Low Temperature Multinuclear NMR Study of the Mechanism of Protonation of $W(H)_2Cl_2(PMe_2Ph)_4$[†]

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Protonation (CF_3SO_3H) of $WH_2Cl_2L_4$ (L = PMe_2Ph) below −70 °C in CD_2Cl_2 gives **A** as the kinetic product. This shows two hydride signals at −85 °C, and inequivalent (A_2M_2) ^{31}P nuclei. By −70 °C, the kinetic product converts completely to the thermodynamic product $W^{VI}(H)_3Cl_2L_4^+$, **B**, which has fluxional hydrides but inequivalent (A_2M_2) ^{31}P nuclei. The W−P coupling constants, the W/H T_1 value of **B**, and the green color of **A** support metal oxidation state IV for **A** and VI for **B**. By −30 °C, **B** reacts further to dissociate one phosphine, to produce stereochemically-rigid, C_3-symmetric $W^{VI}(H)_3Cl_2L_3^+$, **C**. Both the ^1H and ^{31}P NMR spectral patterns and the W−P coupling constant support the claimed oxidation state of W(VI) in **C**. Above 10 °C, **C** decomposes both in solution (CH_2Cl_2 or toluene) and also as a pure solid to a variety of uncharacterized products. Comparison to the result of protonation of $W(H)_2XYL_4$ (XY = Br_2, I_2, ClI, ClBr) support certain structural proposals for **A**−**C** and indicate how the diminished X→W π-donation by the heavier halides influences these oxidative and phosphine dissociation processes.

Introduction

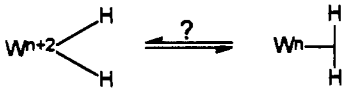
Compounds containing simultaneously halide and H_2 as ligands are rare.[1] We report here the results of a study designed to evaluate the interaction of a weak π-donor ligand (chloride) with coordinated H_2. The combination of the π-acid H_2 ligand with a π-donor could lead to strengthening of H_2 binding by a push/pull interaction. This reasoning suggests that an $L_nMCl(H_2)$ compound might resist H_2 loss.

On the other hand, the *evolution* of H_2 subsequent to protonation of an 18-valence electron metal hydride compound HML_n (eq 1) is very dependent upon the availability of a

$$HML_n + H^+ \rightarrow H_2ML_n^+ \xrightarrow{?} H_2 + ML_n^+ \qquad (1)$$

mechanism to alleviate coordinative unsaturation in ML_n^+. It is for this reason that detection or isolation of $H_2ML_n^+$ is often difficult or impossible when the acid involves a nucleophilic conjugate base (Cl^-, RCO_2^-, etc.),[2] or when the reaction solvent is acetonitrile or acetone, any of which can coordinate to ML_n^+ and thus improve the thermodynamics of H_2 evolution in eq 1. We have presented evidence that the *apparently* unsaturated cationic product of eq 1 can receive significant internal stabilization if one of the "spectator" ligands carries lone pairs on the α-atom. Halides and pseudohalides are prime examples, and explain why IrH_5L_2 is very reluctant to dissociate H_2, yet IrH_4ClL_2 resists H_2 loss with a $\Delta H°$ of less than 9 kcal/mol.[3−5] The rationale for this small enthalpy of H_2 binding is that the "unsaturated" species $Ir(H)_2ClL_2$ benefits from Cl→Ir π-donation.

We have to date demonstrated this effect for the later transition elements, always with a d^6 electron configuration. In seeking another electron configuration to test this, we considered, but rejected, the d^0 configuration. Although a d^0 configuration assures that the product will be an H_2 complex, the resulting lack of back-bonding to the H_2 ligand is certain to result in weak binding.[6] We explore here a case of protonation of a d^2 electron configuration, and with an earlier transition element: $W(H)_2XYL_4$ (X, Y = halide, and L = PMe_2Ph). By choosing tungsten, we benefit from having NMR coupling constants to the metal as a criterion of metal oxidation state, which proves to be a useful aid in deciding whether metal-bound hydrogens are independent ligands (**I**), or have undergone reductive coupling (**II**).



I II

We have chosen to carry out our study in poorly nucleophilic solvents, dichloromethane and toluene. The thermolabile species described here must be characterized at temperatures below −30 °C.

Experimental Section

All manipulations were carried out under an argon atmosphere in glassware dried at 110 °C before use. All solvents were thoroughly dried and degassed: ether, THF, and *n*-pentane over sodium/benzophenone, toluene over sodium, and CH_2Cl_2 (and CD_2Cl_2, respectively) over P_4O_{10}. NMR spectra were recorded on Bruker AM500 and Nicolet NT360 spectrometers. External standards: for ^{31}P, 85% H_3PO_4 (0 ppm); for ^{19}F, neat CF_3COOH (−78.45 ppm); for ^{183}W, a saturated

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[†] Dedicated to Professor Dr. Ekkehard Lindner on the occasion of his 60th birthday.

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(1) Heinekey, D. M.; Oldham, W. J. *Chem. Rev.* **1993**, *93*, 913.

(2) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1716. In $WH_5(PMePh_2)_4^+$, $J_{W,P}$ is 76.6 Hz.

(3) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300.

(4) In contrast, the binding energy of H_2 to the nonagostic (i.e., truly 16-electron) form of $W(CO)_3(PCy_3)_2$ is estimated as 20 ± 7 kcal/mol. See: Gonzalez, A.; Zhang, K.; Nolan, S.; Lopez de la Vega, R.; Mukerjee, S.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

(5) Gusev, D. G.; Hauger, B. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208.

(6) This is the case for protonation of ReH_7L_2. See: Fontaine, X. L. R.; Fowler, E. H.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1988**, 482.

0020-1669/95/1334-2894$09.00/0

solution of Na_2WO_4 in H_2O/D_2O (7:3) (0 ppm). For ^2H NMR, the natural ^2H abundance of the protio solvent served as standard. All negative chemical shifts are upfield. 2D (^1H, ^{183}W) heteronuclear multiple quantum coherence (HMQC) experiments and ^1H and $^{31}P\{^1H\}$ NMR measurements for the protonation studies were made with a 5 mm (inverse) ^1H/broad-band probe on the Bruker AM500 instrument. For the protonation studies, this enabled recording of signals of both nuclei (^1H and ^{31}P) within 15 min without significant temperature change. For the 2D indirect (^1H, ^{183}W) experiments, the 90° pulse lengths were determined as 12.8 μs (^1H) and 30 μs (^{183}W). For the HMQC sequence and sequence 2 (see text), a 16-step phase cycling was employed. Sixteen scans were used for measurements with pulse sequence 2 as well as for every increment of the HMQC experiments. Magnitude mode, zero-filling, and apodization with a shifted sinebell window resulted in the 2D spectra presented. For the calculation of the ^{183}W chemical shifts, the absolute frequency of the cross peaks of the 2D spectra was determined and related to the frequency of a saturated solution of Na_2WO_4 in H_2O/D_2O. At T = 300 K, this frequency was 20.837660 MHz. In the 2D spectra presented, labeling of the F_1 axis (^{183}W) shows the deviation from the employed ^{183}W carrier frequency. The labels of the F_2 axis display directly the ^1H chemical shift in Hz. About 10 mg of compound in 0.5 mL of solvent was used (C_6D_6 for $WH_2Cl_2L_4$, CD_2Cl_2 for $[WH_3Cl_2L_3][CF_3SO_3]$ (**C**)). For $WH_2Cl_2L_4$, 64 increments were distributed over a spectral width of 8000 Hz in the first HMQC experiment; 128 increments over 50 000 Hz were used for **C**.

