

SUPPORTING INFORMATION

Formation of a Cationic Alkylidene Complex *via* Formal Hydride

Abstraction: Synthesis and Structural Characterization of



Aaron Sattler and Gerard Parkin,*

Department of Chemistry,

Columbia University,

New York, New York 10027, USA.

Received xxxx xx, 2011.

EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere unless otherwise specified.¹ Solvents were purified and degassed by standard procedures. ¹H NMR spectra were measured on Bruker 300 DRX, Bruker 300 DPX, Bruker 400 Avance III, Bruker 400 Cyber-enabled Avance III, and Bruker 500 DMX spectrometers. ¹H chemical shifts are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C₆D₅H; δ 3.31 for CD₂HOD, and δ 4.79 for HDO).² ¹³C NMR spectra are reported in ppm relative to SiMe₄ ($\delta = 0$) and were referenced internally with respect to the solvent (δ 49.99 for CD₃OD).² ³¹P chemical shifts are reported in ppm relative to 85% H₃PO₄ ($\delta = 0$) and were referenced using P(OMe)₃ ($\delta = 141.0$) as an external standard.³ Coupling constants are given in hertz. W(PMe₃)₄(η^2 -CH₂PMe₂)H was prepared by the literature method.⁴ LiAlD₄ was purchased commercially (Aldrich).

X-ray structure determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).⁵

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.5 (release 2007) suite of *ab initio* quantum chemistry programs.⁶ Geometry optimizations were performed with the B3LYP density functional⁷ using the 6-31G** (C, H, and P) and LACVP (W) basis sets.⁸ The energies of the optimized structures were reevaluated by additional single point calculations on each optimized geometry using cc-pVTZ(-f) correlation consistent triple- ζ basis set for C, H, and P and LACV3P for W (Table 3).

Molecular orbital analyses were performed with the aid of JIMP2,⁹ which employs Fenske-Hall calculations and visualization using MOPLOT.¹⁰

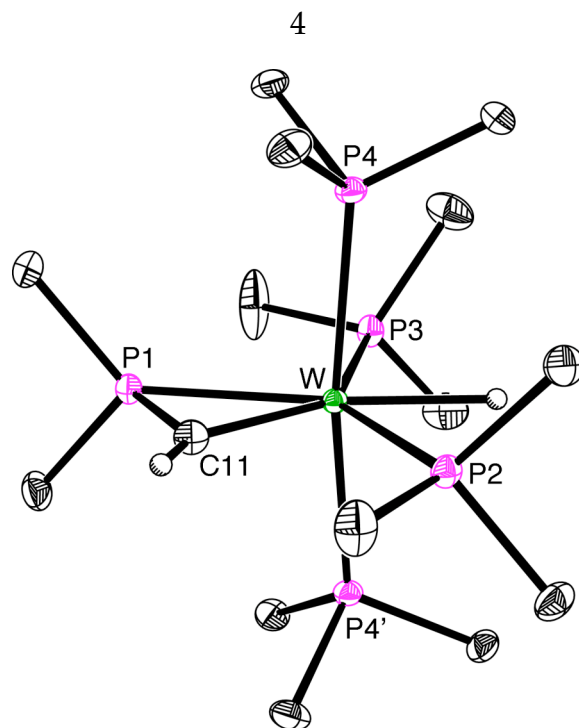
Synthesis of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{I}$

A solution of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ (200 mg, 0.35 mmol) in benzene (3 mL) was treated with iodobenzene (145 mg, 0.71 mmol) giving rise to a dark yellow solution.

The solution was allowed to stand overnight at room temperature, thereby depositing bright blue-purple crystals of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{I}$, together with colorless crystals of $[\text{Me}_3\text{PPh}]\text{I}$, as identified by comparison of the unit cell data with that of the literature [$a = 24.831(6)$ Å, $b = 7.399(2)$ Å, $c = 12.782(3)$ Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$].^{11,12}

The mother liquor was decanted in air and the crystals were washed sequentially with pentane (3×5 mL), Et_2O (2×5 mL), and distilled water (3×5 mL) to remove the colorless crystals of $[\text{Me}_3\text{PPh}]\text{I}$. The sample was then washed with Et_2O (2×5 mL) and pentane (2×5 mL) and dried *in vacuo* to give blue-purple crystals of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{I}$ suitable for X-ray diffraction (120 mg, 49% yield). Anal. Calcd.: C, 26.1%, H, 6.4%. Found: C, 25.6%, H, 5.8%.

