Our results suggest that the structural assignments of fluxional polyhydrides that are based solely on T_1 values may need to be validated by other methods. In cases where the fluxionality of a polyhydride can be frozen out to give several well-separated hydride resonances, deuterium isotope effects on the hydride chemical shift and the $^{2}J_{PH}$ coupling constant may help distinguish between classical and nonclassical structures.

Experimental Section

General. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk techniques. Reagents were purchased from Aldrich Chemical Co. THF, Et_2O, and hexane were distilled from Na/Ph_2CO. CH_2Cl_2 was distilled from CaH_2. $ReOCl_3(AsPh_3)_2$ was prepared according to the literature method.[20] ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker WM 250 and WM 500 spectrometers with CD_2Cl_2 as the solvent unless otherwise stated; ^{1}H and ^{13}C chemical shifts are measured with reference to the residual solvent resonance; ^{31}P chemical shifts are given in ppm downfield from external 85% H_3PO_4. IR spectra were recorded on a Nicolet 5-SX FT-IR instrument. Microanalyses were carried out by the Desert Analytic Co.

Oxotrichloro(1,1′-bis(diphenylphosphino)ferrocene)rhenium(V). A mixture of $AsOCl_3(ASPh_3)_2$ (1.00 g, 1.09 mmol) and dppf (0.60 g, 1.09 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 10 h. The volume of the solution was reduced to 10 mL in vacuo, and Et_2O (40 mL) was added. The greenish solid was filtered, washed with Et_2O (4 × 10 mL), and dried in vacuo. Yield: 0.91 g (97%). Anal. Calcd for $C_{34}H_{28}Cl_3FeOP_2Re$: C, 47.32; H, 3.27. Found: C, 47.09; H, 3.14. IR (Nujol): $\nu_{Re=O}$ 964 cm^{-1}. ^{1}H NMR (298 K): δ 7.4–7.9 (c, 20 H, Ph), 5.31 (br s, 2 H, Cp), 4.78 (br t, 3.1 Hz, 2 H, Cp), 4.50 (br t, 3.0 Hz, 2 H, Cp), 4.39 (br s, 2 H, Cp). ^{31}P{^{1}H} NMR (298 K): δ −26.2.

Other *cis*-$ReOCl_3L_2$ complexes (L_2 = (+)-diop, dppb, dppe′, dppp, dppp′, dpbz) were similarly prepared in 90–95% yields. Their analytical and spectroscopic data are reported in the supplementary material.

Heptahydrido(1,1′-bis(diphenylphosphino)ferrocene)rhenium(VII) (1). $LiAlH_4$ (0.28 g, 7.4 mmol) was added to a suspension of $ReOCl_3$(dppf) (0.80 g, 0.93 mmol) in Et_2O (60 mL). The mixture was stirred at room temperature for 2.5 h. The resulting yellowish suspension was filtered through Celite and the filtrate evaporated to dryness in vacuo. The residue was dissolved in THF (25 mL), cooled to 0 °C, and hydrolyzed by dropwise addition of H_2O (0.6 mL) in 10 mL of THF. The mixture was dried with 5 g of anhydrous Na_2SO_4 and filtered through Celite. The yellow filtrate was concentrated to 5 mL in vacuo. Addition of hexane (40 mL) resulted in the precipitation of a pale-yellow solid that was filtered, washed with hexane (4 × 10 mL), and dried in vacuo. Yield: 0.42 g, 62%. Anal. Calcd for $C_{34}H_{35}FeP_2Re$: C, 59.03; H, 5.10. Found: C, 58.62; H, 5.04. IR (Nujol): ν_{Re-H} 2008, 1951, 1925 cm^{-1}. ^{1}H NMR (298 K): δ 7.3–7.7 (c, 20 H, Ph), 4.32 (pseudotriplet, 1.7 Hz, 4 H, Cp), 4.22 (pseudoquartet, 1.7 Hz, 4 H, Cp), −5.75 (t, $^{2}J_{PH}$ = 16.9 Hz, 7 H, Re–H). ^{1}H NMR (183 K): δ 7.1–8.9 (c, 20 H, Ph), 4.66 (br s, 2 H, Cp), 4.24 (br s, 4 H, Cp), 3.54 (br s, 2 H, Cp), −3.89 (t, $^{2}J_{PH}$ = 32 Hz, 2 H, Re–H), −6.70 (br s, 5 H, Re–H). ^{1}H NMR ($CD_2Cl_2/CFCl_3$ 3:2 (v/v), 153 K): δ 6.9–9.0 (c, 20 H, Ph), 4.65 (br s, 2 H, Cp), 4.29 (br s, 2 H, Cp), 4.21 (br s, 2 H, Cp), 3.54 (br s, 2 H, Cp), −3.95 (br s, 2 H, Re–H), −6.57 (br s, 2 H, Re–H), −7.19 (br s, 3 H, Re–H). Selectively hydride-coupled ^{31}P NMR (298 K): δ 12.9 (octet, $^{2}J_{HP}$ = 16.4 Hz. ^{13}C{^{1}H} NMR (298 K): δ 140.3 (c, C_1 of Ph), 134.4 (t, $^{2}J_{PC}$ = 11.1 Hz, C_2 of Ph), 130.0 (s, C_4 of Ph), 127.9 (t, $^{3}J_{PC}$ = 11.1 Hz, C_3 of Ph), 78.6 (c, C_1 of Cp), 75.8 (t, $^{2}J_{PC}$ = 9.3 Hz, C_2 of Cp), 73.2 (t, $^{3}J_{PC}$ = 7.4 Hz, C_3 of Cp).