The protonation studies, except for the attempts to isolate $[WH_3Cl_2L_3]^+[CF_3SO_3]^-$, were performed directly in NMR tubes which were then quickly introduced in the precooled probe. CD_2Cl_2 was used as a solvent in most cases (CH_2Cl_2 for ^2H experiments). The complexes WH_2XYL_4 (X,Y = F, Cl, Br, I) showed slow decomposition in CD_2Cl_2 over a period of 24 h at 20 °C, but were stable at temperatures below 0 °C. In cases where temperatures below −85 °C were required, 5% of toluene-d_8 was added to the CD_2Cl_2 solutions, which allowed measurements down to −110 °C. However, H/D exchange between CF_3SO_3H and the aromatic part of toluene-d_8[7] led to strongly increased and interfering ^1H NMR peaks in the aromatic region. All metathesis attempts to exchange the halide ligands in WCl_2L_4 or $WH_2Cl_2L_4$ with sodium or potassium salts MX (X = F, Br, I) failed under various conditions (i.e., toluene or THF, up to 80 °C). Only the metathesis of WCl_2L_4 and an excess of LiI resulted in the formation of WI_2L_4 (see below). Use of CsF with 18-crown-6 or $NBu_4F{\cdot}H_2O$ to introduce a fluoride ligand in $WH_2Cl_2L_4$ gave <5% of WH_2ClFL_4 after 7 days in THF at 20 °C. WCl_2L_4,[8] $WH_2Cl_2L_4$,[9] and $NBu_4(SnF_2Ph_3)$[10] were synthesized according to published procedures. Spectral data are collected in Table 1.

$WH_2Br_2L_4$. A 223.5 mg (0.276 mmol) sample of $WH_2Cl_2L_4$ was dissolved in 20 mL of toluene. At 20 °C, an excess of $SiMe_3Br$ (1 mmol) was added and the solution was vigorously stirred for 1 h. Removal of the solvent and washing of the residue three times with 1 mL of n-pentane resulted in the isolation of $WH_2Br_2L_4$ as a bright orange powder in quantitative yield.

$WH_2I_2L_4$. (**a**) A 283.2 mg (0.350 mmol) sample of $WH_2Cl_2L_4$ was added to 2 mL of toluene (not all of the solid dissolved in this volume). After addition of an excess of $SiMe_3I$ (1 mmol) to the suspension, the orange color of the solution slowly turned brownish red due to the formation of WI_2L_4. After 1/2 h of stirring at 20 °C, 5 mL of n-pentane was added. $WH_2I_2L_4$ precipitated, whereas the more soluble WI_2L_4 stayed in solution. The solution was decanted and the remaining orange precipitate was washed twice with 1 mL of n-pentane. $WH_2I_2L_4$ was carefully dried with a stream of H_2. Yield: 302 mg (87%).

(**b**) (**1**) **WI_2L_4.** A 403.2 mg (0.499 mmol) sample of WCl_2L_4 was dissolved in 10 mL of toluene. Then 1368.5 mg (10 mmol) of LiI was added, and the suspension was stirred for 24 h at 20 °C during which time the orange solution turned red. The solution was filtered over Celite. The residue was washed twice with 5 mL of toluene, and the washing liquids were filtered, too. The combined toluene solutions were concentrated almost to dryness (~0.5 mL of toluene left). 2 mL of n-pentane was added. After 12 h at −20 °C, the solution was decanted from an orange-red precipitate. The solid was dried under high vacuum and yielded 455 mg of pure WI_2L_4 (92%). ^1H NMR (toluene-d_8, 25 °C, 500 MHz): 10.9 (t, $^3J_{HH}$ = 6.9 Hz, p-phenyl, 4H), 10.7 (br s, phenyl, 8H), 8.1 (br s, phenyl, 8H), 0.3 (br s, CH_3, 24H).

(**2**) In one arm of a Y-shaped reaction tube, 150.2 mg (0.152 mmol) of WI_2L_4 was dissolved, in a minimum of toluene (~0.7 mL). The solution was frozen, evacuated, and put under 1 atm of H_2. After thawing, the solution was stirred for 12 h at 20 °C. The resulting precipitate of $WH_2I_2L_4$ was allowed to settle, and the solution was carefully decanted into the second arm of the reaction container. The solid was washed twice with 1 mL of n-pentane and dried with a stream of H_2. Yield: 145.2 mg (96%).

WH_2ClFL_4. A 248 mg (0.31 mmol) sample of $WH_2Cl_2L_4$ was dissolved in 5 mL of THF. A 202 mg (0.32 mmol) sample of $NBu_4SnF_2Ph_3$ was added and the solution stirred for 1/2 h at 20 °C. After complete removal of the solvent, the solid showed ^1H and $^{31}P\{^1H\}$ NMR signals for WH_2ClFL_4 and a small amount of $WH_2F_2L_4$ (<2%). The solid was treated with 1 mL of toluene and 2 mL of n-pentane. The suspension was kept at −20 °C for 12 h to yield more solid WH_2ClFL_4. Decanting of the liquid and drying of the residue yielded 189 mg of pure WH_2ClFL_4 (78%). In contrast to WH_2ClXL_4 (X = Br, I), WH_2ClFL_4 is not in equilibrium with $WH_2Cl_2L_4$ and $WH_2F_2L_4$. It is impossible to completely substitute the second chloride ligand in WH_2ClFL_4 by use of a large excess of $NBu_4SnF_2Ph_3$. A 10-fold excess of $NBu_4SnF_2Ph_3$ resulted in the observation of about 40% of $WH_2F_2L_4$. The compound could not be separated from the remaining WH_2ClFL_4.

WH_2BrClL_4 and WH_2ClIL_4. Equimolar amounts of $WH_2Cl_2L_4$ and the corresponding complex $WH_2X_2L_4$ (X = Br, I) were dissolved in toluene and stirred for 16 h. ^1H and $^{31}P\{^1H\}$ NMR investigations indicated the formation of the mixed WH_2ClXL_4 complexes in equilibrium with both starting materials.

Protonations. The protonations followed in all cases the same procedure. As an example, the protonation of $WH_2Cl_2L_4$ is described. A 25.0 mg (0.031 mmol) sample of $WH_2Cl_2L_4$ was dissolved in 0.3 mL of CD_2Cl_2 in an extended-length NMR tube attached to an inert gas valve. In a second container, 4.7 mg (0.031 mmol) of CF_3SO_3H was mixed with 0.2 mL of CD_2Cl_2. Excess acid led to side reactions. The NMR tube was cooled to −85 °C. Via cannula, the CD_2Cl_2 solution of CF_3SO_3H was added. In most cases, the solution turned immediately bright green. If the addition was slow, the local heating was insufficient for the protonation and the solution stayed orange. The solution was then frozen in liquid nitrogen, pumped for 5 min, and flame sealed. The tube was returned to the −85 °C bath. Care was taken to expose almost the whole NMR tube to the cooling liquid. Insufficient cooling during the thawing process, where the CD_2Cl_2 solution started to boil, led to an immediate color change to pink-red indicating the decomposition of the sample. In cases where the solution stayed orange during the whole procedure, the NMR tube was taken out of the cooling liquid, tipped twice, and immediately cooled again. This allowed us to study kinetically-trapped **A**.

Isolation of Compound C, $[W(H)_3(PMe_2Ph)_3Cl_2]SO_3CF_3$. The synthesis was executed at −20 °C in CH_2Cl_2 and the solvent was removed under vacuum at −20 °C. The resulting oily orange residue was triturated for 0.5 h with n-pentane at −40 °C, to yield a yellow precipitate. The precipitate was then washed extensively with cold Et_2O and n-pentane, to ensure complete removal of free phosphine, any excess acid, or $[HPMe_2Ph]O_3SCF_3$. The remaining pale yellow powder was dried under high vacuum at −40 °C. However, when this solid was brought to 25 °C, it became brown and sticky and evolved a gas (H_2 by ^1H NMR). The ^1H NMR spectrum of the foamy residue showed a number of signals.

Results

Synthesis. For the purpose stated in the Introduction, it was necessary to prepare a series of analogous hydrides of general formula $W(H)_2XYL_4$ ($L = PMe_2Ph$). The compounds $W(H)_2$-

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(7) (a) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69. (b) Taylor, R.; Tewson, T. J. *J. Chem. Soc., Chem. Commun.* **1973**, 836. (c) Bakoss, H. J.; Ranson, R. J.; Roberts, R. M. G.; Sadri, A. R. *Tetrahedron* **1982**, *38*, 623.

