SUPPORTING INFORMATION

Dihydrogen activation by a tungsten–alkylidyne complex: toward photoredox chromophores that deliver renewable reducing equivalents

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Contents

A. Syntheses, Spectra, and Reactions

General Procedures. All experiments were performed under a nitrogen atmosphere using standard Schlenk and glovebox techniques. HPLC-grade solvents, stored under nitrogen, were purified by passing them under nitrogen pressure through an anaerobic, stainless-steel system consisting of either two 4.5 in. × 24 in. (1 gal.) columns of activated A2 alumina (CH_3CN, Et_2O, CH_2Cl_2, and THF) or one column of activated A2 alumina and one column of activated BASF R3-11 catalyst (toluene).[1] Benzene-d_6 was dried over Na:K (1:2) alloy. Dichloromethane-d_2 was dried over P_2O_5 or 3A molecular sieves. THF-d_8 was dried over Na:K (1:2) alloy or 3A molecular sieves. Acetonitrile-d_3 was dried over calcium hydride. $W(CPh)(dppe)_2Cl$ (**1**)[2] and $[W(CPh)(dppe)_2Cl][OTf]$ (**1**[OTf])[3] were prepared by standard procedures. Isotopically labeled $[W(^{13}CPh)(H)(dppe)_2Cl][PF_6]$ was prepared by following the procedure below for $[W(CPh)(H)(dppe)_2Cl][PF_6]$ ([**1H**][PF_6]) from the starting material $W(^{13}CPh)(dppe)_2Cl$, with the ^{13}C label being derived from $Ph^{13}C^{13}CPh$.[2,4] All other reagents were obtained from commercial sources and used as received. ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR spectra were recorded using Bruker AF-500 or DRX 400 MHz NMR spectrometers at room temperature unless otherwise noted. Chemical shifts were measured relative to solvent resonances (^1H and ^{13}C) or an external standard of 85% H_3PO_4 (^{31}P).

Synthesis of $[W(CPh)(H)(dppe)_2Cl][PF_6]$ ([1H][PF_6]). To a stirred suspension of **1** (0.160 g, 0.144 mmol) in THF (5 mL) at room temperature was added dropwise a solution of HCl (0.5 mL, 1 M in Et_2O, 0.5 mmol) over 10 min. The color of the reaction mixture changed from dark orange-red to dark golden yellow and a precipitate formed. After 2 h the volatile components were removed under vacuum. The remaining off-white solid was dissolved in acetonitrile (6 mL), and to the resulting yellow solution was added a solution of KPF_6 (0.045 g, 0.244 mmol) in acetonitrile (4 mL) with stirring. A white precipitate formed immediately. After 12 h, the precipitate was removed via filtration from the yellow solution and washed with cold acetonitrile (3 × 5 mL). The volatile components were removed from the yellow filtrate and extracted into dichloromethane (10 mL). The solution was filtered through celite, which removed a small amount of solid, and the volatile components were removed under vacuum. The crude product was recrystallized from acetonitrile (0.5 mL) layered with toluene (2 mL) at –50 ˚C. [**1H**][PF_6] was collected via filtration as an off-white powder from the light yellow solution, washed with Et_2O (15 mL), and dried under vacuum (0.126 g, 0.100 mmol, 69.4% yield).

Selected NMR spectra are shown in Figures S1–S4. ^{1}H NMR (500.13 MHz, CD_3CN): δ 7.42 (m, 8 H, *o*-PPh_2), 7.38 (m, 8 H, *o*-PPh_2), 7.33 (m, 8 H, *p*-PPh_2), 7.21 (m, 8 H, *m*-PPh_2), 7.09 (m, 8 H, *m*-PPh_2), 6.95 (t, 1 H, $^{3}J_{HH}$ = 7 Hz, *p*-C_6H_5), 6.68 (t, 2 H, $^{3}J_{HH}$ = 7 Hz, *m*-C_6H_5), 5.81 (d, 2 H, $^{3}J_{HH}$ = 7 Hz, *o*-C_6H_5), 4.21 (quin with satellites, $^{2}J_{HP}$ = 43 Hz, $^{1}J_{HW}$ = 13 Hz, WH) 3.11 (d, 8 H, PCH_2). ^{1}H NMR (500.13 MHz, CD_2Cl_2): δ 7.42 (m, 8 H, *o*-PPh_2), 7.37 (m, 8 H, *o*-PPh_2), 7.33 (m, 8 H, *p*-PPh_2), 7.19 (m, 8 H, *m*-PPh_2), 7.12 (m, 8 H, *m*-PPh_2), 6.97 (t, 1 H, $^{3}J_{HH}$ = 8 Hz, *p*-C_6H_5), 6.70 (t, 2 H, $^{3}J_{HH}$ = 8 Hz, *m*-C_6H_5), 5.68 (d, 2 H, $^{3}J_{HH}$ = 7 Hz, *o*-C_6H_5), 4.18 (quin with satellites, $^{2}J_{HP}$ = 43 Hz, $^{1}J_{HW}$ = 14 Hz, $^{2}J_{HC}$ = 6 Hz,† WH), 3.01 (m, 8 H, PCH_2). $^{13}C\{^{1}H\}$ NMR (125.78 MHz, CD_3CN): δ 265.67 (quin, $^{2}J_{CP}$ = 12 Hz, $^{1}J_{WC}$ = 190 Hz,† WC), 147.63 (s), 135.23 (s), 134.72 (s), 133.53 (s), 132.51 (s), 132.28 (s), 129.89 (s), 129.44 (s), 128.91 (s), 127.59 (s), 29.41 (br s). $^{31}P\{^{1}H\}$ NMR (125.78 MHz, CD_3CN): δ 45.45 (br s, WP_4), –144.02 (sep, PF_6). $^{31}P\{^{1}H\}$ NMR (125.78 MHz, CD_2Cl_2): δ 46.35 (br s, WP_4), –147.30 (sep, PF_6). *Anal.* Calc. (found) for $C_{59}H_{54}ClF_6P_5W$: C 56.64 (56.45); H 4.35 (4.57). † Datum measured for ^{13}C-labeled [W(^{13}CPh)(H)(dppe)$_2$Cl][PF_6].

