rotate about the axis from Re to its midpoint. Repetition of this type of process in all the equivalent ways would give an averaged ^{1}H NMR spectrum. Such a mechanism would contribute to the observed short T_1(min) values found[7b] for $Re_2H_8(PR_3)_4$ molecules, but we do not believe a reverse argument (i.e., that the short T_1(min) values favor this sort of mechanism in preference to others) is persuasive.

Finally, however, we should like to propose one more mechanism, of a very different type, that is suggested by the crystallographic disorder found in **1a**. This consists of an internal flip of the Re_2 unit within the ligand cage accompanied by slight ligand rearrangements such as shown in Scheme I. Such a motion could have been responsible for creating the disorder present in **1a**. Similar internal-flip mechanisms in different complexes are now gaining general acceptance in the literature.[17]

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Larry R. Falvello for his extremely helpful discussions regarding aspects of the crystallographic work.

Supplementary Material Available: Fully labeled ORTEP drawings and stereoviews of the unit cell packing for complexes **1a** and **1b**, listings of the positional parameters for the hydrogen atoms attached to phenyl rings, full tables of the crystallographic data and anisotropic displacement parameters for complexes **1a** and **1b**, and difference Fourier contour plots with all of the data and data up to (sin θ)/λ of 0.423 for complex **1b** (26 pages); listings of observed and calculated structure factors for **1a** and **1b** (49 pages). Ordering information is given on any current masthead page.

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Structure and Reactivity of $ReH_4(PMe_2Ph)_4^+$

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Protonation of ReH_3P_4 (P = PMe_2Ph) with $HBF_4{\cdot}OEt_2$ in Et_2O gives $ReH_4P_4^+$, which neither exchanges with D_2 nor reacts with PhC≡CPh, CO, MeCN, or C_2H_4 under mild conditions. These results, together with an X-ray crystal structure determination, are consistent with a "classical" tetrahydride formulation for this cation, and the lack of reactivity correlates with the absence of coordinated H_2 as a ligand. NEt_3 will not deprotonate $ReH_4P_4^+$ since it is a weaker base than ReH_3P_4. The implied electron-rich character of ReH_3P_4 thus rationalizes why protonation results in formal oxidation to Re(V), rather than retention of Re(III) as in $Re(H)_2(H_2)P_4^+$. The T_1 value of the hydrogens bound to rhenium is 97 ms at −70 °C and 360 MHz.

Introduction

We have found that protonation of IrH_3P_3[1,2] and OsH_4P_3[3] (P = PMe_2Ph) with $HBF_4{\cdot}OEt_2$ gives dihydrogen complexes with the valuable feature that they participate in equilibrium dissociation of H_2 to produce the unsaturated polyhydrides $IrH_2P_3^+$ and $OsH_3P_3^+$. We were interested in whether it was possible to extend this principle to tetrakis(phosphine) complexes for the influence such increased steric hindrance could have on the resulting hydrogenation of olefins and alkynes. We report here the results of protonation of ReH_3P_4. Earlier reports[4-6] of protonation of other ReH_3L_4 species have not revealed anything about the structure or reactivity of the derived cations.

Experimental Section

Materials and Methods. All manipulations were carried out by using standard Schlenk and glove box techniques under nitrogen or vacuum. Solvents were dried over Na/K benzophenone ketyl (diethyl ether, toluene, hexane) or P_2O_5 (CH_2Cl_2). Absolute ethanol was used as received but degassed prior to use. Deuterated solvents were dried over P_2O_5 ($CDCl_3$, CD_2Cl_2) or Na/K (C_6D_6) and distilled in vacuo. Reagents were dried over P_2O_5 (CH_3CN) or CaH_2 (NEt_3) and distilled under nitrogen. Ethylene, carbon monoxide, deuterium, and diphenylacetylene were used as received. $Re(PMe_2Ph)_3Cl_3$[7] and PMe_2Ph[8] were prepared according to literature procedures.

Spectroscopy. Proton NMR spectra were recorded by using either a Nicolet EM-360 (^{1}H at 360 MHz) or a Bruker 500 (^{1}H at 500 MHz) spectrometer. Carbon NMR spectra were recorded on a Bruker 500 instrument (^{13}C at 125.7 MHz), and all were referenced to Me_4Si. Phosphorus NMR spectra were obtained on a Nicolet 360 spectrometer (^{31}P at 146 MHz) and referenced externally to 85% H_3PO_4. Proton T_1 values were determined by the inversion/recovery method at 360 MHz with a 180°–τ–90° pulse sequence. Infrared spectra were recorded as Nujol mulls by using a Perkin-Elmer 283 spectrophotomer.