¹H NMR (CD_3OD): 1.32 [ddquint, $J_{\text{H-H}} = 12$, $J_{\text{P-H}} = 16$, $^2J_{\text{P-H}} = 37$, $^1J_{\text{W-H}} = 29$, 1H of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\underline{\text{H}}$], 1.60 [d, $^2J_{\text{P-H}} = 10$, 6H of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$], 1.68 [s, 36H of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$], 11.86 [dq, $J_{\text{H-H}} = 12$, $J_{\text{P-H}} = 11$, $J_{\text{W-H}} = 11$, 1H of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\underline{\text{H}}$]. ³¹P{¹H} NMR (CD_3OD): -154.0 [quint, $^2J_{\text{P-P}} = 12$, $^1J_{\text{W-P}} = 81$, 1P of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$], -34.9 [d, $^2J_{\text{P-P}} = 12$, $^1J_{\text{W-P}} = 204$, 4P of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$]. ¹³C{¹H} NMR (CD_3OD): 19.2 [d, $^1J_{\text{P-C}} = 27$, 2C of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$], 26.9 [m, 12C of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}$], 224.4 [dq, $^1J_{\text{P-C}} = 51$, $J_{\text{P-C}} = 13$, 1C of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\underline{\text{H}}$].

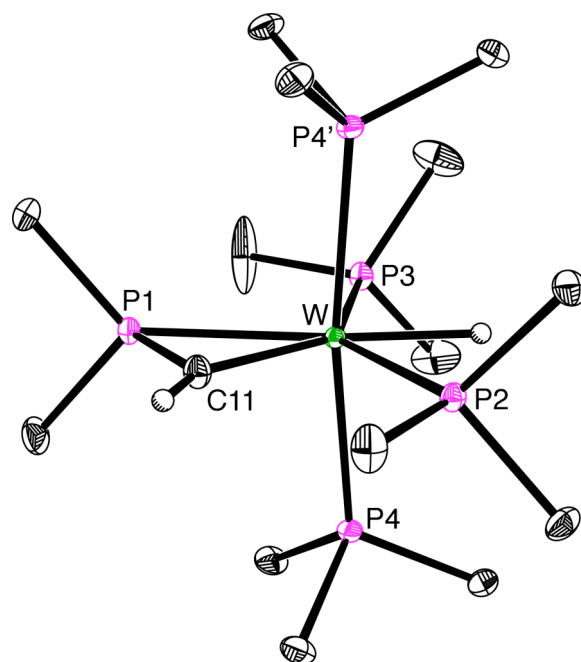


Molecular Structure of [W(PMe₃)₄(η²-CHPMe₂)H]I (iodide counterion not shown)

Synthesis of [W(PMe₃)₄(η²-CHPMe₂)H]Br

A solution of W(PMe₃)₄(η²-CH₂PMe₂)H (400 mg, 0.71 mmol) in benzene (5 mL) was treated with bromobenzene (250 mg, 1.60 mmol) giving rise to a dark yellow solution. The solution was allowed to stand overnight at room temperature, thereby depositing bright blue-purple crystals of [W(PMe₃)₄(η²-CHPMe₂)H]Br, together with some colorless crystals (presumably [Me₃PPh]Br, *vide supra*). The mother liquor was decanted in air, and the crystals were washed sequentially with pentane (3 × 5 mL), Et₂O (2 × 5 mL), and pentane (2 × 5 mL) and dried *in vacuo* to give blue-purple crystals of [W(PMe₃)₄(η²-CHPMe₂)H]Br suitable for X-ray diffraction (260 mg, 57% yield). ¹H NMR (CD₃OD): 1.32 [ddquint, J_{H-H} = 13, J_{P-H} = 16, ²J_{P-H} = 37, ¹J_{W-H} = 29, 1H of W(PMe₃)₄(η²-CHPMe₂)H], 1.59 [d, ²J_{P-H} = 9, 6H of W(PMe₃)₄(η²-CHPMe₂)H], 1.67 [s, 36H of W(PMe₃)₄(η²-CHPMe₂)H], 11.85 [dq, J_{H-H} = 13, J_{P-H} = 10, J_{W-H} = 11, ¹J_{C-H} = 174, 1H of W(PMe₃)₄(η²-CHPMe₂)H]. ³¹P{¹H} NMR (CD₃OD): -153.8 [quint, ²J_{P-P} = 12, ¹J_{W-P} = 82, 1P of W(PMe₃)₄(η²-CHPMe₂)H], -34.7 [d, ²J_{P-P} = 12, ¹J_{W-P} = 204, 4P of W(PMe₃)₄(η²-CHPMe₂)H]. ¹³C{¹H} NMR (CD₃OD): 19.2 [dq, ¹J_{P-C} = 27, ³J_{P-C} = 2, 2C of W(PMe₃)₄(η²-CHPMe₂)H], 26.9 [m, 12C of W(PMe₃)₄(η²-CHPMe₂)H], 224.4 [dq, ¹J_{P-C} = 50, ²J_{P-C} = 13,

