Inorg. Chem. **1990**, *29*, 4437–4441

sequentially binuclear and even more complex molecular architecture by choosing a relatively unhindered, uninegative L, with donor atoms capable of displacing chloride ion.

Acknowledgment. The technical assistance of L. Lardear and V. Cannelongo is gratefully acknowledged.

Supplementary Material Available: Listings of crystallographic data (Table S17), thermal parameters (Tables S1, S5, S9, and S13), hydrogen atom positions (Tables S2, S6, S10, and S14), and complete bond distances and angles (Tables S4, S8, S12, and S16) (19 pages); listings of observed and calculated structure factors (Tables S3, S7, S11, and S15) (35 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Formation and Characterization of the Unsymmetrical Dirhenium Polyhydrides $Re_2H_6(PMe_3)_5$ and $Re_2H_6(SbPh_3)_5$ and Observations Concerning the Mechanism of the Conversion of $Re_2H_8(PMe_3)_4$ to $[Re_2H_5(PMe_3)_6]^+$

Michael T. Costello, Phillip E. Fanwick, Karen E. Meyer, and Richard A. Walton*

Received March 8, 1990

The reaction of $Re_2H_8(PMe_3)_4$ with PMe_3 in methanol proceeds to give $[Re_2H_5(PMe_3)_6]^+$ via the intermediacy of $Re_2H_6(PMe_3)_5$ and $[Re_2H_7(PMe_3)_5]^+$, both of which have been isolated and characterized on the basis of their ^1H and ^{31}P NMR spectra and their electrochemical properties. Measurements of the ^1H NMR spectrum of $Re_2H_6(PMe_3)_5$ in C_7D_8 over the temperature range +50 to −100 °C show that this complex possesses the unsymmetrical structure $(Me_3P)_3HRe(\mu\text{-}H)_3ReH_2(PMe_3)_2$, at least at low temperatures. A similar type of structure has been found in the solid state for $Re_2H_6(SbPh_3)_5$, a complex that is formed by the reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with an excess of $SbPh_3$ and $NaBH_4$ in ethanol. A single-crystal X-ray structure determination on $Re_2H_6(SbPh_3)_5$ has been carried out with the data collected at −100 °C. Crystal data are as follows: monoclinic space group $P2_1/n$, $a = 13.287$ (5) Å, $b = 40.137$ (8) Å, $c = 14.392$ (5) Å, $\beta = 92.55$ (2)°, $V = 7667$ (7) Å^3, and $Z = 4$. The structure was refined to $R = 0.030$ ($R_w = 0.037$) for 7182 data with $I > 3.0\sigma(I)$. The Re–Re distance is 2.5340 (6) Å, and all six hydride ligands (three terminal, three bridging) have been located and refined.

Introduction

Dirhenium polyhydride complexes of stoichiometry $Re_2H_8(PR_3)_4$ (PR_3 represents a monodentate phosphine or half a bidentate phosphine ligand), whose syntheses,(1–10) structures,(8,9,11–13) redox behavior,(14) and chemical reactivities(14–20) have been of considerable recent interest, are potential starting materials for other neutral dirhenium polyhydrides of the types $Re_2H_6(PR_3)_5$ and $Re_2H_4(PR_3)_6$ through sequential reductive elimination of dihydrogen and the coordination of additional PR_3 ligands as shown in eq 1.

$$Re_2H_8(PR_3)_4 \xrightarrow[-H_2]{+PR_3} Re_2H_6(PR_3)_5 \xrightarrow[-H_2]{+PR_3} Re_2H_4(PR_3)_6 \qquad (1)$$

Surprisingly, very few examples of these conversions have been reported, although the first step has been shown to occur when $PR_3 = PMe_2Ph$,(2) and the structure of the resulting complex has been determined.(2a) The second step has been encountered in the case of the reaction between $Re_2H_8(PMe_2Ph)_4$ and the phosphine ligand $P(OCH_2)_3CEt$, which gives $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$,(21) while $Re_2H_8(dppe)_2$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with dppe in THF to give $Re_2H_4(dppe)_3$.(22) The latter two products are readily protonated by HBF_4 to give $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$(21) and $[Re_2H_5(dppe)_3]BF_4$,(22) respectively. The cationic species contain a $[HRe(\mu\text{-}H)_3ReH]$ disposition of hydride ligands and resemble structurally the complex $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$.(14,17)

Recently, in the course of studying the reaction of $Re_2H_8(PMe_3)_4$ with PMe_3 in methanol, we were able to isolate the complex $[Re_2H_5(PMe_3)_6]PF_6$,(16) which we found has a structure closely akin to those of the aforementioned(14,17,21,22) dirhenium pentahydride cations, viz., $[(Me_3P)_3HRe(\mu\text{-}H)_3ReH(PMe_3)_3]^+$. In seeking to understand the mechanism of this reaction, in particular the role that methanol might play,(23) we have carried

---

(1) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.
(2) (a) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695. (b) Roberts, D. A.; Geoffroy, G. L. *J. Organomet. Chem.* **1981**, *214*, 221.
(3) Green, M. A. Ph.D. Thesis, Indiana University, 1982.
(4) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.
(5) Cameron, C. J.; Moehring, G. A.; Walton, R. A. *Inorg. Synth.* **1990**, *27*, 14.
(6) Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C13.
(7) Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 587.
(8) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395.
(9) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 3203.
(10) Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578.
(11) Bau, R.; Carroll, W. E.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872.
(12) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 4522.
(13) Cotton, F. A.; Luck, R. L.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 43.
(14) (a) Allison, J. D.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1983**, 401. (b) Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163.
(15) Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861.
(16) Root, D. R.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2503.
(17) Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159.
(18) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 5137.
(19) Mueting, A. M.; Bos, W.; Alexander, B. D.; Boyle, P. D.; Casalnuovo, J. A.; Balaban, S.; Ito, L. N.; Johnson, S. M.; Pignolet, L. H. *New J. Chem.* **1988**, *12*, 505.
(20) Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642.
(21) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1982**, *104*, 2319.
(22) Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 2239.

