Spectroscopic Study of Dehydrochlorination and Exchange with D_2 in $WH_2Cl_2(PMe_2Ph)_4$: Unexpected Stereochemical Rigidity of Dodecahedra Containing both Hydride and Chloride Ligands. Crystal and Molecular Structure of $W(H)_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$

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$WH_2Cl_2L_4$ (L = PMe_2Ph), formed by oxidative addition of H_2 to WCl_2L_4, is stereochemically rigid, and, in solution, undergoes exchange with D_2 by a mechanism dissociative in L; NMR evidence is consistent with $WH_2Cl_2L_4$ being a crowded molecule. Because of this mechanism, $WH_2Cl_2L_4$ is a catalyst for conversion of HD to H_2 and D_2. $LiDBEt_3$ converts $WH_2Cl_2L_4$ into exclusively one isotopomer of WH_2DClL_4, a dodecahedron which is stereochemically rigid on the time scale of 1 day. The mechanism of this halide substitution also appears to begin with phosphine dissociation. Attempted nucleophilic substitution of one or more chlorides in $WH_2Cl_2L_4$ by $KN(SiMe_3)_2$ or LiR (R = ^{n}Bu, ^{t}Bu, $CH_2{}^t$Bu, Me, NMe_2) leads instead to dehydrohalogenation (followed by ortho-metalation of the P–Ph group, giving a nonfluxional $WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)L_3$) or to β-hydrogen elimination (to give stereochemically-rigid WH_3ClL_4 or $WH_3(\eta^2\text{-}C_6H_4PMe_2)L_3$). The last compound was shown by X-ray diffraction to have a dodecahedral structure of mirror symmetry. Crystal data (−170 °C): a = 13.770 (7) Å, b = 16.567(9) Å, c = 14.245(8) Å, and β = 99.97(2)° with Z = 4 in space group $P2_1/c$. The metalation products are proposed to arise from an intermediate $W^{II}HClL_4$, which is lightly stabilized by Cl → W π donation.

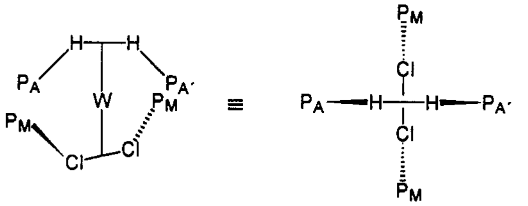
Introduction

We have described[1] reasons why polyhydride compounds of the transition metals which also contain at least one π-donor ligand might exhibit useful reactivity under unusually mild conditions. The halides represent one class of π-donor ligands, with the added virtue that systematic electronic modification is possible by surveying all halides, F–I. Transition metal hydrido/halide compounds are not numerous, and we were attracted to $WH_2Cl_2L_4$ (L = PMe_2Ph), which was reported[2] as the side product (ca. 15% yield) of the synthesis of $W(N_2)_2L_4$. A brief report of its reactivity has appeared, as has its dodecahedral structure (Chart 1, which shows only the inner coordination sphere and gives labeling of phosphorus nuclei).[3] We report here further studies of this hydrido halide and its conversion to WH_3ClL_4, as well as attempts at replacement of chloride ligands by a variety of nucleophiles. Such attempts lead to dehydrohalogenation to form $WH_2Cl(\eta^2\text{-}L)L_3$ or β-H elimination to form $WH_3(\eta^2\text{-}L)L_3$ or WH_4L_4 (η^2-L = $\eta^2\text{-}PMe_2C_6H_4$). All of these compounds except WH_4L_4 are found to display an exceptional resistance to fluxionality.

Experimental Section

General Methods. All manipulations under ambient conditions (25 °C, 1 atm) were carried out in a glovebox under an argon atmosphere. The glassware was rigorously flame dried; NMR tubes were kept at 110 °C in an oven. Aromatic solvents were dried over alkali metal, and hexanes over sodium/benzophenone; all solvents were freshly distilled before use. NMR spectra (values in ppm) were recorded on Bruker AM500 (^{1}H and ^{13}C{^{1}H} NMR) and Nicolet NT360 (^{1}H, ^{31}P{^{1}H}, and ^{2}H{^{1}H} NMR) spectrometers. Eighty-five percent H_3PO_4 served as an external standard for phosphorus chemical shifts, a negative chemical shift being upfield. Infrared spectra were obtained on KBr pellets on a Nicolet 510P FT-IR instrument.

Chart 1



$WCl_2(PMe_2Ph)_4$ and $WH_2Cl_2(PMe_2Ph)_4$. Under an argon atmosphere, 2.0 g (3.3 mmol) of $WCl_4(PMe_2Ph)_2$[4] was dissolved in 150 mL of THF to give an orange solution. Addition of 0.95 mL (6.7 mmol) of PMe_2Ph produced a red solution (due to $WCl_4(PMe_2Ph)_3$). A 40 g amount of 0.4% Na amalgam (~5% excess) was added, and the solution was stirred for 3 h. The THF was removed under vacuum and the residue dissolved in 50 mL of toluene. The resulting orange-brown solution was filtered through 2 cm of Celite to remove NaCl and Hg. The volume of the filtrate was reduced to 10 mL, and 10 mL pentane was added. After 12 h at −20 °C, orange crystals of $WCl_2(PMe_2Ph)_4$ were collected by filtration and washed with pentane (yield 1.75 g, 65%). ^{1}H NMR (C_6D_6, 360 MHz, 25 °C): 10.7 (4H, *para*); 8.59 (8H, *ortho* or *meta*); 7.56 (8H, *meta* or *ortho*); 2.15 (24H, PMe_2Ph), all peaks broadened. No ^{31}P signal was observable.

A solution of 1.0 g (1.239 mmol) of $WCl_2(PMe_2Ph)_4$ in 10 mL of toluene in a 300-mL flask was subjected to three freeze–pump–thaw cycles and placed under ~1.5 atm (25 °C) of H_2. After the solution was stirred for 10 h at room temperature, 10 mL of pentane was added to precipitate $WH_2Cl_2(PMe_2Ph)_4$ in quantitative yield. ^{1}H NMR (toluene-d_8, 25 °C, 500 MHz): 7.29–7.36 (m, Ph H), 7.12–7.19 (m, Ph H), 6.70–7.12 (m, Ph H), 1.60 (12H, vt, N = 7.8 Hz, CH_3–P), 1.52 (12H, vt, N = 8.6 Hz, CH_3–P), −1.52 (2H, m, $^1J_{W,H}$ = 10.4 Hz, H–W). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 146 MHz): −10.9 (t ($^2J_{PP}$ = 14.8 Hz) with W satellites ($^1J_{W,P}$ = 167.8 Hz)); −14.1 (t ($^2J_{P,P}$ = 14.8 Hz) with W satellites ($^1J_{W,P}$ = 191.3 Hz)). IR (KBr, $\nu(WH_2)$): 1894 and 1919 cm^{-1}.

Higher yields (>90% with respect to $WCl_4(PMe_2Ph)_2$) of $WH_2Cl_2(PMe_2Ph)_4$ may be obtained by treating the filtered toluene solution from the above $WCl_2(PMe_2Ph)_4$ synthesis directly with 2 atm of H_2,

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(1) Lunder, D. L.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991,** *113,* 1837.

(2) Dadkeh, H.; Kashef, N.; Richards, R. L.; Hughes, D. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1983,** *255,* C1.

(3) Fakley, M. E.; Richards, R. L. *Transition Met. Chem.* **1982,** *7,* 1.

(4) This was prepared similarly to the preparation of $WCl_4(PMe_3)_3$ (Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* **1990,** *28,* 326). The additional phosphine ligand in the resulting $WCl_4(PMe_2Ph)_3$ was removed at 110 °C under high vacuum for 1 h.

