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# Hydrogenolysis of tetra(allyl)tungsten in the presence of tertiary phosphines: synthesis of tris(dmpm)tungsten (0)

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**Abstract**

Reaction of $W(\eta^3\text{-}C_3H_5)_4$ with $PMe_2Ph$ and $Me_2PCH_2PMe_2$ (dmpm) under 1 atm of $H_2$ in toluene at 110–120 °C yielded $WH_4(PMe_2Ph)_4$ and $W(dmpm)_3$, respectively. Spectroscopic studies on the hydrogenolysis of $W(\eta^3\text{-}C_3H_5)_4$ in the presence of tertiary phosphines $PEt_3$, $PMePh_2$, and $PPh_3$ were consistent with formation of the tungsten phosphine hydride complexes $WH_6(PEt_3)_3$, $WH_4(PMePh_2)_4$ and $WH_6(PPh_3)_3$. $W(\eta^3\text{-}C_3H_5)_4$ has advantages over similar hydrogenolysis of $WMe_6$ in that $W(\eta^3\text{-}C_3H_5)_4$ is considerably more thermally and air stable. Pyrolysis of $WH_4(PMePh_2)_4$ at 400 °C under a hydrogen flow yielded a shiny tungsten powder contaminated by hydrocarbon residues.

*Keywords:* Tungsten; Phosphines; Hydrides; Hydrogenolysis; Hydrogenation

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## 1. Introduction

Tungsten hexahalides are used extensively for the chemical vapor deposition (CVD) of tungsten thin films; however, the corrosivity and water-sensitivity of tungsten halides and their decomposition products continue to generate an interest in volatile organometallic tungsten compounds as alternative precursors for the CVD of tungsten metal in microelectronic devices [1]. Alternative precursors to $WF_6$ include tungsten hexacarbonyl [2], tetra(allyl)tungsten [3], ditungstenhexakis(cyclohexyloxide) [4], bis(cyclopentadienyl)tungsten dihydride [5], tris(methylvinylketone)tungsten, and tris(butadiene)-tungsten [6]. Films deposited from these reagents contain varying amounts of carbon in the product, highly dependant on the deposition conditions. Precursors lacking direct tungsten–carbon bonds are, in principle, attractive as alternative precursors for CVD of tungsten metal due to the absence of direct metal carbon bonds. Hexakis(trifluorophosphine)tungsten, $W(PF_3)_6$, removes the potential for carbon impurities but introduces sufficient phosphorous into the film to limit the utility of $W(PF_3)_6$ as a precursor for tungsten films in electronic applications [7]. In the present paper we describe the hydrogenolysis of tetra(allyl)tungsten in the presence of tertiary phosphines to tungsten phosphine polyhydrides $(WH_x(PR_3)_y$ for $x = 4, 6$, $y = 3, 4$, $R_3 = Et_3$, $Me_2Ph$, $MePh_2$ or $Ph_3)$ and solid state pyrolysis of $WH_4(PMePh_2)_4$.

## 2. Experimental

All compounds were handled using Schlenck techniques, in an M. I. Braun glovebox under a purified nitrogen or argon atmosphere or on a vacuum line equipped with oil diffusion and mechanical pumps ($10^{-3}$ Torr) [8]. Solvents were purified by refluxing over Na/benzophenone (benzene, ether, hexane, pentane, tetrahydrofuran, toluene) and distilled prior to use. $WCl_6$, phosphines and allyl magnesium bromide were purchased from Strem Chemical and used as received. Benzene-$d_6$ was purchased from Cambridge Isotope Laboratories. $^1H$ NMR spectra were recorded on a Varian 300XL spectrometer in either flame sealed 5 mm tubes or in 5 mm tubes equipped with a Teflon valve. Proton chemical shifts are relative to residual protons in the solvent ($C_6D_5H$ $\delta$ 7.15). Authentic samples of $WH_4(PMePh_2)_4$ and $WH_4(PMe_2Ph)_4$ were prepared by literature procedures from $WCl_4(PMePh_2)2$ and $WCl_4(PMe_2Ph)_2$ [11]. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN) and Desert Analytics (Tucson, AZ).