1C of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$. ^{13}C NMR (CD_3OD): 19.2 [dq, $^1J_{P-C} = 27$, $^1J_{H-C} = 129$, 2C of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], 26.9 [q, $^1J_{H-C} = 132$, 12C of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], 224.4 [dd, $^1J_{P-C} = 50$, $^1J_{H-C} = 174$, 1C of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$]. 1H NMR (D_2O): 0.23 [m, 1H of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], 1.56 [d, $^2J_{P-H} = 10$, 6H of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], 1.62 [s, 36H of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], 12.01 [sextet, $J_{P-H} = 11$, $J_{H-H} = 11$, $J_{W-H} = 11$, 1H of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$]. $^{31}P\{^1H\}$ NMR (D_2O): -154.6 [quint, $^2J_{P-P} = 12$, $^1J_{W-P} = 84$, 1P of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$], -35.7 [d, $^2J_{P-P} = 12$, $^1J_{W-P} = 203$, 4P of $W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H$].



Molecular Structure of $[W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H]Br$ (bromide counterion not shown)

Reaction of $W(PMe_3)_4(\eta^2\text{-CH}_2PMe_2)H$ with bromotoluene

A solution of $W(PMe_3)_4(\eta^2\text{-CH}_2PMe_2)H$ (60 mg, 0.11 mmol) in C_6D_6 (ca. 0.7 mL) was treated with *p*-bromotoluene (40 mg, 0.23 mmol) and allowed to stand at room temperature for 12 hours. After this period, the mixture was filtered, removing *inter alia* purple crystals of $[W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H]Br$, and the filtrate was analyzed by 1H NMR spectroscopy, thereby demonstrating the formation of toluene.

Reaction of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{Br}$ with LiAlH_4

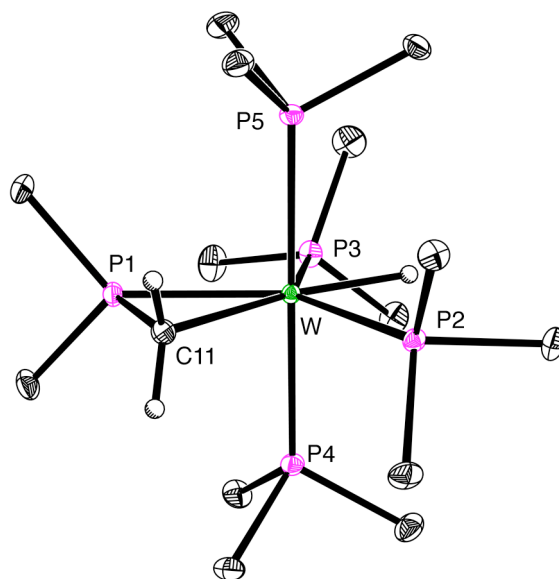
A suspension of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{Br}$ (12 mg, 0.02 mmol) in C_6D_6 (ca. 0.7 mL) was treated with LiAlH_4 (10 mg, 0.26 mmol). Et_2O (ca. 0.1 mL) was then added, thereby resulting in the formation of a bright yellow solution. The mixture was filtered and the filtrate was lyophilized and the solid obtained was extracted into C_6D_6 and analyzed by ^1H NMR spectroscopy, thereby demonstrating the formation of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$.