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since the air sensitivity of $WCl_2(PMe_2Ph)_4$ leads to loss on workup and isolation. Thus, the crude product from Na/Hg reduction of 7.2 g (12 mmol) of $WCl_4(PMe_2Ph)_2$ was dissolved in 50 mL of toluene and treated with H_2 for 10 h at 25 °C. The major portion of $WH_2Cl_2(PMe_2Ph)_4$ had precipitated as fine orange crystals by this time. These were dissolved by addition of 100 mL of THF and 100 mL of toluene. Filtration through 1 cm of Celite removes any NaCl (from the $WCl_4(PMe_2Ph)_2$ reduction). The solution was concentrated in vacuo to a volume of 50 mL, which precipitates most of the $WH_2Cl_2(PMe_2Ph)_4$. These crystals were collected by filtration and slurried for 2 h in 50 mL of hexane to remove residual THF; this treatment is required for effective THF removal, since 6 h of vacuum treatment of the solid product failed to remove all THF. Yield: 6.0 g (62%). Removal of the THF/toluene volatiles from the filtrate, extraction of the brown residue with 30 mL of toluene, filtration (Celite), volume reduction (vacuum) to 10 mL, and addition of 10 mL of hexane precipitates an additional 2.8 g of $WH_2Cl_2(PMe_2Ph)_4$, for a combined yield of 91%.

$WD_2Cl_2(PMe_2Ph)_4$. A 100-mg amount (0.124 mmol) of $WCl_2(PMe_2Ph)_4$ was dissolved in 0.5 mL of toluene. A 3-mL volume of pentane was added carefully to decrease the polarity of the solvent but to keep all $WCl_2(PMe_2Ph)_4$ still in solution. The solution was frozen in liquid nitrogen, pumped, and pressurized with about 1.5 atm (25 °C) of D_2. After the solution was stirred at 20 °C for 8 h, the less-soluble $WD_2Cl_2(PMe_2Ph)_4$ precipitated quantitatively. The solution was removed via cannula, and the remaining (orange) $WD_2Cl_2(PMe_2Ph)_4$ was dried. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): 7.34–7.38 (m, Ph H), 7.17–7.20 (m, Ph H), 6.97–7.08 (m, Ph H), 1.63 (12H, vt, N = 7.6 Hz, CH_3–P), 1.56 (12H, vt, N = 8.4 Hz, CH_3–P). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 146 MHz): −11.1 (t ($^2J_{P,P}$ = 16.3 Hz) of quint ($^2J_{P,D}$ = 8.8 Hz) with W satellites ($^1J_{W,P}$ = 167.9 Hz)), −14.4 (t ($^2J_{P,P}$ = 14.3 Hz) of DD′PP′ spin system with W satellites ($^1J_{W,P}$ = 190.7 Hz)). IR (KBr, $\nu(WD_2)$): 1375 and 1401 cm^{-1}.

$WH_3Cl(PMe_2Ph)_4$. A 126.6-mg amount (0.156 mmol) of $H_2WCl_2L_4$ was dissolved in 20 mL of THF and cooled to −78 °C. A 0.15-mL volume of a 1.0 M solution of $LiHBEt_3$ in THF was carefully added (syringe) to the well-stirred solution. The cooling bath is slowly warmed up to −10 °C and kept at this temperature for 2 h. The color changes from yellow-orange to bright yellow. Conversion to H_6WL_3 (identified by $^{31}P\{^1H\}$ and ^{1}H NMR) partially occurs at temperatures higher than 0 °C. In order to prevent this, the following steps were carried out at −10 °C. The volume is reduced under vacuum to about 1 mL. Addition of hexanes (20 mL) precipitates unreacted $WH_2Cl_2L_4$ and LiCl. The yellow solution was filtered through 1 cm of Celite. Reducing the volume to about 2 mL and cooling this concentrated solution to −78 °C precipitates WH_3ClL_4 as a yellow powder in nearly quantitative yield. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): 7.65–7.69 (m, Ph H), 7.53–7.56 (m, Ph H), 7.34–7.38 (m, Ph H), 7.03–7.16 (m, Ph H), 6.92–6.94 (m, Ph H), 2.15 (1H, m with W satellites ($^1J_{W,P}$ = 5.0 Hz), H_z), 1.82 (6H, vt, N = 6.6 Hz, CH_3–P_M), 1.65 (6H, d, $^2J_{P,H}$ = 6.6 Hz, CH_3–P_A), 1.50 (6H, vt, N = 6.4 Hz, CH_3–P_M), 1.32 (6H, d, $^2J_{P,H}$ = 8.2 Hz, CH_3–P_Q), −2.54 (2H, m with W satellites ($^1J_{W,P}$ = 22.8 Hz), H_x). $^{31}P\{^1H\}$ NMR, (C_6D_6, 25 °C, 146 MHz): 2.12 (P_Q, dt, ($J_{M,Q}$ = 15.2 Hz, $J_{A,Q}$ = 39.3 Hz) with W satellites ($^1J_{W,P}$ = 135.1 Hz)), −11.01 (P_M, dd ($J_{A,M}$ = 15.7 Hz, $J_{M,Q}$ = 15.2 Hz) with W satellites ($^1J_{W,P}$ = 192.1 Hz)), −18.72 (P_A, dt ($J_{A,Q}$ = 39.3 Hz, $J_{A,M}$ = 15.7 Hz) with W satellites ($^1J_{W,P}$ = 128.0 Hz)). Assignment of P_A and P_Q by selective decoupling of phosphorus in ^{1}H NMR on the assumption that from 92.1 and 22.4 Hz, respectively, the greater coupling constant refers to H_z–P_Q *trans* coupling. IR (KBr, $\nu(WH_3)$): 1757, 1883 and 1945 cm^{-1}. Decomposition during recrystallization prevented elemental analysis.

$WD_3Cl(PMe_2Ph)_4$. In a 100-mL flask, 42 mg (0.056 mmol) of $WH_3Cl(PMe_2Ph)_4$ was dissolved in 10 mL of toluene. The solution was frozen in liquid nitrogen and evacuated. Subsequently, the flask was pressurized with 1.5 atm of D_2. After thawing, the solution was stirred for 10 h at 25 °C. In order to ensure isotopically-pure WD_3ClL_4, the gas phase was replaced with pure D_2 and stirred at 25 °C for 10 h. Removal of the toluene under vacuum yielded pure $WD_3Cl(PMe_2Ph)_4$. $^2H\{^1H\}$ NMR (protiotoluene, 25 °C, 55 MHz): 2.03 (1D, br, D_z), −2.61 (2D, br, D_x). $^{31}P\{^1H\}$ NMR chemical shifts are unchanged compared to $WH_3Cl(PMe_2Ph)_4$. Due to P–D coupling, however, all signals are strongly broadened.

$WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$. The following procedure describes the reaction of $WH_2Cl_2P_4$ with 1 equiv of ^{t}BuLi. Reactions with $LiCH_2{}^tBu$ or $KN(SiMe_3)_2$ were carried out similarly (the solid bases were first dissolved in 1 mL of toluene). An 81.1-mg amount (0.100 mmol) of $WH_2Cl_2(PMe_2Ph)_4$ was dissolved in 5 mL of toluene. While the solution was stirring, 56 μL of ^{t}BuLi solution (1.8 M in *n*-hexane) was slowly added via syringe. The color changed from orange to yellow-green. After 5 min of stirring, the solvent was removed and the oily residue dissolved in 4 mL of hexanes. The solution was filtered over Celite and the volume subsequently reduced to 1 mL. After 12 h at −20 °C, yellow crystals were formed (yield: 21 mg = 27%). The mother liquor showed a darkening during concentration of the solution, and storage at −20 °C led simply to decomposition. Even the crystalline compound is thermolabile. In the course of 2 d, it decomposed under argon at 25 °C. ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): 8.45 (1H, m, Ph H*),[5] 7.82 (1H, apparent triplet, 7.3 Hz, Ph H*),[5] 7.73 (1H, apparent triplet, 7.6 Hz, Ph H*),[5] 7.31–7.60 (m, Ph H), 6.91–7.10 (m, Ph H), 6.45 (1H, dd, $^3J_{P,H}$ = 12.4 Hz, $^3J_{H,H}$ = 7.0 Hz, Ph H*),[5] 1.57 (6H, d, $^2J_{P,H}$ = 7.1 Hz, CH_3–P), 1.47 (6H, vt, N = 7.2 Hz, CH_3–P), 1.17 (6H, d, $^2J_{P,H}$ = 8.9 Hz, CH_3–P), 1.17 (6H, vt, N = 6.9 Hz, CH_3–P), −0.82 (2H, d ($^2J_{P,H}$ = 44.9 Hz) of d ($^2J_{P,H}$ = 53.2 Hz) of HH′$P_AP_{A'}$ with W satellites ($^1J_{W,H}$ = 6.9 Hz, W–H)). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 126 MHz): 151.8 (d, $^1J_{P,C}$ = 42.6 Hz, ipso carbon of ortho-metallated ring), 147.9 (d, $^2J_{P,C}$ = 28.5 Hz, C–W), 143.0 (vt, N = 33.1 Hz, ipso carbon of $P_AP_{A'}$), 137.8 (s, Ph C), 136.1 (d, $^1J_{P,C}$ = 21.1 Hz, ipso carbon), 133.1 (d, $J_{P,C}$ = 11.3 Hz, Ph C), 127.3–131.7 (m, Ph C), 125.6 (s, Ph C), 122.2 (d, $J_{P,C}$ = 7.2 Hz, Ph C), 121.9 (s, Ph C), 21.6 (d, $^1H_{P,C}$ = 25.7 Hz, *C*H_3–P), 20.6 (d, $^1J_{P,C}$ = 21.8 Hz, *C*H_3–P), 18.2 (vt, N = 26.6 Hz, *C*H_3–P), 16.6 (vt, N = 22.8 Hz, *C*H_3–P). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 146 MHz) −11.7 (2P, apparent triplet (16.8 Hz) with W satellites ($^1J_{W,P}$ = 188.9 Hz)), −20.5 (1P, d ($^2J_{P,P}$ = 45.0 Hz) of t ($^2J_{P,P}$ = 16.0 Hz) with W satellites ($^1J_{W,P}$ = 125.2 Hz)), −59.4 (1P, d ($^2J_{P,P}$ = 45.0 Hz) of t ($^2J_{P,P}$ = 17.9 Hz) with W satellites ($^1J_{W,P}$ = 133.1 Hz)). IR (KBr, $\nu(WH_2)$): 1848 and 1912 cm^{-1}. Decomposition during recrystallization prevented elemental analysis.

$WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$. The compound was synthesized by reaction of $WH_2Cl_2(PMe_2Ph)_4$ with 2 equiv of the following bases: ^{t}BuLi (as 1.8 M solution in *n*-hexane), $LiCH_2{}^tBu$ (in toluene), LiMe and $LiNMe_2$ (as solids). In addition, $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$ was obtained reacting $WH_3Cl(PMe_2Ph)_4$ with 1 equiv of *n*-BuLi (1.6 M in *n*-hexane) or $WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$ with 1 equiv of ^{t}BuLi or $LiNMe_2$. As an example, the reaction of $WH_2Cl_2(PMe_2Ph)_4$ with 2 equiv of neopentyllithium is described. A 51.3-mg amount (0.063 mmol) of $WH_2Cl_2(PMe_2Ph)_4$ was dissolved in 5 mL of toluene. While the mixture was stirred vigorously, a solution of 9.9 mg (0.127 mmol) of $LiCH_2{}^tBu$ in 2 mL of toluene was slowly added. The orange solution turned yellow-orange. It was stirred for an additional 2 h and filtered over Celite, and the toluene was removed under vacuum. The remaining yellow-orange residue was dissolved in hexanes (∼1 mL). After 12 h at −20 °C, orange crystals of pure $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$ precipitated (yield: 38 mg, 81%). ^{1}H NMR (C_6D_6, 25 °C, 500 MHz): 7.97 (1H, m, Ph H*),[5],6.91–7.75 (m, Ph H), 6.51 (1H, dd, $^3J_{P,H}$ = 12.2 Hz, $^3J_{H,H}$ = 7.1 Hz, Ph H*),[5] 1.425 (6H, vt, N = 5.1 Hz, CH_3–P), 1.418 (6H, vt, N = 5.8 Hz, CH_3–P), 1.39 (6H, d, $^2J_{P,H}$ = 7.7 Hz, CH_3–P), 1.31 (6H, d, $^2J_{P,H}$ = 6.6 Hz, CH_3–P), 0.54 (1H, d ($^2J_{P,H}$ = 51.7 Hz) of t ($^2J_{P,H}$ = 30.1 Hz) of d ($^2J_{P,H}$ = 5.6 Hz) of t ($^2J_{H,H}$ = 7.0 Hz), W–H), −1.44 (2H, d ($^2J_{P,H}$ = 64.5 Hz) of d ($^2J_{P,H}$ = 37.2 Hz) of d ($^2J_{H,H}$ = 7.0 Hz) of HH′$P_BP_{B'}$ with W satellites ($^1J_{W,H}$ = 7.5 Hz), W–H). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C, 126 MHz): 155.6 (d ($^1J_{P,C}$ = 41.5 Hz) of t ($^3J_{P,C}$ = 3.9 Hz) of d ($^3J_{P,C}$ = 1.4 Hz), ipso carbon of ortho-metalated ring), 147.8 (d, $^2J_{P,C}$ = 30.6 Hz, C–W), 146.2 (vt, N = 28.4 Hz, ipso carbon of P_B,$P_{B'}$), 142.7 (d ($^1J_{P,C}$ = 29.2 Hz) of d ($^3J_{P,C}$ = 5.0 Hz) of t ($^3J_{P,C}$ = 2.9 Hz), ipso carbon of P_A), 131.1 (m, Ph C), 130.8 (vt, N = 8.6 Hz, Ph C), 130.5 (d, $J_{P,C}$ = 8.6 Hz, Ph C), 130.3 (d, $J_{P,C}$ = 8.3 Hz, Ph C), 129.8 (d, $J_{P,C}$ = 7.9 Hz, Ph C), 129.2 (s, Ph C), 128.2 (s, Ph C), 127.4–127.5 (m, Ph C), 123.8 (s, Ph C), 123.7 (s, Ph C), 123.4 (d ($J_{P,C}$ = 7.2 Hz) of m, Ph C), 120.6 (d ($J_{P,C}$ = 7.2 Hz) of t ($J_{P,C}$ = 2.9 Hz), Ph C), 27.9 (d, $^1J_{P,C}$ = 26.6 Hz, CH_3), 24.2 (vt, N = 27.1 Hz, CH_3), 23.2 (vt, N = 24.8 Hz, CH_3), 18.5 (d, $^1J_{P,C}$ = 16.2 Hz, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 146 MHz): −8.3 to −9.7 (3P, AB_2 system), −79.5 (1P, d ($^2J_{P,P}$ = 11.4 Hz) of t ($^2J_{P,P}$ = 18.8 Hz) with W satellites ($^1J_{W,P}$ = 129.3 Hz), P_M). IR (KBr, $\nu(WH_3)$): 1788, 1824, and 1874 cm^{-1}.

Isotopic Exchange Catalysis. The exchange of HD with $WH_2Cl_2L_4$ was carried out by treatment of KH in benzene-d_6 with neat D_2O in one arm of an evacuated reaction vessel connected by an inverted U-tube to $WH_2Cl_2L_4$ dissolved in benzene-d_6. KH was used in 5% excess, and the amount of D_2O was calculated to form 1 atm HD in the known reactor volume. The head space gases were sampled at $^1/_2$ and at 3 h and analyzed on an isotope ratio mass spectrometer. The mole ratios (Table 1) revealed the reaction to be essentially at equilibrium after 3 h at 25 °C. The reaction of KH with D_2O was vigorous and difficult to control, and its

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[5] H* signifies protons of the ortho-metalated phenyl group.

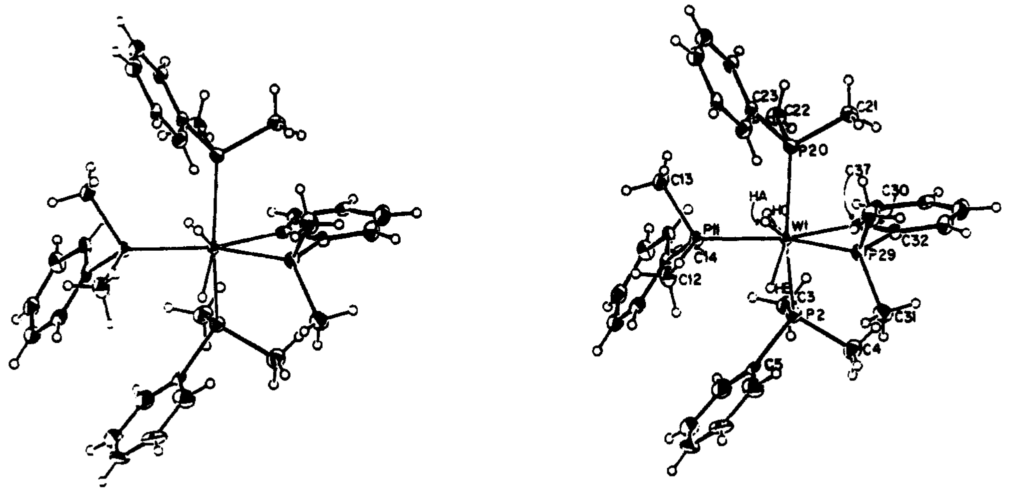

Figure 1. Stereo ORTEP drawing of $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$, showing selected atom labeling. Atoms W(1), P(29), C(32), and C(37) define a noncrystallographic mirror plane of symmetry. Unlabeled atoms are carbon or (open circles) hydrogen.