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### 2.1. Preparation of $W(OPh)_6$ [9]

In a typical procedure, 24 g (0.060 mols) $WCl_6$ were added as a solid to 84 g (0.90 mols) of phenol in a 250 ml flask under nitrogen. The flask was connected to a trap containing aqueous NaOH and heated to reflux for 3 h under nitrogen. During this time the mixture turns dark red accompanied by the evolution of HCl. The temperature was reduced to just below reflux and the mixture heated for an additional 4 h to ensure complete reaction. After cooling to room temperature, absolute ethanol (150 ml) was added and the red insoluble solid, $W(OPh)_6$ (39 g, 88% yield) was collected by filtration and dried under vacuum.

### 2.2. Preparation of $W(\eta^3\text{-}C_3H_5)_4$

Tetra(allyl)tungsten, $W(\eta^3\text{-}C_3H_5)_4$, was prepared using literature procedures with some minor modifications [10]. Hexaphenoxytungsten, $W(OPh)_6$, 12 g (0.016 mols), was dissolved in 50 ml of THF and added to 130 ml (0.13 mols) of a 1.0 M solution of allyl MgBr in diethyl ether at room temperature from an addition funnel. The mixture was stirred overnight. After evaporation of the THF under vacuum, the crude solid was transfered to a Soxhlet extractor and extracted for 8 h with pentane. Evaporation of the pentane solution and sublimation of the pale yellow solid at 80 °C and $10^{-2}$ Torr yielded 3.7 g (60% based on $W(OPh)_6$) of white $W(\eta^3\text{-}C_3H_5)_4$. The product was identified by comparison of the $^1H$ NMR spectrum with literature data [9].

### 2.3. Synthesis of $WH_4(PMe_2Ph)_4$ from $W(\eta^3\text{-}C_3H_5)_4$, dimethylphenylphosphine, and hydrogen

A 2.5 × 40 cm thick wall pyrex tube equipped with a Teflon valve (Chemglass, 2 mm bore) was charged with 0.338 g (0.97 mmols) of freshly sublimed $W(\eta^3\text{-}C_3H_5)_4$ in the glove box. Slightly more than three equivalents of $PMe_2Ph$, 0.44 g (3.2 mmols) was added and the tube was flushed for 20 min with hydrogen. Dried, distilled toluene, 8–10 ml, was degassed by bubbling hydrogen through the solvent for 15 min and added to the reaction vessel, yielding a colorless solution. The tube was sealed and immersed to the depth of 1–2 inches in a 120–130 °C oil bath behind a safety shield for 72 h. The tube was not agitated during the heating process. After each 24 h reaction period, the tube was cooled to room temperature and flushed with fresh hydrogen before heating was continued. Reaction was judged to be complete when the solution was yellow and traces of black solid were observed on the walls of the reaction tube. After cooling to room temperature, the toluene was evaporated under vacuum and the residue extracted with 3 × 15 ml of pentane. The pentane extracts were filtered through a layer of Celite. Solution volume was reduced to about 3–5 ml before chilling to −78 °C. Solid products were collected by removal of the supernatant by syringe. A 0.476 g (80% yield) of yellow $WH_4(PMe_2Ph)_4$ was collected and dried under vacuum. $^1H$ ($C_6D_6$) −2.69 m (4 H, W-*H*), 1.55 d (24 H, P*Me*$_2$Ph), 7.01 t (8 H, aryl protons), 7.12 t (4 H, aryl protons), 7.63 br s (8 H, aryl protons); $^{31}P$ ($C_6D_6$): −8.85 s ($^{183}W$ satellites, −8.2, −9.5 ppm $J_{WP} = 168$ Hz).

