

# The synthesis of tungsten imido hydride complexes by the hydrogenolysis of dialkyl complexes

James M. Boncella \*, Shu-Yu S. Wang, Daniel D. VanderLende

Department of Chemistry and Center for Catalysis, University of Florida, Gainesville, FL 32611-7200, USA

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## Abstract

The reaction of the complexes  $[(\text{TMS})_2\text{pda}]\text{W}(=\text{NPh})(\text{R})_2$ , ( $\text{R} = \text{CH}_2\text{CMe}_3$ ,  $\text{CH}_2\text{CH}_3$ ) ( $[(\text{TMS})_2\text{pda}] = \{o\text{-}[\text{Me}_3\text{SiN}]_2\text{C}_6\text{H}_4\}^{2-}$ ) with dihydrogen in the presence of trialkyl phosphines results in the formation of a series of W(VI) hydride complexes of the general formula  $[(\text{TMS})_2\text{pda}]\text{W}(=\text{NPh})(\text{H})_2(\text{PR}_3)_2$  ( $\text{PR}_3 = \text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $1/2\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ,  $1/2\text{P}(\text{C}_6\text{H}_{11})_3$ ). The reactions of these complexes with olefins are also described. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Tungsten; Imido; Hydride; Alkyl; Hydrogenolysis

## 1. Introduction

Recently, we have studied a series of tungsten and molybdenum complexes with the general formula  $[(\text{TMS})_2\text{pda}]\text{M}(=\text{NPh})(\text{R})_2$  ( $[(\text{TMS})_2\text{pda}] = \{o\text{-}[\text{Me}_3\text{SiN}]_2\text{C}_6\text{H}_4\}^{2-}$ ;  $\text{M} = \text{W}$ ,  $\text{Mo}$ ;  $\text{R} = \text{alkyl}$ ,  $\text{aryl}$ ) [1–5]. Although our initial studies were directed toward the synthesis of metal alkylidene complexes for use as olefin metathesis catalysts, the ease with which a wide variety of dialkyl complexes could be synthesized has led us to study the chemistry of these  $d^0$  dialkyl complexes in more detail. We have found that isocyanides readily insert into the metal carbon bonds of these complexes [6] and that the W complexes with  $\beta\text{-H}$  containing alkyl groups are stable at and above room temperature (r.t.), despite their electronic and coordinative unsaturation [1].

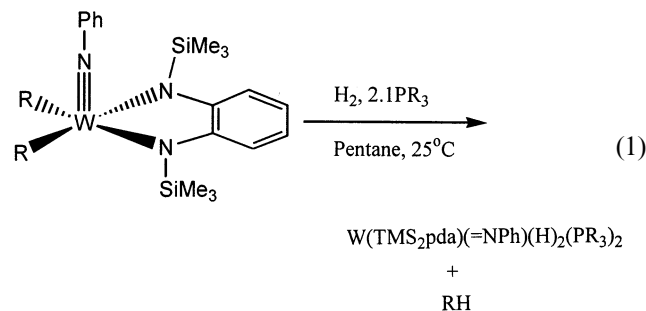
In this paper, we report the reaction of several tungsten dialkyl complexes with  $\text{H}_2$  in the presence of trialkyl phosphines. These reactions result in the formation of a series of new W(VI) imido hydride complexes. Despite the fact that the hydride ligand is the simplest anionic ligand in coordination chemistry, there are relatively few examples of transition metal complexes that contain both the imido and hydride ligands [7–16]. The compounds reported herein afford us the opportunity to study the chemistry of the hydride ligand in the presence of the

tungsten imido group. We have found that these hydride complexes react rapidly with olefins to give the corresponding alkane and W(IV) olefin complexes, and they behave as homogeneous olefin hydrogenation catalysts.