Table 1. Catalysis of HD Disproportionation by $WH_2Cl_2(PMe_2Ph)_4$

	0.5 h	3 h		0.5 h	3 h
H_2, %	14.3	22.6	D_2, %	16.6	29.4
HD, %	69.1	48.0			

Table 2. Crystallographic Data for $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$

chem formula	$C_{32}H_{46}P_4W$	space group	$P2_1/c$
a, Å	13.770(7)	T, °C	−170
b, Å	16.567(9)	λ, Å	0.710 69
c, Å	14.245(8)	ρ_{calcd}, g cm^{-3}	1.533
β, deg	99.97(2)	μ(Mo Kα), cm^{-1}	39.02
V, Å^3	3200.54	R[a]	0.0271
Z	4	R_w[a]	0.0290
fw	738.46		

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

Table 3. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å
W(1)	3114.8(2)	538.4(2)	2587.0(2)	10
P(2)	1348(1)	838(1)	2200(1)	14
P(11)	3504(1)	1793(1)	3466(1)	12
P(20)	4731(1)	482(1)	2037(1)	13
C(21)	5118(6)	−427(5)	1444(5)	20
C(22)	4817(6)	1214(5)	1089(5)	18
P(29)	2983(1)	−935(1)	2742(1)	14
C(30)	4012(6)	−1590(5)	3254(6)	23
C(37)	2733(5)	−173(4)	1217(5)	14
H(A)	397(6)	34(5)	355(6)	48(15)
H(B)	261(4)	45(3)	353(4)	5(11)
H(C)	322(4)	126(3)	185(4)	6(10)

[a] Fractional coordinates are ×10^4 for non-hydrogen atoms and ×10^3 for hydrogen atoms. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$

W(1)–P(2)	2.4498(22)	W(1)–C(37)	2.258(7)
W(1)–P(11)	2.4381(20)	W(1)–H(A)	1.68(8)
W(1)–P(20)	2.4866(21)	W(1)–H(B)	1.63(5)
W(1)–P(29)	2.4609(23)	W(1)–H(C)	1.62(6)
P(2)–W(1)–P(11)	93.68(6)	P(11)–W(1)–H(A)	71.6(27)
P(2)–W(1)–P(20)	147.67(6)	P(11)–W(1)–H(B)	75.0(19)
P(2)–W(1)–P(29)	97.76(6)	P(11)–W(1)–H(C)	70.2(19)
P(2)–W(1)–C(37)	80.67(17)	P(20)–W(1)–H(A)	73.2(27)
P(11)–W(1)–P(20)	93.73(6)	P(20)–W(1)–H(B)	142.3(19)
P(11)–W(1)–P(29)	144.37(6)	P(20)–W(1)–H(C)	68.8(19)
P(11)–W(1)–C(37)	152.20(18)	P(29)–W(1)–H(A)	77.6(27)
P(20)–W(1)–P(29)	94.29(6)	P(29)–W(1)–H(B)	77.6(19)
P(20)–W(1)–C(37)	78.19(17)	P(29)–W(1)–H(C)	144.4(19)
P(29)–W(1)–C(37)	63.35(19)	C(37)–W(1)–H(A)	129.0(27)
W(1)–P(29)–C(32)	88.12(23)	C(37)–W(1)–H(B)	126.8(19)
W(1)–C(37)–C(32)	107.3(5)	C(37)–W(1)–H(C)	82.1(19)
W(1)–C(37)–C(36)	136.0(5)	H(A)–W(1)–H(B)	69.(3)
P(2)–W(1)–H(A)	138.8(27)	H(A)–W(1)–H(C)	123.(3)
P(2)–W(1)–H(B)	69.9(19)	H(B)–W(1)–H(C)	134.8(27)
P(2)–W(1)–H(C)	84.3(19)		

total time of generation was about 0.5 h. Since the evolving HD was exposed to $WH_2Cl_2L_4$ during the entire generation process, the time of the first mass spectral assay is not a reliable indication of rate.

Reaction of D_2 with Solid $WH_2Cl_2(PMe_2Ph)_4$. A 15-mg amount (0.019 mmol) of $WH_2Cl_2L_4$ was dissolved in 5 mL of toluene in a 100-mL flask. The solvent was slowly removed in vacuum in order to cover as much surface of the flask with $WH_2Cl_2L_4$ as possible. To complete the removal of toluene, the sample was pumped at high vacuum for 18 h. The flask was then filled with 1 atm of D_2 (4.1 mmol) and kept at 25 °C for 7 days. D_2 was removed under vacuum and replaced by argon. $^{31}P\{^1H\}$ as well as ^2H NMR of the sample in protiotoluene shows no deuterium incorporation. The $^{31}P\{^1H\}$ spectrum is known to be broadened in $WD_2Cl_2L_4$.

X-ray Diffraction Study of $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$. A suitable, triangular-shaped fragment was cleaved from a larger plate and affixed to the end of a glass fiber. The crystal was then transferred to the goniostat where it was cooled to −170 °C for characterization and data collection (Table 2, 6° < 2θ <45°).[6] All handling was performed in an inert nitrogen atmosphere, although the crystal was later discovered to be quite stable under air at 25 °C. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with systematic absences and symmetry corresponding to the unique monoclinic space group $P2_1/c$. Subsequent solution and refinement confirmed this choice. Data were collected using a continuous θ/2θ scan with fixed background counts at each extreme of the scan. Background corrections were made and the resulting intensities corrected for Lorentz and polarization effects. Equivalent data were averaged to yield a unique set of corrected intensities and estimated errors.

The structure was readily solved by direct methods (MULTAN78) and Fourier techniques. Anisotropic refinement rapidly converged, although two atoms exhibited nonpositive definite thermal parameters. Most hydrogen atoms were visible, although there were numerous peaks of 1.2–3.5 e/Å^3 within 2 Å of the tungsten atom. The R for averaging decreased from 0.048 to 0.018 upon application of the absorption correction, and the residual dropped from 0.049 to 0.032. A difference Fourier clearly revealed the positions of the hydride atoms, and they were included in the final cycles of the refinement. A final difference Fourier revealed only random noise (all peaks less than 0.35 e/Å^3) except for one peak of 1.4 e/Å^3 at the metal site. The results of the structure determination are shown in Tables 3 and 4 and Figure 1.

NMR Spectral Simulations. (a) $WH_2Cl_2L_4$. The hydride multiplet is accurately described as a doublet of doublets of triplets. However, since the spin system is actually $A_2MM'XX'$ (A and M are P, X is H),

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(6) For details of general crystallographic, computer, and diffractometer procedures, see: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

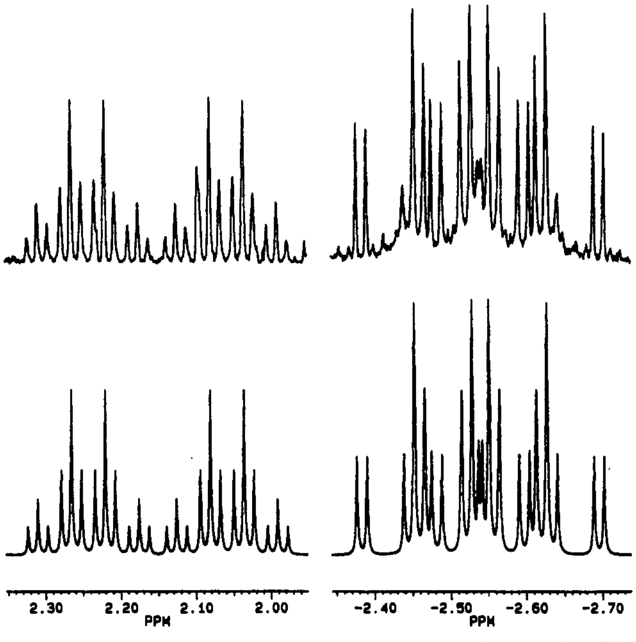


Figure 2. Observed (top) and simulated (bottom) hydride region 500-MHz ^1H NMR spectra of $WH_3Cl(PMe_2Ph)_4$.

the simple first-order appearance is deceptive. The X pattern in an MM'XX' spin system is a virtual triplet whenever $J_{MM'} \gg |J_{MX} + J_{MX'}|$. This is relevant since phosphorus nuclei in $WH_2Cl_2L_4$ are nearly *trans* ($\angle P_M\text{-}W\text{-}P_{M'} = 156.8°$), so $J_{MM'}$ will be larger than the H-P coupling constants. When these are comparable in magnitude, a double doublet (which has two central lines nearly overlapped) can result. We have analyzed the latter deceptively simple spectrum to give the following coupling constants. For $J_{AM} = J_{AM'} = 14.8$ Hz and $J_{AX} = J_{AX'} = 60.5$ Hz, the $J_{MM'}$ coupling has to be in the range 33-38 Hz, resulting in $J_{MX}/J_{M'X}$ pairs of 28.3/47.2 Hz for the lower and 27.4/48.1 Hz for the upper limit of $J_{MM'}$, respectively.