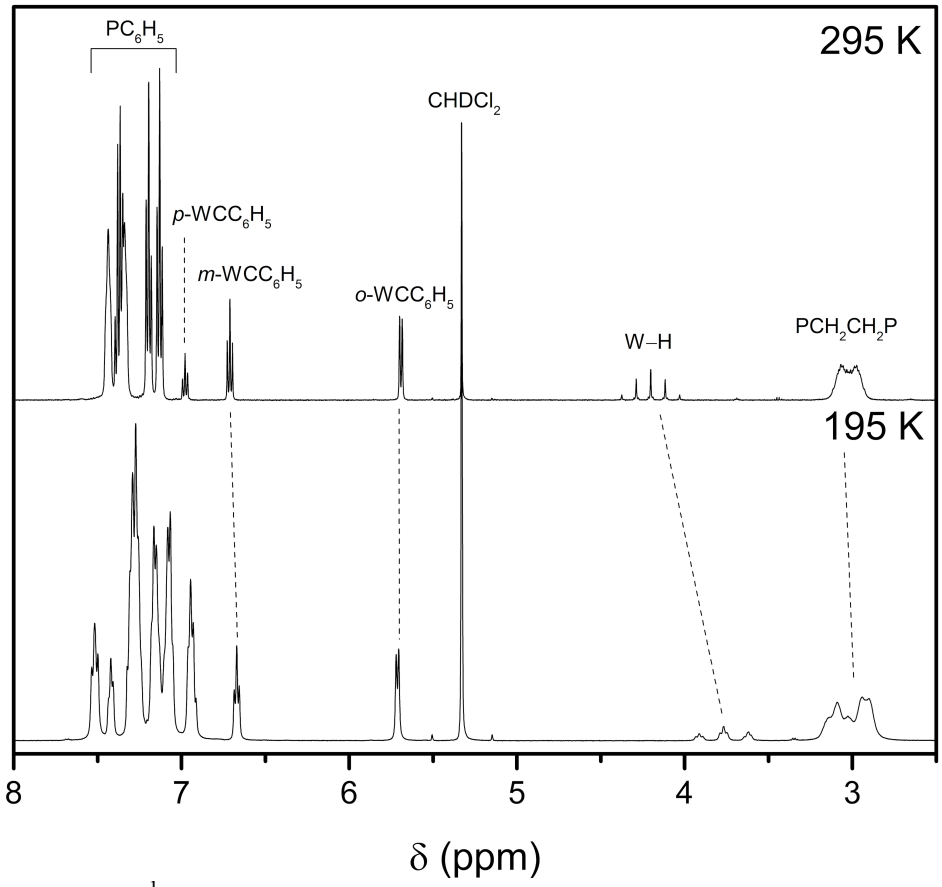

Figure S1. ^{1}H NMR spectra of [**1H**][PF_6] in CD_2Cl_2 at 295 and 195 K.

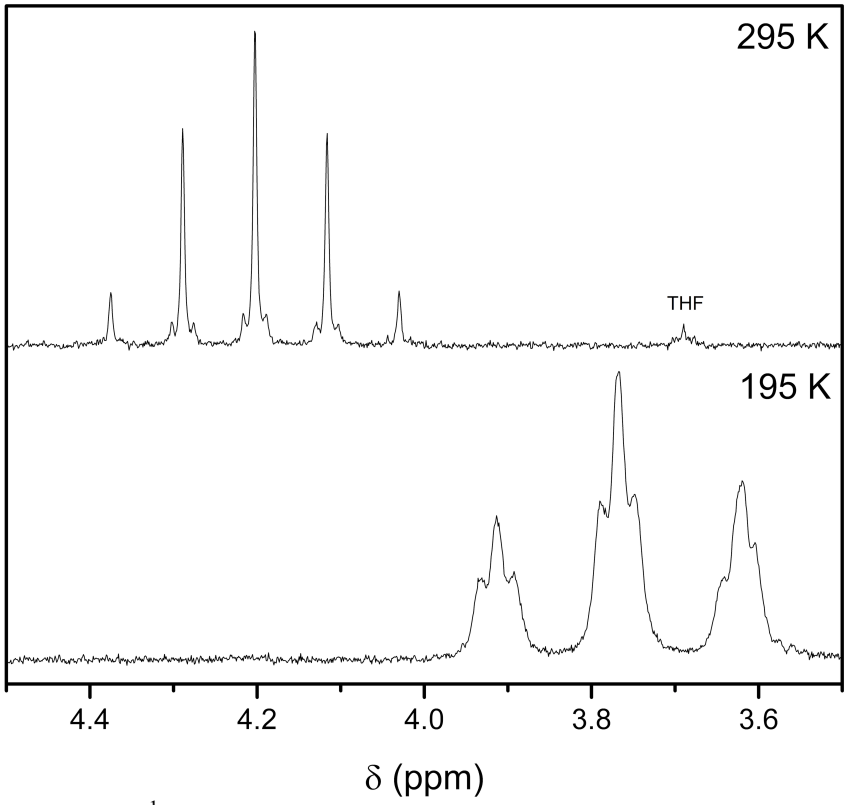

Figure S2. ^{1}H NMR W–*H* resonance of [**1H**][PF_6] in CD_2Cl_2, at 295 K and 195 K.

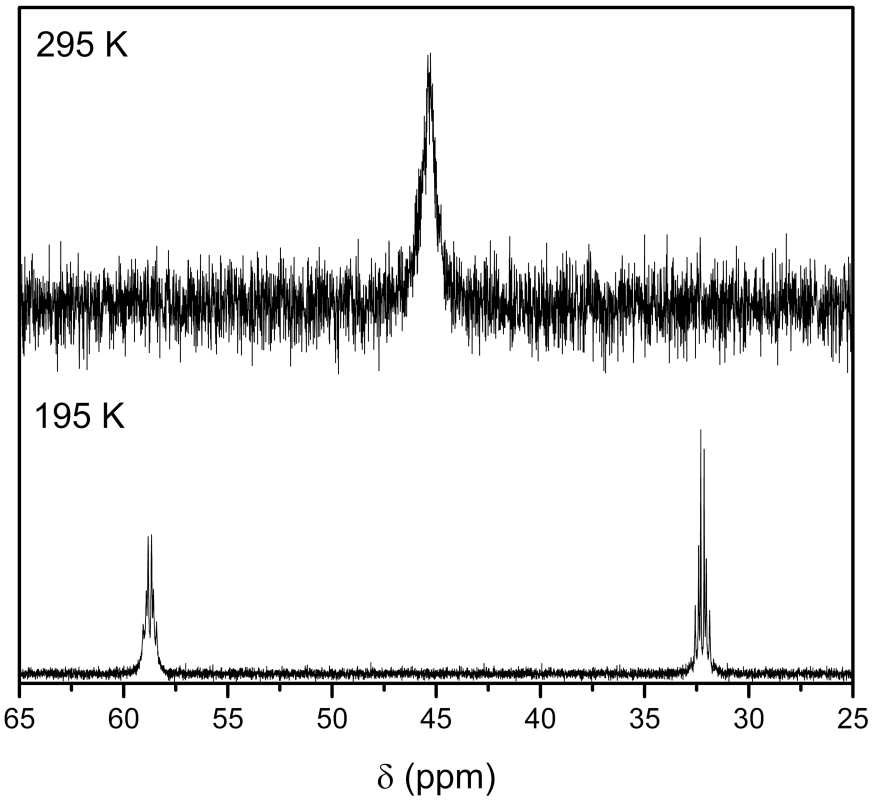

Figure S3. $^{31}P\{^{1}H\}$ NMR spectra of [**1H**][PF_6] in CD_2Cl_2 at 295 K and 195 K.

