Molecular Structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$ in the Solid State and in Solution[‡]

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Abstract: The molecular structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$ has been identified by low temperature ($-123\text{ }^\circ\text{C}$) X-ray diffraction studies as a classical hydride compound, with a tricapped trigonal prismatic geometry in which two of the PMe_3 ligands adopt eclipsed positions on opposite triangular faces of the prism and one PMe_3 ligand caps a rectangular face. The solid state structure is reproduced well by density functional theory geometry optimization calculations on the molecule in the gas phase. NMR spectroscopic studies provide evidence that $\text{W}(\text{PMe}_3)_3\text{H}_6$ also exists as a classical hydride compound in solution. For example, the $T_{1(\text{min})}$ value for the hydride ligands of $\text{W}(\text{PMe}_3)_3\text{H}_6$ is 380 ms at 500 MHz and 310 ms at 400 MHz, values that are more in accord with a classical hydride formulation than a nonclassical one. Likewise, the $\text{W}(\text{PMe}_3)_3\text{H}_{6-x}\text{D}_x$ isotopologues (obtained by isotope exchange with either deuterobenzene or deuterotoluene) exhibit upfield (+13 ppb) deuterium secondary isotope effects on the hydride chemical shift, which are also consistent with a classical description.

Keywords: Tungsten, hydride, polyhydride, dihydrogen, T_1 relaxation, isotopologue, isotope shift.

[‡] Dedicated to Professor T. Don Tilley on the occasion of his 60th birthday. Happy birthday, Don!

INTRODUCTION

Transition metal polyhydride compounds comprise an interesting class of molecules that have had a profound impact on the development of coordination chemistry in terms of their structures, spectroscopic properties and reactivities.¹ For example, with respect to their structures,² polyhydride compounds can exist in either classical or nonclassical (*i.e.* dihydrogen) forms^{3,4,5} and are often fluxional on the NMR timescale in solution.⁶ Such compounds may also exhibit quantum mechanical exchange coupling that is manifested by extremely large coupling constants in their ¹H NMR spectra.⁷ In terms of reactivity, metal hydride compounds play important roles in a large variety of catalytic transformations, including hydrogenation,⁸ hydroformylation^{8,9} and hydrosilylation.^{8,10} While many transition metal polyhydride compounds are known, derivatives of the class $M(PR_3)_xH_y$, which feature tertiary phosphine ligands, have received particular attention.¹ Here, we report on the nature of $W(PMe_3)_3H_6$, as determined by X-ray diffraction studies in the solid state and by T_1 relaxation studies and deuterium isotope shift effects in solution.

RESULTS AND DISCUSSION

1. Molecular Structure of $W(PMe_3)_3H_6$

Tungsten forms three classes of polyhydride compounds of the type $M(PR_3)_xH_y$, namely $W(PR_3)_5H_2$,¹¹ $W(PR_3)_4H_4$,^{11,12} and $W(PR_3)_3H_6$.^{13,14} Of these, the first representative to be obtained was $W(PMe_2Ph)_3H_6$, as prepared by Moss and Shaw *via* the reaction of $W(PMe_2Ph)_2Cl_4$ with $NaBH_4$ in methanol.^{13a} The trimethylphosphine derivative $W(PMe_3)_3H_6$ was subsequently synthesized *via* the reaction of $W(PMe_3)_3Cl_4$ with $LiAlH_4$ ^{13f} and was identified as being fluxional in solution, such that all six hydrides are equivalent, as are the PMe_3 ligands. Although crystals suitable for X-ray diffraction were not obtained, two idealized geometries were considered for the static structure,

namely (i) a tricapped trigonal prism with D_{3h} symmetry,^{*} in which the hydride ligands make up a trigonal prism and the PMe_3 ligands cap the rectangular faces (Figure 1, left),^{12c,13c,d,15} and (ii) a tricapped trigonal prism with C_{2v} symmetry,^{*} in which two of the PMe_3 ligands adopt eclipsed positions on the triangular faces and one PMe_3 ligand caps a rectangular face (Figure 1, right).^{13c,d}

In view of these two suggestions, it is noteworthy that we have determined the low temperature ($-123\text{ }^\circ\text{C}$) molecular structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$ by X-ray diffraction (Figure 2). Significantly, all six hydrogen atoms attached to tungsten could be located and freely refined isotropically, thereby demonstrating that the molecule is best described as having the approximate C_{2v} structure described above, with a PMe_3 ligand on each triangular face and one capping a rectangular face (Figure 1, right).