2–7 were similarly prepared in 40–60% yields. The analytical and spectroscopic data for **4–7** are included in the supplementary material. The isotopomeric mixtures of **1–10** were prepared by treatment of $ReOCl_3L_2$ with 8 equiv of $LiAlD_4$ followed by hydrolysis with H_2O/D_2O (1:1 molar ratio).

ReH_7(dppb) (2). Anal. Calcd for $C_{28}H_{35}P_2Re$: C, 54.27; H, 5.69. Found: C, 54.63; H, 5.82. IR (Nujol): ν_{Re-H} 1971, 1943, 1904 cm^{-1}. ^{1}H NMR (298 K): δ 7.4–7.7 (c, 20 H, Ph), 2.7 (c, 4 H, CH_2P), 1.6–1.8 (c, 4 H, CH_2CH_2P), −6.18 (t, $^{2}J_{PH}$ = 16.2 Hz, 7 H, Re–H). ^{1}H NMR ($CD_2Cl_2/CFCl_3$ 3:2 (v/v), 163 K): δ 7.4–7.7 (c, 20 H, Ph), 2.96 (br s, 2 H, CH_2P), 2.36 (br s, 2 H, CH_2P), 1.88 (c, 2 H, CH_2CH_2P), 1.46 (c, 2 H, CH_2CH_2P), −4.75 (br t, $^{2}J_{PH}$ = 32 Hz, 2 H, Re–H), −7.04 (br s, 5 H, Re–H). ^{31}P NMR (298 K): δ 11.4. ^{13}C{^{1}H} NMR (298 K): δ 141.0 (c, C_1 of Ph), 132.9 (t, $^{2}J_{PC}$ = 9.3 Hz, C_2 of Ph), 129.8 (s, C_4 of Ph), 128.3 (t, $^{3}J_{PC}$ = 9.3 Hz, C_3 of Ph), 31.1 (t, $^{1}J_{PC}$ = 31.4 Hz, CH_2P), 22.4 (t, $^{2}J_{PC}$ = 7.4 Hz, CH_2CH_2P).