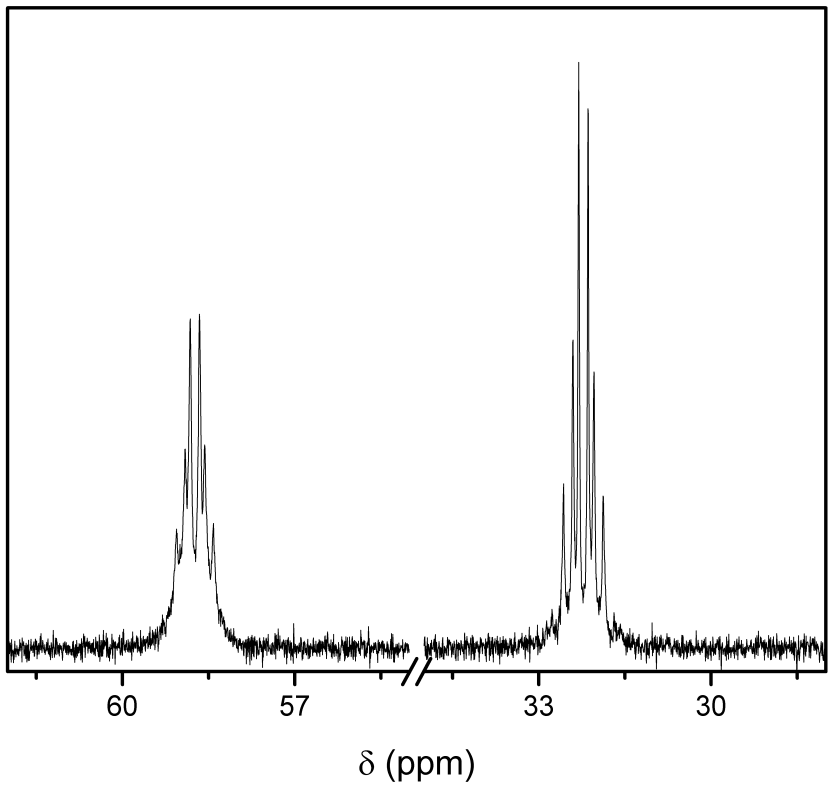

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of [**1H**][PF_6] in CD_2Cl_2 at 195 K.

Thermal stability of [1H][PF_6] in CD_2Cl_2 at 25 ˚C and 60 °C. A sealed NMR sample of [**1H**][PF_6] in CD_2Cl_2 was warmed in an oil bath at 60 ºC. The reaction was monitored periodically by ^{1}H and ^{31}P NMR spectroscopy. The first evidence of signals due to decomposition of [**1H**][PF_6] to unidentified products was observed after 10 d. At the end of 4 weeks [**1H**][PF_6] still represented > 50% of the total ^{1}H- and ^{31}P-NMR intensity, and the experiment was discontinued. A similar NMR sample of [**1H**][PF_6] at room temperature showed no evidence of decomposition over 4 weeks.

Reaction between 1[OTf] and H_2. A Fisher-Porter bottle containing a solution of **1**[OTf] (0.100 g, 0.08 mmol) in CH_2Cl_2 (60 mL) was evacuated and charged with H_2 (44 psi). The reaction mixture was stirred vigorously at room temperature for one week. During this time the color of the reaction mixture changed from orange to brown. Removal of the volatile components under vacuum yielded an off-white solid (ca. 0.08 g). This was extracted with toluene, in which [**1H**][OTf] is insoluble, and the remaining solid was collected by filtration and dried under vacuum. ^{1}H and ^{31}P NMR spectra of this product (Figures S5 and S6) showed it to be > 90% [**1H**][OTf] (0.038 g, 38% yield).

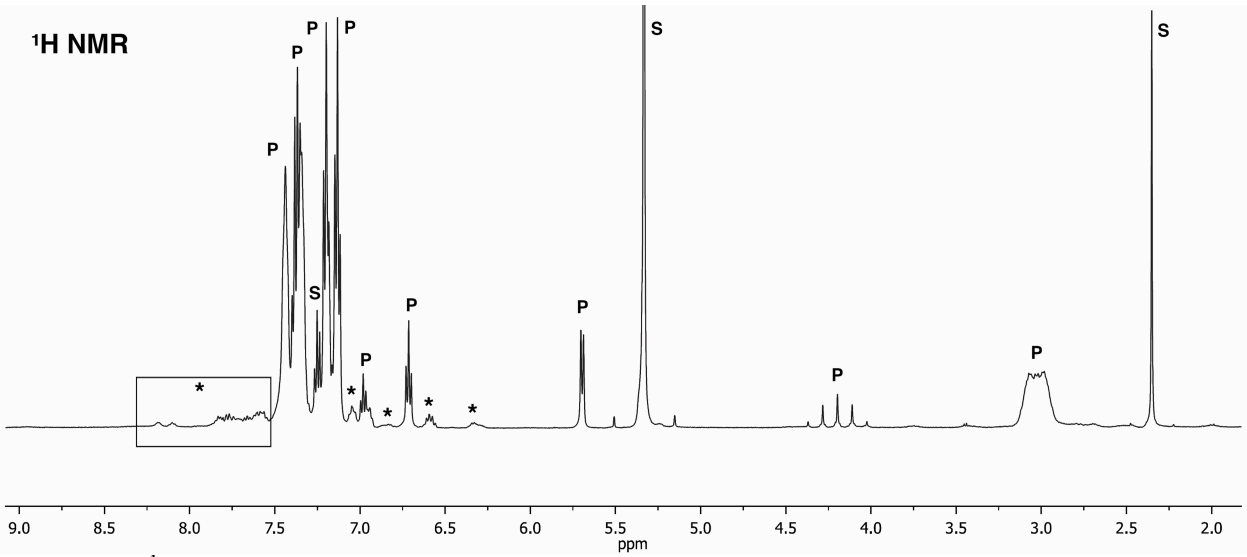

Figure S5. ^{1}H NMR spectrum (CD_2Cl_2) of the toluene-insoluble fraction of the product of the reaction between **1**[OTf] and H_2 (44 psi) in CH_2Cl_2 at 25 ˚C. The resonances due to the **1H**$^+$ product are labeled with a P; solvent resonances (toluene, $CHDCl_2$) are labeled with an S. Resonances denoted with asterisks are due to unidentified reaction side products.