For example, a clear indication that the molecule does not possess D_{3h} symmetry is provided by the fact that there is no C_3 axis; specifically, the P–W–P bond angles (Table 1) deviate substantially from 120° and range from $102.49(3)^\circ$ to $128.57(2)^\circ$. Furthermore, the W–P bond lengths range from $2.4156(8)\text{ \AA}$ to $2.4706(6)\text{ \AA}$,^{†16} which also indicates a deviation from D_{3h} , albeit to a lesser extent than the angular variation. While inconsistent with a D_{3h} geometry, they are, nevertheless, consistent with an idealized C_{2v} geometry in which [P2, H1, H2] and [P2', H1', H2'] form the top and bottom faces of the idealized trigonal prism, while P1 caps the [H1, H2, H1', H2'] rectangular face, and H3 and H4 respectively cap the [P2, H2, H2', P2'] and [P2, H1, H1', P2'] faces (Figure 2, right).

^{*} The D_{3h} and C_{2v} labels refer only to the coordination environment about tungsten and do not consider the positions of the methyl groups.

[†] For comparison, the average W– PMe_3 bond length in structurally characterized compounds listed in the Cambridge Structural Database (Version 5.35) is $2.49\text{ \AA}$. See reference 16.

Support for the experimental structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$ is provided by the fact that it is reproduced well by density functional theory geometry optimization calculations on the molecule in the gas phase, as illustrated in Figure 3. For example, the calculations predict P–W–P angles that deviate markedly from 120° (101.4° , 128.4° and 129.8°).[‡] Furthermore, the calculations also reproduce the fact that the W–P bond length for the PMe_3 ligand that caps the rectangular face ($2.460 \text{ \AA}$) is shorter than the W–P bonds for the two PMe_3 ligands that occupy triangular faces of the trigonal prism ($2.522 \text{ \AA}$ and $2.536 \text{ \AA}$), clearly deviating from a structure with D_{3h} symmetry.¹⁷

Also in accord with the C_{2v} structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$, solid state ^{13}C and ^{31}P NMR spectroscopic studies indicate the presence of two different types of PMe_3 ligand environments.¹⁸ The related complex with a bulky PPhPr_2 ligand, namely $\text{W}(\text{PPhPr}_2)_3\text{H}_6$,^{13c,d} also possesses a C_{2v} symmetric structure similar to that of $\text{W}(\text{PMe}_3)_3\text{H}_6$. Therefore, on the basis that $\text{W}(\text{PMe}_3)_3\text{H}_6$ and $\text{W}(\text{PPhPr}_2)_3\text{H}_6$ possess similar structures despite the very different steric demands of the PR_3 ligands, it is expected that the C_{2v} arrangement will be common for other $\text{W}(\text{PR}_3)_3\text{H}_6$ derivatives.

In addition to the overall geometry of $\text{W}(\text{PMe}_3)_3\text{H}_6$, an important issue is concerned with whether the compound should be classified as a classical or nonclassical hydride complex. Such complexes are distinguished according to the $\text{H}\cdots\text{H}$ distances and, although a continuum of distances has been observed in these systems, $\text{H}\cdots\text{H}$ distances of $\leq 1.0 \text{ \AA}$ are typically considered to be “true” dihydrogen complexes, while distances of $> 1.6 \text{ \AA}$ are considered to be dihydride complexes.^{3c} On this basis, $\text{W}(\text{PMe}_3)_3\text{H}_6$ is classified as a classical hydride derivative in the solid state because the shortest $\text{H}\cdots\text{H}$ distance between the hydride ligands is greater than this threshold.

[‡] A geometry optimization in which $\text{W}(\text{PMe}_3)_3\text{H}_6$ was constrained to C_{3v} symmetry resulted in a structure that is approximately $2.8 \text{ kcal mol}^{-1}$ higher in energy than that without constraints.