(b) WH_3ClL_4. In the case of WH_3ClL_4, the deceptive simplicity is even more accentuated. The MM'XX' spin subsystem has now collapsed to a triplet hydride pattern, and consequently it is only possible to fix sets of limits on $J_{MM'}$, J_{MX}, and $J_{MX'}$. Spectral simulations (Figure 2) yield the following: for a $J_{MM'}$ coupling between 40 and 120 Hz (upper limit arbitrarily stipulated; no higher P-P couplings have previously been observed in these systems) and $J_{AX} = 31.0$ Hz, $J_{QX} = 49.2$ Hz, and $J_{XZ} = 6.7$ Hz, $J_{MX}/J_{M'X}$ lies between 33/43 Hz and 31.5/44.5 Hz, respectively.

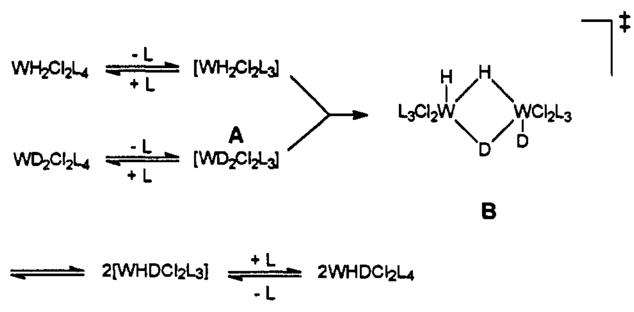
Results

Synthesis of $WH_2Cl_2(PMe_2Ph)_4$. Although the compound was characterized some years ago, there was no rational synthesis for $WH_2Cl_2L_4$ to date. Richards[3] obtained the complex as a side product in the synthesis of $W(N_2)_2L_4$ without knowing the source of the hydride ligands. We were able to form the compound in a quantitative yield by simply exposing WCl_2L_4 to 1.5 atm of hydrogen for 10 h.[7]

$$WCl_2L_4 + H_2 \rightarrow WH_2Cl_2L_4 \qquad (1)$$

Temperature Dependence of the Chemical Shifts in $WH_2Cl_2L_4$. The chemical shifts in both the $^{31}P\{^1H\}$ and the ^1H NMR of $WH_2Cl_2(PMe_2Ph)_4$ are temperature-dependent. For the A_2M_2 system (see Chart 1) in $^{31}P\{^1H\}$ NMR, two well-resolved triplets are observed at 25 °C at δ −10.9 (P_M) and −14.1 (P_A). At lower temperatures, they individually broaden and then (at −80 °C) collapse. There is no significant shift of the signal of nuclei P_M (−11.1 ppm at −80 °C), while the P_A resonance displays strong (3 ppm) temperature dependence. ^1H NMR spectra of $WH_2Cl_2(PMe_2Ph)_4$ reveal a similar behavior. One of the two virtual triplets (δ 1.60) at 25 °C for the methyl protons of the dimethylphenylphosphine ligands shifts by only 0.16 ppm (δ 1.44) at −90 °C, whereas the second signal shows a change of 0.48 ppm in the same temperature range, from δ 1.52 (25 °C) to 1.04 (−90 °C). The hydride signal, which appears at δ −1.52 at 25 °C, undergoes a high-field shift to δ −1.96 at −90 °C. It is remarkable that, at all temperatures, the sharp-lined multiplet structure of the hydride pattern is retained, requiring that all coupling constants in this $AA'M_2XX'$ spin system remain uninfluenced by temperature. This behavior rules out the possibility of substantial structural rearrangement of the inner coordination sphere as an explanation of the observed temperature dependence.

Scheme 1



Therefore, the reason for the temperature dependence of the chemical shifts has to be in the outer sphere of the molecule, suggesting temperature-dependent populations of different rotamers (around the W–P and P–C bonds). We attribute this to the crowding consequent on coordinating *four* phosphines to a single metal. However, despite the highly crowded molecule, no individual rotamers are frozen out between +25 °C and −90 °C. In the ^1H NMR, both methyl signals as well as the lines of the hydride pattern show no significant broadening at low temperatures.

Reactivity of $WH_2Cl_2(PMe_2Ph)_4$. In order to better understand the reactivity of $WH_2Cl_2L_4$, we have studied it for possible exchange with D_2. Treatment of $WH_2Cl_2L_4$ in benzene with excess D_2 (1 atm) gives a mixture of $WD_2Cl_2L_4$ (72%),[8] $WHDCl_2L_4$ (26%), and $WH_2Cl_2L_4$ (2%) within 2.5 h at 25 °C. The ^2H NMR spectrum of the unseparated reaction solution shows that there is no deuteration of the substituents in the PMe_2Ph ligand. The $^{31}P\{^1H\}$ NMR spectrum exhibits complex but symmetrical multiplets due to P–D coupling. A difference in the phosphorus chemical shift of the different H/D isotopic labeled complexes is not observable. The hydride signals of $WHDCl_2L_4$ (−1.50 ppm) and $WH_2Cl_2L_4$ (−1.52 ppm) differ by only 0.02 ppm.

Initially, we assumed that the reverse of eq 1 might be the mechanism of the exchange reaction. However, reductive elimination of H_2 and oxidative addition of D_2 cannot account for the production of $WHDCl_2L_4$. Obviously, a second mechanism has to be involved.

Redistribution of Isotopomers. One possibility to achieve an isotopically-mixed hydride complex is by a hydride-bridged transition state. Therefore, equivalent amounts of $WH_2Cl_2(PMe_2Ph)_4$ and isotopically pure $WD_2Cl_2(PMe_2Ph)_4$ (synthesized from $WCl_2(PMe_2Ph)_4$ and D_2) were dissolved in toluene-d_8 and monitored by ^1H NMR. After 3 h, a statistical distribution of 25% each of $WH_2Cl_2L_4$ and $WD_2Cl_2L_4$ and 50% of $WHDCl_2L_4$ was reached. The reaction implies (Scheme 1) predissociation of phosphine to create an empty metal site (**A**) and subsequent hydride bridging (**B**).

HD Equilibration. $WH_2Cl_2L_4$ seems to catalyze H_2/D_2 equilibration ($H_2 + D_2 \rightleftharpoons 2\,HD$). For confirmation, $WH_2Cl_2L_4$ was treated with 1 atm of HD in deuterated benzene. Mass spectroscopy was used as an analytical tool to determine the

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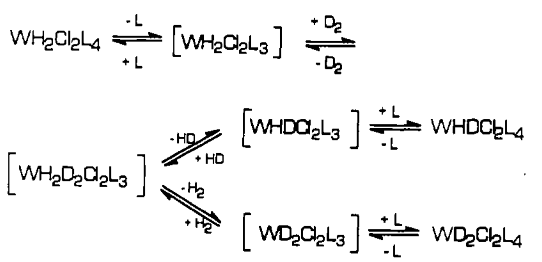
[7] Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808.

[8] Percentages were evaluated by ^1H NMR. The hydride signals furnish a ratio of $WHDCl_2L_4$ to $WH_2Cl_2L_4$, and the methyl signals of the PMe_2Ph ligands allow a determination of the population of all three isotopomers.