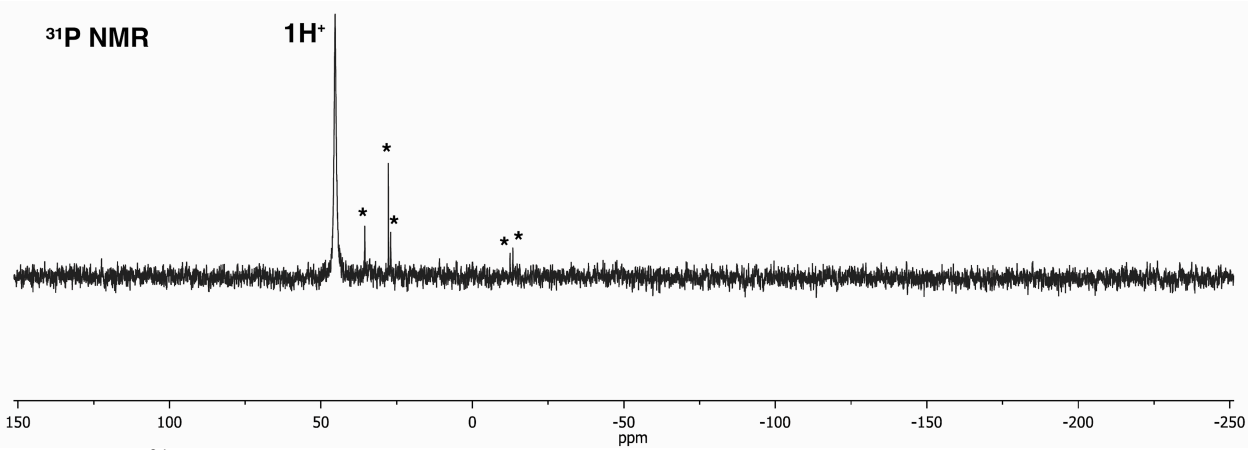

Figure S6. ^{31}P NMR spectrum (CD_2Cl_2) of the toluene-insoluble fraction of the product of the reaction between **1**[OTf] and H_2 (44 psi) in CH_2Cl_2 at 25 ˚C. The resonance due to **1H**$^+$ is indicated. Resonances denoted with asterisks are due to unidentified reaction side products.

B. Single Crystal X-ray Diffraction Structural Determination of [1H][PF_6].

Procedures. An irregular broken fragment (0.20 × 0.10 × 0.10 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained that samples approximately all of reciprocal space to a resolution of 0.75 Å using 0.3˚ steps in ω with 15 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT.[5] Absorption corrections were applied using SADABS[5] based on redundant diffractions.

The space group was determined as P1(bar) based on systematic absences and intensity statistics. Patterson methods were used to locate the W and P atoms. Repeated difference Fourier maps allowed recognition of all expected C, Cl and F atoms. Following anisotropic refinement of all non-hydrogen atoms, ideal H atom positions were calculated. Final refinement was anisotropic for W, P, Cl, C and F atoms and isotropic-riding for H atoms. No anomalous bond lengths or thermal parameters were noted. The C_7H_8 solvent and PF_6 are slightly disordered based on larger thermal ellipsoids. While NMR spectroscopy has confirmed that there is a H atom bonded to W, the residual electron density mainly associated with this heavy atom precludes confirmation of the presence or position of this H atom. ORTEP representations are shown in Figures S7–S10. Crystallographic data are set out in Tables S1 and S2.

Equations of interest:

(1) $R_{int} = \Sigma|F_o^2 - \langle F_o^2 \rangle| / \Sigma|F_o^2|$

(2) $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

(3) $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

where: $w = q / \sigma^2(F_o^2) + (aP)^2 + bP$;

q, a, b, P as defined in ref. [5].

(4) $GooF = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)^{1/2}$

n = number of independent reflections;

p = number of parameters refined.

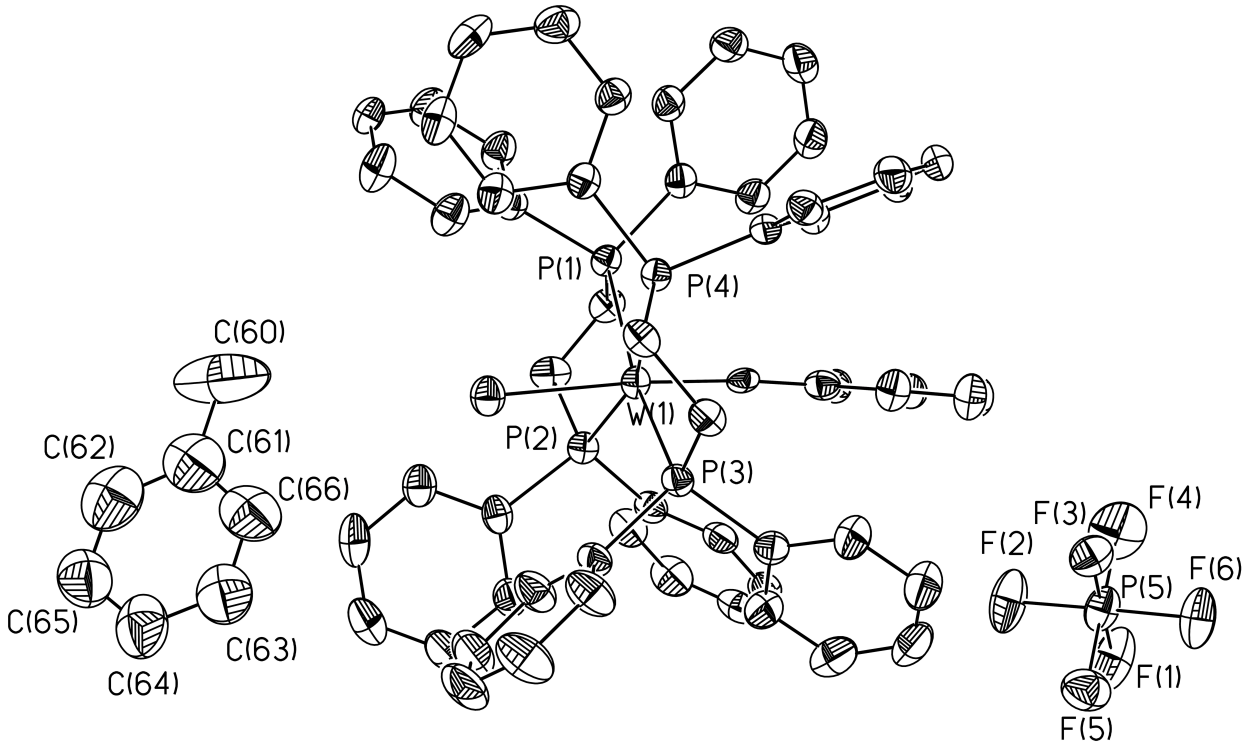

Figure S7. ORTEP representation (50% probability ellipsoids) of [**1H**][PF_6]•C_7H_8. Hydrogen atoms are omitted for clarity.

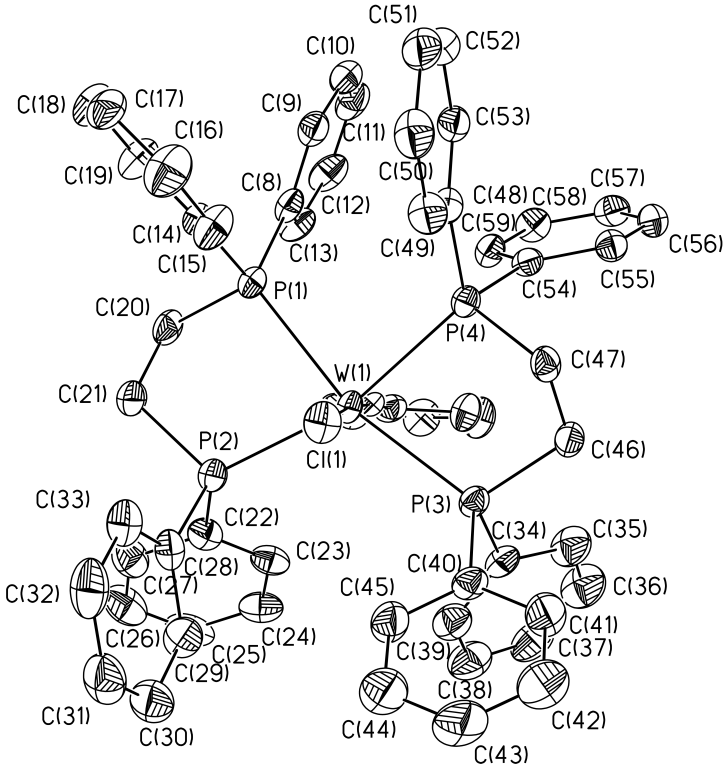

Figure S8. ORTEP representation (50% probability ellipsoids) of **1H**$^+$ ion of [**1H**][PF_6]•C_7H_8. Hydrogen atoms are omitted for clarity.