Specifically, the shortest distance in the experimental structure is 1.647 Å, while that in the calculated structure is 1.914 Å.¹⁷

2. T_1 Relaxation Studies

T_1 relaxation studies provide evidence that $\text{W}(\text{PMe}_3)_3\text{H}_6$ also exists as a classical hydride compound in solution. The essential basis of the T_1 method is that, for short distances (r) between protons, dipole-dipole relaxation is a major contributor to the total spin-lattice relaxation rate constant (R) *via* the relationship $R \propto 1/r^6$. As such, $T_1 \propto r^6$, thereby enabling the value of T_1 to help differentiate between classical and nonclassical hydrides.^{19,20,21,22,23} However, despite the existence of the relationship between T_1 and r , extraction of internuclear distances from the value of T_1 is complicated by the fact that dipole-dipole relaxation is also dependent on the correlation time (τ_c), which is temperature dependent^{22,24,25} and generally unknown.²⁶ Fortunately, the correlation time of a molecule has a precise value of $0.62/\omega$ (where ω is the Larmor frequency) at the temperature at which T_1 has its minimum value (*i.e.* $T_{1(\text{min})}$), which thus allows r to be extracted.^{19a,20} For example, for a system involving only two hydrogen atoms that undergo relaxation *via* the dipole-dipole mechanism, the distance between the two hydrogen atoms, r (in Å), is related to $T_{1(\text{min})}$ (in seconds) *via* the expression $r = 5.815[T_{1(\text{min})}/\nu]^{1/6}$, where ν is the spectrometer frequency in MHz.²²

Therefore, we have measured the temperature dependence of the T_1 relaxation times of $\text{W}(\text{PMe}_3)_3\text{H}_6$, as illustrated in Table 2 and Figure 4. At 500 MHz, the minimum value of T_1 occurs at *ca.* 210 K and has a value of 380 ms, whereas at 400 MHz the minimum value is 310 ms at *ca.* 195 K, a difference that is in accord with the fact that $T_{1(\text{min})}$ is directly proportional to field strength.^{19,20} Since classical hydride compounds are generally considered to possess $T_{1(\text{min})}$ values > 200 ms at 500 MHz, whereas well-defined nonclassical hydride compounds have values < 80 ms,^{19b} it is evident that $\text{W}(\text{PMe}_3)_3\text{H}_6$ can be identified as a classical hydride in solution.

It should, however, be noted that the T_1 relaxation time of a proton in a polyhydride compound is dependent not only on interactions with the other hydride ligands, but also on interactions with all other magnetically active nuclei.^{19,20,27} In this regard, the average relaxation rate for the hydride ligands of $\text{W}(\text{PMe}_3)_3\text{H}_6$ is a sum of components due to (i) interactions between the hydride ligands (R_{HWH}), (ii) interactions between the hydride ligands and the hydrogen atoms of the methyl groups (R_{HMe}), and (iii) interactions between the hydride ligands and the phosphorus nuclei (R_{HP}).²⁰ These components have been calculated for the DFT geometry optimized structure and, as would be expected, the dominant component is due to interactions between the hydride ligands ($R_{\text{HWH}} = 2.89 \text{ s}^{-1}$), but relaxation due to the methyl groups ($R_{\text{HMe}} = 0.97 \text{ s}^{-1}$) is also significant. On the other hand, relaxation due to the phosphorus nuclei ($R_{\text{HP}} = 0.08 \text{ s}^{-1}$)[§] provides only a minor component.^{**} The total relaxation rate for the hydride ligands of $\text{W}(\text{PMe}_3)_3\text{H}_6$ is, therefore, estimated to be $R_{\text{tot}} = 2.89 + 0.97 + 0.08 = 3.94 \text{ s}^{-1}$ at 500 MHz, which corresponds to a value of 253 ms for $T_{1(\text{min})}$.

This calculated value is in sufficient agreement with the experimental value (380 ms) that it supports the classification of $\text{W}(\text{PMe}_3)_3\text{H}_6$ as a classical hydride in solution. The observation that the calculated $T_{1(\text{min})}$ is less than the experimental value does, nevertheless, suggest that the hydride ligands in the geometry optimized structure are, on average, closer together than those in the actual structure in solution.^{††} However, in

[§] This value is calculated *via* the expression $R_{\text{HP}} = 0.027n \text{ s}^{-1}$, where n is the number of phosphorus nuclei. See reference 20.