## 2. Results and discussion

### 2.1. Synthesis

The reaction of the complex  $[(\text{TMS})_2\text{pda}]\text{W}(=\text{NPh})(\text{CH}_2\text{CMe}_3)_2$  (**1**) with  $\text{H}_2$  (ca. 2 atm) and two equivalents of trialkyl phosphine results in the formation of the seven-coordinate dihydride complexes,  $[(\text{TMS})_2\text{pda}]\text{W}(=\text{NPh})(\text{H})_2(\text{PR}_3)_2$  (**2–4**), as shown in Eq. (1). In the case of  $\text{PCy}_3$ , only one phosphine can coordinate to the metal for steric reasons and the product is  $[(\text{TMS})_2\text{pda}]\text{W}(=\text{NPh})(\text{H})_2(\text{PCy}_3)$  (**5**).



$\text{R} = \text{CH}_2\text{CH}_3$ ,  $\text{CH}_2\text{CMe}_3$

\* Corresponding author. Fax: +1-352-392 3255.

E-mail address: boncella@chem.ufl.edu (J.M. Boncella)

Although single crystals of **2** have been obtained, their quality has not resulted in an X-ray diffraction study that is completely refined and therefore publishable. The results of the structural study do however indicate that the phenyl imido group and one amide from the TMS<sub>2</sub>pda ligand are *trans* with respect to one another. The other silylamide group is *cis* to the NPh ligand as are the two PMe<sub>3</sub> ligands which are mutually *transoid*. A structure that is derived from a pentagonal bipyramid with the imido group occupying an axial position is consistent with these observations, as shown in Fig. 1.

The r.t. <sup>1</sup>H-NMR spectrum of **2** displays two peaks that are assigned to inequivalent Si(CH<sub>3</sub>)<sub>3</sub> groups as well as a hydride resonance at 9.26 ppm that integrates to two protons. The PMe<sub>3</sub> protons appear as a broad singlet at 1.04 ppm. The inequivalence of the Me<sub>3</sub>Si groups is consistent with a structure that has the NSiMe<sub>3</sub> groups occupying sites that are *cis* and *trans* to the imido group, while the broadness of the hydride and PMe<sub>3</sub> peaks suggests that the compound is fluxional at r.t.

The low-temperature NMR spectra are consistent with this structural assignment. At –50°C the hydride peak of **2** is a sharp doublet of doublets because the hydrides are the AA' part of an AA'XX' spin system (the <sup>31</sup>P nuclei being the XX' part.). The PMe<sub>3</sub> protons resolve into a virtual triplet with a peak separation of 3 Hz. This is consistent with the pseudotrans disposition of the PMe<sub>3</sub> groups in the equatorial plane of the pentagonal bipyramid. The <sup>31</sup>P{<sup>1</sup>H} spectra of **2** display a singlet with tungsten satellites (<sup>1</sup>J<sub>W-P</sub> = 188 Hz) from 25 to –50°C.

The NMR spectral parameters of **3** are similar to those of **2** and are also consistent with the proposed structure. The difference is that **3** is more fluxional than **2**. At r.t., the hydride signal is observed as a broad singlet, and at –50°C, this resonance has only decoalesced into a broad triplet that is similar to the one observed for **2** at r.t. It is likely that the fluxionality in **2** and **3** involves dissociation of the PR<sub>3</sub> ligand and the larger steric demands of PMe<sub>2</sub>Ph versus PMe<sub>3</sub> lead to a lower activation barrier for dissociation.

The NMR spectra of complex **4** are also consistent with a structure that is derived from a pentagonal bipyramid, as shown in Fig. 1. This structure has an axial phenylimido group with the TMS<sub>2</sub>pda ligand amido groups occupying equatorial sites, while the phosphines of the DPPE group occupy one equatorial site and the axial site *trans* to the imido group. The hydrides are symmetrically disposed in the equatorial plane. This structure has a mirror plane that contains the phosphorus atoms of the DPPE group as well as the imido N atom. This mirror plane renders the SiMe<sub>3</sub> protons of the TMS<sub>2</sub>pda ligand chemically equivalent as is observed in the proton NMR spectrum. The PPh<sub>2</sub> groups of the DPPE ligand are chemically inequivalent and are observed as a pair of doublets in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **4**. The hydride ligands give rise to a four line pattern with <sup>183</sup>W satellites that is the A<sub>2</sub> part of an A<sub>2</sub>XY spin system where X and Y are the <sup>31</sup>P nuclei of the DPPE ligand.