### 2.4. Synthesis of $W(dmpm)_3$ from $W(\eta^3\text{-}C_3H_5)_4$, bis(dimethylphosphino)methane, (dmpm), and hydrogen

A 2.5 × 40 cm thick wall pyrex tube equipped with a Teflon valve (Chemglass, 2 mm bore) was charged with 0.391 g (1.12 mmols) of freshly sublimed $W(\eta^3\text{-}C_3H_5)_4$ in the glove box. Slightly more than two equivalents, 0.358 g (2.63 mmols), of dmpm was added and the tube was flushed for 20 min with hydrogen. Dried, distilled toluene, 8–10 ml, was degassed by bubbling hydrogen through the solvent for 15 min and added to the reaction vessel, yielding a colorless solution. The tube was sealed and immersed to the depth of 1–2 inches in a 120–130 °C oil bath behind a safety shield for 60 h. The tube was not agitated during the heating process. After each 24 h reaction period, the tube was cooled to room temperature and flushed with fresh hydrogen before heating was continued. Reaction was judged to be complete when the solution was red and small amounts of black solid were observed on the walls of the reaction tube. After cooling to room temperature, the toluene was evaporated under vacuum and the residue extracted with 5 × 10 ml of hexane. The hexane extracts were filtered through a layer of Celite. Solution volume was reduced to about 3–5 ml before chilling to −78 °C. A 0.100 g (20% yield) of orange solid $W(dmpm)_3$ was isolated by removal of the supernatant by syringe and subsequent drying of the product under vacuum. Anal. Calc. for $C_{15}H_{42}P_6W$: 30.42% C, 7.15% H; found: 30.11% C, 7.14% H. $^1H$ ($C_6D_6$): $\delta$ 1.64 t (12 H, *Me*$_2$P-), 4.28 m (2 H, PC*H*$_2$P); $^{31}P$ ($C_6D_6$): $\delta$ −54.9 s ($^{183}W$ satellites −53.8, −55.9 $J_{WP} = 258$ Hz).

### 2.5. Attempted synthesis of $H_6W(PEt_3)_3$ from $W(\eta^3\text{-}C_3H_5)_4$, triethylphosphine, and hydrogen

A 2.5 × 40 cm thick wall pyrex tube equipped with a Teflon valve (Chemglass, 2 mm bore) was charged with 0.150 g (0.43 mmols) of freshly sublimed $W(\eta^3\text{-}C_3H_5)_4$ in the glove box. Slightly more than two equivalents, 0.223 g (1.89 mmols), of $PEt_3$ was added and the tube was flushed for 20 min with hydrogen. Dried, distilled toluene, 8–10 ml, was degassed by bubbling hydrogen through the solvent for 15 min and added to the reaction vessel, yielding a colorless solution. The tube was sealed and immersed to the depth of 1–2 inches in a

100–120 °C oil bath behind a safety shield. The tube was not agitated during the heating process. After 18 h, the tube was cooled to room temperature and flushed with fresh hydrogen before heating was continued for an additional 6 h. Reaction was judged to be complete when the solution was brown and small amounts of black solid were observed on the walls of the reaction tube. After cooling to room temperature, the toluene was evaporated under vacuum and the residue extracted with 5 × 10 ml of hexane. The hexane extracts were filtered through a layer of Celite. Solution volume was reduced to about 3–5 ml before chilling to $-78$ °C The product was a brown oil which could not be purified further. $^1$H ($C_6D_6$) $\delta$ $-3.81$ q (6 H, W-$H$, $J_{PH} = 36$ Hz), 0.86 t (27 H, $\mathrm{PCH_2C}\mathit{H}3$), 1.09 q of d (18 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH}_3$). $^{31}$P ($C_6D_6$) $\delta$ 25.8 s ($^{183}$W satellites, 25.4, 26.2 ppm, $J_{WP} = 75$ Hz).

### 2.6. General procedure for NMR studies of the reaction of W($\eta^3$-$C_3H_5$)$_4$ with tertiary phosphines under hydrogen

The same procedure was used for all reactions of W($\eta^3$-$C_3H_5$)$_4$ with phosphines under hydrogen. W($\eta^3$-$C_3H_5$)$_4$ was placed in a 5 mm NMR tube equipped with a Teflon valve in the glove box. A solution of phosphine ($PEt_3$, $PMePh_2$, $PPh_3$, $Me_2PCH_2PMe_2$) in $C_6D_6$ was added. The sample was removed from the glove box and degassed with three freeze/pump/thaw cycles on a vacuum line ($10^{-3}$ Torr). The tube was filled with hydrogen and sealed. The sample was heated to 60 °C in an oil bath and the progress of the reaction monitored by $^1$H NMR spectroscopy. The tube was periodically charged with fresh hydrogen using the procedure described above. In each case, disappearance of the resonances for W($\eta^3$-$C_3H_5$)$_4$ was accompanied by the appearance of resonances for propane, $C_3H_8$, at $\delta$ 0.88 (t, 6 H, $\mathrm{C}\mathit{H}_3\mathrm{CH_2C}\mathit{H}_3$) and 1.28 (multiplet, 2 H, $\mathrm{CH_3C}\mathit{H}_2\mathrm{CH}_3$), propene, at $\delta$ 1.54 d ($\mathrm{C}\mathit{H}_3\mathrm{CH_2CH_2}$), 4.96 m, ($\mathrm{CH_3C}\mathit{H}_2\mathrm{CH}_2$), 5.72 m ($\mathrm{CH_3CH_2C}\mathit{H}_2$), and resonances for $WH_x(PR_3)_y$ as described below. The solutions remained homogeneous throughout the experiment.