^{**} Furthermore, relaxation due to ^{183}W is negligible, such that the hydride ligands attached to ^{183}W (as represented by the tungsten satellites) are calculated to have similar $T_{1(\text{min})}$ values to those attached to non- ^{183}W nuclei (*i.e.* the central signal).

^{††} An alternative explanation for the calculated $T_{1(\text{min})}$ to be less than the experimental value is that the hydrogen atoms of the PMe_3 ligands are closer to the hydride ligands in the calculated structure than in the actual structure. However, this is considered to

view of the r^6 dependence of $T_{1(\min)}$, only small differences in structure are needed to modify the value $T_{1(\min)}$ by amounts of this magnitude.

For comparison, $T_{1(\min)}$ data for related tungsten compounds^{13g,28,29} are compiled in Table 3 and are scaled to the values at 500 MHz.^{19,20} From these data, it is evident that, whereas each of the neutral compounds may be identified as classical, the protonated complexes are nonclassical.

3. Deuterium Isotope Effects

In addition to T_1 relaxation measurements on the protio compounds, NMR spectroscopic studies on partially deuterated isotopologues also provide valuable information concerned with the nature of the polyhydride compound in solution. For example, the observation of a substantial J_{H-D} coupling constant (> 15 Hz) is generally inferred to be indicative of a dihydrogen tautomer.^{21,30,31} Likewise, the occurrence of a substantial secondary deuterium isotope shift³² in the hydride region of the 1H NMR spectrum is indicative of the presence of a dihydrogen species. Therefore, to obtain more evidence for the nature of $W(PMe_3)_3H_6$ in solution, we have generated a series of isotopologues, namely $W(PMe_3)_3H_{6-x}D_x$, by hydrogen/deuterium exchange with either deuterobenzene or deuterotoluene (Scheme 1).

Of note, both 1H and 2H NMR spectroscopy demonstrate that deuterium incorporation also occurs into the PMe_3 groups, although incorporation into the hydride sites is more facile. For example, after 8 days at 40 °C, the ratio of deuterium incorporation into the hydride and PMe_3 groups is approximately 10:1. Isotope exchange reactions of this type involving polyhydrides are well known,³³ with some early illustrations being provided by $Re(PR_3)_2H_7$,³⁴ $Ta(Me_2PCH_2CH_2PMe_2)_2H_5$,³⁵ $Ir(PR_3)_2H_5$,³⁶ $M(PR_3)_4H_4$ ($M = Mo, W$)³⁷ and Cp_2MH_3 ($M = Nb, Ta$).^{36a,38} By analogy with

be less important because the relaxation is dominated by interactions between the hydride ligands.

the aforementioned examples, the mechanism for deuterium incorporation into the hydride sites presumably involves a sequence of (i) reductive elimination of H₂, (ii) oxidative addition of Ar-D, (iii) reductive elimination of Ar-H and (iv) oxidative addition of H₂,[‡] while incorporation into the PMe₃ ligands involves an additional cyclometallation³⁹ sequence that features oxidative addition of a C-H bond.⁴⁰ As such, deuterium incorporation into the PMe₃ groups is less facile than incorporation into the hydride sites.

With respect to the oxidative addition of the C-H bond, reactions involving toluene typically exhibit a preference for cleavage of the phenyl rather than methyl C-H bonds. Furthermore, the *ortho/meta/para* selectivity is highly dependent on the system, except for the fact that cleavage of the *ortho* bond is rarely observed. For example, with respect to cleavage of the phenyl C-H bonds, photolysis of Cp₂WH₂ in toluene gives Cp₂W(C₄H₄Me)H as a 0.1:1 ratio of *meta* and *para* isomers.^{41,§§} In contrast, photolysis of [Tp^{Me2}]Rh(CNNp)(η²-PhNCNNp) in toluene gives [Tp^{Me2}]Rh(CNNp)(C₆H₄Me)H as a kinetic 1.33:1 ratio of *meta* and *para* isomers, which converts to the statistical 2:1 ratio after heating at 100°C for 12 hours.^{42,***} The site selectivity for cleaving the C-H bonds in toluene has been examined for several other systems,⁴³ from which it is evident that there can be a kinetic preference for cleaving either the *meta* or *para* C-H bonds. Therefore, we have examined the extent of ¹H incorporation into the phenyl sites of toluene and observe that incorporation into the *meta* and *para* sites⁴⁴ is statistical throughout the process, as illustrated in Figure 5.