Reaction of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{Br}$ with LiAlD_4

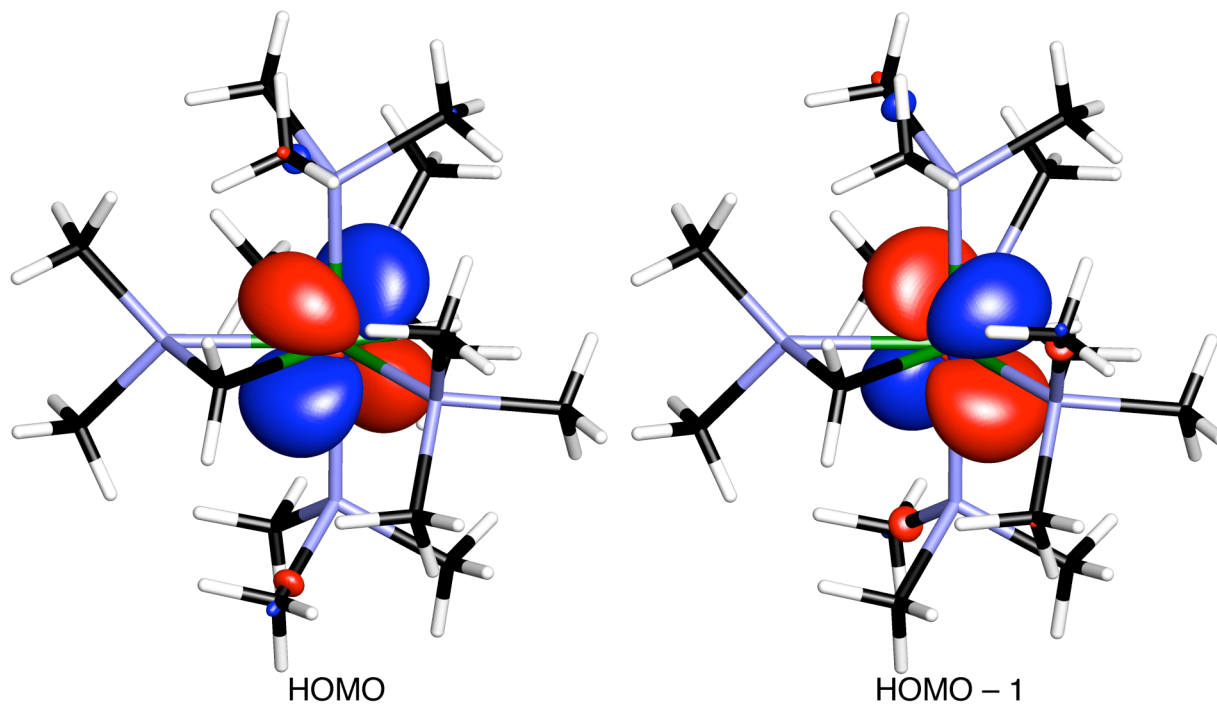
A suspension of $[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{Br}$ (50 mg, 0.08 mmol) in benzene (1 mL) was treated with a solution of LiAlD_4 (3 mg, 0.07 mmol) in Et_2O (ca. 0.2 mL). The resulting mixture was shaken for 1 minute and filtered. The filtrate was lyophilized and the yellow powder was extracted into C_6D_6 (ca. 0.7 mL) and analyzed by ^1H NMR spectroscopy, thereby demonstrating the formation of an isotopologue of $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$ in which deuterium primarily resided in the methylene site, namely $\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHDPMe}_2)\text{H}$.

Crystal Structure and Molecular Orbital Analysis of $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$

Crystals of $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$ suitable for X-ray diffraction were obtained from a solution in pentane at $-15\text{ }^\circ\text{C}$.