(8) Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808.

(9) Rothfuss, H.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 2946.

(10) Gingras, M. *Tetrahedron Lett.* **1991**, *32*, 7381.

Table 1. NMR Spectral Data[p]

	$\delta(^1H)$, ppm	$\delta(^{31}P\{^1H\})$, ppm
$WH_2F_2L_4$[c]	1.45 (vt, $N = 7.9$ Hz, 12H, CH_3−P), 1.40 (vt, $N = 6.8$ Hz, 12H, CH_3−P), 0.09 (m, 2H, H−W)	2.3 {t ($J_{P,P} = 18.2$ Hz) of vt (FF′PP′, $N = 168.8$ Hz), 2P}, −6.1 {t ($J_{P,P} = 18.2$ Hz) of t ($J_{P,F} = 47.3$ Hz), 2P}
$WH_2Br_2L_4$	7.38−7.41 (m, 4H, Ph−H), 7.27−7.30 (m, 4H, Ph−H), 6.94−7.08 (m, 12H, Ph−H), 1.69 (vt, $N = 7.7$ Hz, 12H, CH_3−P), 1.61 (vt, $N = 8.3$ Hz, 12H, CH_3−P), −2.60 (t ($J_{P,H} = 60.7$ Hz) of HH′PP′ ($J_{P,H} + J_{P,H'} = 77.0$ Hz (with satellites ($J_{W,H} = 14.7$ Hz)), 2H, H−W)	−18.7 {t ($J_{P,P} = 16.2$ Hz) with satellites ($J_{W,P} = 154.7$ Hz), 2P}, −23.2 {t ($J_{P,P} = 16.2$ Hz) with satellites ($J_{W,P} = 182.0$ Hz), 2P}
$WH_2I_2L_4$[a,b]	7.38−7.41 (m, 8H, Ph−H), 6.94−7.09 (m, 12H, Ph−H), 1.83 (vt, $N = 7.5$ Hz, 12H, CH_3−P), 1.64 (vt, $N = 8.2$ Hz, 12H, CH_3−P), −4.35 (t ($J_{P,H} = 62.0$ Hz) of HH′PP′ ($J_{P,H} + J_{P,H'} = 79.6$ Hz (with satellites ($J_{W,H} = 18.4$ Hz)), 2H, H−W)	−32.2 {t ($J_{P,P} = 18.1$ Hz) with satellites ($J_{W,P} = 155.3$ Hz), 2P}, −40.1 {t ($J_{P,P} = 18.1$ Hz) with satellites ($J_{W,P} = 173.9$ Hz), 2P}
WH_2ClFL_4[d,e]	6.98−7.57 (m, 20H, Ph−H), 1.82 (d, $J_{P,H} = 7.9$ Hz, 6H, CH_3−P), 1.59 (vt, $N = 7.1$ Hz, 6H, CH_3−P), 1.42 (vt, $N = 6.7$ Hz, 6H, CH_3−P), 1.08 (d, $J_{P,H} = 8.4$ Hz, 6H, CH_3−P), −0.70 (d, $J_{F,H} = 13.1$ Hz), −0.70 (d ($J_{F,H} = 13.1$ Hz) of d ($J_{P,H} = 49.1$ Hz) of d ($J_{P,H} = 66.2$ Hz) of HH′PP′ ($J_{P,H} + J_{P,H'} = 73.7$ Hz), 2H, H−W)	0.4 {t ($J_{P,P} = 12.2$ Hz) of d ($J_{P,P} = 56.5$ Hz) of d ($J_{P,F} = 64.6$ Hz), 1P}, −6.7 {t ($J_{P,P} = 12.6$ Hz) of d ($J_{P,P} = 56.5$ Hz) of d ($J_{P,F} = 83.5$ Hz), 1P}, −10.8 (apparent triplet (d of d: 12.2 and 12.6 Hz) of d ($J_{P,F} = 53.3$ Hz), 2P}
WH_2BrClL_4[e,f]	1.49 (d, $J_{P,H} = 8.4$ Hz, 6H, CH_3−P), −2.00 (d ($J_{P,H} = 59.2$ Hz) of d ($J_{P,H} = 61.9$ Hz) of HH′PP′ ($J_{P,H} + J_{P,H'} = 76.3$ Hz) with satellites ($J_{W,H} = 10.8$ Hz), 2H, H−W)	−14.0 {d ($J_{P,P} = 60.1$ Hz) of t ($J_{P,P} = 15.7$ Hz) with satellites ($J_{W,P} = 174.0$ Hz), 1P}, −19.2 {d ($J_{P,P} = 60.1$ Hz) of t ($J_{P,P} = 15.8$ Hz) with satellites ($J_{W,P} = 180.4$ Hz), 1P}, −20.4 {apparent triplet (d of d: 15.7 and 15.8 Hz) with satellites ($J_{W,P} = 187.8$ Hz), 2P}
WH_2ClIL_4[a,f,g]	2.21 (vt, $N = 8.1$ Hz, 6H, CH_3−P), 2.03 (vt, $N = 8.2$ Hz, 6H, CH_3−P), 1.79 (d, $J_{P,H} = 8.0$ Hz, 6H, CH_3−P), 1.29 (d, $J_{P,H} = 8.9$ Hz, 6H, CH_3-P), −2.76 (d ($J_{P,H} = 58.0$ Hz) of d ($J_{P,H} = 64.9$ Hz) of HH′PP′ ($J_{P,H} + J_{P,H'} = 77.8$ Hz), 2H, H−W)	−25.5 {apparent triplet, 2P}, −26.5 {d ($J_{P,P} = 65.0$ Hz) of t ($J_{P,P} = 17.2$ Hz), 1P}
A[e,h,i]	+2.4 (br), −2.5 (apparent quintet, H−W)	16.3 {br ($\Delta = 883$ Hz), 2P}, −1.6 {br ($\Delta = 373$ Hz), 2P}
$[WH_3Cl_2L_4]$-$[CF_3SO_3]$, **B**[c,h,k]	7.32−7.48 (m, 12H, Ph−H), 7.14 (m, (br), 4H, Ph−H), 7.01 (m, (br), 4H, Ph−H), 2.91 (t ($J_{P,H} = 39.4$ Hz) of t ($J_{P,H} = 63.7$ Hz) with satellites ($J_{W,H} = 39.1$ Hz), 3H, H−W), 1.75 (m, 12H, CH_3−P), 1.65 (m, 12H, CH_3−P)	−3.9 {t ($J_{P,P} = 47.1$ Hz) with satellites ($J_{W,P} = 58.5$ Hz), 2P}, −12.0 {t ($J_{P,P} = 47.1$ Hz) with satellites ($J_{W,P} = 103.1$ Hz), 2P}
$[WH_3Cl_2L_3]$-$[CF_3SO_3]$, **C**[c,h,l]	7.17−7.89 (m, Ph−H), 2.75 (m, spacing of outer lines: 190.7 Hz, 3H, H−W), 1.66 (m, 18H, CH_3−P)	2.9[m] {s with satellites ($J_{W,P} = 81.4$ Hz)}
B-ClBr[e,h,n]		−6.9 {d ($J_{P,P} = 50.6$ Hz) of t ($J_{P,P} = 52.2$ Hz), 1P}, −12.3 {d ($J_{P,P} = 50.6$ Hz) of t ($J_{P,P} = 44.1$ Hz), 1P}, −18.7 {d ($J_{P,P} = 52.2$ Hz) of d ($J_{P,P} = 44.1$ Hz), 2P}
B-Br_2[e,h,k]	7.01−7.44 (m, 20H, Ph−H), 1.69−1.92 (m, 24H, CH_3−P), 1.76[o] (m, 3H, H−W)	−14.4 {t ($J_{P,P} = 48.6$ Hz) with satellites ($J_{W,P} = 54.6$ Hz), 2P}, −25.4 {t ($J_{P,P} = 48.6$ Hz) with satellites ($J_{W,P} = 96.5$ Hz), 2P}
C-Br_2[c,h,l]	7.16−7.81 (m, Ph−H), 1.71 (m, 18H, CH_3−P), 1.25 (m, spacing of outer lines: 187.6 Hz, 3H, H−W)	−11.1 {s with satellites ($J_{W,P} = 74.9$ Hz)}