The NMR spectra of **5** are consistent with a structure that is derived from an octahedron in which the PCy<sub>3</sub> group and the phenyl imido ligand are mutually *trans*. This leaves the hydride ligands in *cis* positions as proposed in Fig. 1. The proton NMR spectrum of **5** displays a doublet for the chemically equivalent hydride protons (<sup>2</sup>J<sub>P-H</sub> = 83 Hz) and a single peak that is assigned to the Me<sub>3</sub>Si protons that are equivalent due to the mirror plane that contains the N, W and P atoms. Furthermore, the value of J<sub>W-P</sub> (56 Hz) is significantly smaller than that of **2** and **3** as would be expected given the strong *trans* influence of the W=N group.

## 2.2. Reactivity studies

Although our initial discovery of these complexes occurred when we were examining the interaction of complex **1** with H<sub>2</sub> in the presence of phosphines, a more efficient and economical synthesis involves the reaction of the complex [o-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]W(=NPh)(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> (**7**) with H<sub>2</sub> in the presence of the desired phosphine ligand. As part of this procedure, crude **7** was allowed to react with an excess of the phosphine in the presence of ca. 2 atm of

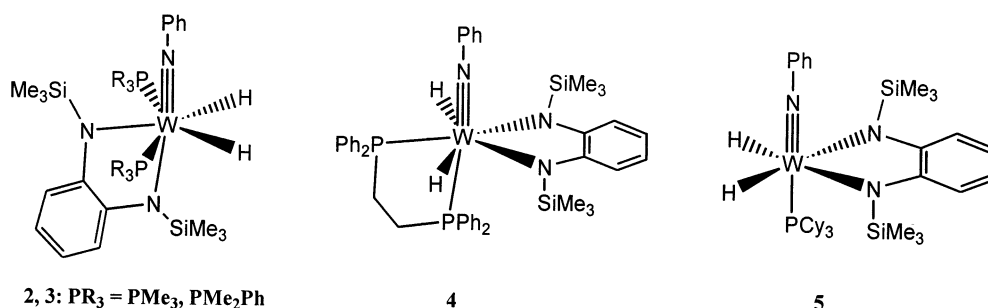
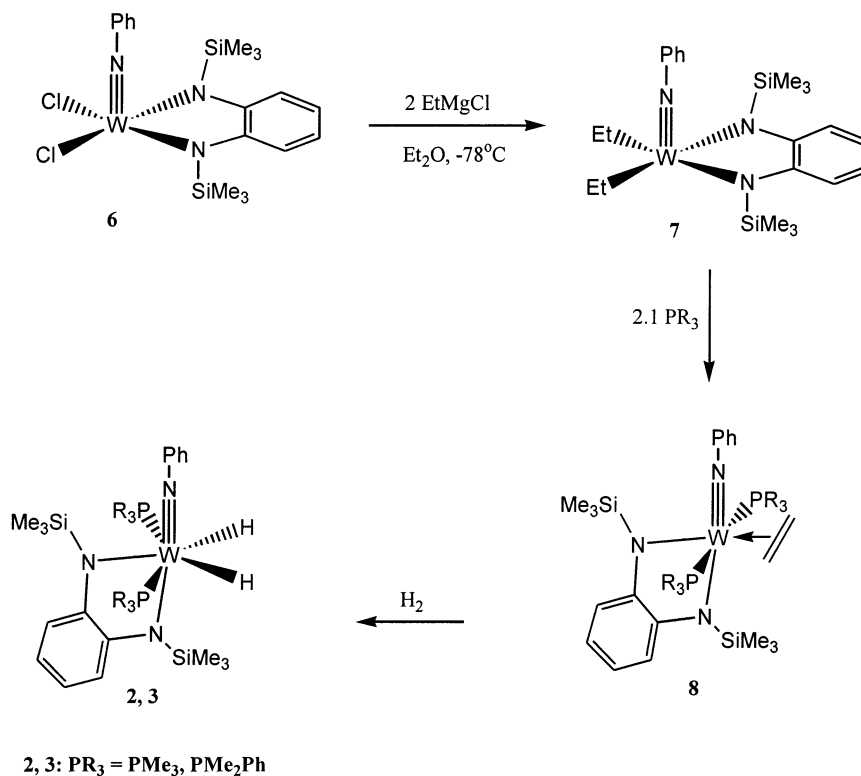


Fig. 1. Proposed structures of compounds **2**–**5**.