Scheme 2



composition of the gas phase. The initial mole ratio of $WH_2Cl_2L_4$:HD was 1:8.5. As is evident from Table 1, the gas composition after 3 h is close to a statistical distribution of H_2, HD, and D_2. It appears obvious that a combination of reductive elimination of H_2 and oxidative addition of HD (according to eq 1) and hydride bridging would serve as a completely satisfactory explanation of the observed equilibration. However, the synthesis of $WH_2Cl_2L_4$ via oxidative addition of H_2 to WCl_2L_4 showed that even under a large head space of H_2 and vigorous stirring, the reaction is very slow and cannot account for the fast equilibration of HD, particularly under the condition of a many-fold excess of HD which would require 8.5 times the oxidative addition of HD per molecule WCl_2L_4. Therefore, other mechanisms have to be taken into consideration.

Exchange Mechanism. If one excludes an HCl-elimination mechanism (which is discussed later), these observations implicate an intermediate containing *four* hydrogen atoms in some bonding form (i.e., WH_4L_n, $W(H_2)H_2L_n$, or $W(H_2)_2L_n$).

(a) Associative Mechanism. One conceivable mechanism involves direct coordination of H_2 to $WH_2Cl_2L_4$, involving a 20e$^-$ species as a transition state. To investigate this possibility under conditions where phosphine dissociation is hindered, we subjected a solid sample of $WH_2Cl_2L_4$ to a large excess of D_2. After 7 d, a thin layer dispersed on the interior of a glass vessel showed no sign of any deuteration (^{31}P and ^2H NMR assay), suggesting that, in the solid state, a 20e$^-$ transition state is not capable of effecting exchange of $WH_2Cl_2L_4$ with D_2. This also provides supporting evidence that, when phosphine dissociation is prevented, the exchange mechanism observed in solution is also stopped.

(b) Pre-equilibrium Dissociation of HCl. An alternative source of a monodeuteride complex and HD from $WH_2Cl_2L_4$ and D_2 would involve a mechanism involving reductive elimination of HCl. Subsequent D_2 addition, loss of HD, and oxidative addition of HCl would also lead to a complex of the composition $WHDCl_2L_4$.

$$WH_2Cl_2L_4 \underset{+HCl}{\overset{-HCl}{\rightleftharpoons}} [WHClL_4] \underset{-D_2}{\overset{+D_2}{\rightleftharpoons}} WHD_2ClL_4 \underset{+HD}{\overset{-HD}{\rightleftharpoons}}$$

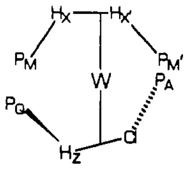
$$[WDClL_4] \underset{-HCl}{\overset{+HCl}{\rightleftharpoons}} WHDCl_2L_4$$

However, WH_3ClL_4 (analogous to WHD_2ClL_4 in the above proposed mechanism) is an isolable species whose spectral characteristics are well established (see below). None of it is detected in separate experiments where $WH_2Cl_2L_4$ is exposed to H_2. Thus, HCl reductive elimination is not a viable mechanism for scrambling of HD, and we are left with preequilibrium phosphine dissociation as most consistent with the full body of observations.

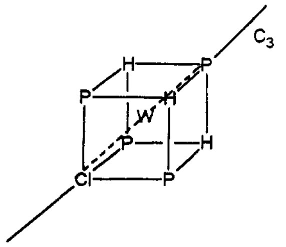
(c) Phosphine Dissociation. Evidently phosphine dissociation must be the initial step (Scheme 2). Unfortunately, no intermediate "$WH_4Cl_2L_3$" could be detected in ^1H and $^{31}P\{^1H\}$ NMR studies of $WH_2Cl_2L_4$ under 1 atm H_2 in a temperature range from +25 to −85 °C. Independent investigations[9] of the mechanism for the synthesis of $WH_2I_2(PMe_3)_4$ from $WI_2(PMe_3)_4$ and H_2 have also shown phosphine dissociation as the first step. Our bulkier phosphine should enhance phosphine dissociation. Consistent with this result is our observation that $WH_2Cl_2L_4$ is completely consumed within 3 h at 25 °C by excess PMe_3. The corresponding amount of free PMe_2Ph is also observed in this trapping of transient "$WH_2Cl_2L_3$".

Synthesis of $WH_3Cl(PMe_2Ph)_4$. Reaction of equimolar $WH_2Cl_2L_4$ and $LiBEt_3H$ in THF at or below 0 °C gives clean conversion to WH_3ClL_4, which can be isolated. The molecule is soluble in organic solvents but has a tendency to decompose in solution (even hydrocarbons) to PMe_2Ph and WH_6L_3. Such decomposition is not halted by added PMe_2Ph.

The $^{31}P\{^1H\}$ NMR spectrum of WH_3ClL_4 consists of an AM_2Q pattern, indicating the presence of a mirror plane of symmetry. In the ^1H NMR spectrum, the hydride ligands appear as two different chemical shifts, +2.15 and −2.54 ppm, with intensities 1:2. The former is in a sufficiently unusual region that its detection was initially overlooked. It was first detected by recording the $^2H\{^1H\}$ NMR spectrum of WD_3ClL_4 (see below for synthesis), where the +2.15 ppm multiplet is not obscured by aliphatic protons. Each hydride resonance is a well-resolved multiplet which conforms to the X and Z part of an AMM′QXX′Z spin system. Together, these results are consistent with a dodecahedral structure (**C**, which shows atom labels for the inner coordination sphere) derived by replacing one Cl by H in the structure of $WH_2Cl_2L_4$. This structure requires four PMe proton chemical shifts, consistent with what is observed. The two methyl signals from P_M and $P_{M'}$ appear as virtual triplets while those on P_A and P_Q are doublets. It bears mention that the number of hydrides might suggest a structure derived from an ideal cube by retention of its C_3 axis (**D**, which shows an idealized cube of ligating atoms around the tungsten). This, however, is inconsistent with the observed spectra. Moreover, although this would appear to be easily formed from **C**, the activation energy for this deformation must be large: **D** would effect site exchange of the three hydrides (and of three of the four phosphorus nuclei), but the molecule is observed to be (surprisingly) rigid.



C



D

Stereochemistry of Replacement of Chloride by Hydride in $WH_2Cl_2L_4$. We have investigated the stereochemistry of the transformation of $WH_2Cl_2L_4$ into WH_3ClL_4. Reaction in THF of $WH_2Cl_2L_4$ with equimolar $LiBEt_3D$ does not begin until −40 °C. At this temperature, the ^2H NMR spectrum shows only one W–D signal, at −2.5 (due to H_x in **C**), together with the single

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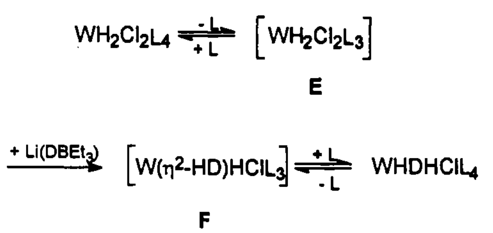
[9] Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353. Phosphine dissociation is also implicated for $WCl_2(PMePh_2)_4$. See: Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402. Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483.

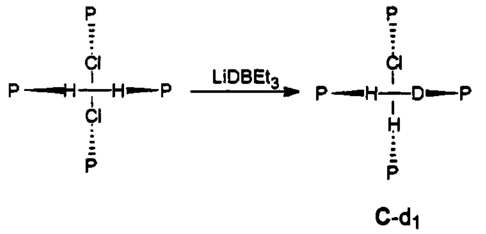
Scheme 3



(average) resonance of the rapid equilibrium in eq 2. The $^{31}P\{^1H\}$

$$Et_3BD^- + BEt_3 \rightleftharpoons Et_3B\text{–}D\text{–}BEt_3^- \qquad (2)$$

NMR spectrum at this point shows only $WH_2Cl_2L_4$ and WH_2DClL_4. As the temperature is raised to -30 °C and then -20 °C, $WH_2Cl_2L_4$ disappears and more WH_2DClL_4 appears (by ^{31}P NMR), and only the H_x signal of WH_2DClL_4 grows.[10] The reaction is thus selective for forming C-d_1 (eq 3); it does *not* simply place D in a chloride site of an undisturbed dodecahedron. Most remarkably, this molecule is stereochemically rigid on the time scale of 1 *day*: in $^2H\{^1H\}$ NMR C-d_1 shows less than 20% migration of deuterium to the Z site (see C) after 24 h.