[a] In toluene-d_8. [b] Due to the equilibrium in eq 2, ^1H NMR spectra contain additional signals of free H_2, PMe_2Ph, and WI_2L_4. [c] $\delta(^{19}F)$: −225.1 ppm (m). Pure $WH_2F_2L_4$ is not obtainable by metathesis of $WH_2Cl_2L_4$ and $[NBu_4][SnF_2Ph_3]$ (see discussion). Therefore phenyl protons are not assigned. [d] $\delta(^{19}F)$: −223.4 ppm (m). [e] $^{31}P\{^1H\}$ NMR at 202 MHz. [f] There is overlap of signals with $WH_2Cl_2L_4$ and $WH_2X_2L_4$ (X = Br, I) in the phenyl and the methyl region. [g] In $^{31}P\{^1H\}$ NMR, one signal group not assignable due to overlap with $WH_2Cl_2L_4$ or $WH_2I_2L_4$. [h] In CD_2Cl_2. [i] At −85 °C. Phenyl and methyl signals were obscured by signals of $WH_2Cl_2L_4$, **B**, and already formed **C**. ^1H NMR signals were confirmed by $^2H\{^1H\}$ NMR in a control experiment: $WD_2Cl_2L_4 + CF_3SO_3D$ in CH_2Cl_2. [k] At −40 °C. [l] At −10 °C. Phenyl region contains in addition signals of free PMe_2Ph. [m] In ^{31}P NMR: apparent quartet with a spacing of outer lines of 192.0 Hz. [n] At −60 °C. Due to the presence of $WH_2Cl_2L_4$ and $WH_2Br_2L_4$ during the protonation, ^1H NMR spectra are uninformative. [o] Signal partially covered by methyl signals. Initially found for $WH_2Br_2L_4 + CF_3SO_3D$ in CH_2Cl_2. [p] General conditions: solvent C_6D_6 at 25 °C; ^1H NMR: 500 MHz; ^{19}F NMR: 340 MHz, $^{31}P\{^1H\}$ NMR: 146 MHz, or noted otherwise.

X_2L_4 (X = Br and I) are conveniently prepared from $W(H)_2Cl_2L_4$ and excess Me_3SiX in toluene. The reaction is instantaneous and the product is precipitated by addition of *n*-pentane. This may involve silicon as an electrophile, since chloride in $W(H)_2Cl_2L_4$ will have enhanced nucleophilicity due to d_π/Cl(p_π) filled−filled repulsions.[11] It is remarkable that the Me_3SiX reagent does not attack the hydride ligands.

In order to avoid decomposition according to eq 2,[12] any removal of solvent from $W(H)_2I_2L_4$ solutions was done by purging with an H_2 stream. $W(H)_2I_2L_4$ is not accessible from $W(H)_2Cl_2L_4$ by metathesis with alkali metal iodide. However, excess LiI (but not NaI or KI) does convert WCl_2L_4 in toluene to WI_2L_4. The size mismatch of LiI is apparently crucial. Treatment of WI_2L_4 in toluene with H_2 then leads to formation of $W(H)_2I_2L_4$, although the equilibria in eq 2 are responsible for some WI_2L_4 remaining under 1 atm of H_2.

$$W(H)_2I_2L_4 \overset{\pm L}{\rightleftharpoons} W(H)_2I_2L_3 \overset{\pm H_2}{\rightleftharpoons} WI_2L_3 \overset{\pm L}{\rightleftharpoons} WI_2L_4 \quad (2)$$

In an attempt to obtain fluoro analogs, several approaches were tested. M^IF (M^I = Na, K, and Cs) failed to replace chloride in $W(H)_2Cl_2L_4$. 18-Crown-6 was ineffective as a halide exchange promoter except in the case of CsF, where a small conversion to $W(H)_2ClFL_4$ was noted (^1H and $^{31}P\{^1H\}$ NMR)

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(11) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

(12) Compare Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353.

(13) This is one of the strongest acids known. See: Viggiano, A. A.; Henchman, M. J.; Dale, F.; Deakyne, C. A.; Paulson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 4299.

(14) A reviewer has suggested that the color might be due to MLCT excitation. This is a viable alternative.

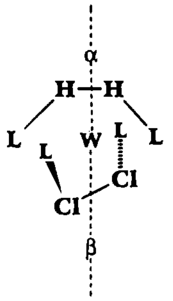
after 1 week. The reagent $[(n\text{-}Bu)_4N]SnPh_3F_2$ is more effective; in THF, it converts $W(H)_2Cl_2L_4$ (1:1 mole ratio) quantitatively to $W(H)_2ClFL_4$. However, a complete substitution of the second chloride proved impossible since this conversion is an equilibrium process. Even a large excess (i.e., a saturated THF solution) of the tin reagent gave only 40% conversion to $W(H)_2F_2L_4$.

Mixed halide complexes $W(H)_2ClYL_4$ (Y = Br or I) are rapidly obtained by mixing equimolar $W(H)_2Cl_2L_4$ and $W(H)_2Y_2L_4$ in toluene (eq 3). These are equilibrium reactions and so the mixed halide species cannot be isolated pure.

$$W(H)_2Cl_2L_4 + W(H)_2Y_2L_4 \rightleftharpoons 2W(H)_2ClYL_4 \qquad (3)$$

Two Products of Protonation. Addition of a CD_2Cl_2 solution of CF_3SO_3H[13] to a CD_2Cl_2 solution of an equimolar amount of $WH_2Cl_2L_4$ (L = PMe_2Ph) at −90 °C gives an immediate color change to bright green (**A**). The visible absorption by this product indicates that it still contains the d electrons of W(IV), since the d^0 configuration of W(VI) in $W(H)_3Cl_2L_4]^+$ would be less likely to have low energy excitations.[14] This might suggest that **A** is the dihydrogen compound $W(H_2)(H)Cl_2L_4]^+$. A sample of **A** in CD_2Cl_2 was produced and sealed in an NMR tube at −90 °C, then placed in an NMR probe precooled to −85 °C. Under these conditions, the green species **A** was the major component (in addition to $WH_2Cl_2L_4$ and **B**; see below), and exhibited two equally intense, broad ($\Delta\nu_{1/2}$ = 370 and 880 Hz) $^{31}P\{^1H\}$ NMR resonances at 14.0 and −2.4 ppm. Species **A** showed two hydride signals at −2.5 and +2.4 ppm. Whereas the low field signal was broad and unresolved, the high field signal displayed a fine structure (apparent quintet). Overlap of the hydride resonance of **B** and the methyl protons prevented a meaningful integration of the low field signal. The methyl region of the ^1H NMR spectrum is not useful due to the presence of $WH_2Cl_2L_4$ and of product **B** (see below).

Alternatively, **A** could be an adduct of $WH_2Cl_2L_4$ and CF_3SO_3H, with the latter located on the C_2 axis of the former, either on the hydride side (α) or on the chloride side (β).



The interaction at α will be of a proton in the acid with the electron-rich hydride ligands. The interaction at β will be with the chloride lone pairs. Because of the filled−filled interactions in $WH_2Cl_2L_4$, the HOMO will have significant chlorine, in addition to tungsten, character. This interaction might equally well be called a charge transfer complex. In either case, the symmetry of the ^{31}P nuclei is in agreement with that observed, and the two hydrogen chemical shifts will be those of hydrides and the acid proton. Because of the metastability of **A**, we were unable to measure T_1 and thus distinguish these several structural models for **A**.