### 2.7. $PR_3 = PEt_3$

0.0138 g (0.04 mmols) W($\eta^3$-$C_3H_5$)$_4$ and 0.0150 g (0.13 mmols) $PEt_3$ in 1 ml $C_6D_6$ were reacted under 650 Torr $H_2$ at 80 °C for 24 h. $^1$H ($C_6D_6$) $\delta$ $-3.81$ q (6 H, W-$H$, $J_{PH} = 36$ Hz), 0.86 t (27 H, $\mathrm{PCH_2C}\mathit{H}_3$), 1.09 q of d (18 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH}_3$). $^{31}$P ($C_6D_6$) $\delta$ 25.8 s ($^{183}$W satellites, 25.4, 26.2 ppm, $J_{WP} = 75$ Hz). The only other resonance observed in the $^{31}$P NMR, at $-19$ ppm, was assigned to unreacted $PEt_3$ by comparison with a known sample.

### 2.8. $PR_3 = PMePh_2$

Approx. 10–15 mg W($\eta^3$-$C_3H_5$)$_4$ and 13 equivalents of $PMePh_2$ (from integration of the $^1$H NMR spectrum) in 1 ml $C_6D_6$ were reacted under 650 Torr $H_2$ at 80 °C for 24 h. $^1$H ($C_6D_6$) $-1.7$ (W-$H$, complex multiplet), 1.72 d, ($\mathrm{P}\mathit{Me}\mathrm{Ph}_2$), 7.08, 7.59 br s ($\mathrm{PMe}\mathit{Ph}_2$). $^{31}$P ($C_6D_6$) $\delta$ 12.7 ($^{183}$W satellites, 11.9, 13.3 ppm $J_{WP} =$ 150 Hz). The only other resonance observed in the $^{31}$P NMR, at $-26$ ppm, was assigned to unreacted $PMePh_2$ by comparison with a known sample.

### 2.9. $PR_3 = PPh_3$

Approx. 10–15 mg W($\eta^3$-$C_3H_5$)$_4$ and 3 equivalents $PPh_3$ (as determined by integration of the $^1$H NMR spectrum) in 1 ml $C_6D_6$ were reacted under 650 Torr $H_2$ at 80 °C for 24 h. $^1$H ($C_6D_6$) $\delta$ $-0.34$ (W-$H$, quartet, 6 H), 6.85 br s, (27 H, $\mathrm{P}\mathit{Ph}_3$), 7.68 br s (18 H, $\mathrm{P}\mathit{Ph}_3$); $^{31}$P ($C_6D_6$) $\delta$ 41.8 t. The only other resonance observed in the $^{31}$P NMR, at $-5$ ppm, was assigned to unreacted $PPh_3$ by comparison with a known sample.

### 2.10. $PR_3 = Me_2PCH_2PMe_2$

0.044 g (0.125 mmols) W($\eta^3$-$C_3H_5$)$_4$ and 0.024 g (0.176 mmols) $Me_2PCH_2PMe_2$ in 1 ml $C_6D_6$ were reacted under 650 Torr $H_2$ in a 110 °C oil bath for 118 h. $^1$H ($C_6D_6$): no W–H resonances observed between 0 and $-17$ ppm. $^1$H ($C_6D_6$): $\delta$ 1.64 t (12 H, $\mathit{Me}_2$P-), 4.28 m (2 H, $\mathrm{PC}\mathit{H}_2\mathrm{P}$). $^{31}$P ($C_6D_6$): $\delta$ $-54.9$ ppm, $^{183}$W satellites $-53.8$, $-55.9$ $J_{WP} = 258$ Hz. No other resonances were observed in the $^{31}$P NMR after 6 h of reaction.