[‡] In accord with this mechanism, HD is formed catalytically *via* H/D exchange between H₂ and deuterotoluene in the presence of W(PMe₃)₃H₆.

^{§§} In addition, cleavage of the methyl C-H bond is also observed to give Cp₂W(C₄H₄Me)(CH₂Ph). See reference 41.

^{***} A significant amount of methyl C-H bond cleavage is also observed in this system. See reference 42.

Each $\text{W}(\text{PMe}_3)_3\text{H}_{6-x}\text{D}_x$ isotopologue that contains at least one hydrogen on the tungsten center can be observed in the ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectra, with the signals being progressively shifted upfield upon increasing deuterium incorporation, as illustrated in Figure 6.

The isotopic perturbation of the chemical shift of a polyhydride compound is a manifestation of both (i) an intrinsic isotope effect and (ii) an effect due to the relative classical/nonclassical site preferences of deuterium and hydrogen. With respect to intrinsic isotope effects, two-bond $^2\Delta^1\text{H}(\text{D})$ isotope shifts are typically upfield.³² For example, CH_4 , CH_3D , CH_2D_2 and CHD_3 exhibit upfield shifts of *ca.* 15 ppb.^{45,46,47} On the other hand, isotope effects resulting from the relative classical/nonclassical site preferences of deuterium and hydrogen can be either upfield or downfield, depending upon both (i) whether the classical or nonclassical site is more upfield and (ii) whether deuterium prefers to reside in the classical or nonclassical site.

Transition metal polyhydride compounds have been observed to exhibit both upfield and downfield $^2\Delta^1\text{H}(\text{D})$ secondary isotope shifts.^{†††} For example, upfield isotope shifts have been noted for $\text{Re}(\text{PCy}_3)_2\text{H}_7$,⁴⁸ $\text{Re}(\text{PPh}_3)_2\text{H}_7$,⁴⁹ $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Mo}(\eta^2\text{-H}_2)\text{H}]^+$,⁵⁰ $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2]\text{Mo}(\eta^2\text{-H}_2)\text{H}]^+$,⁵¹ and Cp_2NbH_3 ,⁵² and $\text{Re}(\text{AsMePh}_2)_4(\eta^2\text{-H}_2)\text{Cl}$, while downfield isotope shifts have been observed for $\text{Os}(\text{PTol}_3)_3\text{H}_4$,²⁰ $[\{\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3\}\text{Os}(\text{H})(\eta^2\text{-H}_2)]^+$,⁵³ and $[\text{Tp}]\text{Ir}(\text{PMe}_3)(\eta^2\text{-H}_2)\text{H}]^+$.⁵⁴

Since two-bond intrinsic isotope shifts are typically upfield, downfield shifts are normally associated with nonclassical hydride compounds. As an illustration, $^2\Delta^1\text{H}(\text{D})$

^{†††} In the $^n\Delta\text{X}(\text{Y})$ notation, the value corresponds to the chemical shift of X in the molecule with the lighter isotope of Y minus the chemical shift of X in the molecule with the heavier isotope of Y, such that an upfield shift for the heavier isotope is characterized by a positive value of $^n\Delta\text{X}(\text{Y})$.^{32a,b} It should be noted that the opposite sign convention has also been used in the literature^{32c-e} and so care should be taken when interpreting literature values.

for the H_2D isotopologue of $\{[Tp]Ir(PMe_3)(\eta^2-H_2)H\}^+$ varies from -228 ppb at 215 K to -149 ppb at 281 K,⁵⁴ and both the downfield nature of the shift and its temperature dependence have been rationalized by suggesting that the deuterium prefers to reside in a classical site that is upfield of the nonclassical site.⁵⁴ Upfield shifts may also be associated with nonclassical hydride compounds if their values are anomalously large. For example, incorporation of deuterium into $[Me_2Si(C_5Me_4)_2]Mo(\eta^2-H_2)H]^+$ results in upfield shifts with incremental values (50 ppb and 90 ppb) that are (i) considerably larger than those for typical hydride compounds and (ii) significantly different from each other.^{50,††} Both the magnitude of these shifts and their variation indicate that the upfield isotope shifts for this complex are not intrinsic but are instead a consequence of the relative site preferences of hydrogen and deuterium. In contrast, the constant (13 ppb per deuterium) upfield shifts for the $W(PMe_3)_3H_{6-x}D_x$ isotopologues, which are comparable in magnitude to those for CH_4 and other organic compounds, are consistent with an intrinsic isotope effect and a classical hydride description for the compound. In accord with the classical hydride suggestion, none of the signals exhibit an observable J_{H-D} coupling.^{§§§}