Syntheses. $ReH_3(PMe_2Ph)_4$.[9] To a solution of 1.0 g (1.41 mmol) of $ReCl_3P_3$ in 50 mL of degassed absolute ethanol were added 1.0 mL (7.05 mmol) of PMe_2Ph and 1.0 g (26.5 mmol) of $NaBH_4$. The orange mixture was heated to reflux under nitrogen. After 3 h, the bright yellow suspension was cooled to room temperature and the solvent removed under vacuum. Extraction with toluene and filtration over Celite gave a yellow solution. The toluene was removed under vacuum and the resulting yellow semisolid dissolved in hot hexane. When the mixture was cooled to room temperature, golden yellow crystals of ReH_3P_4 appeared and were collected by filtration and dried under vacuum. Yield: 80%. ^{1}H NMR (C_6D_6): δ (ppm) −6.80 (quintet, J = 20 Hz, Re–H), 1.48 (s, P–CH_3), 7.0–7.3 (m, P–C_6H_5 (meta, para)), 7.75 (s, P–C_6H_5 (ortho)). ^{31}P{^{1}H} NMR (C_6D_6): δ (ppm) −19.7 (s). IR (Nujol): ν(Re–H) 1782 cm^{-1}.

$[ReH_4(PMe_2Ph)_4]BF_4$. A 60-mg sample (0.082 mmol) of ReH_3P_4 was weighed into a 100-mL Schlenk flask. A 25-mL quantity of diethyl ether was added, resulting in a yellow solution. A 10-μL portion (0.082 mmol) of $HBF_4{\cdot}OEt_2$ was added by syringe, after which the solution immediately became colorless and a white precipitate formed. After 15 min of stirring, the mixture was allowed to settle. The solvent was removed by

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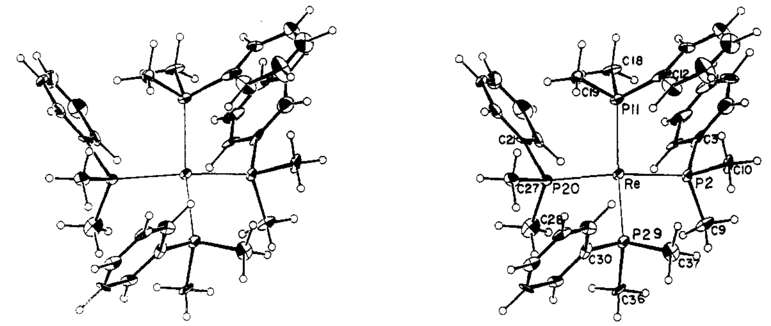

Figure 1. Stereo ORTEP drawing of $ReH_4(PMe_2Ph)_4^+$, showing selected atom labeling. Open circles are hydrogen. Hydrides on rhenium were not located.

Table I. Crystal Data for $[ReH_4(PMe_2Ph)_4]BF_4$

chem formula	$C_{32}H_{48}BF_4P_4Re$	space group	*Pcab*
a, Å	18.930 (3)	T, °C	−156
b, Å	20.319 (3)	λ, Å	0.71069
c, Å	18.880 (3)	ρ_{calcd}, g cm^{-3}	1.518
V, Å^3	7262.21	μ(Mo Kα), cm^{-1}	36.05
Z	8	R	0.0678
fw	829.63	R_w	0.0629

cannula and the remaining white solid dried under vacuum. ^1H NMR (CD_2Cl_2): δ (ppm) −4.33 (m, Re–H), 1.59 (s, P–CH_3), 7.41 (s, P–C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) −26.9 (s, becomes a quintet upon selective decoupling of only the methyl and phenyl protons). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 24.9 (s, P–CH_3), 128.9 (s, P–C_6H_5 (ortho)), 130.0 (s, P–C_6H_5 (meta)), 130.4 (s, P–C_6H_5 (para)), 141.2 (m, P–C_6H_5 (ipso)). IR (Nujol): ν(Re–H) 1933 cm^{-1}. Anal. Calcd for $C_{32}H_{48}BF_4P_4Re$: C, 46.33; H, 5.83. Found: C, 45.91; H, 5.67.

Reactivity Studies. (1) $[ReH_4P_4]BF_4$ with Ethylene. $[ReH_4P_4]BF_4$ (0.082 mmol) was dissolved in 20 mL of CH_2Cl_2 in a 100-mL flask, which was frozen in liquid nitrogen and placed under vacuum. Ethylene was added to the reaction vessel to a pressure of 1 atm, and the reaction mixture was stirred for 30 h at room temperature. The solvent was removed by vacuum, leaving a white semisolid shown by ^1H NMR spectroscopy to contain only starting material. The complex was also recovered unchanged from a stainless-steel vessel pressurized to 500 psi with ethylene and then heated to 90 °C for 3.5 h.

(2) $[ReH_4P_4]BF_4$ with PhCCPh. A solution of 30 mg (0.16 mmol) of PhCCPh in 10 mL of CH_2Cl_2 was transferred by cannula into a 100-mL Schlenk flask containing 0.082 mmol of $[ReH_4P_4]BF_4$ in 10 mL of CH_2Cl_2. The colorless solution was stirred at room temperature under an atmosphere of nitrogen. After 20 h, only starting material was detected by ^{31}P NMR spectroscopy. The reaction was repeated in refluxing CH_2Cl_2 (40 °C) for 30 h. After removal of solvent, again only starting material remained.