ReH_7{(+)-diop} (3). Anal. Calcd for $C_{31}H_{39}O_2P_2Re$: C, 53.82; H, 5.68. Found: C, 53.66; H, 5.75. IR (Nujol): ν_{Re-H} 1984, 1953, 1928 cm^{-1}. ^{1}H NMR (298 K): δ 7.3–7.9 (c, 20 H, Ph), 3.84 (c, 2 H, OCH), 3.68 (c, 2 H, CH_2P), 2.61 (c, 2 H, CH_2P), 1.27 (s, 6 H, Me), −6.11 (t, $^{2}J_{PH}$ = 16.2 Hz, 7 H, Re–H). ^{1}H NMR ($CD_2Cl_2/CFCl_3$ 3:2 (v/v), 153 K): δ 7.3–7.8 (c, 20 H, Ph), 3.70 (c, 2 H, OCH), 3.58 (c, 2 H, CH_2P), 2.60 (c, 2 H, CH_2P), 1.22 (s, 6 H, Me), −4.60 (br s, 2 H, Re–H), −6.97 (br s, 5 H, Re–H). ^{31}P NMR (298 K): δ 0.9. ^{13}C{^{1}H} NMR (298 K): δ 144.8 (c, C_1 of Ph), 135.1 (c, C_1 of Ph′), 134.4 (t, $^{2}J_{PC}$ = 11.1 Hz, C_2 of Ph), 131.0 (t, $^{2}J_{PC}$ = 9.3 Hz, C_2 of Ph′), 129.8 (s, C_4 of Ph and Ph′), 128.7 (t, $^{3}J_{PC}$ = 9.3 Hz, C_3 of Ph), 128.4 (t, $^{3}J_{PC}$ = 9.3 Hz, C_3 of Ph′), 108.2 (s, Me_2C), 78.5 (t, $^{2}J_{PC}$ = 7.4 Hz, OCH), 39.7 (t, $^{1}J_{PC}$ = 31.2 Hz, CH_2P), 26.9 (s, Me).

$ReH_6(SiPh_3)$(dppf). NaH (60% dispersion in mineral oil, 52 mg, 1.3 mmol) was added to a THF (10 mL) solution of ReH_7(dppf) (100 mg, 0.13 mmol) and Ph_3SiH (260 mg, 1.0 mmol). The mixture was heated at reflux for 5 min and then allowed to cool to room temperature. Me_2SO_4 (120 μL, 1.3 mmol) was added. After being stirred for 10 min, the suspension was filtered through Celite. The yellow filtrate was concentrate to 0.5 mL in vacuo. Addition of Et_2O (5 mL) and hexane (30 mL) precipitated a yellow solid, which was filtered, washed with hexane (3 × 10 mL), and dried in vacuo. Yield: 102 mg, 76%. Anal. Calcd for $C_{52}H_{49}FeP_2ReSi$: C, 62.08; H, 4.91. Found: C, 61.65; H, 4.82. IR (Nujol): ν_{Re-H} 2041, 1953, 1905 cm^{-1}. ^{1}H NMR (298 K): δ 7.1–7.5 (c, 35 H, Ph), 4.32 (s, 4 H, Cp), 4.26 (s, 4 H, Cp), −5.11 (t, $^2J_{PH}$ = 16.2 Hz, 6 H, Re–H). ^{1}H NMR (213 K): δ 7.1–7.6 (c, 35 H, Ph), 4.27 (s, 4 H, Cp), 4.16 (br s, 4 H, Cp), −3.33 (t, $^2J_{PH}$ = 31.2 Hz, 2 H, Re–H), −6.25 (d, $^2J_{PH}$ = 15.4 Hz, 4 H, Re–H). ^{1}H NMR (CD_2Cl_2/$CFCl_3$ 3:2 (v/v), 173 K): δ 6.1–8.0 (c, 35 H, Ph), 4.72 (br s, 2 H, Cp), 4.29 (br s, 2 H, Cp), 4.20 (br s, 2 H, Cp), 3.58 (br s, 2 H, Cp), −3.38 (br t, $^2J_{PH}$ = 31 Hz, 2 H, Re–H), −6.20 (br s, 2 H, Re–H), −6.50 (br s, 2 H, Re–H). Selectively hydride-coupled ^{31}P NMR (298 K): δ 17.7 (heptet, $^2J_{HP}$ = 15.7 Hz). ^{13}C{^{1}H} NMR (298 K): δ 149.4 (s, C_1 of $SiPh_3$), 139.8 (c, C_1 of PPh_2), 136.4 (s, C_2 of $SiPh_3$), 134.1 (t, $^2J_{PC}$ = 11.1 Hz, C_2 of PPh_2), 130.0 (s, C_4 of PPh_2), 127.9 (t, $^3J_{PC}$ = 10.2 Hz, C_3 of PPh_2), 127.3 (s, C_4 of $SiPh_3$), 127.0 (s, C_3 of $SiPh_3$), 78.5 (c, C_1 of Cp), 75.7 (t, $^2J_{PC}$ = 9.3 Hz, C_2 of Cp), 73.2 (t, $^3J_{PC}$ = 5.6 Hz, C_3 of Cp).