0020-1669/90/1329-4437$02.50/0

out additional studies that have led to the isolation of $Re_2H_6(PMe_3)_5$ and a study of its properties. We have also isolated the analogous triphenylstibine derivative $Re_2H_6(SbPh_3)_5$ and determined its X-ray crystal structure. These studies are described in the present report.

Experimental Section

Starting Materials. The complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$,[24] $Re_2H_8(PMe_3)_4$,[9] and $ReOCl_3(SbPh_3)_2$[10] were prepared according to reported methods. Trimethylphosphine was obtained from Strem Chemicals, while triphenylstibine was purchased from Pressure Chemical Co. Both were used without further purification. The remaining reagents and solvents were obtained from commercial sources and used without further purification. Solvents were deoxygenated prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen gas with standard Schlenk techniques.

A. Reaction of $Re_2H_8(PMe_3)_4$ with PMe_3. (i) $Re_2H_6(PMe_3)_5$. A quantity of $Re_2H_8(PMe_3)_4$ (0.053 g, 0.077 mmol) was placed in a round-bottom flask equipped with a stir bar and a septum. The octahydride was dissolved in 5.0 mL of benzene, and 0.015 mL (0.15 mmol) of PMe_3 was added to the solution. The orange solution darkened within a few minutes of stirring. After 5 h, the solvent was removed by evaporation under a N_2 atmosphere, and the red-brown residue was collected and placed under vacuum to dry; yield 0.050 g (77%). Anal. Calcd for $C_{17}H_{52}P_5Re_2$ (i.e. $Re_2H_6(PMe_3)_5\cdot{}^1/_3C_6H_6$): C, 26.01; H, 6.82. Found: C, 26.11; H, 7.12. The amount of lattice benzene present was confirmed by ^1H NMR spectroscopy (recorded in C_7D_8); the benzene signal at δ +7.3 showed the correct integration relative to the methyl doublets centered at δ +1.9 and δ +1.7.

(ii) $[Re_2H_7(PMe_3)_5]BF_4$. A solution that contained 0.04 g (0.05 mmol) of $Re_2H_6(PMe_3)_5$ dissolved in 5.0 mL of benzene was treated with 0.015 mL of 85% $HBF_4\cdot Et_2O$. A green product formed upon stirring, and after 5 min, the solvent was removed by evaporation and the residue was collected. Recrystallization of the oily material from CH_2Cl_2/diethyl ether gave a dark green solid; yield 0.03 g (70%). Anal. Calcd for $C_{15}H_{52}BF_4P_5Re_2$: C, 21.28; H, 6.19. Found: C, 20.52; H, 5.49. The presence of a small amount of lattice CH_2Cl_2 in the crystals were confirmed by ^1H NMR spectroscopy on a solution of this complex in $(CD_3)_2CO$. This may account for the slightly low C and H microanalyses that were consistently obtained.

B. Syntheses of $Re_2H_6(SbPh_3)_5$. A mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.30 g, 0.27 mmol), $SbPh_3$ (1.0 g, 2.8 mmol), and $NaBH_4$ (0.30 g, 7.9 mmol) was refluxed in 30 mL of ethanol for 5 days. The dark purple precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (3 × 15 mL), and dried under vacuum; yield 0.50 g (86%). Several attempts were made to obtain satisfactory microanalyses for this complex, but in each instance the carbon and hydrogen microanalyses were low, perhaps due to incomplete combustion during the analysis procedure. However, since the ^1H NMR spectrum and cyclic voltammetric properties of this complex gave no hint of contamination by significant amounts of impurities and since we confirmed the identity of this product by X-ray crystallography, we are confident that this procedure gave a pure product.

C. Synthesis of $ReH_5(SbPh_3)_3$. A mixture of $ReOCl_3(SbPh_3)_2$ (0.17 g, 0.17 mmol) and $SbPh_3$ (0.61 g, 1.7 mmol) was stirred with 15 mL of ethanol in an ice/acetone bath (−10 °C). After 30 min, an excess of $NaBH_4$ (0.22 g, 5.8 mmol) was added and the resulting suspension stirred for 24 h. The light yellow precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (2 × 15 mL), and dried under vacuum; yield 0.13 g (60%). Anal. Calcd for $C_{54}H_{54}O_2ReSb_3$ (i.e. $ReH_5(SbPh_3)_3\cdot 2H_2O$): C, 50.42; H, 4.23. Found: C, 50.45; H, 4.24. ^1H NMR spectroscopy (in CD_2Cl_2) confirmed the presence of water (δ +1.55). This was substantiated by the IR spectrum of this product (Nujol mull), which showed ν(OH) at ca. 3350 (m, br) cm^{-1} and δ(OH) at ca. 1650 (w) cm^{-1}. The presence of lattice water is not unreasonable given the propensity of certain rhenium polyhydrides to form hydrates.[9,10]

Preparation of Single Crystals for Structure Determination. Suitable crystals of $Re_2H_6(SbPh_3)_5$ were obtained by diffusion of pentane into a dichloromethane solution of this complex over a period of several days.