### 2.11. Reaction with $PEt_3$ in the absence of $H_2$

Approx. 10–15 mg W($\eta^3$-$C_3H_5$)$_4$ and 5 equivalents of $PEt_3$ (from integration of the $^1$H NMR spectrum) in 1 ml $C_6D_6$ were reacted at 80 °C for 288 h. No changes were observed in the spectrum.

### 2.12. Reaction with $H_2$ in the absence of $PEt_3$

Approx. 10–15 mg W($\eta^3$-$C_3H_5$)$_4$ and 600 Torr $H_2$ in 1 ml $C_6D_6$ were reacted at ambient temperature for 24 h. Formation of a black precipitate was observed after a few hours concurrently with the observation of propene in the $^1$H NMR spectrum.

### 2.13. Reaction with ethylene

0.0201 g (0.058 mmols) W($\eta^3$-$C_3H_5$)$_4$ and 0.020 mols $C_2H_4$ in 1 ml of $C_6D_6$ were reacted at 80 °C for 72 h, yielding a black precipitate and the observation of propene in addition to the ethylene present in solution.

### 2.14. Reaction with ethylene and $H_2$

Approx. 10–15 mg (≈ 0.03–0.04 mmols) $W(\eta^3\text{-}C_3H_5)_4$, 0.10 mmols $C_2H_4$ and 500 Torr $H_2$ in 1 ml $C_6D_6$ were reacted at 80 °C for 72 h. The ratio of $C_2H_6$ to $C_2H_4$ was observed to be 14:1 and propene was the only other product observed in the reaction.

### 2.15. Pyrolysis studies of $WH_4(PMePh_2)_4$

0.237 g (0.24 mmols) of $WH_4(PMePh_2)_4$ were placed in a quartz boat in the center of a 1 × 14 inch pyrex tube in a Lindbergh tube furnace. The tube was kept under a flow of dry, oxygen-free hydrogen (flow rate = 5 ml $min^{-1}$, Novapure™ Inert Gas Purifier, Novapure Corporation, Danbury, CT 06810) while the oven temperature was raised to 400 °C. The $WH_4(PMePh_2)_4$ was pyrolyzed for 6 h at 400 °C before cooling to room temperature overnight under a continuous hydrogen flow. The shiny, silvery powder, 0.049 g (20.6% ceramic yield compared to theoretical ceramic yield of 18.6% based on complete decomposition to W metal) remaining in the boat analyzed for 1.57% C and 0.28% H.

## 3. Results

### 3.1. Reactions of $W(\eta^3\text{-}C_3H_5)_4$ with tertiary phosphines and hydrogen

Reaction of tetra(allyl)tungsten with dimethylphenylphosphine under hydrogen leads to the loss of all four allyl groups as propane/propene mixtures and isolation of $WH_4(PMe_2Ph)_4$ in 66% yield. The product was identified by comparison of the $^1H$ and $^{31}P$ NMR spectra with literature data for $WH_4(PMe_2Ph)_4$ prepared by lithium aluminum hydride reduction of $WCl_4(PMe_2Ph_2)_2$. Hydrogenolysis of tetra(allyl)tungsten in the presence of the chelating phosphine, bis(dimethylphosphino)methane (dmpm), however, yielded the homoleptic tris(phosphine) derivative $W(dmpm)_3$ in 20% yield. A similar compound, $W(dmpe)_3$, has been prepared by metal vapor synthesis from W atoms and dmpe in 50% yield and in 10% yield from reduction of $WCl_6$, dmpe and $LiAlH_4$. Reactions of $W(\eta^3\text{-}C_3H_5)_4$ with triethylphosphine and hydrogen yielded an oil which could not be crystallized although spectroscopic evidence was consistent with the formation of a tungsten hexahydride $WH_6(PEt_3)_3$. The effect of hydrogen pressure and agitation of the reaction mixtures on the rate of conversion were not investigated.