Scheme 1.

$\text{H}_2$  over the course of several hours at r.t. This reaction sequence is an efficient synthesis of **2** from  $[o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4]\text{W(=NPh)(Cl)}_2$  (**6**). It appears that the reaction sequence proceeds as shown in Scheme 1. Addition of  $\text{PR}_3$  to the diethyl complex rapidly induces  $\beta\text{-H}$  abstraction to generate the ethylene complex **8** [4]. Hydrogenation of **8** in the presence of  $\text{PR}_3$  leads to the desired hydride products. We have confirmed that **8** reacts with  $\text{H}_2$  under the same conditions as employed here to generate complex **2**.

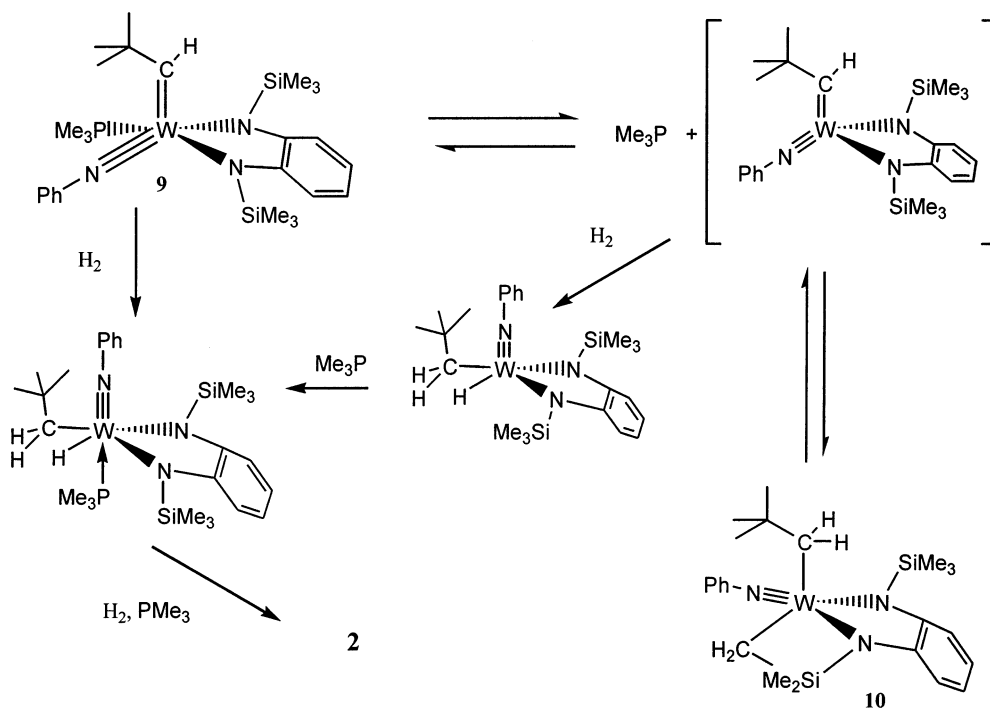
An alternative route to complex **2** involves hydrogenolysis of the alkylidene complex  $\text{W(NPh)[}o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4\text{](CHCMe}_3\text{)(PMe}_3\text{)}$  (**9**) in the presence of one equivalent of  $\text{PMe}_3$ . In this reaction, the alkylidene is completely hydrogenated to form neopentane and the metal ends up as **2**. Reactions that were performed in an NMR tube reveal essentially quantitative conversion of **9** to **2**. If the reaction was performed in the absence of added  $\text{PMe}_3$ , then a 50% yield of **2** was observed. The remaining W containing material is the metallated  $\text{TMS}_2\text{pda}$  complex **10** [3], shown in Scheme 2.