(3)

C-d_1

Mechanism of Formation of $WH_2DCl(PMe_2Ph)_4$. A general consideration of the characteristics of the mechanism of eq 3 reveals two requirements. The reaction must destroy the symmetry of the two hydrides in $WH_2Cl_2L_4$. It must also make one of the original hydrides equivalent to the arriving deuteride. This latter could be accomplished either early or late in the mechanism. One mechanism which would make H and D equivalent very early in the reaction pathway is deprotonation of $WH_2Cl_2L_4$ (eq 4). In subsequent steps, lithium-assisted removal of a chloride ligand and oxidative addition of HD would show the observed stereoselectivity.

$$WH_2Cl_2L_4 + LiBEt_3D \rightarrow Li^+ + [WHCl_2L_4^-] + HD + BEt_3 \qquad (4)$$

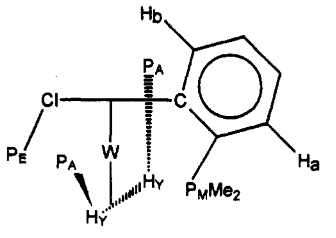
To test this mechanism, we have carried out the reaction of $WH_2Cl_2L_4$ with $LiBEt_3H$ at -20 °C under 1 atm of D_2. The reaction was executed in a vessel with a large head space, large liquid surface area, and vigorous stirring, to ensure solution saturation with D_2 and optimal mixing of D_2 with any liberated H_2. After 30 min, when the reaction had proceeded 50% to completion, there was no evidence (^1H and ^2H NMR of the hydride signals) for deuterium incorporation.[11] We therefore conclude that a mechanism involving deprotonation of $WH_2Cl_2L_4$, with liberation of HD into the bulk solution (eq 4), may be excluded.

Therefore, we again considered a mechanism (Scheme 3) dissociative in phosphine (E) followed by replacement of chloride by deuteride. Loss of phosphine leaves the metal electron-poor and thus favors formation of an η^2-HD ligand, in which H and D are equivalent (F). Subsequent phosphine association increases the electron density at the tungsten and cleaves the H–D bond. Similar considerations may explain the lack of facile site exchange via phosphine dissociation in WH_2DClL_4.

Attempted Replacement of Halide Ligands by Nucleophiles. (a) Attempted Single Chloride Replacement. It was our goal to transform $WH_2Cl_2(PMe_2Ph)_4$ into a hydrido compound which also contained a stronger π-donor ligand than chloride. This was attempted by reaction of $WH_2Cl_2(PMe_2Ph)_4$ with alkali metal amides and alkoxides, using both noncoordinating (toluene) and coordinating (THF) solvents. The general consequence of these studies is to reinforce the conclusion of Richards[2] (using NEt_3 as base) that $WH_2Cl_2(PMe_2Ph)_4$ is quite prone to dehydrochlorination by an added Brønsted base.

In THF solvent, we find that HCl elimination is apparently followed by THF coordination, to give paramagnetic products (no ^1H or $^{31}P\{^1H\}$ NMR signals). No significant amount of phosphine is liberated in these reactions. Attempted isolation and crystallization gave only variable yields of $WH_3Cl(PMe_2Ph)_4$, and this effort was therefore abandoned. A change to toluene solvent with MOR (M = Na, K; OR = $OCMe(CF_3)_2$, $OSiMe_2Ph$) yielded similar results.

In toluene, alkali metal amides showed very different behavior. Dehydrochlorination was followed by *ortho*-metalation of a phosphine phenyl ring. Thus, from $KN(SiMe_3)_2$ and $WH_2Cl_2(PMe_2Ph)_4$ in toluene at 25 °C, there is an immediate color change. Workup yields $WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$, identified as *ortho*-metalated by an A_2EM $^{31}P\{^1H\}$ NMR pattern with a remarkably high-field shift (to -59.6 ppm) of the M nucleus (compare E at -20.9 and A at -12.4 ppm). Structure G (lines connect ligands which form trapezoids of the dodecahedron and are not chemical bonds) is consistent with this information and predicts four P–Me ^1H NMR chemical shifts, which is what is observed. Moreover, two of these methyl signals are virtual triplets, which we assign to the diastereotopic methyls on P_A and P_A'. Two aryl protons fall at the limits of the typical aryl region. These, at 6.4 and 8.3 ppm, we assign to the hydrogens most influenced by metalation: H_a and H_b in structure G. The two hydrides in structure G, being related by a mirror plane of symmetry, appear as a single chemical shift (-0.89 ppm) but as a non-first-order multiplet (15 lines of a AA'EMYY' spin system).



G

This reaction of $KN(SiMe_3)_2$ with $WH_2Cl_2(PMe_2Ph)_4$ in toluene also produces smaller amounts of dark red side products (altogether ~10%). These, as well as the amine $NH(SiMe_3)_2$, are difficult to separate from the highly soluble $WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$. Therefore, $WH_2Cl_2(PMe_2Ph)_4$ was reacted in toluene with 1 equiv of ^tBuLi in *n*-hexane or neopentyllithium. The reactions are instantaneous and form the desired $WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$ in yields above 95% (by $^{31}P\{^1H\}$ NMR). However, its hexane solubility as well as its thermal sensitivity result in yields of only 30% after crystallization. As a working hypothesis, we suggest that the *ortho*-metalation implies the intermediacy of a reduced, unsaturated species (eq 5, η^2-L = η^2-$C_6H_4PMe_2$).

$$WH_2Cl_2L_4 + MR \underset{-MCl}{\overset{-RH}{\rightarrow}} [WHClL_4] \rightarrow WH_2Cl(\eta^2\text{-}L)L_3 \qquad (5)$$

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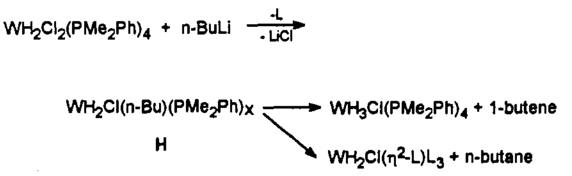
[10] The ^2H NMR signal due to eq 2 moves further upfield as the equilibrium shifts away from the -0.7 ppm position of $LiBEt_3D$ in THF.

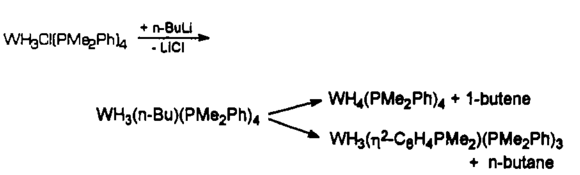
[11] At this temperature, the D_2 exchange of $WH_2Cl_2L_4$ and WH_3ClL_4 is very slow and in the course of the experiment not detectable by NMR. However, to avoid any D_2 contamination of the starting material or the product by D_2 exchange, all manipulations until the removal of D_2 from the gas phase had to be done at -20 °C.

It is reasonable that a coordinating solvent (THF) could intercept $WHCl(PMe_2Ph)_4$ before metalation of the phenyl group could occur, and this would be the source of the paramagnetic products we encountered in THF solvent. In order to test our hypothesis, and to use this dehydrochlorination for some rational purpose, $WH_2Cl_2(PMe_2Ph)_4$ was reacted (25 °C) with 1 equiv of *n*-BuLi in toluene in the presence of excess H_2. We anticipated that H_2 would trap $WHCl(PMe_2Ph)_4$, and we indeed observe over 70% yield of $WH_3Cl(PMe_2Ph)_4$. However, $WH_3Cl(PMe_2Ph)_4$ is *also* produced by this same reaction (at −40 °C) in the *absence* of H_2 (together with a small amount of $WH_2Cl(\eta^2\text{-}L)L_3$), implicating a different mechanism for an alkyl reagent containing β-hydrogens (eq 6) from that in eq 5.



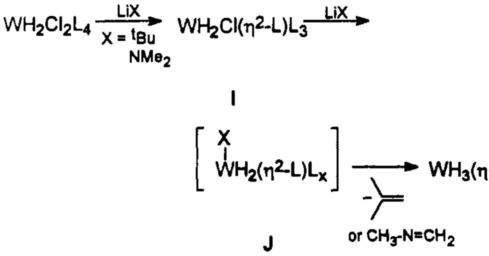
(6)

(b) Attempted Double Chloride Replacement. The above results implicate an alkyl intermediate **H**, which β-hydrogen eliminates at a rate competitive with its reductive elimination of butane. Consistent with this hypothesis, if $WH_2Cl_2(PMe_2Ph)_4$ is reacted with 2 equiv of *n*-BuLi (or correspondingly $WH_3Cl(PMe_2Ph)_4$ with 1 equiv *n*-BuLi), then mainly $WH_4(PMe_2Ph)_4$ (the product of two β-hydrogen eliminations) but also $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$ (25% yield,[12] as the product of one β-hydrogen elimination and one ortho-metalation) are observed (eq 7).