The hydrogenolysis of $W(\eta^3\text{-}C_3H_5)_4$ in the presence of a series tertiary phosphines was followed by $^1H$ and $^{31}P$ NMR spectroscopy. Only a single tungsten hydride resonance was observed in each of these reactions. The number of phosphine and hydride ligands can be readily determined from integration of the W–H and phosphine proton resonances as well as from the splitting of the W–H resonances by the phosphine ligands (Table 1). In reactions involving $PEt_3$ and $PPh_3$, quartet patterns (1 : 3 : 3 : 1 ratio) for the W–H resonance were consistent with formation of hexahydrides of formula $WH_6(PR_3)_3$ ($PR_3 = PEt_3$, $PPh_3$). $^{31}P$ NMR spectra consist of singlets with low intensity doublets due to phosphorus coupling to $^{183}W$ ($I = 1/2$, 14% natural abundance).

Hydrogenolysis of $W(\eta^3\text{-}C_3H_5)_4/PMePh_2$ mixtures yielded $WH_4(PMePh_2)_4$ as detemined by NMR spectroscopy and comparison with literature data [12,14]. $WH_4(PMePh_2)_4$ and $WH_4(PMe_2Ph)_4$ show a complex W–H resonance (AA′A″A‴XX′X″X‴ pattern) at ambient temperature which resolves into a quintet upon heating [11].

In the absence of hydrogen, no reaction was observed between $W(\eta^3\text{-}C_3H_5)_4$ and excess $PEt_3$ after 12 days of reaction at 80 °C. When the phosphine was replaced by ethylene, the rate of decomposition was faster, with significant decomposition (to propene and black, carbonaceous residues [3b]) being observable only after 3 days at 80 °C. Hydrogenation of ethylene to ethane was observed in mixtures of $W(\eta^3\text{-}C_3H_5)_4$, $H_2$ and ethylene

Table 1
Products from reactions of $W(\eta^3\text{-}C_3H_5)_4$, tertiary phosphines and hydrogen

| Phosphine | Product | $^1H$ NMR (W–H) | $^{31}P$ NMR ($J_{WP}$) |
|---|---|---|---|
| $PMe_3$ | $WH_4(PMe_3)_4$ | −3.92 | −27.3 (169) |
| $PEt_3$ | $WH_6(PEt_3)_3$ | −3.81 q | 25.8 (75 Hz) |
| $PMe_2Ph$ | $WH_4(PMe_2Ph)_4$ | −2.6 m [a] | −8.85 (168) |
|  | $WH_6(PMe_2Ph)_3$ | −1.94 q [13]<br>−2.18 q [a] |  |
| $P^iPr_2Ph$ | $WH_6(P^iPr_2Ph)_3$ | −3.4 q [16] | 55.5 (63) [16] |
| $PMePh_2$ | $WH_4(PMePh_2)_4$ | −2.7 m | 12.7 (150) |
| $PPh_3$ | $WH_6(PPh_3)_3$ | −0.34 q | 41.8 |
| $Ph_2PCH_2PPh_2$ (dppm) | $W(dppm)_3$ | – | −25.7 |
| $Me_2PCH_2PMe_2$ (dmpm) | $W(dmpm)_3$ | – | −54.9 (258) |

[a] −2.8 ppm Ref. 11.

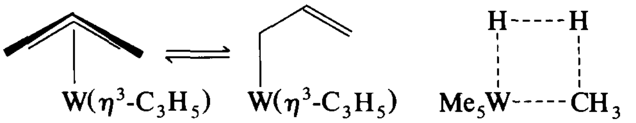
only after heating to 80 °C for 5 days. The olefin hydrogenation was accompanied by the formation of propane and partial decomposition of the tetra(allyl)tungsten to a black solid. By comparison, the first signs of decomposition of $W(\eta^3\text{-}C_3H_5)_4$ to a black solid and propene as the major soluble product were observed after 6 h at room temperature [3b]. Under a hydrogen atmosphere, this decomposition is equally rapid, yielding a mixture of propene and propane as determined by $^1H$ NMR.

### 3.2. Solid state pyrolysis study of $WH_4(PMePh_2)_4$

Thermal decomposition of $WH_4(PMePh_2)_4$ at 400 °C under a continuous flow of hydrogen led to isolation of a shiny metallic powder which analyzed for 1.57% C and 0.28% H, corresponding to a formula $W_4CH_2$. The observation of residual carbon was consistent with the observed ceramic yield, 20.6% vs. 18.6%, theoretically.