(3) $[ReH_4P_4]BF_4$ with CH_3CN. $[ReH_4P_4]BF_4$ (0.082 mmol) was dissolved in $CDCl_3$ in an NMR tube and 17 μL (0.33 mmol) of CH_3CN was added. Spectra taken after 8 h showed only starting materials.

(4) $[ReH_4P_4]BF_4$ with CO. The reaction was performed as in part 1, with 1 atm of CO at room temperature. After 24 h, evaporation of solvent again yielded only starting material.

(5) $[ReH_4P_4]BF_4$ with D_2. $[ReH_4P_4]BF_4$ (0.082 mmol) was dissolved in $CDCl_3$, and a ^1H NMR spectrum was recorded for reference purposes. The solution was transferred to a 100-mL Schlenk flask and the solvent removed under vacuum. A 25-mL portion of CH_2Cl_2 was added, the solution was frozen in liquid nitrogen, and the flask was placed under vacuum. D_2 was introduced into the vessel to a pressure of 1 atm (i.e., 4 mmol). After 72 h of stirring at 25 °C, the solvent was removed under vacuum and the residue dissolved in $CDCl_3$. The ^1H NMR spectrum showed no significant change in the pattern or intensity of the multiplet at −4.4 ppm.

(6) $[ReH_4P_4]BF_4$ with NEt_3. $[ReH_4P_4]BF_4$ (0.082 mmol) was dissolved in 25 mL of CH_2Cl_2, and 11 μL (0.082 mmol) of NEt_3 as added. After 24 h of stirring at room temperature, no reaction was detected by ^1H NMR.

(7) ReH_3P_4 with $[HNEt_3]Br$. A 60-mg sample (0.082 mmol) of ReH_3P_4 was placed in a 100-mL Schlenk flask and dissolved in 20 mL of CH_2Cl_2. A 15-mg quantity (0.082 mmol) of $HNEt_3Br$ was added to the yellow solution. After 15 h of stirring at room temperature, the solvent was removed under vacuum to leave a yellow semisolid. ^1H NMR ($CDCl_3$): δ (ppm) −4.39 (m, Re–H), 1.63 (s, P–CH_3), 7.42 (s, P–C_6H_5).

Crystal Structure Determination. $[ReH_4P_4]BF_4$ (50 mg) was dissolved in 5 mL of CH_2Cl_2, and 15 mL of hexane was layered over the colorless solution. When the mixture was allowed to stand at room temperature for 5 days, colorless crystals precipitated.

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for $[ReH_4(PMe_2Ph)_4]BF_4$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Re(1)	1510.2 (3)	718.5 (3)	2695.6 (3)	10
P(2)	2578 (2)	662 (2)	2008 (2)	12
C(3)	2917 (7)	−187 (7)	1850 (9)	17
C(4)	2975 (9)	−443 (9)	1169 (10)	27
C(5)	3197 (9)	−1115 (9)	1122 (9)	27
C(6)	3390 (8)	−1469 (8)	1700 (11)	30
C(7)	3355 (8)	−1196 (8)	2365 (11)	26
C(8)	3104 (7)	−562 (6)	2452 (9)	17
C(9)	3352 (8)	1053 (7)	2389 (9)	22
C(10)	2566 (8)	1015 (7)	1127 (9)	22
P(11)	933 (2)	−114 (2)	1990 (2)	13
C(12)	1000 (8)	−19 (8)	1023 (9)	24
C(13)	1319 (9)	−496 (8)	595 (9)	24
C(14)	1398 (9)	−399 (9)	−132 (9)	30
C(15)	1127 (9)	182 (10)	−420 (9)	29
C(16)	804 (10)	645 (10)	−8 (9)	34
C(17)	747 (8)	546 (8)	698 (8)	24
C(18)	1192 (8)	−961 (7)	2131 (8)	19
C(19)	−27 (8)	−164 (8)	2069 (8)	20
P(20)	884 (2)	440 (2)	3766 (2)	12
C(21)	749 (9)	−438 (7)	3944 (8)	18
C(22)	100 (8)	−750 (8)	3952 (8)	21
C(23)	26 (9)	−1412 (8)	4054 (9)	24
C(24)	602 (10)	−1799 (8)	4170 (10)	30
C(25)	1287 (10)	−1520 (8)	4177 (9)	29
C(26)	1346 (8)	−836 (7)	4049 (7)	17
C(27)	−3 (8)	795 (7)	3880 (8)	17
C(28)	1312 (8)	686 (8)	4578 (9)	25
P(29)	1654 (2)	1866 (2)	2996 (2)	13
C(30)	831 (7)	2291 (7)	3259 (8)	15
C(31)	315 (8)	2390 (6)	2763 (8)	15
C(32)	−303 (8)	2722 (7)	2917 (9)	20
C(33)	−402 (7)	2949 (7)	3598 (9)	16
C(34)	111 (9)	2835 (7)	4147 (8)	19
C(35)	736 (7)	2512 (7)	3951 (8)	16
C(36)	2270 (7)	2091 (7)	3711 (9)	18
C(37)	1945 (9)	2409 (7)	2271 (9)	23
B(38)	3547 (9)	2749 (10)	896 (9)	21
F(39)	3579 (5)	2433 (5)	1553 (5)	30
F(40)	3037 (6)	3219 (6)	930 (8)	58
F(41)	4208 (6)	3006 (5)	743 (6)	44
F(42)	3382 (7)	2271 (6)	391 (5)	57