One possible mechanism for the conversion of **9** to **2** involves initial dissociation of  $\text{PMe}_3$  from **9**. Hydrogenolysis of the intermediate base-free alkylidene complex would generate a base-free hydrido neopentyl complex that could be trapped by  $\text{PMe}_3$  to give **2** by reductive elimination, followed by oxidative addition of  $\text{H}_2$ . If there is not enough  $\text{PMe}_3$  present in the reaction mixture, then **10** is formed along with **2**. Complex **10**

does in fact react with  $\text{H}_2$  much more slowly to give a material that has a peak in the hydride region of the  $^1\text{H-NMR}$  spectrum that is converted to **2** when it is allowed to react with  $\text{PMe}_3$ . The direct hydrogenolysis of the alkylidene group of **9** could also lead to **2**.

We have explored the reaction of various hydride sources with the dichloride complex **6** as an alternative route to these complexes. Unfortunately, the use of  $\text{KH}$ ,  $\text{LiAlH}_4$ ,  $\text{LiBEt}_3\text{H}$ ,  $\text{LiAl(O-}i\text{-Bu)}_3\text{H}$  and  $\text{NaBH}_4$  did not give satisfactory results. While hydride complexes were formed in all cases, there were significant quantities of impurities that proved extremely difficult to separate from the desired products. The most efficient synthesis of these phosphine hydride complexes appears to be generating the diethyl complex **7**, followed by its in situ hydrogenolysis in the presence of excess phosphine ligand.

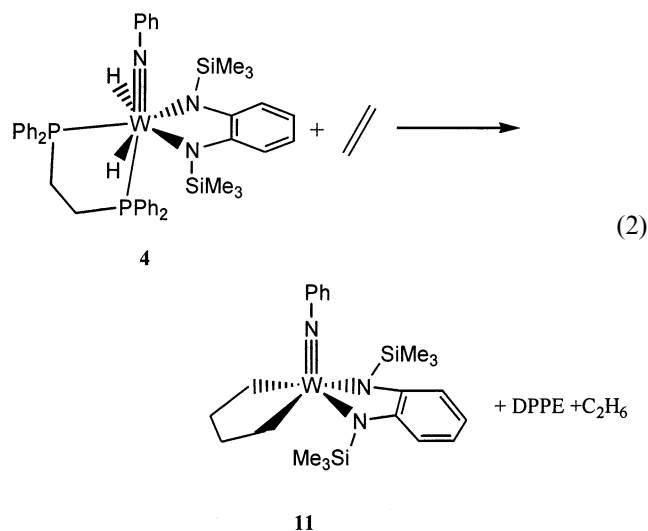
When a solution of compound **2** was exposed to ethylene at r.t. and 1 atm pressure, the ethylene complex **8** was observed along with one equivalent of ethane. Compound **2** does function as an olefin hydrogenation catalyst though the turnover frequency is very low. Thus, styrene is hydrogenated to form ethylbenzene ( $\text{TON} \sim 3/\text{h}$ ) and cyclohexadiene is converted to cyclohexene with 98% selectivity. We believe that the low turnover frequency and the inability to hydrogenate cyclohexene at an appreciable rate is due to the inhibitory effect of the  $\text{PMe}_3$  and the formation of a stable cyclohexene complex, respectively. Both of these



Scheme 2.

factors could inhibit the oxidative addition of  $\text{H}_2$  to the metal center and would thereby inhibit the hydrogenation reaction.

When complex **4** was exposed to excess ethylene, a rapid reaction occurred that produced ethane and the metallacyclopentane complex **11** [5] (Eq. (2)). We were surprised by the identity of the W complex formed in this reaction. Evidently, the DPPE ligand in **4** is displaced once the complex is exposed to excess ethylene. Presumably, the formation of a W(VI) ethylene complex occurs as it does with **2** and **3**, but in this case, the DPPE does not bind strongly enough to prevent the formation of the W(VI) metallacyclopentane complex **11**.



Indeed, when **2** is exposed to an excess of ethylene over the period of weeks at r.t., **11** is the final product of the reaction. In all cases, the driving force for the formation of W(VI) leads to the observed thermodynamic product, the W(VI) metallacyclopentane complex.