X-ray Crystallography. The structure of $Re_2H_6(SbPh_3)_5$ was determined by the application of standard procedures. The crystal data are listed in Table I. The cell constants were determined by means of a least-squares analysis on 25 reflections with $18.0 < \theta < 21.0°$. Three standard reflections were measured after every 5000 s of beam time during data collection; there was no systematic variation in intensity. Calculations were performed on a MicroVAX II computer using the Enraf-Nonius structure determination package.

Table I. Crystallographic Data for $Re_2H_6(SbPh_3)_5$

chem formula	$Re_2Sb_5C_{90}H_{81}$	Z	4
fw	2143.80	T, °C	−100
space group	$P2_1/n$ (No. 14)	radiation (λ, Å)	Mo Kα (0.71073)
a, Å	13.287 (5)	ρ_{calcd}, g cm^{-3}	1.858
b, Å	40.137 (8)	μ(Mo Kα), $cm^{-1}1$	49.79
c, Å	14.392 (5)	transm coeff	1.000–0.815
β, deg	92.55 (2)	R^a	0.025
V, Å^3	7667 (7)	$R_w{}^b$	0.029

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

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for Non-Phenyl Ring Atoms of $Re_2H_6(SbPh_3)_5$ and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re(1)	0.19955 (2)	0.11542 (1)	0.34777 (2)	1.299 (6)
Re(2)	0.17159 (2)	0.13261 (1)	0.17917 (2)	1.179 (6)
Sb(11)	0.12185 (4)	0.14081 (1)	0.49182 (4)	1.57 (1)
Sb(12)	0.31384 (4)	0.06942 (1)	0.41573 (4)	1.58 (1)
Sb(21)	0.03131 (4)	0.17363 (1)	0.12263 (4)	1.53 (1)
Sb(22)	0.32709 (4)	0.16794 (1)	0.13795 (4)	1.52 (1)
Sb(23)	0.09914 (4)	0.07730 (1)	0.12243 (4)	1.45 (1)
H(11)	0.299 (5)	0.134 (2)	0.416 (4)	2 (1)*
H(12)	0.128 (6)	0.084 (2)	0.382 (5)	0 (2)*
H(21)	0.689 (8)	0.370 (2)	0.579 (7)	3 (3)*
H(B1)	0.192 (5)	0.157 (2)	0.290 (5)	1 (2)*
H(B2)	0.271 (5)	0.104 (2)	0.243 (5)	1 (2)*
H(B3)	0.086 (5)	0.123 (2)	0.267 (5)	1 (2)*

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl ring carbon atoms are included in the supplementary material. Values marked with an asterisk denote atoms that were refined isotropically.

The X-ray data were collected at low temperature. A suitable single crystal was mounted on a glass fiber with vacuum grease and cooled to −100 °C in a cold stream of gaseous N_2 by using an Enraf-Nonius Type 524 temperature controller. The crystal was found to belong to the monoclinic space group $P2_1/n$ (standard space group $P2_1/c$, No. 14). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Three bridging hydride ligands and three terminally bound hydrides were tentatively located following anisotropic refinement of all non-hydrogen atoms. Their refinement as H^- gave reasonable Re–H bond distances. Hydrogen atoms of the phenyl groups were calculated by assuming idealized geometries and C–H bond distances of 0.95 Å. We also assumed that the value of B(H), i.e., the isotropic thermal parameters for the hydrogen atoms, was equal to $1.3[B_{eqv}(C)]$ at the time of the inclusion of this parameter in the refinement procedure. While these hydrogen atoms were used in the calculation of F_c, their positions were not refined. An empirical absorption correction was used,[25] the linear absorption coefficient being 49.79 cm^{-1}. No corrections for extinction were applied. The structure was refined by full-matrix least-squares methods where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The non-hydrogen atoms of the dirhenium complex were refined anisotropically; corrections for anomalous scattering were applied to all atoms so refined.[26] The largest peak in the final difference Fourier map (0.56 e/Å^3) was not at bonding distance to any of the atoms of the dirhenium molecule.

Positional parameters and their errors for the non-phenyl group atoms of $Re_2H_6(SbPh_3)_5$ are listed in Table II. Important intramolecular bond distances and angles are given in Table III. Tables giving full details

---

(23) These mechanistic questions were first raised in a very fruitful discussion with Professor K. G. Caulton of Indiana University. We are most grateful to Professor Caulton for the insights he provided.

(24) Barder, T. J.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2510.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(26) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*; Table 2.2B.

(27) As with many rhenium polyhydrides, this chemical shift is markedly solvent dependent, cf. δ −6.68 in C_6D_6 and δ −7.40 in CD_2Cl_2 (see ref 9).

Table III. Important Bond Distances (Å) and Bond Angles (deg) for $Re_2H_6(SbPh_3)_5$