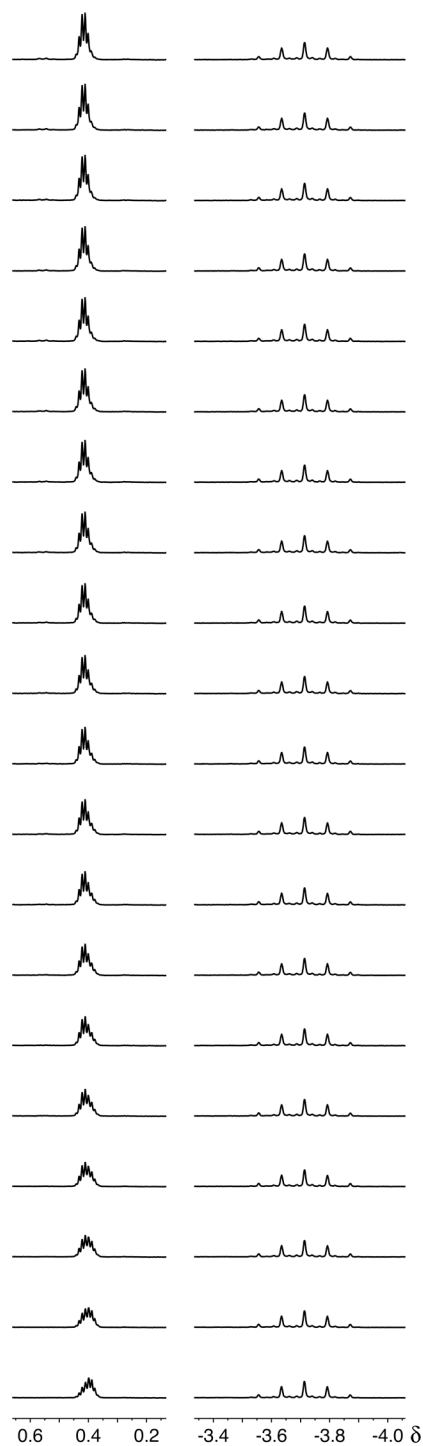
Molecular Structure of $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$



The highest occupied molecular orbitals of $W(PMe_3)_4(\eta^2-CH_2PMe_2)H$ indicate a d^4 configuration

Kinetics of isomerization of $W(PMe_3)_4(\eta^2-CHDPM_2)H$

A suspension of $[W(PMe_3)_4(\eta^2-CHPMe_2)H]Br$ (100 mg, 0.16 mmol) in benzene (1 mL) was treated with a solution of $LiAlD_4$ (5 mg, 0.12 mmol) in Et_2O (*ca.* 0.2 mL). The resulting mixture was shaken for 1 minute and filtered. The filtrate was lyophilized and the yellow powder of $W(PMe_3)_4(\eta^2-CHDPM_2)H$ obtained was extracted into C_6D_6 (*ca.* 2.1 mL) and filtered into a vial. Mesitylene (1 μ L) was added as an internal integration standard, and the solution was divided evenly into 3 NMR tubes equipped with J. Young valves. Two of the samples were treated with PMe_3 and the kinetics of the isomerization of $W(PMe_3)_4(\eta^2-CHDPM_2)H$ were measured at 30°C by monitoring the increase in intensity of the methylene signal in the 1H NMR spectrum. Using a similar procedure, the kinetics were also measured at 53°C and 64°C in the probe of the NMR spectrometer, as summarized in Table 1. Within experimental error, the rate constant data are not influenced by the presence of PMe_3 .



NMR spectra for isomerization of $W(PMe_3)_4(\eta^2-CHDPMe_2)H$ at 53 °C.

The methylene signal is on the left, and the hydride is on the right. The first spectrum is at the bottom and subsequent spectra were recorded every 1.59 minutes, with only every 5th spectrum being shown. In addition to the methylene signal growing in intensity, the shape of the signal changes because the [CHD] and [CH₂] groups have slightly different chemical shifts.

Table 1. Rate constant data (k_1) for isomerization of $W(PMe_3)_4(\eta^2\text{-CHDPMe}_2)H$.^a

Temperature/°C	[PMe ₃]/mM	k_1/s^{-1}
30	–	$1.6(5) \times 10^{-5}$
30	1.9	$2.0(2) \times 10^{-5}$ ^b
30	9.4	$1.3(4) \times 10^{-5}$
53	–	$2.08(8) \times 10^{-4}$
64	–	$9.9(5) \times 10^{-4}$

(a) Activation parameters: $\Delta H^\ddagger = 24(2)$ kcal mol⁻¹; $\Delta S^\ddagger = -3(6)$ cal mol⁻¹ K⁻¹.

(b) The hydride signal of d_1 - $W(PMe_3)_4(\eta^4\text{-CH}_2\text{PMe}_2)H$, rather than that of mesitylene, was used as the integration standard due to a small amount of decomposition during this experiment. In this regard, although deuterium is incorporated into the hydride site during the course of the reaction, the statistical variation in its intensity (from 1.00 to 0.98) is small compared to other sources of error in the experiment. Thus, any error introduced by using the hydride signal is considered to be negligible.