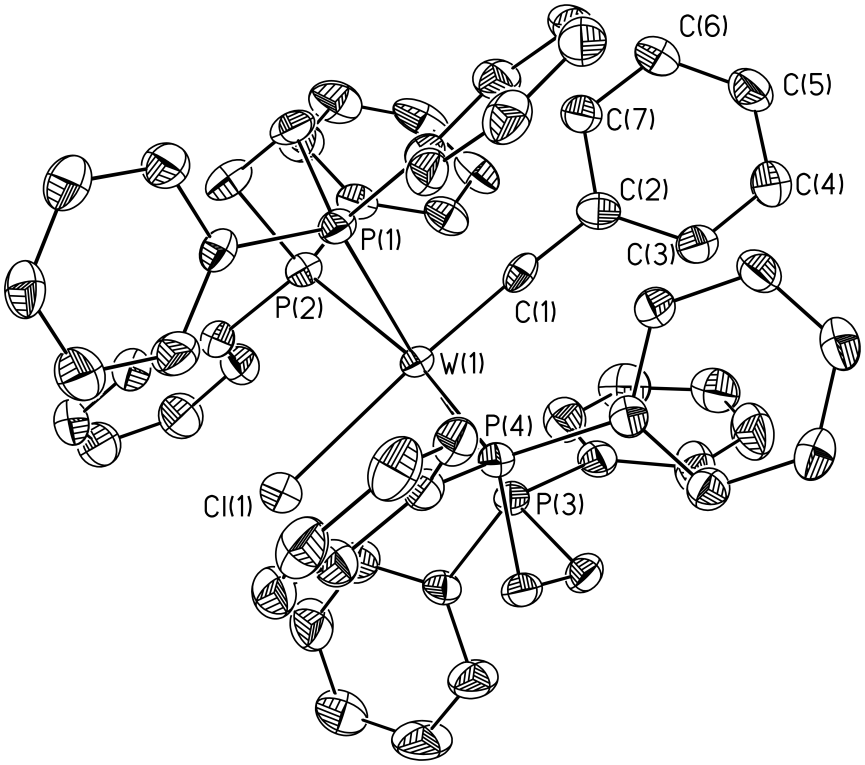

Figure S9. ORTEP representation (50% probability ellipsoids) of $\mathbf{1H}^+$ ion of [**1H**][PF_6]•C_7H_8. Hydrogen atoms are omitted for clarity.

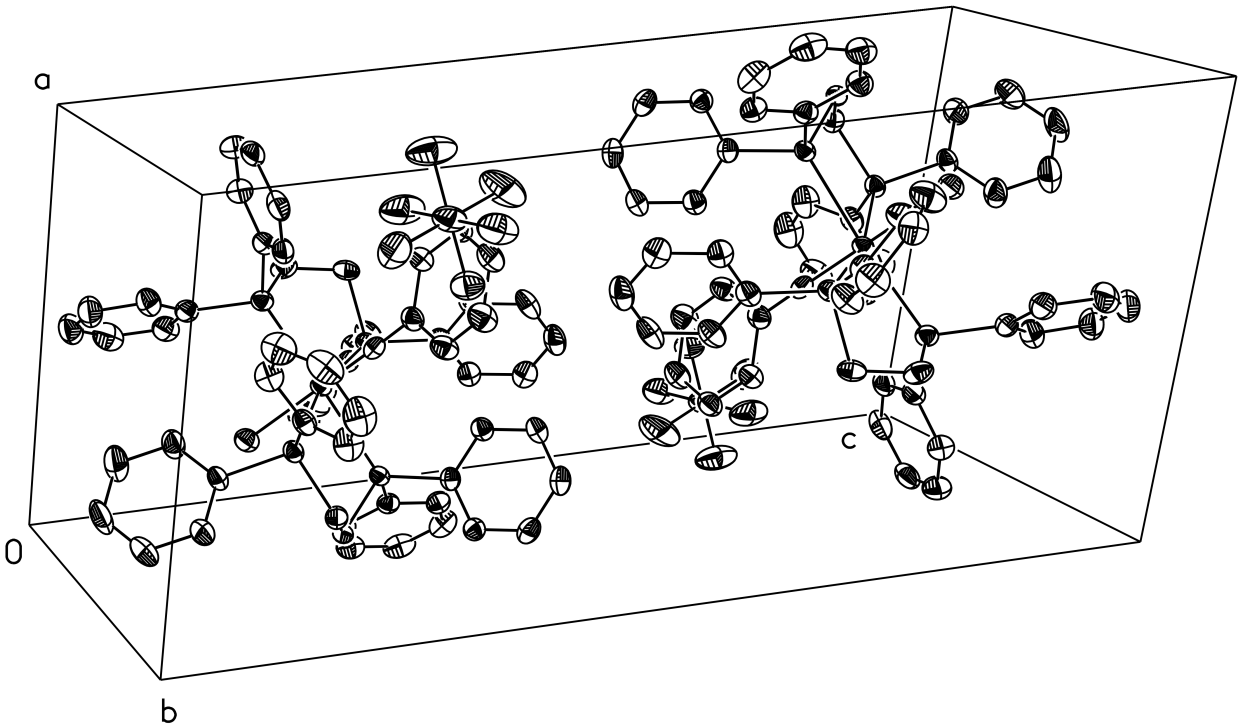

Figure S10. ORTEP representation (50% probability ellipsoids) of unit cell of [**1H**][PF_6]•C_7H_8. Hydrogen atoms are omitted for clarity.

Table S1. Crystal and Structure Refinement Data for [**1H**][PF_6]•C_7H_8.