	Distances		
Re(1)–Re(2)	2.5340 (5)	Re(2)–Sb(21)	2.5908 (7)
Re(1)–Sb(11)	2.5678 (7)	Re(2)–Sb(22)	2.5962 (7)
Re(1)–Sb(12)	2.5570 (7)	Re(2)–Sb(23)	2.5876 (7)
Re(1)–H(11)	1.77 (8)	Re(2)–H(21)	1.5 (1)
Re(1)–H(12)	1.67 (9)	Re(2)–H(B1)	1.87 (8)
Re(1)–H(B1)	1.86 (8)	Re(2)–H(B2)	1.94 (9)
Re(1)–H(B2)	1.87 (9)	Re(2)–H(B3)	1.78 (9)
Re(1)–H(B3)	1.88 (9)		
	Angles		
Re(2)–Re(1)–Sb(11)	128.16 (2)	Re(1)–Re(2)–Sb(22)	106.45 (2)
Re(2)–Re(1)–Sb(12)	128.47 (2)	Re(1)–Re(2)–Sb(23)	99.10 (2)
Re(2)–Re(1)–H(11)	119 (2)	Re(1)–Re(2)–H(21)	153 (5)
Re(2)–Re(1)–H(12)	115 (3)	Sb(21)–Re(2)–Sb(22)	98.62 (2)
Sb(11)–Re(1)–Sb(12)	103.36 (2)	Sb(21)–Re(2)–Sb(23)	100.26 (2)
Sb(11)–Re(1)–H(11)	73 (2)	Sb(22)–Re(2)–Sb(23)	132.10 (2)
Sb(11)–Re(1)–H(12)	79 (3)	Sb(21)–Re(2)–H(21)	84 (5)
Sb(12)–Re(1)–H(11)	71 (2)	Sb(22)–Re(2)–H(21)	70 (5)
Sb(12)–Re(1)–H(12)	71 (3)	Sb(23)–Re(2)–H(21)	69 (5)
H(11)–Re(1)–H(12)	125 (4)	Re(1)–H(B1)–Re(2)	85 (3)
Re(1)–Re(2)–Sb(21)	123.13 (2)	Re(1)–H(B2)–Re(2)	83 (3)
		Re(1)–H(B3)–Re(2)	88 (4)

of the crystal data and data collection parameters (Table S1), listings of all positional parameters (Tables S2 and S3), the thermal parameters (Table S4), and complete bond distances (Table S5) and bond angles (Table S6) are available as supplementary material. A figure (Figure S1) giving the atomic numbering scheme is also available.

Physical Measurements. IBM Instruments IR/32 and Perkin-Elmer 1800 FTIR spectrometers were used to record IR spectra of compounds as Nujol mulls supported in KBr plates in the region 4800–400 cm^{-1}. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, the ferrocenium/ferrocene couple is at $E_{1/2}$ = +0.47 V vs Ag/AgCl. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +7.20 in C_6D_6, δ +7.10 (C_6H_5) and δ +2.10 (CH_3) in C_7D_8, δ +3.35 (CH_3) and δ +4.75 (OH) in CD_3OD, and δ +2.17 in $(CD_3)_2CO$). Phosphorus resonances were referenced externally to 85% H_3PO_4. Conductivity measurements were performed on solutions of the samples at a concentration of ca. 1.0 × 10^{-3} M by utilizing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

(a) Reaction of $Re_2H_8(PMe_3)_4$ with Trimethylphosphine. In a previous study, we showed that the final product from the reaction of $Re_2H_8(PMe_3)_4$ with 2 equiv of PMe_3 in *methanol* was the $[Re_2H_5(PMe_3)_6]^+$ cation, which could be isolated as its orange PF_6^- salt.[16] Aerial oxidation of the monocation in solution gave the purple paramagnetic dicationic species $[Re_2H_5(PMe_3)_6]^{2+}$. Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy on $[Re_2H_5(PMe_3)_6]PF_6$ confirmed that its structure is correctly represented as $[(Me_3P)_3HRe(\mu\text{-}H)_3ReH(PMe_3)_3]^+$.

In order to unravel the mechanistic details, we first monitored the reaction of $Re_2H_8(PMe_3)_4$ with PMe_3 in CD_3OD over time with the use of ^1H NMR spectroscopy. The results obtained in the high-field region are displayed in Figure 1. The resonance at δ −7.49 (Re–*H*, pentet, J_{PH} = 9.0 Hz)[27] is due to $Re_2H_8(PMe_3)_4$, while the unresolved multiplet at δ −8.80 in the final spectrum is assigned to $[Re_2H_5(PMe_3)_6]^+$. This conversion is accompanied both by loss of H_2 (δ +4.52) and HD (δ +4.47, triplet, J_{HD} = 43.2 Hz) in that order and also involves the sequential formation of two polyhydride intermediates characterized by δ ca. −6.5 and δ ca. −9.3 (Figure 1). Since the resonance at δ −9.3 has a chemical shift upfield of $Re_2H_8(PMe_3)_4$, we anticipated that it might be due to $Re_2H_6(PMe_3)_5$, a logical intermediate in this reaction (see eq 1).[28] Accordingly, we set out to devise ways of isolating this complex by alternative means.

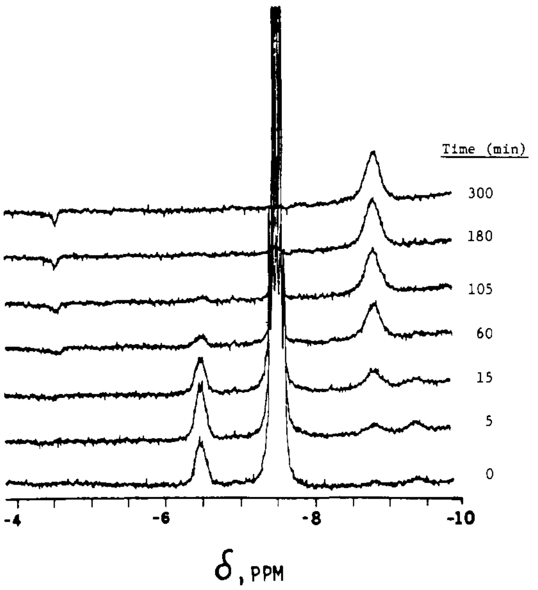


Figure 1. ^1H NMR spectra of a solution in the high-field region containing $Re_2H_8(PMe_3)_4$ (1 equiv) and PMe_3 (4 equiv) in CD_3OD monitored over a period of ca. 5 h. The signal at δ −7.49 is due to $Re_2H_8(PMe_3)_4$ and it diminishes in intensity with time, while the signal at δ −8.80 (due to $[Re_2H_5(PMe_3)_6]^+$) increases in intensity. The resonances at δ ca. −6.5 and δ ca. −9.4 are due to intermediates (see text).