This work demonstrates the viability of W(VI) imido hydride complexes. One interesting aspect of the reactivity of these compounds is their ability to cycle between the W(IV) and W(VI) formal oxidation states. Unlike typical  $d^0$  complexes that are olefin hydrogenation catalysts [17], the hydrogenation reaction appears to be proceeding via a mechanism that involves both oxidative addition and reductive elimination steps. It is possible that the imido group somehow facilitates the  $d^2/d^0$  couple that is necessary for such reactions. We are actively investigating the oxidative addition and reductive elimination reactivities of this class of compounds.

### 3. Materials and experimental methods

All syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. The compounds  $\text{W}(=\text{NPh})\text{Cl}_4(\text{OEt}_2)$  (**6**) [18],  $[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{W}(=\text{NPh})(\text{CH}_2\text{CH}_3)_2$  (**7**) [1],  $\text{W}(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{C}_2\text{H}_4)(\text{PMe}_3)_2$  (**8**) [5], and  $\text{W}(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{CHCMe}_3)(\text{PMe}_3)$  (**9**) [2], were synthesized according to literature procedures. Tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ), and pentane were distilled from sodium benzophenone ketyl. Benzene was distilled from sodium. NMR solvents were

stored over molecular sieves and degassed prior to use. NMR spectra were acquired on either Varian VXR 300 or Gemini 300 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are referenced to the residual proton peaks of the deuterated solvents and are reported relative to TMS. Elemental analyses were performed by Atlantic Micro-labs, Inc., or by the analytical services of this department.

### 3.1. $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{H})_2(\text{PMe}_3)_2$ (**2**)

#### 3.1.1. Method 1

In a glass tube with a Teflon Young's joint,  $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{CH}_2\text{C}(\text{CH}_3)_3)_2$  (**10**) (1.66 g, 2.48 mmol) was dissolved in 25 ml of hexanes.  $\text{PMe}_3$  (0.64 ml, 6.20 mmol) was added via syringe. The solution was then placed in liquid nitrogen while a vacuum was applied. Once the solution was frozen solid under vacuum, the flask was sealed. The neck of the flask was then purged with hydrogen gas and the  $\text{H}_2$  hose was wired securely to the flask. The flask was opened until the  $\text{H}_2$  reached a pressure of 10 PSIG. The flask was then resealed and the  $\text{H}_2$  line removed. The reaction was then allowed to warm to r.t. After 4 h of stirring, the color of the solution changed from brown to magenta, and magenta crystals precipitated from solution. The remaining solution was transferred to a Schlenk tube and cooled to  $-10^\circ\text{C}$  to give additional magenta crystals. The mother liquors were concentrated and cooled to give another crop of crystals. Total yield of **2**: 1.48 g (88%).  $^1\text{H}$ -NMR ( $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 0.79 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 0.81 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 1.04 (s, 18H,  $-\text{PMe}_3$ ); 6.80–7.45 (m, 9H, aromatic); 9.26 (br t, 2H, W-H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ): 4.92 ( $\text{Si}(\text{CH}_3)_3$ ); 6.43 ( $-\text{Si}(\text{CH}_3)_3$ ); 15.99 (s,  $-\text{PMe}_3$ ); 115.21, 116.53, 118.17, 119.20, 123.31, 126.71, 128.68, 151.13 (aromatic).  $^1\text{H}$ -NMR ( $-50^\circ\text{C}$ ,  $\text{C}_7\text{D}_8$ ): 0.69 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 0.75 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 0.84 (t, separation = 3 Hz, 18H,  $-\text{PMe}_3$ ); 6.74–7.38 (m, 9H, aromatic); 9.0 (d of d, 2H,  $^2J_{\text{P-H}} = 37, 41$  Hz, W-H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $-24.46$  (s,  $^1J_{\text{W-P}} = 188$  Hz). Anal. Calc. for  $\text{C}_{24}\text{H}_{47}\text{N}_3\text{P}_2\text{Si}_2\text{W}$ : C, 42.41; H, 6.97; N, 6.18. Found: C, 42.18; H, 6.79; N, 6.03.