Warming the sample above −70 °C completed the protonation (i.e., $WH_2Cl_2L_4$ was consumed) but also converted all **A** to **B**. The solution was now yellow-orange, consistent with[15] a redox change to a d^0 configuration for species **B**. We assign formula $W^{VI}(H)_3Cl_2L_4^+$ to **B**.

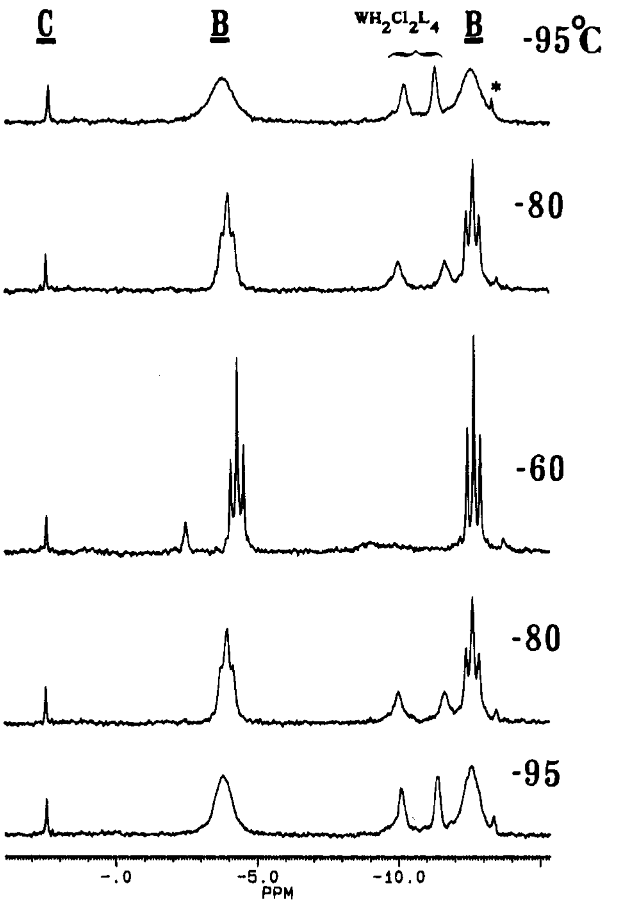


Figure 1. $^{31}P\{^1H\}$ NMR spectra showing the thermal reversal of the equilibrium for protonation of WH_2Cl_2 to $WH_3Cl_2L_4^+$ (**B**). One cycle from −95 to −60 °C and then to −95 °C has already been executed, to consume all **A**, and the cycle portrayed here begins at the bottom. Each higher spectrum involves a time delay of 30 min, for thermal equilibration. A small and constant amount of **C** is present, along with a trace impurity (asterisk).

Protonation Is an Equilibrium Process.[16] Remarkably, the protonation of $WH_2Cl_2L_4$ is reversible below −70 °C. Cooling the solution containing solely **B** (prepared at −70 °C) down to −80 °C led to re-formation of $WH_2Cl_2L_4$ (20%). The amount of $WH_2Cl_2L_4$ increased to 25% upon further cooling to −95 °C.

To study the reversibility of this reaction, a sample was subjected to two temperature cycles. Prepared at −90 °C, the solution was then cooled to −95 °C, subsequently warmed to −80 and −60 °C in the same steps, and then recooled to −95 °C. At every temperature, ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded (Figure 1 displays the $^{31}P\{^1H\}$ NMR spectra of the second temperature cycle). The results were highly reproducible and the ratio $[WH_2Cl_2L_4]/[\mathbf{B}]$ could be reestablished within 10 min. For the corresponding $WH_2Br_2L_4$, no such equilibrium was found under the same conditions.

Surprisingly, **A** could not be detected during the second equilibration cycle. We considered that adding a warm CD_2-

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(15) A reviewer notes that a d^0 configuration is not a *necessary* condition for only high energy transitions (yellow color).

(16) For studies of protonation and hydrogen bonding equilibria with even weak acids (e.g., alcohols), see: Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069. Epstein, L. M.; Shubina, E. S.; Krylov, A. N.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1993**, *447*, 277. Shubina, E. S.; Krylov, A. N.; Kreindlin, A. Z.; Rybinskaya, M. I.; Epstein, L. M. *J. Organomet. Chem.* **1994**, *465*, 259.

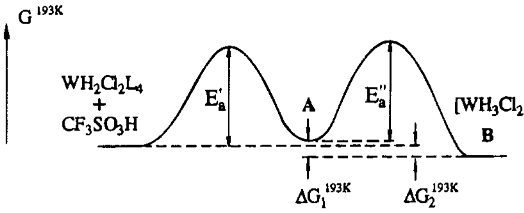


Figure 2. Semiquantitative free energy diagram for the equilibrium in eq 4.

Cl_2 solution of CF_3SO_3H (25 °C) to a solution of $WH_2Cl_2L_4$ in CD_2Cl_2 at −85 °C might have generated the energy necessary to form **A**, by local heating. To study this possibility, pure CF_3SO_3H was added to $WH_2Cl_2L_4$ in CD_2Cl_2 at −95 °C. The acid froze immediately at this temperature and dissolved slowly into the orange-yellow solution. Only in the vicinity of the frozen acid was noted some green color indicating formation of a small amount of **A**. At −85 °C, ^1H and $^{31}P\{^1H\}$ NMR spectra showed no formation of **B** and only the weak hydride and $^{31}P\{^1H\}$ NMR signals of **A** . Thus, the sample contained mostly $WH_2Cl_2L_4$ and the composition did not change for 1 h. Obviously, the protonation reaction is very slow at −85 °C or below. Subsequently, the sample was quickly taken out of the probe and manipulated twice so that its contents came in contact with the warmer top part of the tube. The solution immediately turned bright green and the $^{31}P\{^1H\}$ NMR spectrum now showed a significant amount of **A** (~20%) and a small amount of **B** (<5%) in addition to $WH_2Cl_2L_4$. Keeping the sample for 1 h at −85 °C did not change the composition, clearly demonstrating that both the protonation reaction and isomerization of **A** to **B** were kinetically trapped at −85 °C.

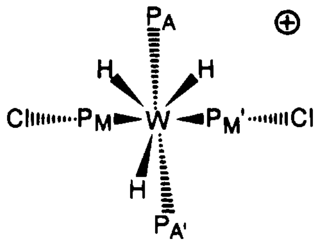
Figure 2 depicts a possible energy profile for the reactions. Both the protonation of $WH_2Cl_2L_4$ to complex **A** as well as the conversion of **A** to **B** require a higher energy than available at

$$WH_2Cl_2L_4 + CF_3SO_3H \rightleftharpoons \mathbf{A} \rightleftharpoons \underset{\mathbf{B}}{W(H)_3Cl_2L_4{}^+CF_3SO_3{}^-} \qquad (4)$$

−85 °C. Upon heating higher than −80 °C, kinetically-trapped **A** slowly transforms to **B**. The equilibrium is established and at −70 °C only **B** is observed by ^1H and $^{31}P\{^1H\}$ NMR. In the temperature range where a true equilibrium exists between the starting compound $WH_2Cl_2L_4$ and $W(H)_3Cl_2L_4{}^+$, the amount of **A** present is apparently too small to be detected by NMR.

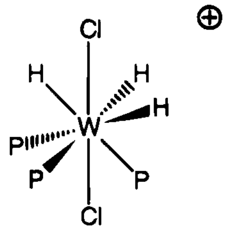
These observations permit some thermodynamic conclusions. For the transformation of $WH_2Cl_2L_4$ into **B**, ΔH must be positive. In this case, increase in starting material upon cooling requires $\Delta S > 0$ and $\Delta H < T\Delta S$. For the former to be true, CF_3SO_3H must not be dissociated in methylene chloride (see eq 4). Increased intramolecular mobility in **B** (where the hydrides are fluxional) may also contribute to the gain in entropy. At −80 °C, the proportion of $WH_2Cl_2L_4$ is approximately 20%. ΔG_2 (193 K) (see Figure 2) can be estimated (with a starting concentration of CF_3SO_3H of ~0.1 M) as being ≥ −2 kcal/mol. Due to the fact that **A** is not observed NMR spectroscopically at equilibrium, $|\Delta G_1(193\ K)| > |\Delta G_2(193\ K)|$. Under the assumption that up to 5% of **A** may stay undetected (due to its broad $^{31}P\{^1H\}$ NMR lines), $|\Delta G_1(193\ K)| - |\Delta G_2(193\ K)|$ has to be larger than 0.5 kcal.