## 4. Discussion

Tungsten hydrides of general formula $WH_x(PR_3)_y$ ($x = 2, 4, 6$; $y = 5, 4, 3$, respectively, $PR_3$ = alkyl, aryl and mixed tertiary alkyl(aryl)phosphines) have been known for over 20 years and can be prepared from lithium aluminum hydride or sodium borohydride reduction of $WCl_4(PR_3)_2$ as well as by hydrogenolysis of hexamethyltungsten in the presence of phosphines [15–17]. The generation of metal-hydrides from hydrogenolysis of late transition metal allyl complexes is also well documented (e.g. HRh(dmope) from $\eta^3\text{-}2\text{-}CH_3C_3H_4\text{-}Rh(dmope)$ where dmope refers to $(MeO)_2PCH_2CH_2P(OMe)_2$. The formation of $WH_4(PMe_2Ph)_4$, $WH_4(PMePh_2)_4$, $WH_6(PEt_3)_3$ and $WH_6(PPh_3)_3$ from $H_2$, $W(\eta^3\text{-}C_3H_5)_4$ and phosphines is therefore not surprising. There are, nevertheless, differences between the synthetic methods worthy of further comment. The synthesis of $WH_4(PMe_3)_4$ from $WMe_6 \cdot PMe_3$ requires precisely three equivalents of $PMe_3$ and 3 atm $H_2$ [15]. An excess of $PMe_3$ leads to the isolation of $WH_2(PMe_3)_5$. While yields of $WH_2(PMe_3)_5$ and $WH_4(PMe_3)_4$ were essentially quantitative, yields of polyhydrides with more sterically hindered ligands (e.g. $PiPr_2Ph$) were only about 10%. Spectroscopic studies of the reaction between $W(\eta^3\text{-}C_3H_5)_4$, phosphines and $H_2$, however, suggest that ≈ 1 atm of hydrogen and, in some cases, even excess phosphine still lead to the formation of $WH_4(PMe_2Ph)_4$, $WH_4(PMePh_2)_4$, $WH_6(PEt_3)_3$ and $WH_6(PPh_3)_3$. Curiously, the preparation of $WH_6(PiPr_3)_3$, $WH_6(PiPr_2Ph)_3$, and $WH_4(PMe_2Ph)_4$ from hexamethyltungsten and the appropriate phosphine was performed under 250 atm of hydrogen [16]. Comparison of the preparative methods for $WH_4(PMe_2Ph)_4$ indicates yields of 30%, 66%, and 15%, respectively, for hydrogenolysis of $WMe_6$, hydrogenolysis of $W(\eta^3\text{-}C_3H_5)_4$, and reduction of $WCl_4(PMe_2Ph)_4$). The overall yield of $WH_4(PMe_2Ph)_4$ from $W(OPh)_6$ is 70%, the best yield of the three methods for synthesis of this compound. A possible explanation for the improved yields of $WH_4(PMe_2Ph)_4$ at lower hydrogen pressures starting from $W(\eta^3\text{-}C_3H_5)_4$ may be the ability of the allyl ligand to undergo hapticity changes from $\eta^3$ to $\eta^1$, generating coordinatively unsaturated intermediates capable of activating hydrogen. In contrast, the hydrogenation of $WMe_6$ requires a σ-bond metathesis pathway involving a four-centered intermediate (Scheme 1) [15].



Scheme 1.

Tungsten phosphine polyhydrides, $WH_x(PR_3)_y$, represent a class of potential precursors for CVD of tungsten in which there are no tungsten–carbon bonds. Tungsten phosphine polyhydrides do not appear to be volatile; however, in situ, gas phase formation of $WH_x(PR_3)_y$ from volatile $W(\eta^3\text{-}C_3H_5)_4$ (sublimes 80 °C at $10^{-2}$ Torr), a low molecular weight phosphine and a hydrogen carrier gas is attractive as a precursor for tungsten CVD. From the perspective of CVD, tetra(allyl)tungsten has considerable advantages over $WMe_6$ in that it is air stable for short periods and thermally stable up to ≈ 60 °C whereas $WMe_6$ is highly sensitive to oxygen and decomposes (at times explosively) above −25 °C [17]. While the gas phase formation of $WH_x(PR_3)_y$ from $W(\eta^3\text{-}C_3H_5)_4$ is the subject of current investigations, the utility of $WH_x(PR_3)_y$ was evaluated through solid state pyrolysis experiments on $WH_4(PMePh_2)_4$. Under a continuous flow of hydrogen at 400 °C, solid $WH_4(PMePh_2)_4$ was converted to a shiny powder which contained tungsten and hydrocarbon residues. The relatively low vapor pressure of $PMePh_2$ (≈ 120 °C, 2 mmHg) and potentially reactive C–H bonds (*o*-metallation of aryl groups) [18] may contribute to the carbon and hydrogen impurities observed in the final product. The effects of reaction temperature, particle size and the choice of phosphine on the purity of the final product will be the subject of further studies.