#### 3.1.2. Method 2

$W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{CHCMe}_3)(\text{PMe}_3)$  (**9**) (50 mg, 0.07 mmol) was dissolved in  $\text{C}_6\text{D}_6$  in an NMR tube fitted with a Teflon Young's joint. One equivalent of  $\text{PMe}_3$  (7  $\mu\text{l}$ , 0.07 mmol) was added via a microliter syringe. The NMR tube was then fitted with a Schlenk adapter, frozen in liquid nitrogen, and placed under vacuum. The tube was then sealed while frozen under vacuum. Hydrogen gas was then purged through the Schlenk adapter for 5 min. The Teflon seal was opened to allow the  $\text{H}_2$  to fill the vacuum in the NMR tube. The NMR tube was charged with ca. 15 PSIG of  $\text{H}_2$ .

Over a period of less than 2 h, complete conversion of **9** to **2** was observed by  $^1\text{H}$ -NMR.

#### 3.1.3. Method 3

The compound  $[(\text{TMS})_2\text{pda}]\text{M}(\text{=NPh})(\text{Et})_2$  (**7**) was generated by the addition of 2.1 equivalents of  $\text{EtMgCl}$  to a diethyl ether solution of  $[(\text{TMS})_2\text{pda}]\text{M}(\text{=NPh})(\text{Cl})_2$  at  $-78^\circ\text{C}$ . The solution was allowed to warm to r.t. and was stirred for 30 min. The  $\text{Et}_2\text{O}$  was removed under reduced pressure and the resultant residue was extracted with pentane ( $3 \times 20$  ml) and the combined extracts were then filtered into a tube with a Teflon valve. At this time, 2.1 equivalents of  $\text{PMe}_3$  was added to the solution resulting in a change from red to purple. The reaction mixture was stirred for 1 h and then frozen in liquid  $\text{N}_2$  and evacuated. The flask was then charged with  $\text{H}_2$  (ca. 10–15 PSIG) as described above. The solution was allowed to warm to r.t. and was stirred for 24 h. The solution turned the characteristic magenta color of compound **2**. The crystals that deposited were collected and the mother liquors were cooled to  $-20^\circ\text{C}$  to harvest further compound from the reaction. The yield of **2** using this procedure is ca. 80% based on the  $[(\text{TMS})_2\text{pda}]\text{W}(\text{=NPh})(\text{Cl})_2$  starting material. The identity of **2** was confirmed by  $^1\text{H}$ -NMR spectroscopy.

### 3.2. $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{H})_2(\text{PMe}_2\text{Ph})_2$ (**3**)

This compound was synthesized according to the procedure used for **2** by substituting  $\text{PMe}_2\text{Ph}$  for  $\text{PMe}_3$  and following either Method 1 or Method 3, as described above. The yield was ca. 85%.  $^1\text{H}$ -NMR ( $25^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 0.53 (s, 18H,  $-\text{Si}(\text{CH}_3)_3$ ); 1.22 (s, 12H,  $-\text{PMe}_2\text{Ph}$ ); 6.72–7.29 (m, 9H, aromatic); 9.63 (br s 2H, W-H).  $^1\text{H}$ -NMR ( $-50^\circ\text{C}$ ,  $\text{C}_7\text{D}_8$ ): 0.53 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 0.59 (s, 9H,  $-\text{Si}(\text{CH}_3)_3$ ); 1.19 (t, peak separation = 4 Hz, 12H,  $-\text{PMe}_2\text{Ph}$ ); 6.72–7.29 (m, 9H, aromatic); 9.56 (br t,  $^2J_{\text{P-H}} = 40$  Hz, 2H, W-H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ): 4.92 ( $\text{Si}(\text{CH}_3)_3$ ); 6.43 ( $-\text{Si}(\text{CH}_3)_3$ ); 15.99 (s,  $-\text{PMe}_3$ ); 115.21, 116.53, 118.17, 119.20, 123.31, 126.71, 128.68, 151.13 (aromatic).  $^{31}\text{P}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $-17.4$  (s,  $^1J_{\text{W-P}} = 164$  Hz). Anal. Calc. for  $\text{C}_{34}\text{H}_{51}\text{N}_3\text{P}_2\text{Si}_2\text{W}$ : C, 50.81; H, 6.39; N, 5.22. Found: C, 50.52; H, 6.19; N, 5.03.