CONCLUSIONS

In summary, both X-ray diffraction studies in the solid state and NMR spectroscopic studies in solution, namely T_1 relaxation measurements and deuterium isotope effects, indicate that $W(PMe_3)_3H_6$ exists as a classical hydride compound. Specifically, X-ray diffraction demonstrates that the structure may be described as a tricapped trigonal prism in which two of the PMe_3 ligands adopt eclipsed positions on opposite faces of

†† $\{[H_2C(C_5H_4)_2]Mo(\eta^2-H_2)H\}^+$ exhibits similar behavior upon isotopic substitution. See reference 51.

§§§ An upper limit of *ca.* 2 Hz for J_{HD} may be estimated on the basis that the linewidth of the hydride signal of $W(PMe_3)_5HD$ in the 1H NMR spectrum is 4 Hz.

the prism and one PMe_3 ligand adopts a capping position, a geometry that is reproduced well by density functional theory geometry optimization calculations on the molecule in the gas phase.

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.⁵⁵ Solvents were purified and degassed by using standard procedures. ^1H NMR spectra were measured on Bruker Avance III 500 and Avance III 400SL spectrometers. ^1H chemical shifts are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity (δ 2.08 for $\text{C}_7\text{D}_7\text{H}$).⁵⁶ $\text{W}(\text{PMe}_3)_3\text{H}_6$ was prepared by photolysis of $\text{W}(\text{PMe}_3)_4\text{H}_4$ with H_2 .¹⁴

X-ray structure determination

Crystals of $\text{W}(\text{PMe}_3)_3\text{H}_6$ suitable for X-ray diffraction were obtained from a solution in pentane at -15°C . X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Table 4. The structure was solved by using direct methods and standard difference map techniques, and was refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.10).⁵⁷

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.5 (release 2007) suite of *ab initio* quantum chemistry programs.⁵⁸ Geometry optimizations were performed with the B3LYP density functional⁵⁹ using the 6-31G** (C, H, and P) and LACVP (W) basis sets.⁶⁰

T_1 Measurements

T_1 measurements were performed by using the standard 180– τ –90 inversion recovery method. Each T_1 experiment used 13 mixing times ranging from 1 ms to 15 s, depending upon the value of T_1 . For each mixing time, the spectrum was composed of four scans with a delay time of $> 5T_1$. The T_1 value was measured for each component of the hydride quartet and averaged to give the values listed in Table 2. Calculations to estimate the $T_{1(\text{min})}$ value of $\text{W}(\text{PMe}_3)_3\text{H}_6$ were performed on the geometry optimized structure of $\text{W}(\text{PMe}_3)_3\text{H}_6$ using a previously described method.²⁰

Generation of $\text{W}(\text{PMe}_3)_3\text{H}_{6-x}\text{D}_x$ Isotopologues

A solution of $\text{W}(\text{PMe}_3)_3\text{H}_6$ (3 mg, 0.007 mmol) in C_7D_8 (0.7 mL) was heated at 40 °C and was monitored by ^1H and $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy, thereby demonstrating the sequential formation of $\text{W}(\text{PMe}_3)_3\text{H}_{6-x}\text{D}_x$ isotopologues over a period of several days. Deuterium incorporation into the PMe_3 groups was also demonstrated by ^2H NMR spectroscopy, albeit at a slower rate than into the hydride sites. Isotope exchange was also observed by using C_6D_6 as the solvent.

APPENDIX A. Supplementary Material

Crystallographic data in CIF format (CCDC #1003445). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi: <http://dx.doi.org/10.1016/j.ica.xxxxxx>.

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Scheme 1.

Figure 1. High symmetry structures proposed^{13f} for $\text{W}(\text{PMe}_3)_3\text{H}_6$ (blue dashed lines show the trigonal prism, while the blue arrows represent the primary symmetry axis).