[a] Isotropic values for these atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crysatllogr.* **1959**, *12*, 609.

An irregular shaped fragment of suitable overall size was mounted with silicone grease and transferred to a goniostat where it was cooled to −156 °C for characterization and data collection (see Table I). A systematic search of a limited hemisphere of reciprocal space revealed a set of diffraction maxima which could be indexed consistent with orthorhombic symmetry. An inspection after complete data collection (6° ≤ 2θ ≤ 46°) revealed systematic absences that uniquely determined space group *Pcab*. Data processing[10] gave a residual of 0.035 for 201 unique

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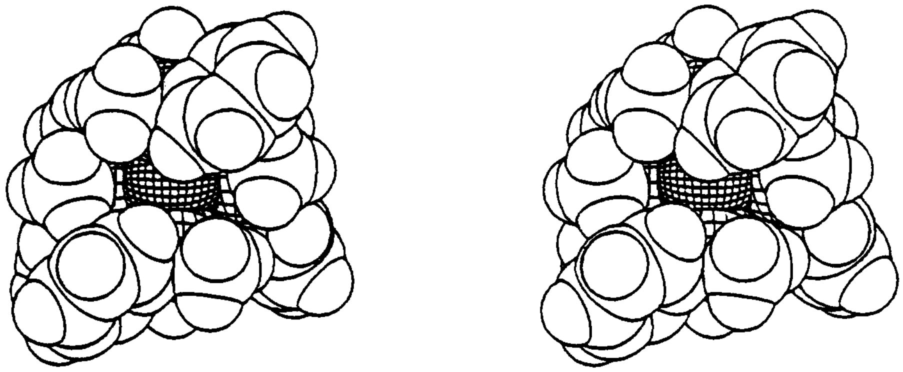

Figure 2. Stereo space-filling drawing of $ReH_4(PMe_2Ph)_4^+$, viewed as in Figure 1. All C–H distances are fixed at 1.05 Å.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[ReH_4(PMe_2Ph)_4]BF_4$

Re(1)–P(2)	2.406 (4)	F(39)–B(38)	1.399 (18)
Re(1)–P(11)	2.415 (4)	F(40)–B(38)	1.359 (22)
Re(1)–P(20)	2.410 (4)	F(41)–B(38)	1.386 (20)
Re(1)–P(29)	2.414 (4)	F(42)–B(38)	1.396 (22)
P(2)–Re(1)–P(11)	92.83 (13)	Re(1)–P(20)–C(21)	116.7 (5)
P(2)–Re(1)–P(20)	148.74 (13)	Re(1)–P(20)–C(27)	117.1 (5)
P(2)–Re(1)–P(29)	94.45 (12)	Re(1)–P(20)–C(28)	115.3 (6)
P(11)–Re(1)–P(20)	94.35 (13)	Re(1)–P(29)–C(30)	114.8 (5)
P(11)–Re(1)–P(29)	148.98 (13)	Re(1)–P(29)–C(36)	118.9 (5)
P(20)–Re(1)–P(29)	94.88 (13)	Re(1)–P(29)–C(37)	116.0 (5)
Re(1)–P(2)–C(3)	114.8 (4)	F(39)–B(38)–F(40)	108.1 (14)
Re(1)–P(2)–C(9)	116.4 (6)	F(39)–B(38)–F(41)	108.6 (13)
Re(1)–P(2)–C(10)	117.8 (5)	F(39)–B(38)–F(42)	107.2 (15)
Re(1)–P(11)–C(12)	116.3 (5)	F(40)–B(38)–F(41)	112.7 (16)
Re(1)–P(11)–C(18)	117.6 (5)	F(40)–B(38)–F(42)	111.3 (14)
Re(1)–P(11)–C(19)	116.4 (5)	F(41)–B(38)–F(42)	108.8 (14)

intensities which had been observed more than once. Four standard reflections, measured after every 300 reflections collected, showed no decay of intensity. Because there were no well-defined faces on the crystal, no attempt was made to accurately measure its size and to correct for absorption.