Empirical formula	$C_{59}H_{53}ClP_4W + PF_6 + C_7H_8$	
Formula weight	1342.30	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space Group	P1(bar)	
Unit cell dimensions	a = 11.066(3) Å	α = 78.017(4)°
	b = 12.217(3) Å	β = 79.887(4)°
	c = 22.205(6) Å	γ = 80.575(4)°
Volume	2865.5(14) Å^3	
Z	2	
Density (calculated)	1.556 Mg/m^3	
Absorption coefficient	2.264 mm^{-1}	
F(000)	1354	
Crystal size, color, habit	0.20 × 0.10 × 0.10 mm, orange, fragment	
Theta range for data collection	1.72 – 28.31°	
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-28 \le l \le 29$	
Reflections collected	33,829	
Independent reflections	13,542 (R_{int} = 0.0298)	
Reflections with I > 4σ(F_o)	11,867	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.852	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = q\,[\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where:	
	$P = (F_o^2 + 2F_c^2)/3$, a = 0.0391, b = 0.0, q = 1	
Data / restraints / parameters	13542 / 0 / 713	
Goodness-of-fit on F^2	1.018	
Final R indices [I > 2 sigma(I)]	R1 = 0.0357, wR2 = 0.0784	
R indices (all data)	R1 = 0.0426, wR2 = 0.0806	
Largest diff. peak and hole	2.198, –0.799 e Å^{-3}	

Table S2. Bond Lengths (Å) and Angles (deg) for [**1H**][PF_6]•C_7H_8.

C(1)-C(2)	1.396(5)	C(37)-C(38)	1.357(6)
C(1)-W(1)	1.858(3)	C(38)-C(39)	1.395(6)
C(2)-C(7)	1.409(5)	C(40)-C(41)	1.376(5)
C(2)-C(3)	1.411(5)	C(40)-C(45)	1.386(5)
C(3)-C(4)	1.375(5)	C(40)-P(3)	1.835(3)
C(4)-C(5)	1.383(5)	C(41)-C(42)	1.380(5)
C(5)-C(6)	1.369(5)	C(42)-C(43)	1.359(6)
C(6)-C(7)	1.377(5)	C(43)-C(44)	1.357(6)
C(8)-C(9)	1.390(5)	C(44)-C(45)	1.377(5)
C(8)-C(13)	1.396(5)	C(46)-C(47)	1.527(5)
C(8)-P(1)	1.824(4)	C(46)-P(3)	1.825(3)
C(9)-C(10)	1.384(5)	C(47)-P(4)	1.828(3)
C(10)-C(11)	1.381(5)	C(48)-C(53)	1.384(5)
C(11)-C(12)	1.374(6)	C(48)-C(49)	1.402(5)
C(12)-C(13)	1.378(5)	C(48)-P(4)	1.825(4)
C(14)-C(19)	1.379(5)	C(49)-C(50)	1.383(5)
C(14)-C(15)	1.393(5)	C(50)-C(51)	1.369(6)
C(14)-P(1)	1.819(3)	C(51)-C(52)	1.383(6)
C(15)-C(16)	1.396(5)	C(52)-C(53)	1.392(5)
C(16)-C(17)	1.352(6)	C(54)-C(55)	1.384(5)
C(17)-C(18)	1.364(5)	C(54)-C(59)	1.403(5)
C(18)-C(19)	1.389(5)	C(54)-P(4)	1.821(3)
C(20)-C(21)	1.522(5)	C(55)-C(56)	1.387(5)
C(20)-P(1)	1.833(4)	C(56)-C(57)	1.382(5)
C(21)-P(2)	1.821(4)	C(57)-C(58)	1.379(5)
C(22)-C(23)	1.378(5)	C(58)-C(59)	1.390(5)
C(22)-C(27)	1.401(5)	C(60)-C(61)	1.501(9)
C(22)-P(2)	1.826(4)	C(61)-C(66)	1.394(9)
C(23)-C(24)	1.396(5)	C(61)-C(62)	1.410(9)
C(24)-C(25)	1.373(6)	C(62)-C(63)	1.378(9)
C(25)-C(26)	1.375(6)	C(63)-C(64)	1.393(8)
C(26)-C(27)	1.373(6)	C(64)-C(65)	1.364(7)
C(28)-C(33)	1.382(5)	C(65)-C(66)	1.383(8)
C(28)-C(29)	1.402(5)	Cl(1)-W(1)	2.5215(10)
C(28)-P(2)	1.819(4)	F(1)-P(5)	1.599(3)
C(29)-C(30)	1.387(5)	F(2)-P(5)	1.590(3)
C(30)-C(31)	1.367(6)	F(3)-P(5)	1.591(2)
C(31)-C(32)	1.365(6)	F(4)-P(5)	1.580(3)
C(32)-C(33)	1.403(6)	F(5)-P(5)	1.585(3)
C(34)-C(39)	1.373(5)	F(6)-P(5)	1.593(2)
C(34)-C(35)	1.386(5)	P(1)-W(1)	2.5922(10)
C(34)-P(3)	1.819(4)	P(2)-W(1)	2.5020(10)
C(35)-C(36)	1.383(6)	P(3)-W(1)	2.5196(10)
C(36)-C(37)	1.370(6)	P(4)-W(1)	2.5876(10)

C(2)-C(1)-W(1)	175.5(3)	C(10)-C(9)-C(8)	120.6(4)
C(1)-C(2)-C(7)	121.2(3)	C(11)-C(10)-C(9)	120.4(4)
C(1)-C(2)-C(3)	121.7(3)	C(12)-C(11)-C(10)	119.2(4)
C(7)-C(2)-C(3)	117.1(3)	C(11)-C(12)-C(13)	121.2(4)
C(4)-C(3)-C(2)	121.1(4)	C(12)-C(13)-C(8)	120.1(4)
C(3)-C(4)-C(5)	120.3(4)	C(19)-C(14)-C(15)	117.9(3)
C(6)-C(5)-C(4)	119.7(4)	C(19)-C(14)-P(1)	120.8(3)
C(5)-C(6)-C(7)	121.1(4)	C(15)-C(14)-P(1)	121.3(3)
C(6)-C(7)-C(2)	120.7(3)	C(14)-C(15)-C(16)	120.2(4)
C(9)-C(8)-C(13)	118.5(3)	C(17)-C(16)-C(15)	120.6(4)
C(9)-C(8)-P(1)	121.2(3)	C(16)-C(17)-C(18)	120.2(4)
C(13)-C(8)-P(1)	120.2(3)	C(17)-C(18)-C(19)	120.0(4)