$ReH_6(SiPh_3)$(dppb) and $ReH_6(SiPh_3)${(+)-diop} were similarly prepared. Their analytical and spectroscopic data are included in the supplementary material.

Acknowledgment. We thank the National Science Foundation for support, Dr. Peter Demou for assistance, and Dr. Judith A. K. Howard for neutron diffraction data of ReH_7(dppe).

Supplementary Material Available: Analytical and spectroscopic data for *cis*-$ReOCl_3L_2$ complexes, ReH_7L_2 complexes **4–7**, $ReH_6(SiPh_3)$(dppb), and $ReH_6(SiPh_3)${(+)-diop} (5 pages). Ordering information is given on any current masthead page.

Flexibility of the Zeolite RHO Framework. In Situ X-ray and Neutron Powder Structural Characterization of Divalent Cation-Exchanged Zeolite RHO

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Abstract: Zeolite RHO has an unusual three-dimensional monolayer surface with a topology that gives equal access to either side of the surface. In the absence of supporting structural subunits, e.g., smaller cages or channels, RHO exhibits atypical framework flexibility with large displacive rearrangements. These have been investigated by in situ X-ray powder diffraction studies of zeolite RHO exchanged with various divalent cations. The unit cell variation (e.g., Ca,H-RHO (400 °C), a = 13.970 (5) Å; Sr-RHO (250 °C), a = 14.045 (1) Å; Ba-RHO (200 °C), a = 14.184 (2) Å; Cd-RHO (350 °C), a = 14.488 (3) Å; Na,Cs-RHO (25 °C), a = 15.031 (1) Å) is a particularly sensitive function of cation and temperature. Rietveld analysis of neutron diffraction data was used to refine the structures of two samples, Ca,ND_4-RHO and Ca,D-RHO. Ca,D-RHO shows the largest reported deviation from $Im\bar{3}m$ symmetry (a = 13.9645 (7) Å) for a RHO structure. The calcium atom is located in the center of the double 8-ring, distorting the framework to generate a tetrahedral environment. The in situ X-ray studies of zeolite RHO with both monvalent and divalent cations together with the Rietveld results for the extreme end member of this structural field confirm the largest displacive distortion observed for a molecular sieve framework with a unit cell volume increase of 25% when the calcium ions of Ca,H-RHO are replaced with hydrogen ions to give H-RHO.

Zeolites are crystalline aluminosilicate materials with open framework structures of molecular dimensions. The term "open framework" indicates the presence of intracrystalline voids—that is, cages and channels or pore openings. It is the shape and size of these pore openings that give a zeolite its molecular sieving ability and hence shape and size selectivity when used as a catalyst, support, or absorbent. For many years, zeolite frameworks have been known to exhibit small distortions.[1] Recent studies have shown distortions resulting in a change of symmetry on sorption of different solvents[2a] or as a function of temperature.[2b] The observed distortions and their effects on the pore openings are insignificant when compared to the flexiblity and distortions observed in the framework of zeolite RHO.[3] The flexibility in zeolite RHO offers an oppotunity to introduce a high degree of catalytic selectivity by controlled cation siting at reaction temperatures. Our studies of the selective synthesis of dimethylamine from methanol and ammonia over zeolite RHO showed it to exhibit a unique selectivity and activity compared to other small-pore zeolites.[4] This observation led us to further investigate the flexibility of this zeolite framework.

The framework of RHO (Figure 1) is composed of a body-centered cubic arrangement of truncated cubo-octahedra or α-cages linked via double 8-rings. X-ray powder structural studies

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