The structure was solved by a combination of direct methods and Fourier techniques. After the non-hydrogen atoms had been located and partially refined, a difference Fourier map revealed only a few of the anticipated 48 hydrogen atoms. The 44 hydrogen atoms bonded to carbon atoms were placed in fixed calculated positions to improve the refinement of the non-hydrogen atoms to which they are attached. The final cycles of least-squares refinement, in which the non-hydrogens were refined with anisotropic thermal parameters, gave $R(F) = 0.068$.

The final difference map had 24 peaks in the range of 1–2 e/Å^3; i.e., it was not a clean map. This, together with the fact that most of the hydrogens on the carbon atoms could not be located earlier, leaves no reason to suppose that the four anticipated hydride atoms on Re can be located, on the basis of this study. The results of the structure study are shown in Tables II and III and Figures 1 and 2.

Reaction of $ReH_3[PMe_2Ph]_4$ with C_2H_4. A 60-mg sample (0.082 mmol) of ReH_3P_4 was weighed into a 100-mL Schlenk flask and 10 mL CH_2Cl_2 added. The resulting yellow solution was frozen and placed under vacuum. C_2H_4 was added to a pressure of 1 atm (3.7 mmol). After thawing, the solution was stirred at room temperature for 11 h. The ^1H NMR spectrum (C_6D_6) showed only starting material.

Reaction of $ReH_3[PMe_2Ph]_4$ with D_2. A solution of 60 mg (0.082 mmol) of ReH_3P_4 in 10 mL of toluene inside a 100-mL Schlenk flask was frozen and evacuated. D_2 was introduced into the flask to a pressure of 1 atm (3.7 mmol). The solution was stirred at room temperature for 72 h. The ^1H NMR spectrum showed complete conversion to $Re(H,D)_5(PMe_2Ph)_3$. ^1H NMR (C_6D_6) (δ, ppm): –6.10 (q, J = 19 Hz, Re–H), 1.67 (d, P–Me), 7.05 (m, P–Ph (meta, para)), 7.57 (br m, P–Ph (ortho)). The simplicity (i.e., only slight broadening) of the hydride region and the reduced intensity of the 7.57 ppm resonance (compared to an authentic sample of $ReH_5[P(CH_3)_2C_6H_5]_3$) are consistent with major transfer of deuterium from Re to carbon.

Results

Synthesis and Characterization. Reaction of ReH_3P_4 with equimolar $HBF_4{\cdot}OEt_2$ in Et_2O immediately precipitates the white solid $[ReH_4P_4]BF_4$. The $^{31}P\{^1H\}$ NMR spectrum of the cation in CD_2Cl_2 shows a single line that becomes a quintet on selectively decoupling the 0–10 ppm ^1H NMR region. The ^1H NMR spectrum is also very simple: one methyl resonance and a single (accidentally degenerate) phenyl resonance, together with one hydride multiplet. The hydride resonance is a non-first-order (at both 360 and 500 MHz) five-line multiplet with sharp outer lines flanking a broad three-line pattern. The hydride pattern is unchanged at –80 °C. It is a singlet on phosphorus decoupling. The hydride pattern (phosphorus-coupled) changes appearance in the range 23–52 °C to resemble more closely a binomial quintet, indicating the more rapid occurrence of fluxionality. This variable-temperature ^1H NMR spectral behavior mimics that seen for MH_4P_4 (M = Mo, W).[11] While the hydride resonance pattern resembles the AA′A″A‴XX′X″X‴ pattern of the *tetrahydride* $MoH_4(PMePh_2)_4$, it could also be consistent with one H_2 and two hydride ligands at intermediate rates of exchange. We therefore undertook chemical reactivity studies.

Reactivity Studies. $[ReH_4P_4]BF_4$ showed no reaction with ethylene under conditions as vigorous as 500 psi, at 90 °C for 3.5 h. The generally more reactive unsaturate PhC≡CPh was also unreactive over 30 h at 40 °C. Since acetonitrile readily displaces the H_2 ligands in $H_4IrP_3^+$ and $H_5OsP_3^+$, we stirred $ReH_4P_4^+$ with 4 equiv of the "slender" Lewis base MeCN for 8 h. The cation was recovered unchanged. Carbon monoxide is another reagent that efficiently scavenges unsaturated species; upon treatment of $ReH_4P_4^+$ with 1 atm of CO for 24 h at 25°, the cation was recovered unchanged.

Our standard method for detecting H_2 dissociation (however small, and *regardless* of whether H_2 is the structural form of the coordinated "hydrogen")[12] is facile exchange with D_2. We find (^1H NMR) that $[ReH_4P_4]BF_4$ in CH_2Cl_2 undergoes no detectable exchange after treatment with 1 atm of D_2 for 72 h.