### 3.3. $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{H})_2(\text{DPPE})$ (**4**)

In a glass tube with a Teflon Young's joint,  $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{CH}_2\text{C}(\text{CH}_3)_3)_2$  (**10**) (0.65 g, 0.98 mmol) and DPPE (0.39 g, 0.98 mmol) were dissolved in 30 ml of hexanes. The solution was then placed in liquid nitrogen while a vacuum was applied.  $\text{H}_2$  gas was introduced as described for **2**. The reaction was then allowed to warm to r.t. After 8 h of stirring, the color of the solution had changed from brown to

purple. Purple solid had also precipitated from solution. The solution was transferred to a Schlenk tube, concentrated to 10 ml, and cooled to  $-10^{\circ}\text{C}$  to give additional purple solid. Total yield: 0.71 g (78%).  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^{\circ}\text{C}$ ): 0.49 (s, 18H,  $-\text{Si}(\text{CH}_3)_3$ ); 2.23 (m, 2H,  $\text{PCH}_2\text{CH}_2\text{P}$ ); 2.42 (m, 2H,  $\text{PCH}_2\text{CH}_2\text{P}$ ); 6.72–7.69 (aromatic); 10.56 (m, 2H, W-H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^{\circ}\text{C}$ ): 30.43 (d,  $^2J_{\text{P-P}} = 83$  Hz);  $-12.70$  (d,  $^2J_{\text{P-P}} = 83$  Hz). Anal. Calc. for  $\text{C}_{44}\text{H}_{53}\text{N}_3\text{Si}_2\text{P}_2\text{W}$ : C, 57.08; H, 5.77; N, 4.54. Found: C, 57.33; H, 5.84; N, 4.54.

### 3.4. $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{H})_2(\text{PCy}_3)$ (**5**)

In a glass tube with a Teflon Young's joint,  $W(\text{NPh})[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4](\text{CH}_2\text{C}(\text{CH}_3)_3)_2$  (**10**) (1.06 g, 1.58 mmol), and  $\text{PCy}_3$  (0.476 g, 1.70 mmol) were dissolved in ca. 30 ml of pentane. The solution was then placed in liquid nitrogen while a vacuum was applied. Once the solution was frozen solid under vacuum, the flask was sealed. The neck of the flask was then purged with hydrogen gas and the  $\text{H}_2$  hose was wired securely to the flask. The flask was opened until the  $\text{H}_2$  reached a pressure of 10 PSIG. The flask was then resealed and the  $\text{H}_2$  line removed. The reaction was then allowed to warm to r.t. After 12 h of stirring, the color of the solution changed from brown to red. The solution was transferred to a Schlenk tube and concentrated to ca. 10 ml and cooled to  $-10^{\circ}\text{C}$  to give red crystals. The mother liquors were concentrated and cooled to give a second crop of crystals. Total yield: 1.04 g (82%).  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^{\circ}\text{C}$ ): 0.81 (s, 18H,  $-\text{Si}(\text{CH}_3)_3$ ); 1.04–1.93 (m, 33H,  $\text{PC}_6\text{H}_{11}$ ); 6.81 (t, 1H, *p*-Ph H); 6.95 (m, 2H *pda* ring H); 6.99 (t, 2H *m*-Ph-H) 7.18 (d, 2H *o*-Ph-H); 7.47 (m, 2H, *pda* ring H); 11.35 (d,  $^2J_{\text{P-H}} = 85$  Hz,  $^1J_{\text{W-H}} = 64$  Hz, W-H).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{C}_6\text{D}_6$ ,  $25^{\circ}\text{C}$ ): 66.71 (s,  $^1J_{\text{W-P}} = 56$  Hz). Anal. Calc. for  $\text{C}_{36}\text{H}_{53}\text{N}_3\text{Si}_2\text{P}_2\text{W}$ : C, 54.13; H, 6.69; N, 5.26. Found: C, 53.98; H, 6.64; N, 5.23.

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