Reaction of $W(PMe_3)_4(\eta^2\text{-CHDPMe}_2)H$ towards bromotoluene

A sample of $W(PMe_3)_4(\eta^2\text{-CHDPMe}_2)H$ was prepared by the above procedure employing $[W(PMe_3)_4(\eta^2\text{-CHPMe}_2)H]Br$ (200 mg, 0.31 mmol), benzene (1.5 mL) and a solution of $LiAlD_4$ (10 mg, 0.24 mmol) in Et_2O (ca. 0.4 mL). The resulting mixture was shaken for 1 minute and then filtered. The precipitate was extracted with benzene (1 mL), filtered and the filtrates were combined and lyophilized. The bright yellow powder was then extracted with d_6 -benzene (ca. 0.7 mL), filtered into an NMR tube equipped with a J. Young valve and treated with *p*-bromotoluene (150 mg, 0.88 mmol). The sample was monitored by ¹H NMR spectroscopy, which demonstrated that the toluene formed contained ca 40% deuterium in the *para* position.

Table 2. Crystal, intensity collection and refinement data.

	$[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{I}$	$[\text{W}(\text{PMe}_3)_4(\eta^2\text{-CHPMe}_2)\text{H}]\text{Br}$
lattice	Tetragonal	Tetragonal
formula	$\text{C}_{15}\text{H}_{44}\text{IP}_5\text{W}$	$\text{C}_{15}\text{H}_{44}\text{BrP}_5\text{W}$
formula weight	690.10	643.11
space group	$P4_2/m$	$P4_2/m$
$a/\text{\AA}$	13.598(3)	13.476(3)
$b/\text{\AA}$	13.598(3)	13.476(3)
$c/\text{\AA}$	14.392(3)	14.118(4)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	90	90
$V/\text{\AA}^3$	2661.3(11)	2563.8(11)
Z	4	4
temperature (K)	150(2)	125(2)
radiation (λ , \AA)	0.71073	0.71073
ρ (calcd.) g cm^{-3}	1.722	1.666
μ (Mo $K\alpha$), mm^{-1}	5.799	6.373
θ max, deg.	31.50	31.76
no. of data collected	45502	44100
no. of data	4582	4516
no. of parameters	125	124
$R_1 [I > 2\sigma(I)]$	0.0220	0.0188
$wR_2 [I > 2\sigma(I)]$	0.0469	0.0410
R_1 [all data]	0.0295	0.0261
wR_2 [all data]	0.0497	0.0433
GOF	1.054	1.042

Table 2 (cont). Crystal, intensity collection and refinement data.

W(PMe₃)₄(η²-CH₂PMe₂)H	
lattice	Monoclinic
formula	C ₁₅ H ₄₅ P ₅ W
formula weight	564.21
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	14.8321(4)
<i>b</i> /Å	9.4806(3)
<i>c</i> /Å	18.0198(5)
α /°	90
β /°	106.6870(10)
γ /°	90
<i>V</i> /Å ³	2427.19(12)
<i>Z</i>	4
temperature (K)	125(2)
radiation (λ , Å)	0.71073
ρ (calcd.) g cm ⁻³	1.544
μ (Mo K α), mm ⁻¹	5.084
θ max, deg.	30.51
no. of data collected	14235
no. of data	7349
no. of parameters	208
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0208
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0461
<i>R</i> ₁ [all data]	0.0259
<i>wR</i> ₂ [all data]	0.0478
GOF	1.011

Table 3. Cartesian Coordinates and Single Point Energies for Geometry Optimized Structures (Energies in parentheses correspond to the basis set used for geometry optimization).

W(PMe₃)₄(η²-CHPMe₂)H⁺				
-2372.97560102073 Hartrees				
(-2372.62930166812 Hartrees)				
atom	x	y	z	
W	0.164082868	-0.089603817	-0.167022673	
H	-1.239494374	-0.024419274	0.910893201	
P	1.980306506	-0.675512003	-1.814177339	
P	-0.078439617	2.053727985	1.124539735	
P	-1.103831833	-2.378419567	-0.418658167	
P	-1.378158841	0.831860353	-2.004413818	
C	1.76355099	0.811925229	-0.880554604	
C	2.101872875	-0.341239712	-3.64014632	
C	1.195072857	3.380049798	0.88182646	
H	0.96104997	4.247829479	1.505365651	
H	1.222066085	3.696474019	-0.163836014	
H	2.187216435	3.010651846	1.152742405	
C	-1.631359594	3.056272261	0.926037913	
C	-0.380538369	-3.59852926	-1.605518973	
H	-0.978123357	-4.514649888	-1.643701081	
H	0.638608566	-3.846395543	-1.299163154	
H	-0.336015734	-3.15609425	-2.603556765	
C	-1.36146638	-3.421858669	1.095881622	
C	-3.16629139	1.191429284	-1.659571286	
C	-1.573581972	-0.114239939	-3.598372455	