Hydride T_1 Measurement. The T_1 relaxation time of the hydride nuclei in $[ReH_4P_4]BF_4$ at –70 °C and 360 MHz in acetone-d_6 was measured at 97 (±18) ms. This value is short (shorter still at 250 MHz, where any value below 80–100 ms has been proposed[13] as being diagnostic of coordinated H_2) compared to the 524 ms value for WH_4P_4 in toluene-d_8 at –70 °C. The ReH_3 T_1 (–69 °C, 400 MHz, CD_2Cl_2) of $ReH_3(PMePh_2)_4$ is 192 ms (note, however, that this phosphine is not the one in our $ReH_4(PMe_2Ph)_4^+$); this trihydride has coupling constants consistent with the *absence* of any coordinated H_2. However, given recent results[14] which imply that, particularly for rhenium, the T_1 threshold for H_2 should be considerably lower than 80–100 ms at 250 MHz, we conclude that the T_1 value for $ReH_4P_4^+$ is not a decisive criterion of structure.

Structure. The X-ray study (Figure 1) shows solid $[ReH_4(PMe_2Ph)_4]BF_4$ to consist of well-separated cations and anions. The BF_4^- and phenyl rings have their conventional geometry. Since the hydride hydrogens were not evident in the X-ray diffraction data, the following discussion will focus on the non hydrogen atom geometry. The cation has an ReP_4 geometry that

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[11] Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muetterties, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467.

[12] For a case where a dihydride will lose H_2 in vacuo, see: Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113.

[13] Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.

[14] Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181.

is intermediate between tetrahedral and planar. This geometry has been termed "flattened tetrahedral".[15] The approximate S_4 symmetry of the ReP_4 unit indicates that the four hydrogens must also be symmetry-related and thus preclude an $Re(H)_2(H_2)(PMe_2Ph)_4^+$ formulation. The close approach to S_4 symmetry is, however, consistent with an $Re(H)_4(PMe_2Ph)_4^+$ formulation with dodecahedral coordination geometry. The two orthogonal (87.6°) trapezoidal $Re(H)_2P_2$ planes of such a dodecahedron are defined by Re, P(2), and P(20) and by Re, P(11), and P(29); two hydrides will lie in each plane, each located crudely *transoid* to a phosphorus.

Each phosphine adopts a rotational conformation about the Re–P bond such that the transoid C–P–Re–P–C units are entirely (±0.06 Å) planar, and in a W conformation; the carbons in this array are methyl groups (C(10), C(27), C(18), C(36)). This directs the other two substituents on any phosphorus into the octants "vacated" by the two cis phosphines. The location of the phenyl group on P(2) destroys what would otherwise be S_4 symmetry of the cation, but this has no influence on the bond distances or angles involving P(2). There is no graphitic (face-to-face) stacking of phenyl rings within the cation (Figure 2).

The structure of $ReH_4(PMe_2Ph)_4^+$ is quite similar to that of dodecahedral $Mo(H)_4(PMePh_2)_4$[15] and also (remarkably!) to that of $Rh(PMe_2Ph)_4^+$ (which crystallizes in a different space group[16]). While the approximate S_4 symmetry of the ReP_4 unit is consistent with a tetrahydride formulation, it must be admitted that it could also be interpreted in terms of an $Re(H_2)_2(PMe_2Ph)_4^+$ formulation. Only the less symmetric $Re(H)_2(H_2)(PMe_2Ph)_4^+$ formulation is strongly excluded. The "openness" around the metal in Figure 2 indicates ample room to accommodate the hydride ligands.

Proton-Transfer Reactivity. To explore the possibility that the lack of reactivity of $ReH_4P_4^+$ was due to steric inhibition, we attempted transfer of a small and highly mobile ligand: simple proton transfer to NEt_3. We find no reaction between these reagents over 24 h in CH_2Cl_2. To test whether this, too, was kinetic[17] or thermodynamic in origin, we attempted to establish equilibrium 1 from the left side. In fact, ReH_3P_4 reacts with

$$ReH_3P_4 + HNEt_3^+ \rightleftharpoons ReH_4P_4^+ + NEt_3 \qquad (1)$$

equimolar $[HNEt_3]Br$ in CH_2Cl_2 to give complete proton transfer to rhenium! ReH_3P_4 is a stronger base than NEt_3.

Further Reactivity Studies. The reactivity of ReH_3P_4 was briefly examined. We find no reaction of ReH_3P_4 with 1 atm of ethylene in 11 h. To further explore the possibility of H_2 dissociation (eq 2), ReH_3P_4 was treated with 1 atm of D_2. Over a period of 72

$$ReH_3P_4 \overset{?}{\rightleftharpoons} ReHP_4 + H_2 \qquad (2)$$

h in toluene, there is complete conversion to $ReH_nD_{5-n}P_3$.[18] The primary reactivity of ReH_3P_4 is thus replacement of one phosphine by hydrogen, a reaction contrary to eq 2, but consistent with eq 3, followed by scavenging of ReH_3P_3 by D_2 to give $ReH_3D_2P_3$ as

$$ReH_3P_4 \rightleftharpoons ReH_3P_3 + P \qquad (3)$$

the primary product. Equation 3 has been observed to be photopromoted.[9] These several results are consistent with an $Re^{III}(H)_3$ structure assignment for this compound.