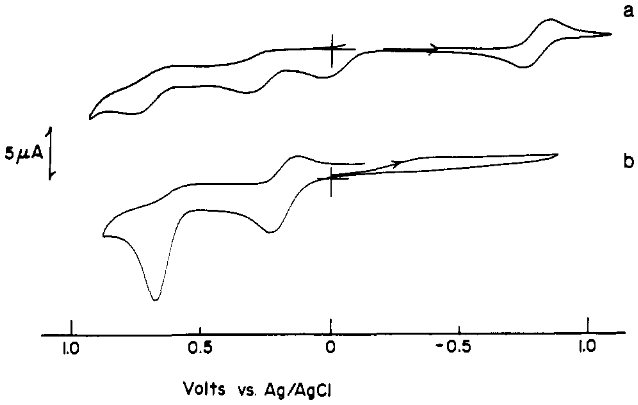


Figure 2. Cyclic voltammograms of (a) $Re_2H_6(PMe_3)_5$ and (b) $[Re_2H_7(PMe_3)_5]BF_4$ in 0.1 M TBAH–CH_2Cl_2 recorded at 200 mV s^{-1} with the use of a Pt-bead electrode.

While we were unable to isolate $Re_2H_6(PMe_3)_5$ when methanol was the reaction solvent, it proved to be the main product (isolated yield of ca. 75%) upon switching to benzene; this reaction is accompanied by H_2 evolution. The IR spectrum (Nujol mull) of this complex shows a strong band at 938 cm^{-1} due to the PMe_3 ligands, as well as a weak broad band at 1918 cm^{-1} in addition to even weaker features at 2016 and 1868 cm^{-1} that are assigned to ν(Re–H).

Cyclic voltammetric measurements on solutions of $Re_2H_6(PMe_3)_5$ in 0.1 M TBAH–CH_2Cl_2 showed a reversible redox process at $E_{1/2}$ = −0.79 V and three irreversible oxidations at $E_{p,a}$ = +0.05 V and $E_{p,a}$ = +0.33 and +0.83 V vs Ag/AgCl (Figure 2). The reversible process corresponds to the one-electron oxidation of $Re_2H_6(PMe_3)_5$, but attempts to obtain this product chemically with the use of $C_7H_7PF_6$ as oxidant were unsuccessful. However, a solution of $[Re_2H_6(PMe_3)_5]^+$ in 0.1 M TBAH–CH_2Cl_2 was generated electrochemically upon bulk electrolysis at −0.7 V. This blue solution gives a cyclic voltammogram identical with

---

(28) As phosphine for hydride ligand substitution increases, there is usually an upfield shift of the Re–*H* resonance; at room temperature, δ −6.22 for $Re_2H_8(PMe_2Ph)_4$ in C_6D_6[9] versus δ −8.26 for $Re_2H_6(PMe_2Ph)_5$ in C_7D_8.[2a]

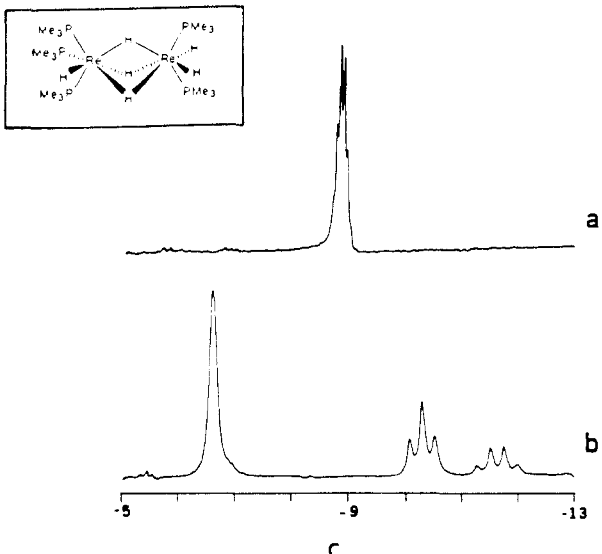
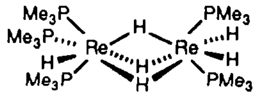


Figure 3. ^1H NMR spectra of $Re_2H_6(PMe_3)_5$ recorded in C_7D_8 at temperatures of (a) +50 and (b) −100 °C. Coalescence occurs at ca. −40 °C.

that of its parent, with the exception that the reversible process at $E_{1/2} = -0.79$ V now corresponds to a reduction. ESR spectral measurements on such a solution (at −160 °C) confirmed the paramagnetic nature of $[Re_2H_6(PMe_3)_5]^+$ through the presence of a broad signal centered at 3080 G ($g_{av} \simeq 2.12$); some rhenium hyperfine structure ($A_{Re} \simeq 110$G) was resolved.

The ^1H NMR spectrum of $Re_2H_6(PMe_3)_5$ in CD_3OD showed that this complex is very unstable in methanol; it converts rapidly to the species with δ −6.46 (vide infra), although there is a weak broad resonance at δ −9.28 due to unreacted $Re_2H_6(PMe_3)_5$ in freshly prepared solutions. On the other hand, solutions of $Re_2H_6(PMe_3)_5$ in C_6D_6 are quite stable and show two doublets at δ +1.74 and δ +1.90 ($^2J_{HP}$ = 10 Hz), with a relative intensity of 3:2, which are assigned to the methyl groups of two sets of inequivalent phosphine ligands. A Re–*H* resonance at δ −8.56 appears as a sextet (J_{PH} = 11.8 Hz), confirming the presence of five PMe_3 ligands. The corresponding $^{31}P\{^1H\}$ NMR spectrum consists of two singlets at δ −25.0 and δ −30.3, with a relative intensity of 3:2.