## References

[1] (a) A. Sherman, *Chemical Vapor Deposition for Microelectronics*, Noyes Publications, Park Ridge, NJ, 1987; (b) S.S. Wong and S. Furukawa (eds.), *Tungsten and Other Refractory Metals for VLSI Applications*, Vol. V, Materials Research Society, Pittsburgh, PA, 1990.

[2] (a) I.M. Watson, J.A. Connor and R. Whyman, *Polyhedron, 8* (1989) 1794; (b) M. Diem, M. Fisk and J.Goldman, *Thin Solid*

*Films, 107* (1983) 39; (c) G.J. Vogt, *Vac. Sci. Technol., 20* (1982) 1336; (d) N.S. Gluck, G.J. Wolga, C.E. Bartosch, W. Ho and Z. Ying, *J. Appl. Phys., 61* (1987) 998; (e) D.K. Flynn, J.I. Steinfeld and D.S. Sethi, *J. Appl Phys., 59* (1984) 3914; (f) T. Kado and Y. Noda, *J. Electrochem. Soc., 136* (1989) 2184; (g) G.I. Christianz, T.J. Elms, G.N. Pain and R.R. Pierson, *J. Cryst. Growth, 93* (1988) 589.

[3] (a) R.U. Kirss, *Appl. Organometal. Chem., 6* (1992) 609; (b) R.U. Kirss, J. Chen, J. and R.B. Hallock, *Mater. Res. Soc., 250* (1992) 303.

[4] D.V. Baxter, M.H. Chisholm, V. DiStasi and J.A. Klang, *Chem. Mater., 3* (1991) 221.

[5] B. Niemer, A.A. Zinn, W.K. Stovall, P.E. Gee, R.F. Hicks and H.D. Kaesz *J. Appl. Phys, 61* (1992) 1793.

[6] R.U. Kirss, D.G. Gordon, P.S. Kirlin, *Mater. Res. Soc., 282* (1993) 275.

[7] (a) E. Sirtl, US Patent, 3 619 288, 1971; (b) K. Hieber, J. Von Tomkewitsch, H. Treichel, T. Kruck and O. Spindler, Eur. Pat. Appl. EP 338, 206, 1989.

[8] D.F. Shriver, *Manipulation of Air Sensitive Compounds*, McGraw Hill, New York, 1969.

[9] H. Funk and W. Baumann, *Z. Anorg. Allg. Chem., 231* (1937) 264.

[10] R. Benn, T.H. Brock, M.C.F.B Dias, P.W. Jolly, A. Rufinska, G. Schroth, K. Seevogel and B.Wassmuth, *Polyhedron, 9* (1990) 11.

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

[12] F.G.N. Cloke, P.J. Fyne, V.C. Gibson, M.L.H. Green, M.-J. Ledoux and R.N. Perutz, *J. Organometal. Chem., 277* (1984) 61.

[13] (a) B. Bell, J. Chatt, G.J. Leigh and T. Ito, *J. Chem. Soc., Chem. Commun.,* (1972) 34; (b) J.R. Moss and B.L. Shaw, *J. Chem. Soc., Dalton Trans.,* (1972) 1910.

[14] M.D. Fryzuk, *Organometallics, 1* (1982) 408.

[15] K.W. Chiu, R.A. Jones, G. Wilkinson, A.M.R. Galas, M.B. Hursthouse and K.M.A. Malik, *J. Chem.Soc., Dalton Trans.,* (1981) 1204.

[16] D. Gregson, J.A.K. Howard, J.N. Nicholls, J.L. Spencer and D.G. Turner, *J. Chem. Soc., Chem. Commun.,* (1980) 572.

[17] A.L. Galyer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.,* (1976) 2235.

[18] C.M. Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole, Monterey, CA, 1985.