Discussion

There is increasing evidence that the presence of intact H_2 as a ligand, especially in a polyhydride complex, confers high reactivity, under mild conditions, upon Lewis bases, olefins, alkynes, etc. This occurs by H_2 dissociation (eq 4) and ligand trapping[19]

$$L_nM(H_2)^+ \rightleftharpoons L_nM^+ + H_2 \qquad (4)$$

$$L_nM^+ + L' \rightarrow L_nML'^+ \qquad (5)$$

(eq 5), although one cannot expect that every H_2 complex will display reversible H_2 dissociation.

The sum total of the reactivity tests and structural results we present here is consistent with the idea that $ReH_4P_4^+$ is a tetrahydride complex (containing no H_2 ligands) and, moreover, that it shows no tendency for H_2 loss under the conditions examined. It is thus consistent with the idea that a lack of *facile* chemical reactivity can provide supporting evidence for the absence of intact H_2 on a metal.

The proton-transfer results we report here show that a strong acid (e.g., $HBF_4{\cdot}OEt_2$) is not required to protonate ReH_3P_4. It is sufficiently basic to be protonated by $[HNEt_3]Br$ and is thus a stronger base than NEt_3. Note also that the salt resulting from this protonation, $[ReH_4P_4]Br$, shows no tendency to form ReH_2BrP_4 by displacement of any H_2 by Br^-. This represents another nucleophile that does not bind, even with the additional Coulombic attraction aiding such a process.

Given the indicated high Brønsted basicity, hence high electron density, of rhenium in $ReH_3(PMe_2Ph)_4$, it is understandable that the form $Re^V(H)_4P_4^+$ is favored over the reduced form $Re^{III}(H)_2(H_2)P_4^+$, containing H_2. Thus, the controlled production of new H_2 complexes by protonation of metal hydrides (eq 6) will

$$L_nM^qH + H^+ \rightarrow L_nM^{q-1}(H_2)^+ \qquad (6)$$

succeed only when the ancillary ligand set L_n and the initial metal oxidation state q are primed to resist oxidation. In $ReH_3(PMe_2Ph)_4$, this is not the case.

Transition-metal polyhydrides most commonly contain tertiary phosphines as companion ligands: $MH_m(PR_3)_n$. Some polyhydrides are also known with Cp and phosphine as coligands: $CpIr(PMe_3)H_3^+$,[20,21] Cp^*IrH_4,[22] and Cp^*ReH_6.[23] Noticeably absent are polyhydride carbonyls, $MH_m(CO)_n$ ($n \geq 3$). We suggest, on the basis of the results reported here, that such compounds are nonexistent because π-acid companion ligands make the metal more difficult to oxidize, thus favoring H_2 as the ligand. The resulting H_2 complex I (eq 7), with little of the back-donation to H_2 that would be required for strong binding of H_2, can dissociate to the 16-electron species II, leading to (hydride-bridged) clusters.[24] The consistent occurrence of multiple hydride ligands accompanied by strong donor ligands is thus comprehensible. Moreover, as the number of donor ligands declines, aggregation is observed even for phosphine as coligand (eq 8).

$$\begin{tikzcd}
(OC)_nH_{m-2}M(H)_2 \arrow[r, shift left, "?"] & (OC)_nH_{m-2}M(H)_2 \arrow[l, shift left] \arrow[r, shift left] & (OC)_nH_{m-2}M + H_2 \arrow[l, shift left] \\
 & \mathrm{I} & \mathrm{II} \arrow[d] \\
 & & \text{clusters} \qquad (7)
\end{tikzcd}$$

$$\begin{tikzcd}
ReH_7(PPh_3)_2 \arrow[r, shift left] & ReH_5(PPh_3)_2 + H_2 \arrow[l, shift left] \arrow[d, "-2H_2"'] \qquad (8) \\
 & {}^1/_2Re_2H_8(PPh_3)_4
\end{tikzcd}$$

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Registry No. $ReH_3(PMe_2Ph)_4$, 79245-24-2; $ReCl_3(PMe_2Ph)_3$, 15613-32-8; $[ReH_4(PMe_2Ph)_4]BF_4$, 123674-41-9; PhCCPh, 501-65-5; CH_3CN, 75-05-8; CO, 630-08-0; D_2, 7782-39-0; $[HNEt_3]Br$, 636-70-4; ethylene, 74-85-1.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table S1) and full crystallographic data (Table S2) (3 pages); a listing of observed and calculated structure factors (Table S3) (10 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Studies of Nickel(II) Complexes of 14-Membered *trans*-N_2O_2 and *trans*-N_2S_2 Quadridentate Macrocycles