The variable-temperature ^1H NMR spectrum of $Re_2H_6(PMe_3)_5$ was recorded in C_7D_8 over the range +50 to −100 °C. As the temperature is lowered, the Re–*H* sextet broadens until coalescence occurs at −40 °C. Upon further cooling of the solution to −100 °C, three distinct Re–*H* resonances were observed (see Figure 3). There is a broad singlet at δ −6.58 due to bridging hydrido ligands, a triplet centered at δ −10.28 (J_{PH} = 44 Hz) that arises from coupling of terminal hydrides to two phosphine ligands, and a quartet at δ −11.49 (J_{PH} = 49 Hz) due to a terminal hydride that is coupled to three phosphines. The ratio of the relative intensities of these three resonances is 3:2:1. These results, along with the $^{31}P\{^1H\}$ NMR spectral data, confirm that $Re_2H_6(PMe_3)_5$ has the same unsymmetric structure I that has been shown to be



I

the case for the crystallographically characterized dimethylphenylphosphine analogue $Re_2H_6(PMe_2Ph)_5$.[2a]

As mentioned before, $Re_2H_6(PMe_3)_5$ is unstable in methanol and converts to the same species (δ ca. −6.5) that is formed as an intermediate in the conversion of $Re_2H_8(PMe_3)_4$ to $[Re_2H_5(PMe_3)_6]^+$ in this solvent. This resonance has the appearance of a poorly resolved sextet (implying that five phosphine ligands are present) and is shifted downfield of the $Re_2H_6(PMe_3)_5$ resonance by ca. 2 ppm, the magnitude of which is not out of line with the downfield chemical shift observed upon converting $Re_2H_8(PR_3)_4$ to $[Re_2H_9(PR_3)_4]^+$ (R = Me or Ph).[9,15,16] Accordingly, we made the assumption that this species was $[Re_2H_7(PMe_3)_5]^+$. In other words, it is formed upon protonation of the other intermediate $Re_2H_6(PMe_3)_5$ by methanol. To confirm this supposition, we independently prepared the salt $[Re_2H_7(PMe_3)_5]BF_4$ (70% yield) through the reaction of $Re_2H_6(PMe_3)_5$ with $HBF_4{\cdot}Et_2O$ in benzene.

The IR spectrum of $[Re_2H_7(PMe_3)_5]BF_4$ displays intense bands at 948 and 1056 cm^{-1} that are assigned to PMe_3 and ν(B–F) of $[BF_4]^-$, respectively, as well as a well-defined, albeit weak, ν(Re–H) mode at 1956 cm^{-1}. This complex dissolves in acetone to give a solution with a conductivity characteristic of a 1:1 electrolyte (Λ_m = 171 Ω^{-1} cm^2 mol^{-1}). The cyclic voltammogram of a solution of $[Re_2H_7(PMe_3)_5]BF_4$ in 0.1 TBAH–CH_2Cl_2 is quite different from that of $Re_2H_6(PMe_3)_5$ (Figure 2), with a reversible redox process at $E_{1/2}$ = +0.25 V and an irreversible oxidation at $E_{p,a}$ = +0.76 V vs Ag/AgCl. The process at +0.25 V corresponds to a one-electron oxidation of the bulk complex, but attempts to generate $[Re_2H_7(PMe_3)_5]^{2+}$ chemically (using $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ or $(Ph_3C)PF_6$ as oxidants) or electrochemically were not successful; the solutions decomposed. This dirhenium heptahydride cation bears comparison with the complexes $[Re_2H_7(PPh_3)_4L]PF_6$ (L = MeCN, EtCN, PhCN, *t*-BuNC) that we prepared previously by reacting $Re_2H_8(PPh_3)_4$ with $(Ph_3C)PF_6$ in nitrile solvents.[14] The $[Re_2H_7(PPh_3)_4L]PF_6$ complexes possess electrochemical properties that are very similar to those of $[Re_2H_7(PMe_3)_5]BF_4$ (Figure 2); e.g. for L = MeCN, $E_{1/2}$(ox) = +0.01 V and $E_{1/2}$(ox) = +0.73 V vs SCE, while for L = *t*-BuNC, $E_{1/2}$(ox) = +0.19 V and $E_{1/2}$(ox) = +0.94 V vs SCE.[14] Similarities also exist between the ^1H and $^{31}P\{^1H\}$ NMR spectra (vide infra).