Structure of $W(H)_3Cl_2L_4{}^+$. At −40 °C, **B** shows two triplets in the $^{31}P\{^1H\}$ NMR spectrum, and its P-CH_3 protons appear as two virtual triplets. **B** thus contains four phosphines, and the structure must have a C_2 axis or a mirror plane of symmetry. **B** shows one hydride resonance (+2.9 ppm), a triplet of triplets consistent with the A_2M_2 phosphorus pattern. The three hydrides are fluxional, but their mutual site exchange does not average the phosphorus nuclei (which are different with respect to the halides). Cooling the sample revealed strong broadening of the hydride resonance at −90 °C and decoalescence by −100 °C. At −110 °C, two separate signals were resolved. One of these (at ~2 ppm) overlapped with the P−CH_3 protons, preventing comparison of its intensity to the second signal at 3.8−4.8 ppm. The T_1(min) relaxation time of the hydrides at −40 °C and 500 MHz was determined to be 281 ms, which indicates that **B** is indeed a classical trihydride and thus W(VI). This number should be compared to 200 ms for $WH_2Cl_2L_4$ at −30 °C as T_1(min) and also 220 ms at −40 °C; all values are at 500 MHz. We propose a structure where a *facial* arrangement of three hydrides is arrayed around the C_2 axis of the $WH_2Cl_2L_4$ structure. The postulate of a facial $W(H)_3$ arrangement permits hydride fluxionality which does not average the A and M phosphorus environments. In comparison to the parent $WH_2Cl_2L_4$ molecule, the P_A-P_M coupling constant is much larger (47.1 Hz in **B** vs 14.8 Hz in $WH_2Cl_2L_4$); this may indicate a larger P_A-P_M angle after protonation. The significant decrease in W−P coupling constants (58.5 and 103.1 Hz in **B** vs 167.8 and 191.3 Hz in $WH_2Cl_2L_4$) is consistent with claimed tungsten oxidation state six in **B**.[2,17]



B

Further Reaction of $W(H)_3Cl_2L_4{}^+$. Like **A**, **B** is metastable. Above −30 °C, **B** dissociates a phosphine ligand (coordination number nine is apparently too unstable when four ligands are bulky phosphines) to form a species we characterize as $W(H)_3Cl_2L_3]^+$, **C**. Cooling **C** to −60 °C in the presence of equimolar PMe_2Ph does not reform **B**. The $^{31}P\{^1H\}$ NMR spectrum is a singlet (with $J_{W,P}$ = 81.4 Hz), but the proton-coupled ^{31}P NMR spectrum shows a higher order pattern whose outer lines have a 192 Hz spacing. The hydrides of **C** also appear (+2.75 ppm) as a higher order multiplet whose outermost lines have spacing of 191 Hz. This pattern excludes the possibility that some hydrogens are present as H_2 and shows the rigidity of the hydride ligands. The identical spacing in both ^1H and ^{31}P NMR spectra proves that the numbers of the hydride and phosphorus ligands are the same. We conclude that **C** has an AA′A″XX′X″ spin system, i.e., three chemically-equivalent hydrides and three phosphorus nuclei. Consistent



C

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(17) Compare $J_{P,W}$ = 62.5 Hz in $W^{VI}(H)_6(P^iPr_2Ph)_3$. Gregson, D.; Howard, J. A. K.; Nicholls, J. N.; Spencer, J. L.; Turner, D. G. *J. Chem. Soc., Chem. Commun.* **1980**, 572.

with these conclusions, only one $P-CH_3$ ^1H NMR multiplet is observed. Structure **C** (with a C_3 axis of symmetry) is consistent with all of these observations.

Cation **C** decomposes at 10 °C in solution. Isolated at −40 °C, it proved to be unstable even in the solid state at room temperature.

We wished an independent confirmation that **C** contains *three* phosphine ligands, and turned to ^{183}W NMR. Previous reports[18−20] of indirect heteronuclear metal NMR observation with short experimental times of dilute solutions of metallorganic compounds (<10 mg, ~1 h) drew our attention to 2D (^1H, ^{183}W) NMR. For our heteronuclear shift correlation experiments, we used the following HMQC sequence:[21] $\pi/2(^1H)-\Delta-\pi/2(^{183}W)-t_1/2-\pi(^1H)-t_1/2-\pi/2(^{183}W)-$acquisition($^1H$). Due to the large chemical shift range of ^{183}W (~11 000 ppm),[22] it is crucial to find the appropriate tungsten frequency. This can be accomplished by running the experiment first with a large frequency window (up to 50 000 Hz) and thereby a poor resolution in the F_1 (^{183}W) dimension. A second experiment with the corrected frequency in a smaller window leads to the resolution-enhanced spectrum. Nevertheless, several experiments with a large spectral width may be necessary to find the correct ^{183}W frequency. A much shorter variation to circumvent this difficulty involves the use of the following pulse sequence 2: $\pi/2(^1H)-\Delta-\pi/2(^{183}W)-\pi(^1H)-\pi/2(^{183}W)-\Delta-$acquisition-($^1H$). Subsequently, the HMQC experiments were carried out with this frequency. Originally thought to suppress the parent signal in an HX system (X = nucleus with low natural abundance) and to deliver the pure satellite spectrum, this sequence is an easy tool to determine approximately the ^{183}W frequency. The pure satellite spectrum is only obtained if the ^{183}W frequency employed is close to resonance. This experiment normally requires 16 scans and is easily executed within 5 min. Variation of the ^{183}W frequency in steps of 50 000 Hz leads to the appropriate ^{183}W resonance frequency in a rather short time. In order to test the method for our complicated high-order spin systems and to get the approximate tungsten frequency for this type of complex, we first investigated $WH_2Cl_2L_4$. Figure 3 shows the result. The top spectrum is the hydride signal in a one-dimensional ^1H NMR spectrum. $WH_2Cl_2L_4$ has an $HH'P_AP'_A(P_M)_2$ spin system. In the one-dimensional spectrum, the tungsten satellites are already recognizable. The second spectrum is the pure satellite spectrum obtained from the proton projection of the 2D experiment. For the ^{183}W projection, a triplet of triplets is expected (due to the P_A and P_M), and is observed. Due to the high-order spin system, the center lines of the hydride pattern are lower in intensity in ^1H NMR. Because ^{183}W is observed via protons, this lack of intensity is also reflected in a suppressed intensity of the center triplet (indicated with arrows) in the tungsten dimension.

For $W(H)_3Cl_2L_3]^+$ (**C**), the corresponding spectra are depicted in Figure 4. Due to the AA′A″PP′P″ spin system, there are multiple lines in the inner part of the pattern, which result in two broad central humps without significant fine structure (see top spectrum in Figure 4). All of the center lines are low in intensity. For the ^{183}W projection, this leads to the observation of only the sharp and intense outer lines of the pattern, and the central part does not show any observable tungsten satellite intensity. The same ^1H NMR spectrum was duplicated by using pulse sequence 2. Also here, the one-dimensional (^1H, ^{183}W) experiment was run first to determine the correct ^{183}W resonance frequency and the necessary W−H coupling constant for the 2D experiment. The tungsten satellites were unobservable ($J_{W,P}$ = 4.0 Hz) in an uncorrelated one-dimensional ^1H NMR spectrum. For sequence 2, Δ (= $^1/_2 J_{W,H}$) was first deliberately set to 100 ms, which allows the observation of $^1H/^{183}W$ interaction from 0.5−10 Hz.