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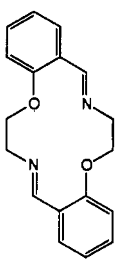
Triphenylphosphine reacts with 2-(2-azidoethoxy)benzaldehyde in an aza-Wittig reaction to give a 98% yield of the unsaturated 14-membered *trans*-N_2O_2 diimine macrocycle 6,7,15,16-tetrahydrodibenzo[*f,m*][1,8,4,11]dioxadiazacyclotetradecine (**1**), presumably via seven-membered 2,3-dihydro-1,4-benzoxazepine (**7**). Reduction of diimine **1** with lithium aluminum hydride gives the *trans*-N_2O_2 diamine macrocycle 6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11]dioxadiazacyclotetradecine (**2**). The structure of $[NiCl_2(\mathbf{2})]$ has been determined by X-ray diffraction. The dichloronickel(II) complex of the corresponding *trans*-N_2S_2 macrocycle 6,7,8,9,15,16,17,18-octahydrodibenzo[*f,m*][1,8,4,11]dithiadiazacyclotetradecine (**4**) has also been prepared and structurally characterized. For $[NiCl_2(\mathbf{2})]$ at −150 °C: space group $P\bar{1}$ (No. 2), $a = 9.092\ (4)$ Å, $b = 9.803\ (4)$ Å, $c = 10.431\ (4)$ Å, $\alpha = 92.34\ (3)°$, $\beta = 104.34\ (3)°$, $\gamma = 97.31\ (3)°$, $Z = 2$, $R = 0.044$ for 1309 data with $I > 3\sigma(I)$. For $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ at −150 °C: space group $P2_1/n$ (nonstandard No. 14), $a = 8.901\ (2)$ Å, $b = 12.031\ (3)$ Å, $c = 19.120\ (5)$ Å, $\beta = 98.50\ (2)°$, $Z = 4$, $R = 0.046$ for 1712 data with $I > 3\sigma(I)$. In octahedral $[NiCl_2(\mathbf{2})]$ the arrangement of the macrocyclic donor atoms around the metal ion is approximately square planar. In $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ the *trans*-N_2S_2 ligand adopts a folded conformation with the metal ion situated outside of the binding cavity. These structures suggest that the binding cavity of the *trans*-N_2S_2 macrocycle is smaller than that of the *trans*-N_2O_2 ligands, in contrast to the situation for similar *cis*-N_2X_2 macrocycles.

Introduction

Structural, kinetic, thermodynamic, and spectroscopic studies on a variety of macrocyclic complexes of nickel(II) have shown that there is a correlation between the radius of the binding cavity of the macrocycle and the covalent radius of the metal ion.[1-4] In particular, studies of quadridentate macrocycles with N_2X_2 (X = N, O, S) donor atom sets have demonstrated that high-spin nickel(II) is best accommodated by macrocyclic rings containing 15 or 16 atoms and that 14-membered rings are the minimum size for the ion.[1,2] Those studies estimated the binding cavity radius (R_A in Figure 1) of a macrocycle in its planar chelating conformation by subtracting the mean value of the radii of the donor atoms from the mean of the centroid–donor atom distances (R_H in Figure 1).[5] It is apparent from Figure 1, however, that the binding cavities of *trans*-N_2X_2 macrocycles will be smaller than the cavities of similar *cis*-N_2X_2 macrocycles when the radii of the X donors are larger than the radii of the N donors. A better estimate of R_H in *trans*-N_2X_2 macrocycles would be obtained by considering the centroid–X donor bond distances only. This point has not been adequately investigated hitherto because of the small number of *trans*-N_2X_2 macrocycles available.

We have recently reported the syntheses of 14- and 16-membered dibenzo-substituted *trans*-N_2S_2[6,7] and *trans*-As_2N_2[8] macrocycles. We now describe a convenient synthesis of the corresponding *trans*-N_2O_2 macrocycles **1** and **2** and the crystal and molecular structure of $[NiCl_2(\mathbf{2})]$. For comparison we have also prepared $[NiCl_2(\mathbf{4})]\cdot 0.5H_2O$ and determined its structure. Since the crystal and molecular structures of the dichloronickel(II) complexes of the cis analogues of **2** and **4** are known,[3,9] we were therefore able to compare the relative merits of the two types of chelating agents for the nickel(II) ion.



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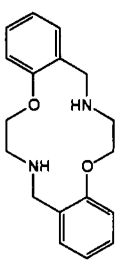

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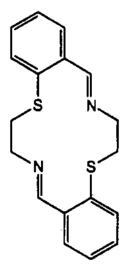

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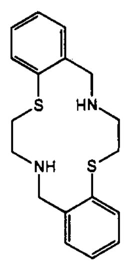

4

Results and Discussion

Syntheses. The diiodonickel(II) complex of the *trans*-N_2O_2 diimine macrocycle **1** was originally prepared in low yield by prolonged heating of bis((iodoethyl)salicylideneaminato)nickel(II) in boiling acetone.[9] The cyclization of the *iodoethyl complex* also occurred when the solid was heated at 140 °C for 3–16 h in vacuo. The free ligand **1** was subsequently obtained from the complex by displacement with sodium ethylenediaminetetraacetate. We

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