C	-0.805697071	2.446770096	-2.717542157
P	1.436058872	-1.137067256	1.803820091
C	3.656571974	-1.432678716	-1.536196701
C	-0.126370997	1.986833031	2.981633239
C	-2.887600773	-2.347721055	-0.934663593
C	0.588871083	-1.44879818	3.425573318
C	2.267170636	-2.791267447	1.588904273
C	2.920087372	-0.159776348	2.339768252
H	-1.932650773	-2.848082182	1.830318055
H	-1.931915686	-4.318078438	0.833340313
H	-0.422567081	-3.735701455	1.549835591
H	-3.028221271	-1.907196883	-1.920706851
H	-3.283272315	-3.367803564	-0.955075712
H	-3.458442077	-1.766899136	-0.205499885
H	2.993486896	-2.751799225	0.777071322
H	2.788551121	-3.071890934	2.509432917
H	1.545232299	-3.573421633	1.350401913
H	-0.208994218	-2.181957411	3.299631347
H	1.307473706	-1.837215761	4.153908464
H	0.148103861	-0.533453779	3.817157317
H	2.633941603	0.846473016	2.64931827
H	3.431692163	-0.654615512	3.171379429
H	3.610936561	-0.065953324	1.498667309
H	0.799574516	1.591161267	3.400244606
H	-0.2824426	2.990729202	3.388010387
H	-0.957775368	1.350807204	3.295808539
H	1.332025658	0.363002019	-3.955276843
H	3.079384547	0.089600242	-3.877523966

H	1.984732536	-1.267648926	-4.211178453
H	3.682602819	-2.462532755	-1.90587843
H	4.420325848	-0.855851116	-2.066715478
H	3.906268113	-1.435831967	-0.475324111
H	-2.492517088	2.441523899	1.199988671
H	-1.600666043	3.927607983	1.587235059
H	-1.760353097	3.410603757	-0.097243461
H	-2.016713206	-1.096513991	-3.428014964
H	-2.218358453	0.439582861	-4.288134975
H	-0.604684877	-0.265867344	-4.074402165
H	0.190790231	2.317301329	-3.146246837
H	-1.490814228	2.791737849	-3.498443581
H	-0.737790126	3.212137069	-1.943000675
H	-3.268767387	1.897701797	-0.837146577
H	-3.641540533	1.61307987	-2.550734897
H	-3.690723424	0.274859658	-1.38598271
H	2.397221888	1.694762605	-0.886918957

W(PMe₃)₄(η²-CH₂PMe₂)H

-2373.74059082820 Hartrees

(-2373.38785945076 Hartrees)

atom	x	y	z
W	13.60632047	1.886785418	12.10612604
H	12.66065599	0.797247755	11.08577664
P	11.96673674	1.759747191	13.95212043
P	15.24243765	2.067398384	10.26260918
P	11.83827553	2.998871653	10.74470989

P	14.26106312	-0.475256407	12.57539499
P	14.63552813	3.848056954	13.15325075
C	12.52192716	1.54241052	15.73779171
H	11.65946828	1.562521849	16.41249384
H	13.20236244	2.347467438	16.02553763
H	13.05103403	0.600446971	15.87787847
C	10.84248028	3.221225339	14.32720116
H	10.15063343	2.983238739	15.14247556
H	10.2585387	3.519038516	13.45596635
H	11.44797351	4.079331773	14.62676945
C	10.65788895	0.417972733	13.94810914
H	9.956500543	0.524874037	14.7835584
H	11.14138991	-0.559960756	14.02380645
H	10.10431694	0.442273533	13.00722514
C	15.07780004	0.944038919	8.775475066
H	15.8984239	1.084864416	8.062358416
H	14.12953254	1.144805359	8.27148082
H	15.06445272	-0.09912736	9.102400678
C	15.43769913	3.689084095	9.330714409
H	16.05398419	3.555297704	8.434695983
H	15.91806715	4.430634815	9.969645928
H	14.46847779	4.090884209	9.033525938
C	17.08260069	1.812012781	10.56257559
H	17.66288477	2.102689429	9.680311498
H	17.29612448	0.766675542	10.7869028
H	17.42009319	2.409029921	11.41344195
C	10.07344902	2.394077358	10.88908026
H	9.409810691	2.970109929	10.23497986