C(14)-C(19)-C(18)	121.1(4)	C(8)-P(1)-C(20)	103.44(16)
C(21)-C(20)-P(1)	107.6(2)	C(14)-P(1)-W(1)	123.40(12)
C(20)-C(21)-P(2)	108.6(2)	C(8)-P(1)-W(1)	118.14(11)
C(23)-C(22)-C(27)	118.5(4)	C(20)-P(1)-W(1)	104.76(12)
C(23)-C(22)-P(2)	122.4(3)	C(28)-P(2)-C(21)	103.68(17)
C(27)-C(22)-P(2)	118.8(3)	C(28)-P(2)-C(22)	101.63(17)
C(22)-C(23)-C(24)	120.8(4)	C(21)-P(2)-C(22)	104.11(18)
C(25)-C(24)-C(23)	119.8(4)	C(28)-P(2)-W(1)	117.23(12)
C(24)-C(25)-C(26)	119.7(4)	C(21)-P(2)-W(1)	110.48(12)
C(27)-C(26)-C(25)	121.0(4)	C(22)-P(2)-W(1)	117.98(12)
C(26)-C(27)-C(22)	120.2(4)	C(34)-P(3)-C(46)	104.68(17)
C(33)-C(28)-C(29)	118.9(3)	C(34)-P(3)-C(40)	103.31(16)
C(33)-C(28)-P(2)	121.9(3)	C(46)-P(3)-C(40)	103.46(16)
C(29)-C(28)-P(2)	119.2(3)	C(34)-P(3)-W(1)	115.86(12)
C(30)-C(29)-C(28)	120.3(4)	C(46)-P(3)-W(1)	110.61(11)
C(31)-C(30)-C(29)	120.5(4)	C(40)-P(3)-W(1)	117.46(12)
C(32)-C(31)-C(30)	119.8(4)	C(54)-P(4)-C(48)	103.89(15)
C(31)-C(32)-C(33)	121.0(4)	C(54)-P(4)-C(47)	102.49(15)
C(28)-C(33)-C(32)	119.5(4)	C(48)-P(4)-C(47)	102.28(16)
C(39)-C(34)-C(35)	118.0(4)	C(54)-P(4)-W(1)	116.62(11)
C(39)-C(34)-P(3)	119.3(3)	C(48)-P(4)-W(1)	123.40(11)
C(35)-C(34)-P(3)	122.7(3)	C(47)-P(4)-W(1)	105.35(11)
C(36)-C(35)-C(34)	120.7(4)	F(4)-P(5)-F(5)	180.0(2)
C(37)-C(36)-C(35)	120.7(4)	F(4)-P(5)-F(2)	90.61(17)
C(38)-C(37)-C(36)	118.9(4)	F(5)-P(5)-F(2)	89.41(16)
C(37)-C(38)-C(39)	121.0(4)	F(4)-P(5)-F(3)	90.39(16)
C(34)-C(39)-C(38)	120.5(4)	F(5)-P(5)-F(3)	89.58(14)
C(41)-C(40)-C(45)	117.3(3)	F(2)-P(5)-F(3)	90.49(14)
C(41)-C(40)-P(3)	122.2(3)	F(4)-P(5)-F(6)	90.34(16)
C(45)-C(40)-P(3)	120.5(3)	F(5)-P(5)-F(6)	89.64(15)
C(40)-C(41)-C(42)	121.2(4)	F(2)-P(5)-F(6)	179.03(17)
C(43)-C(42)-C(41)	120.7(4)	F(3)-P(5)-F(6)	89.71(13)
C(44)-C(43)-C(42)	119.0(4)	F(4)-P(5)-F(1)	89.64(18)
C(43)-C(44)-C(45)	121.0(4)	F(5)-P(5)-F(1)	90.38(17)
C(44)-C(45)-C(40)	120.8(4)	F(2)-P(5)-F(1)	90.03(14)
C(47)-C(46)-P(3)	108.3(2)	F(3)-P(5)-F(1)	179.47(15)
C(46)-C(47)-P(4)	107.2(2)	F(6)-P(5)-F(1)	89.76(14)
C(53)-C(48)-C(49)	118.9(3)	C(1)-W(1)-P(2)	93.23(10)
C(53)-C(48)-P(4)	121.2(3)	C(1)-W(1)-P(3)	91.64(10)
C(49)-C(48)-P(4)	119.9(3)	P(2)-W(1)-P(3)	117.14(3)
C(50)-C(49)-C(48)	120.3(4)	C(1)-W(1)-Cl(1)	175.32(9)
C(51)-C(50)-C(49)	120.3(4)	P(2)-W(1)-Cl(1)	87.39(4)
C(50)-C(51)-C(52)	120.2(4)	P(3)-W(1)-Cl(1)	83.97(3)
C(51)-C(52)-C(53)	120.1(4)	C(1)-W(1)-P(4)	97.73(10)
C(48)-C(53)-C(52)	120.2(4)	P(2)-W(1)-P(4)	162.01(3)
C(55)-C(54)-C(59)	118.5(3)	P(3)-W(1)-P(4)	76.90(3)
C(55)-C(54)-P(4)	122.0(3)	Cl(1)-W(1)-P(4)	82.85(3)
C(59)-C(54)-P(4)	119.5(3)	C(1)-W(1)-P(1)	87.76(10)
C(54)-C(55)-C(56)	120.9(3)	P(2)-W(1)-P(1)	77.45(3)
C(57)-C(56)-C(55)	120.2(3)	P(3)-W(1)-P(1)	165.40(3)
C(58)-C(57)-C(56)	119.9(3)	Cl(1)-W(1)-P(1)	96.90(3)
C(57)-C(58)-C(59)	120.2(3)	P(4)-W(1)-P(1)	88.73(3)
C(58)-C(59)-C(54)	120.3(3)		
C(66)-C(61)-C(62)	115.9(7)		
C(66)-C(61)-C(60)	120.4(7)		
C(62)-C(61)-C(60)	123.7(8)		
C(63)-C(62)-C(61)	123.9(7)		
C(62)-C(63)-C(64)	117.3(6)		
C(65)-C(64)-C(63)	120.9(7)		
C(64)-C(65)-C(66)	120.9(7)		
C(65)-C(66)-C(61)	121.0(6)		
C(14)-P(1)-C(8)	102.28(16)		
C(14)-P(1)-C(20)	102.09(16)		

C. Density Functional Theory Calculation on $1H^+$.

Methodology. A density functional theory (DFT) calculation of the geometry of $\mathbf{1H}^+$ in the gas phase was performed using Gaussian 09.[6] The calculation employed the B3P86 functional,[7,8] which has been benchmarked as providing accurate geometries for tungsten–alkylidyne complexes[3,9] and third-row transition-metal compounds.[10] The LANL2DZ basis and effective core potential[11] was used for tungsten, and the 6-31G* basis set[12,13] was used for other atoms. The geometry was optimized without symmetry constraints. A subsequent vibrational analysis demonstrated the absence of imaginary frequencies. The calculated structure and selected bond distances and angles are reported in Figure S11, and the Cartesian coordinates of the optimized structure are set out in Table S3.