The ^1H NMR spectrum of $[Re_2H_7(PMe_3)_5]BF_4$ (recorded in $(CD_3)_2CO$) displays a pair of overlapping doublets at δ +1.18 and δ +1.16 ($^2J_{HP}$ = 9.8 and 9.0 Hz; relative intensity 3:2) due to the methyl resonances of the PMe_3 ligands. The Re–*H* resonance, which is centered at δ −7.05, appears as a triplet of quartets (J_{PH} = 13.4 and 7.7 Hz) due to inequivalent phosphorus–hydride coupling; this accords with the preservation of an unsymmetrical structure in which three PMe_3 ligands are bound to one Re atom and two are bound to the other. Two singlets at δ −19.8 and δ −24.5, of intensity ratio 3:2, are observed in the $^{31}P\{^1H\}$ NMR spectrum recorded in $(CD_3)_2CO$; in CD_3OD, these resonances are at δ −19.9 and δ −24.3. These features generally resemble the related NMR spectra of $[Re_2H_7(PPh_3)_4L]PF_6$, which show the Re–*H* resonance at δ ca. −5.0 and two separate phosphine signals in the $^{31}P\{^1H\}$ NMR spectra.[14] In CD_3OD, the hydride resonance of $[Re_2H_7(PMe_3)_5]BF_4$ appears as an apparent sextet (J_{PH} = 7.6 Hz) at δ −6.47, a chemical shift identical with that of the second dirhenium intermediate formed in the conversion of $Re_2H_8(PMe_3)_4$ into $[Re_2H_5(PMe_3)_6]^+$ (Figure 1). Furthermore, we find that $[Re_2H_7(PMe_3)_5]BF_4$ reacts with 1 equiv of PMe_3 in CD_3OD to give $[Re_2H_5(PMe_3)_6]BF_4$. This reaction, which was monitored by ^1H NMR spectroscopy, proceeds cleanly with loss of H_2.

On the basis of the aforementioned spectroscopic studies and isolation and characterization of the complexes $Re_2H_6(PMe_3)_5$ and $[Re_2H_7(PMe_3)_5]PF_6$, the mechanism for the conversion of $Re_2H_8(PMe_3)_4$ to $[Re_2H_5(PMe_3)_6]^+$ in CD_3OD can be represented as follows:

step 1 $Re_2H_8(PMe_3)_4 + PMe_3 \rightarrow Re_2H_6(PMe_3)_5 + H_2$

step 2 $Re_2H_6(PMe_3)_5 + CD_3OD \rightarrow [Re_2H_6D(PMe_3)_5]^+OCD_3^-$

step 3 $[Re_2H_6D(PMe_3)_5]^+OCD_3^- + PMe_3 \rightarrow [Re_2H_5(PMe_3)_6]^+OCD_3^-$ (or $[Re_2H_4D(PMe_3)_6]^+OCD_3^-$) + HD (or H_2)

Note that step 1 is the same as the first part of eq 1, but we have no evidence that $Re_2H_4(PMe_3)_6$ is formed at any subsequent stage, even though complexes of the type $Re_2H_4(PR_3)_6$ are known and have been found to protonate quite easily to give $[Re_2H_5(PR_3)_6]^+$.[21,22] In a nonprotic solvent such as benzene, the reaction

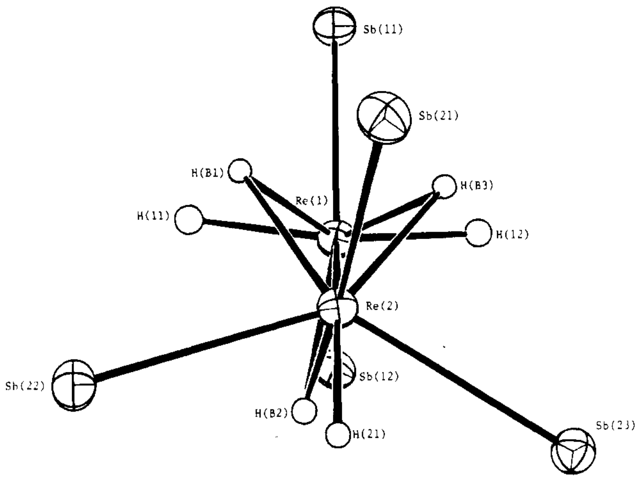


Figure 4. ORTEP representation of the structure of $Re_2H_6(SbPh_3)_5$ as viewed along the Re–Re vector with the phenyl rings omitted. The thermal ellipsoids are drawn at the 50% probability level except for the hydride ligands which are circles of arbitrary radius.

terminates at this first stage, namely, $Re_2H_6(PMe_3)_5$. All attempts by us to deprotonate $[Re_2H_5(PMe_3)_6]^+$ to give $Re_2H_4(PMe_3)_6$ were unsuccessful. By monitoring the gas evolution (with the use of ^1H NMR spectroscopy), we find that H_2 evolution precedes that of HD and continues throughout the course of the reaction. This is consistent with the evolution of H_2 *and* HD in step 3.

(b) The Isolation and Characterization of $Re_2H_6(SbPh_3)_5$. Although we have unambiguously established the structure of $Re_2H_6(PMe_3)_5$ in solution by the use of NMR spectroscopy (vide supra), there is only one example of a molecule of the type $Re_2H_6(PR_3)_5$ whose structure has been established previously by X-ray crystallography, viz., $Re_2H_6(PMe_2Ph)_5$.[2a] While we were unsuccessful in our attempts to grow suitable X-ray quality crystals of $Re_2H_6(PMe_3)_5$, we were successful in so doing in the case of the triphenylstibine analogue $Re_2H_6(SbPh_3)_5$. This compound was obtained in studies that followed up on our recent isolation of the dirhenium octahydride complex $Re_2H_8(SbPh_3)_4$.[10]

We had found that $Re_2H_8(SbPh_3)_4$ can be obtained as a red solid upon reacting $ReOCl_3(SbPh_3)_2$ with an excess of $NaBH_4$ in ethanol at −10 °C for ca. 1 day.[10] When this same reaction is carried out in the presence of a large excess of $SbPh_3$, then the pentahydride complex $ReH_5(SbPh_3)_3{\cdot}2H_2O$ is obtained. The presence of water of crystallization was confirmed by IR and NMR spectroscopies (see Experimental Section). This complex is characterized by a singlet for the Re–*H* resonances in its ^1H NMR spectrum at δ −7.48 (in C_6D_6),[29] and ν(Re–H) modes at 1946 (m-w), 1924 (m-w), 1862 (m-w), and 1816 (w) cm^{-1} in its IR spectrum (Nujol mull). The cyclic voltammetric properties of this complex (recorded in 0.1 M TBAH–CH_2Cl_2) are typical of a rhenium pentahydride complex[30] with a reversible oxidation at $E_{1/2}$ = +0.64 V and an irreversible oxidation at $E_{p,a}$ = +1.50 V vs Ag/AgCl.