Due to this absence of any observable intensity of the central part of the ^{183}W-correlated hydride pattern, no ^{183}W lines (information) can be expected in the center of the ^{183}W multiplet and thus here only the outer lines are observed. The separation of these lines is a multiple of the W−P coupling constant and is a measure for the multiplicity of the WP_x system. With the known W−P coupling constant of 81.4 Hz from $^{31}P\{^1H\}$ NMR, the line separation of 242 Hz in the ^{183}W projection is in excellent agreement with the expected tripled $J_{W,P}$ value. This confirms our conclusion that **C** contains three phosphine ligands.

Protonation of Other Halide Species. Although protonation of $W(H)_2Br_2L_4$ at −85 °C proceeds similarly to the chloride case, **A**-Br_2 is only visible as a faint green color and, even at −85 °C, transforms to **B**-Br_2. There is no NMR evidence for **A**-Br_2, and the ^1H and $^{31}P\{^1H\}$ NMR spectra at −85 °C show only **B**-Br_2 along with <5% of **C**-Br_2. The ^{31}P chemical shifts of the dibromo species lie 10−13 ppm upfield of their chloro analogs. The hydride chemical shift of **B**-Br_2 was obtained from the ^2H NMR spectrum of the product of CF_3SO_3D and $W(H)_2Br_2L_4$ in CH_2Cl_2,since its ^1H NMR signal is masked by the methyl signal of the coordinated phosphine. Conversion of **B**-Br_2 to **C**-Br_2 does not begin below −20 °C, but **C**-Br_2 already transforms (with H_2 evolution) at −10 °C. The hydride chemical shift of **C**-Br_2 lies 1.5 ppm upfield of **C**-Cl_2. The higher stability (compared to chloride) of $W(H)_3Br_2L_4^+$ is consistent with the greater ability of chloride π donation to stabilize a ligand-loss product.[23] Moreover, for the 18-electron species $W(H)_3X_2L_4^+$, the filled−filled interactions are larger for the stronger π-donor chloride, so phosphine ligand loss is encouraged. Bromide in **C**-Br_2 supplies less π-electron density to the metal than does chloride, and so H_2 dissociation (decomposition of **C**) is favored.

To establish that **C** still contains *both* halides, and is not the species $W(H)_3XL_3$ (solvent or triflate)$^{n+}$, $W(H)_2BrClL_4$ (as a component of an equilibrium) was treated with CF_3SO_3H. No green **A**-BrCl was detected by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy at −85 °C. At −60 °C, **B**-BrCl was detected, together with 25% each of **B**-Br_2 and **B**-Cl_2. The *three* $^{31}P\{^1H\}$ NMR signals of **B**-BrCl at −6.9 (1P), −12.3 (1P) and −18.7 (2P) ppm are broad at low temperature. Upon warming to −20 °C, the unit intensity signals become doublets of triplets, while that at −18.7 becomes a doublet of doublets. At −10 °C, no $^{31}P\{^1H\}$ NMR signals are detectable, and the ^1H NMR spectrum shows paramagnetic products. If **C** had been a monohalide species, protonation of $W(H)_2BrClL_4$ would have produced the *two* species observed from protonation of $W(H)_2Cl_2L_4$ and $W(H)_2Br_2L_4$. This is not the case, and supports the assignment of **C**-X_2 as a dihalide. Protonation of $W(H)_2I_2L_4$ was not as clean or informative as for the other halides, presumably because of the presence of a significant amount of WI_2L_4 (eq 2); this species then leads to the paramagnetic products we observe.

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(18) Benn, R.; Brevard, C.; Rufińska, A.; Schroth, G. *Organometallics* **1987**, *6*, 938.

(19) Kozik, M.; Acerete, R.; Hammer, C. F.; Baker, L. C. W. *Inorg. Chem.* **1991**, *30*, 4429.

(20) (a) Benn, R.; Rufińska, A. *Magn. Reson. Chem.* **1988**, *26*, 895, and references therein. (b) Templeton, J. L.; Philipp, C. C.; Pregosin, P. S.; Ruegger, H. *Magn. Reson. Chem.* **1993**, *31*, 58.

(21) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.

(22) Rehder, D. *Coord. Chem. Rev.* **1991**, *110*, 161.

(23) Poulton, J. T.; Sigalas, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 5490.

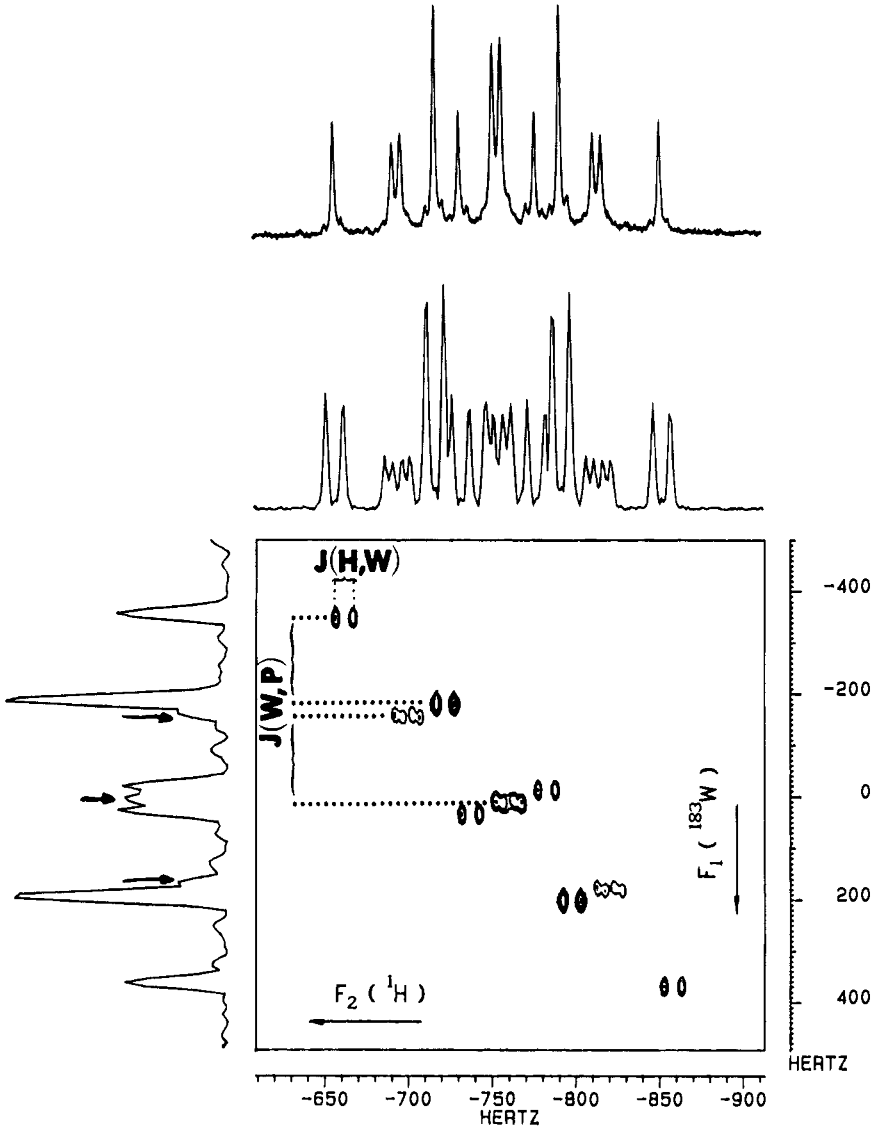

Figure 3. Top: One-dimensional ^1H NMR spectrum of the hydride signal of $WH_2Cl_2L_4$ in C_6D_6 at 300 K. Bottom: Section of the two-dimensional (^1H, ^{183}W) spectrum of $WH_2Cl_2L_4$ in C_6D_6 at 300 K and the projections on the F_1 (^{183}W) and F_2 (^1H) axes. Spectral widths were 5000 Hz (2K datapoints) in the F_2 dimension (large window necessary due to foldover problems) and 1000 Hz (64 increments) in the F_1 dimension. A Δ of 50 ms was used ($J_{W,H} = 10.4$ Hz). Offset of the chemical shift of $WH_2Cl_2L_4$ from the employed ^{183}W resonance frequency of 20.804 685 MHz by +10 Hz resulting in $\delta(^{183}W) = -1582.0$ ppm. Arrows mark the low intensity center triplet (see text).