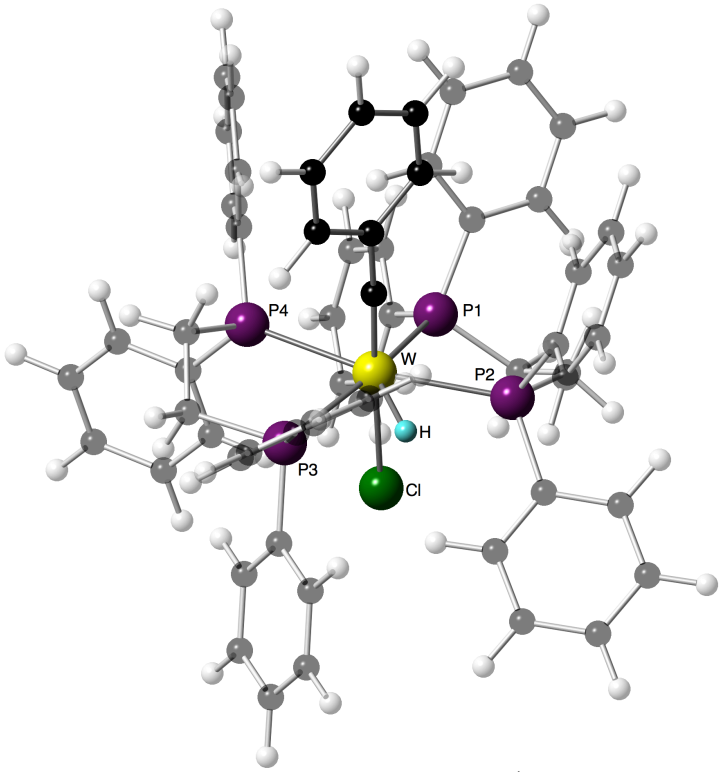

Figure S11. Calculated (DFT) gas-phase structure of the $\mathbf{1H}^+$ ion. Selected bond distances (Å) and angles (deg): W–C(1) 1.812, W–H 1.722, W–Cl 2.560, W–P(1) 2.628, W–P(2) 2.549, W–P(3) 2.531, W–P(4) 2.601, P(2)–W–P(3) 117.92, P(1)–W–P(4) 88.58, P(1)–W–P(2) 76.29, P(3)–W–P(4) 77.41, C(1)–W–P(1) 100.91, C(1)–W–P(2) 94.17, C(1)–W–P(3) 91.93, C(1)–W–P(4) 85.99.

Table S3. Cartesian Coordinates (Å) of DFT Optimized Geometry of **1H**$^+$.

W	-0.210188	0.148840	-0.139351
Cl	-0.321630	1.933684	-1.971554
P	1.629456	1.285064	1.306298
P	-1.549101	1.727143	1.316677
H	-1.929336	0.198367	-0.229415
P	-1.472299	-1.255604	-1.851864
P	1.683240	-0.749771	-1.725304
C	-0.233494	-1.141481	1.132141
C	-0.292264	-2.122110	2.185634
C	-0.759525	-1.774867	3.471124
C	-0.779024	-2.708645	4.499816
C	-0.344490	-4.013823	4.272776
C	0.108305	-4.377538	3.005787
C	0.137142	-3.446509	1.974824
C	3.032851	0.254731	1.879202
C	2.861563	-0.694391	2.896323
C	3.937117	-1.468738	3.324756
C	5.191596	-1.313917	2.738463
C	5.366615	-0.378818	1.721630
C	4.296997	0.404308	1.295371
C	2.435037	2.894856	0.942969
C	2.126236	3.614935	-0.213630
C	2.695725	4.870563	-0.430352
C	3.577236	5.411477	0.499294
C	3.895376	4.694880	1.653739
C	3.328991	3.445434	1.875516
C	0.752994	1.706930	2.885908
C	-0.458131	2.568268	2.568069
C	-2.882334	0.968859	2.324149
C	-3.357887	-0.320794	2.070920
C	-4.404470	-0.848337	2.825046
C	-4.988639	-0.095214	3.838399
C	-4.528285	1.196126	4.093649
C	-3.486892	1.726175	3.339991
C	-2.412498	3.125062	0.505119
C	-3.800366	3.096533	0.322461
C	-4.450695	4.160009	-0.299611
C	-3.723810	5.260529	-0.745543
C	-2.341283	5.289871	-0.577936
C	-1.686700	4.226768	0.034943
C	-2.192287	-2.801342	-1.178918
C	-1.410194	-3.950596	-1.021040
C	-1.967844	-5.118007	-0.506457
C	-3.306750	-5.146947	-0.126028
C	-4.087439	-4.001735	-0.262233
C	-3.536892	-2.836352	-0.789258
C	-2.896323	-0.521756	-2.745748
C	-3.394032	0.750588	-2.460807
C	-4.495644	1.245384	-3.157221
C	-5.109241	0.476905	-4.140514
C	-4.622995	-0.798538	-4.427056
C	-3.525186	-1.295210	-3.734680
C	-0.367492	-1.834670	-3.240876
C	0.851604	-0.935589	-3.365822
C	2.367715	-2.415753	-1.383100
C	2.666451	-3.316511	-2.416111
C	3.263198	-4.542394	-2.134868
C	3.590588	-4.877015	-0.822116
C	3.309813	-3.983756	0.208145
C	2.694105	-2.764747	-0.069028
C	3.180330	0.219417	-2.172679
C	4.465009	-0.298738	-1.965489
C	5.586619	0.418588	-2.375182
C	5.440440	1.656449	-2.995267
C	4.165237	2.176652	-3.204510
C	3.039393	1.467175	-2.796697
H	-1.127694	-0.770351	3.649774
H	-1.143199	-2.418337	5.481076
H	-0.363379	-4.743218	5.077138
H	0.442907	-5.394154	2.819429
H	0.497674	-3.733191	0.995241
H	1.891366	-0.847281	3.356615
H	3.790862	-2.190077	4.123413
H	6.030279	-1.914933	3.077468
H	6.341313	-0.248102	1.260831
H	4.452668	1.140725	0.513965
H	1.439144	3.191748	-0.939406
H	2.447509	5.421843	-1.332773
H	4.020005	6.388417	0.328096
H	4.587207	5.109806	2.380889
H	3.597956	2.889838	2.770123
H	0.452286	0.776742	3.375388
H	1.445021	2.231603	3.552838
H	-0.141579	3.526575	2.143254
H	-1.032638	2.789467	3.472090
H	-2.897897	-0.922100	1.294671
H	-4.753569	-1.855658	2.618939
H	-5.802462	-0.508545	4.426927
H	-4.985449	1.795244	4.875511
H	-3.168033	2.747241	3.530359
H	-4.380228	2.250410	0.677170
H	-5.529616	4.130583	-0.421903
H	-4.232281	6.093148	-1.222644
H	-1.766904	6.140793	-0.931511
H	-0.605651	4.258979	0.130067
H	-0.358250	-3.944620	-1.294456
H	-1.352445	-6.007023	-0.404199
H	-3.740879	-6.059397	0.271639
H	-5.134962	-4.018154	0.024671
H	-4.162907	-1.958736	-0.919120
H	-2.910440	1.370732	-1.716139
H	-4.862340	2.241507	-2.928381
H	-5.965136	0.866476	-4.683949
H	-5.101554	-1.409086	-5.187014
H	-3.175652	-2.301748	-3.950532
H	-0.069027	-2.868260	-3.043763
H	-0.948794	-1.831564	-4.167342
H	0.559909	0.075564	-3.665129
H	1.560630	-1.308316	-4.111729
H	2.449111	-3.066919	-3.449822
H	3.481946	-5.231484	-2.945266
H	4.065565	-5.829526	-0.605980
H	3.563714	-4.230517	1.234656
H	2.469446	-2.080926	0.742667
H	4.595054	-1.264491	-1.489519
H	6.576676	0.001150	-2.215369
H	6.316123	2.211158	-3.319345
H	4.042022	3.139084	-3.692258
H	2.050998	1.884446	-2.961021

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