As an alternative synthetic strategy, we reacted $(n\text{-}Bu_4N)_2Re_2Cl_8$ with an excess of $SbPh_3$ and $NaBH_4$ in ethanol, a method that works well in the case of the corresponding arsine ligand to give $Re_2H_8(AsPh_3)_4$.[10] However, in the case of the stibine system, a mixture of $Re_2H_8(SbPh_3)_4$ and $Re_2H_6(SbPh_3)_5$ is produced. When the reaction times were progressively increased from a few hours to a few days, the amount of the octahydride progressively decreased as the hexahydride increased (as monitored by ^1H NMR spectroscopy). This implies that the conversion of $Re_2H_8(SbPh_3)_4$ to $Re_2H_6(SbPh_3)_5$ under these reaction conditions proceeds in a fashion analogous to the conversion of $Re_2H_8(PMe_3)_4$ to $Re_2H_6(PMe_3)_5$. With the use of a reaction time of 5 days, the complex $Re_2H_6(SbPh_3)_5$ could be obtained in excellent yield.

The complex $Re_2H_6(SbPh_3)_5$ shows a singlet in its ^1H NMR spectrum (recorded in C_7D_8) at δ −9.14 for the Re–*H* resonance, approximately 2.2 ppm upfield of the corresponding signal in the spectrum of $Re_2H_8(SbPh_3)_4$ (recorded in C_6D_6). When the spectrum is measured over the temperature range +10 to −100 °C, the signal at δ −9.14 broadens and shifts downfield slightly to δ −8.94 as the temperature is decreased to −100 °C, but is otherwise unchanged. The cyclic voltammogram of a solution of $Re_2H_6(SbPh_3)_5$ in 0.1 M TBAH–CH_2Cl_2 consists of a reversible process at $E_{1/2}$ = −0.25 V vs Ag/AgCl that corresponds to an oxidation and an irreversible oxidation at $E_{p,a}$ = +0.55 V vs Ag/AgCl. On a second voltammetric sweep, a process at $E_{p,c}$ = −0.43 V is observed that is attributable to the formation of a chemical product following the irreversible oxidation at $E_{p,a}$ = +0.55 V. The process at $E_{1/2}$ = −0.25 V is at a more negative potential than the reversible oxidation of $Re_2H_8(SbPh_3)_4$ at $E_{1/2}$ = +0.05 V;[10] this is almost exactly the same shift as that between the corresponding $E_{1/2}$(ox) values of $Re_2H_6(PMe_3)_5$ (Figure 2) and $Re_2H_8(PMe_3)_4$.[9]

The identity of $Re_2H_6(SbPh_3)_5$ has been confirmed by the results of a single-crystal X-ray structure analysis. As far as we can tell, this structure shows a striking resemblance to that reported for $Re_2H_6(PMe_2Ph)_5$,[2a] with regard to the disposition of the stibine/phosphine ligands, the numbers of bridging versus terminal Re–H bonds, and the Re–Re bond distances (2.5340 (5) Å for $Re_2H_6(SbPh_3)_5$ and 2.589 (1) Å for $Re_2H_6(PMe_2Ph)_5$). The Re–Re distances are also similar to those in the dirhenium octahydride complexes $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ (PR_3 = $PEtPh_2$[11] and PPh_3[12]) that have been structurally characterized and also to several cationic dirhenium pentahydride species that contain a $Re(\mu\text{-}H)_3Re$ unit.[17,21,22]

An ORTEP representation of the main skeleton of the structure (with the phenyl rings omitted) is shown in Figure 4. Important bond distances and angles for this structure are given in Table III. The Re–H distances and Re–H–Re angles are in acceptable agreement with similar parameters reported from the X-ray structure determination of $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]^+$.[17] The angle Sb(11)–Re(1)–Sb(12) about the less sterically congested Re atom is 103.36 (2)°, a value that is within the range of P–Re–P angles (ca. 103–108°) in the structures of $Re_2(\mu\text{-}H)_4H_4(PR_3)_4$ (PR_3 = $PEtPh_2$[11] or PPh_3[12]). The Sb–Re–Sb angles about Re(2) reflect both the increased steric congestion and the presence of a terminal hydride ligand between Sb(22) and Sb(23). Note also the slightly longer Re–Sb bond lengths about Re(2) (2.59–2.60 Å) compared with those about Re(1) (2.56–2.57 Å).

Acknowledgment. Support from the National Science Foundation, through Grant No. CHE88-07444 to R.A.W. and Grant No. CHE86-15556 for the purchase of the MicroVAX II computer and diffractometer, is gratefully acknowledged. We also acknowledge the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers.

Supplementary Material Available: Tables giving full details of crystal data and data collection parameters (Table S1), positional parameters (Tables S2 and S3), thermal parameters (Table S4), and bond distances and bond angles (Tables S5 and S6, respectively) and a figure (Figure S1) showing the atomic numbering scheme for the phenyl group carbon atoms (28 pages); a table of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

---

(29) In CD_2Cl_2 this resonance is at δ −8.30. The magnitude of the chemical shift difference between solutions of this complex in C_6D_6 and CD_2Cl_2 is in accord with data for other rhenium polyhydrides (see ref 10).

(30) Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563.