(7)

However, $WH_3(\eta^2\text{-}L)L_3$ can be obtained (eq 8) in >80% yield

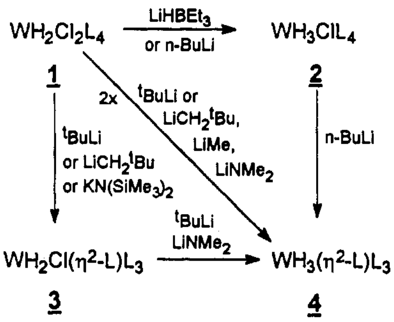


(8)

by the reaction of $WH_2Cl_2L_4$ with *2* equiv of ${}^tBuLi$ or $LiNMe_2$. $WH_3(\eta^2\text{-}L)L_3$ here is thus the product of monodehydrochlorination (see **I** in eq 8) and a β-hydrogen elimination after successful substitution of the second chloride ligand by the nucleophile (**J** in eq 8). For confirmation, $WH_2Cl(\eta^2\text{-}L)L_3$ was reacted with 1 equiv of ${}^tBuLi$ and $LiNMe_2$, respectively. This yields exclusively $WH_3(\eta^2\text{-}L)L_3$. Use of $KN(SiMe_3)_2$ as base for reaction with $WH_2Cl_2L_4$ even in a 5-fold excess yields only $WH_2Cl(\eta^2\text{-}L)L_3$. A substitution of the last chloride ligand by this bulky amide is not possible. These reactions are summarized in Scheme 4.

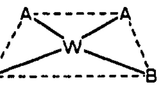
Surprisingly, a 1:2 reaction of $WH_2Cl_2L_4$ with MeLi or Me_3CCH_2Li (both of which lack β-hydrogens) forms $WH_3(\eta^2\text{-}L)L_3$ in high yields. To exclude the solvent, toluene, as the source of hydrogen, the reaction was executed in toluene-d_8. After completion of the reaction, all volatiles were removed. The remaining organometallic product showed (by ^2H NMR) no evidence for any deuteration. Furthermore, for reaction with Me_3CCH_2Li, the volatiles were investigated by GC/MS, revealing at least six organic products, one of which is 2,2,5,5-tetramethylhexane. All products show a MS pattern typical for aliphatic hydrocarbons. None was present in the solvent employed. Therefore, the third hydride ligand derives from α- or γ-elimination. The resulting carbenes react unselectively to give a mixture of different organic products.[13]

Scheme 4



Orange crystals of $WH_3(\eta^2\text{-}L)L_3$ obtained from a hexane solution were suitable for an X-ray diffraction structure determination.

Structure of $WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$. The results of the X-ray diffraction structure determination both confirm and extend the conclusions from NMR spectroscopy. All hydrogens, including the hydrides, were located and refined. The molecule is eight-coordinate (Figure 1) and based on a dodecahedral form. Atoms P(2), P(20), H(A), and H(B) define one trapezoidal plane. The H_A–W–H_B angle is 69° with an H_A/H_B distance of 1.88 Å. Atoms P(11), H(C), C(37), and P(29) define another trapezoidal plane, which is also an idealized mirror plane of symmetry of the molecule. These two planes are approximately orthogonal. The bulkier phosphorus nuclei always occupy the less-hindered B sites of the trapezoidal (see **K**) planes which define a dodecahedron, with hydride and carbon at the more crowded A sites. The rotational conformation about the W–P(2) and W–P(20) bonds directs two phenyl rings away from the (crowded) region where the metalated phenyl ring is bonded to tungsten. The WPCC ring involving the metalated carbon incorporates very small P(29)–W–C(37) (63.35°), W–P(29)–C(32) (88.12°), and P(29)–C(32)–C(37) (101.1°) angles. While the P(29)–C(32) distance is short, 1.791(7) Å (compare the other P–C *ipso* distances of 1.827(7)–1.846(6) Å), the C/C distances in the metalated ring show no unusual features. The W–P distances show an unusually large range of values (2.438(2)–2.487(2) Å), but these do not conform to the mirror symmetry of the inner coordination sphere and thus may originate from steric pressure on the aryl rings. Note particularly that the *ortho*-metalated phosphine has a W–P distance in the middle of the range.



K

Solution Behavior of $WH_3(\eta^2\text{-}L)L_3$. An AB_2M $^{31}P\{^1H\}$ NMR pattern is observed at 25 °C for **4**, in agreement with the solid-state structure. The phosphorus P_M in the *ortho*-metalated ring shows a chemical shift (−79.7 ppm) to even higher field than in **3** (−59.6 ppm). The solid-state structure requires four methyl chemical shifts, two of which (on P_A and P_A') overlap to give one multiplet. Consistent with the solid-state structure, two hydride chemical shifts are observed (rather downfield, at −1.44 and +0.55 ppm), with intensities of 2:1. Overall, these observations establish

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[12] Yield calculated by ^1H and $^{31}P\{^1H\}$ NMR.

[13] This GC/MS study excludes moisture in solvent or on the glass wall as a source of the hydride ligands.

that compound **4** in solution is a stereochemically-rigid molecule with structure identical to that found in the solid.

Discussion

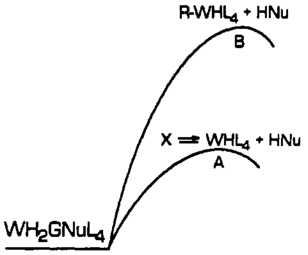
A remarkable aspect of these results is the stereochemical *rigidity* of the eight-coordinate polyhydrides $WH_2Cl_2L_4$ and WH_3ClL_4. Eight-coordinate compounds are generally highly fluxional (although some notable exceptions exist[14]), and polyhydrides are almost universally fluxional. The finding (via the selectively-labeled WH_2DClL_4) of a species which is stereochemically rigid on the time scale of 1 *day* is unprecedented. For reference, $WH_4(PMe_2Ph)_4$ is fluxional (10^2 sec^{-1} at 28 °C), although the rearrangement barrier (15 kcal/mol) is somewhat higher than for many polyhydrides.[15]

The reactions of $WH_2Cl_2L_4$ with the nucleophiles KOR, $KN(SiMe_3)_2$, and LiR fail to give isolable chloride substitution products (eq 9), yielding instead product distributions more

$$WH_2Cl_2L_4 + Nu^- \not\longrightarrow WH_2Cl(Nu)L_4 + Cl^- \qquad (9)$$

suggestive of dehydrochlorination reactions. However, a more complete analysis of the results reported here show that not *all* of the reactions can be initiated by simple proton transfer to the base (nucleophile). This conclusion follows since proton transfer would produce the single species $WHCl_2L_4^-$, yet the observed reactions are different for different nucleophiles. Moreover, the product WH_3ClL_4 from *n*-BuLi implies β-hydrogen elimination from an *n*-butyl intermediate (i.e., a product of chloride substitution).

Scheme 5



The problem thus seems to originate not from a failure to substitute for chloride but rather from inherent instabilities (i.e., unimolecular reactivity) of the desired $WH_2Cl(Nu)L_4$. The facile occurrence of the proposed reductive elimination from this intermediate is, we feel, due to stabilization of the six-coordinate elimination product by lone pairs on the chloride ligand (Scheme 5, where G = X carries a lone pair while G = R has none). The preferred reagent for synthesis of a hydrido/π-donor mixed-ligand compound is thus WH_3ClL_4, since the initial product of chloride substitution is now kinetically inhibited from reductive elimination (it lies on curve B in Scheme 5). In general, this reasoning predicts special problems (i.e., instability) will be associated with trying to synthesize hydride/π-donor mixed-ligand compounds when there is more than one π-donor present.

Acknowledgment. This work was supported by the National Science Foundation. We also thank Steve Studley for mass spectral analyses.

Supplementary Material Available: Tables listing full crystallographic details, full atomic coordinates and *B* values, anisotropic thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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