Figure 2. Molecular structure of $W(PMe_3)_3H_6$ (left) and a view showing the trigonal prismatic geometry with hollow lines for the triangular faces (right). W, P1, H3 and H4 lie on a crystallographic mirror plane.

Figure 3. DFT geometry optimized structure of $\text{W(PMe}_3)_3\text{H}_6$.

Figure 4. Variation in T_1 of the hydride ligands of $\text{W}(\text{PMe}_3)_3\text{H}_6$ as a function of temperature at 400 (black) and 500 (red) MHz.

Figure 5. ^1H incorporation into the *meta* and *para* sites of deuterotoluene relative to the *ortho* site upon treatment with $\text{W}(\text{PMe}_3)_3\text{H}_6$ at 40°C as measured by integration of the ^1H NMR spectra.

Figure 6. 1H (left) and $^1H\{^{31}P\}$ (right) NMR spectra of the hydride signal of $W(PMe_3)_3H_6$ (bottom) in C_7D_8 and after heating for 8 days at 40°C (top). The $W(PMe_3)_3H_{6-x}D_x$ isotopologues in the top right spectrum are indicated by the number of hydrogen atoms in the hydride site, while tungsten satellites are marked by an asterisk (*).

Table 1. Selected bond lengths and angles for $\text{W}(\text{PMe}_3)_3\text{H}_6$.

	Bond lengths/Å
W-P1	2.4156(8)
W-P2	2.4706(6)
W-P2'	2.4706(6)
W-H1	1.62(4)
W-H2	1.62(4)
W-H3	1.38(5)
W-H4	1.59(7)
W-H1'	1.62(4)
W-H2'	1.62(4)
	Bond angles/°
P1-W-P2	128.57(2)
P1-W-P2'	128.57(2)
P2-W-P2'	102.49(3)

Table 2. T_1 relaxation times for the hydride ligands of $\text{W}(\text{PMe}_3)_3\text{H}_6$ as a function of temperature.

Temperature/K	T_1 (400 MHz)/ms	T_1 (500 MHz)/ms
300	2370	2070
270	1300	1170
250	950	730
240	800	580
230	570	460
220	440	390
210	360	380
205	340	420
200	310	500
195	310	560
190	320	650
185	340	

Table 3. $T_{1(\text{min})}$ values for some tungsten phosphine hydride compounds at 11.7 T (*i.e.* 500 MHz).

Compound	$T_{1(\text{min})}/\text{ms}$	Reference
$\text{W}(\text{PMe}_3)_3\text{H}_6$	380	this work
$\text{W}(\text{PPh}_3)_3\text{H}_6$	245 ^a	29
$\text{W}[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2]\text{H}_6$	206, 252 ^{b,c}	28
$\{\text{W}[\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2](\eta^2\text{-H}_2)_x\text{H}_{7-x}\}^+$	42 ^d	28
$\{\text{W}[\text{PhP}(\text{C}_6\text{H}_4\text{-}o\text{-PPh}_2)_2](\eta^2\text{-H}_2)_x\text{H}_{7-x}\}^+$	64 ^e	28

(a) converted from a value of 147 ms at 300 MHz.

(b) converted from values of 103 ms and 126 ms at 250 MHz.

(c) chemically inequivalent hydride ligands.

(d) converted from a value of 21 ms at 250 MHz.

(e) converted from a value of 32 ms at 250 MHz.

Table 4. Crystal, intensity collection and refinement data.

	W(PMe₃)₃H₆
lattice	Orthorhombic
formula	C ₉ H ₃₃ P ₃ W
formula weight	418.11
space group	<i>Cmc2₁</i>
<i>a</i> /Å	15.4496(13)
<i>b</i> /Å	9.7885(8)
<i>c</i> /Å	11.3022(9)
α /°	90
β /°	90
γ /°	90
V /Å ³	1709.2(2)
<i>Z</i>	4
temperature (K)	150(2)
radiation (λ , Å)	0.71073
ρ (calcd.), g cm ⁻³	1.625
μ (Mo K α), mm ⁻¹	7.010
θ max, deg.	31.47
no. of data collected	14256
no. of data	2950
no. of parameters	84
R_1 [$I > 2\sigma(I)$]	0.0147
wR_2 [$I > 2\sigma(I)$]	0.0353
R_1 [all data]	0.0150
wR_2 [all data]	0.0355
GOF	1.081