Discussion

$WH_2Cl_2L_4$ is established[9] to be a crowded molecule; its inherent reactivity is reversible loss of PMe_2Ph. It is therefore understandable that the kinetic product on reaction with H^+ could involve attack on a hydride ligand, with formation of coordinated H_2.[24] The barrier to conversion to the trihydride species **B** almost certainly involves some rearrangement of the (bulky) heavy atom $WCl_2(PMe_2Ph)_4$ substructure. We have ^1H NMR evidence[9] that rotation about W−P and P−C bonds is slow at low temperature, which suggests that, at the observation temperatures employed here, the energy required for such a process is not present.

It is of interest that there is a thermodynamic preference for $W^{VI}(H)_2$ over $W^{IV}(H_2)$ in the protonation product **B**. This shows the ease of oxidation of tungsten even in the presence of two halide ligands. What is remarkable is that the $W(H)_3Cl_2L_4^+$ species reacts by loss not of H_2, but of phosphine. Apparently reduction to W^{IV} (implicit in the loss of H_2) is unfavorable *relative to* relief of repulsions among the four bulky phosphine ligands. Such steric "pressure" is accentuated due to the increased coordination number which accompanies protonation. This stands as a noteworthy contrast to the more usual loss of H_2, and must be due in part to the preference of 5d metals for high oxidation states. What is also remarkable is that product **C**, $W(H)_3Cl_2L_3^+$ is stereochemically rigid. While there has been a generalization (working hypothesis?) that high coordination numbers are always fluxional, a growing number of exceptions have been documented.[25] Certainly this stereochemical rigidity is strong evidence that product **C** does not coordinate $CF_3SO_3^-$ since coordination number nine is unlikely to be stereochemi-

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(24) It has been discussed that protonation of a metal hydride compound gives an H_2 complex as the primary product. See: Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161. Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429. Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1993**, 3431. Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 441.

(25) Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 1424. Chiu, K. W.; Jones, R. W.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1981**, 1204. Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227. Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1992**, *114*, 4611.

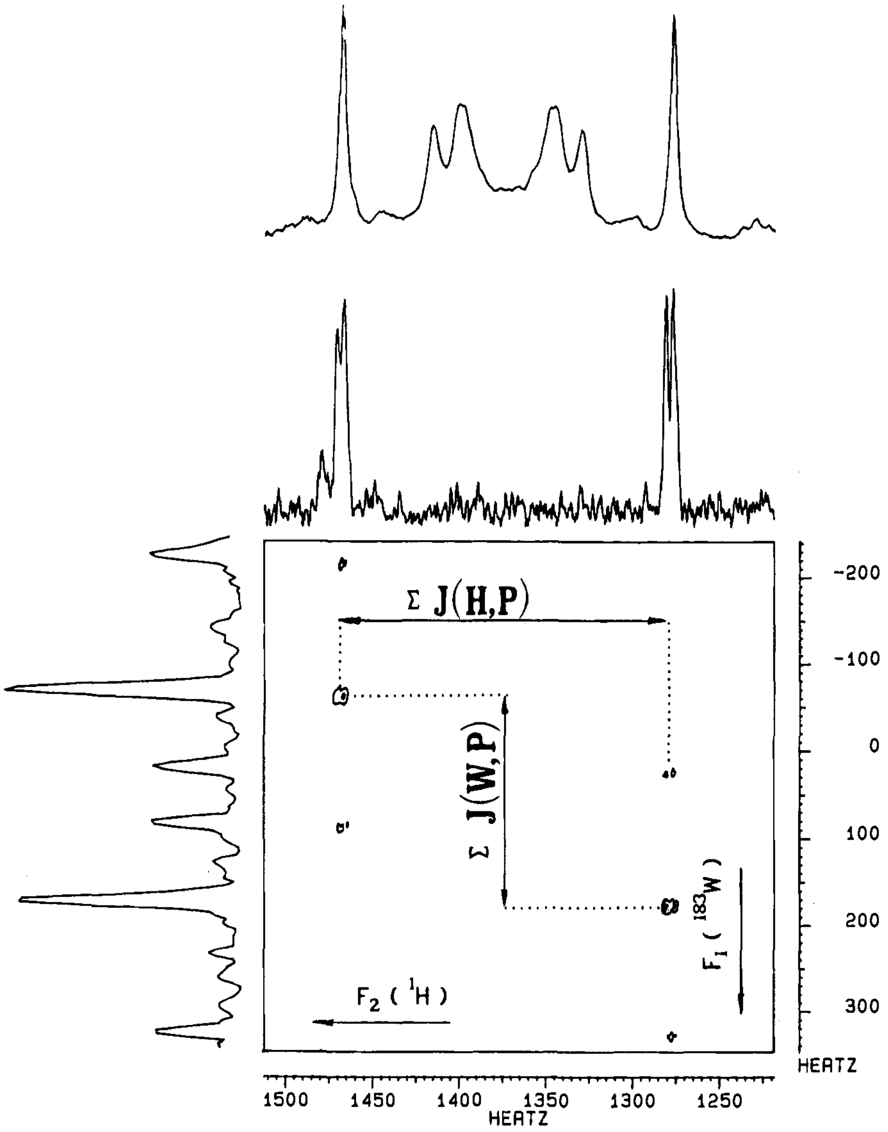

Figure 4. Top: One-dimensional ^{1}H NMR spectrum of the hydride signal of $[WH_3Cl_2L_3][CF_3SO_3]$ (**C**) in CD_2Cl_2 at 263 K. No tungsten satellites are visible. Bottom: Section of the two-dimensional (^{1}H, ^{183}W) spectrum of **C** in CD_2Cl_2 at 263 K and the projections on the F_1 (^{183}W) and F_2 (^{1}H) axes. Spectral widths were 3000 Hz (4K datapoints) in the F_2 dimension and 1000 Hz (128 increments) in the F_1 dimension. With $J_{W,H} = 4.0$ Hz, Δ was set on 114 ms. The employed ^{183}W frequency (20.794978 MHz) was +59 Hz off-resonance, giving a $\delta(^{183}W) = -2045.5$ ppm for **C**.

cally rigid. It would also be true that such a species could not have C_3 symmetry. Since the spectral data for **C** are unchanged when the reaction solvent is toluene, solvent coordination can also be excluded.

Cation **C** is formally unsaturated (if each halide is a pure σ ligand). The fact that phosphine loss from **B** is thermodynamically favored (and has an activation energy low enough to be surmounted at −30 °C) must rely on $Cl \rightarrow W$ π-donation to alleviate such unsaturation. Particularly in a crowded environment, multiple bonding to halide is a more efficient way of filling a low-lying empty orbital than is addition of another ligand.

It is remarkable that the protonation of $WH_2Cl_2L_4$ to give $W(H)_3Cl_2L_4^+$, **B**, is a (reversible!) equilibrium process in the temperature range −70 to −95 °C. This appears to be related to the fact that dissolved CF_3SO_3H in CH_2Cl_2 will be molecular and probably associated (via hydrogen bonding), as well as that it will partially freeze out at these low temperatures, thus lowering its solution concentration.

We have recently reported[26] that CF_3SO_3H protonation of the (unsaturated) hydride chloro complexes $OsH_2Cl_2(P^tBu_2Me)_2$ and $PtHCl(P^tBu_3)_2$ are selective for protonation *at chloride*. In each case, chloride is abstracted as HCl. These results are notably different from those reported here. They show that hydrido/halide complexes represent a good test for selectivity of protonation but that a consistent behavior pattern has yet to emerge.

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[26] (a) Kuhlman, R.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 1788. (b) Gusev, D. G.; Hauger, B. E.; Notheis, J. U.; Rambo, J. R.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.*, to be submitted for publication.