H	9.695758973	2.454082318	11.90892694
H	10.05165462	1.34500504	10.58021931
C	11.58925888	4.836056817	10.96128802
H	10.75232088	5.214513322	10.36411319
H	12.50432503	5.354634755	10.66117116
H	11.40804296	5.058816164	12.01534335
C	11.84955856	2.915237488	8.875356627
H	10.9732571	3.422579809	8.456918836
H	11.82388857	1.863299608	8.577246372
H	12.74683513	3.368193454	8.452799185
C	15.92493241	-1.137417764	12.04411561
H	16.03465086	-2.187702683	12.33443915
H	16.71749669	-0.555190177	12.52034122
H	16.03913421	-1.063616349	10.96042305
C	13.18967814	-1.81364543	11.85703914
H	13.52696305	-2.810659261	12.16218103
H	13.21030951	-1.740129396	10.7668599
H	12.15687043	-1.664540847	12.17918035
C	14.36289799	-1.093043952	14.33590074
H	14.79835835	-2.097275288	14.36870881
H	13.36773905	-1.137712945	14.78285587
H	14.98352161	-0.41711856	14.92862024
C	15.28424313	2.256297969	13.65999122
H	15.12433908	2.010378368	14.71291886
H	16.33088078	2.092505194	13.3890112
C	14.10298805	4.881744101	14.61383155
H	14.97170068	5.197836973	15.20104013
H	13.43194175	4.318510102	15.26185672

H	13.5738149	5.776521413	14.26725238
C	16.01963118	4.966363832	12.58522621
H	16.59883599	5.317198775	13.44568833
H	15.62072418	5.838764603	12.05604166
H	16.69256305	4.433498968	11.91405939

REFERENCES

- (1) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23.
(b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.
(c) Shriver, D. F.; Drezdson, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.
- (2) (a) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. J. *Org. Chem.* **1997**, *62*, 7512-7515.
(b) Reference for methanol and water
- (3) "Nuclear Magnetic Resonance Spectroscopy" Nelson, J. H. Prentice Hall, New Jersey (2003), p 79.
- (4) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. J. *Chem. Soc., Dalton Trans.* **1986**, 2227-2236.
- (5) (a) Sheldrick, G. M. SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen, Göttingen, Federal Republic of Germany, 1981.
(b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.
- (6) Jaguar 7.5, Schrödinger, LLC, New York, NY 2008.
- (7) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
(b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098-3100.
(c) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
(d) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200-1211.
(e) Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. 4: The Self-Consistent Field for Molecules and Solids*; McGraw-Hill: New York, 1974.

- (8) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283.
(b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284-298.
(c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.
- (9) (a) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768-775.
(b) Bursten, B. E.; Jensen, J. R.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320-3321.
(c) Manson, J.; Webster, C. E.; Pérez, L. M.; Hall, M. B.
<http://www.chem.tamu.edu/jimp2/index.html>
- (10) Version 2.0, June 1993; Lichtenberger, D. L. Department of Chemistry, University of Arizona, Tuscon, AZ 85721.
- (11) Schüdel, H.; Näther, C.; Bock, H, *Acta Cryst.* **1995**, *C51*, 1841-1844.
- (12) ^1H NMR of $[\text{Me}_3\text{PPh}]\text{I}$ (D_2O): 2.21 [d, $^2J_{\text{P-H}} = 15$, 9H of $\underline{\text{Me}_3\text{P}}$], 7.73 [m, 2H of $\underline{\text{PPh}}$], 7.84 [m, 1H of $\underline{\text{PPh}}$], 7.90 [m, 2H of $\underline{\text{PPh}}$]. $^{31}\text{P}\{^1\text{H}\}$ NMR of $[\text{Me}_3\text{PPh}]\text{I}$ (D_2O): 21.2 [s, 1P of Me_3PPh].