STRUCTURAL ANALYSIS OF TUNGSTEN BASED HYDROGEN STORAGE MATERIALS

Carly C. Carter^b, Brandon R. Allen^a, Daniel V. Bui^a, Delroy A. Daley^a, Christopher M. Holinej^a, Julia M. Goncalves^a, Sherlin Lira^a, David E. Muniz^a, Alanis I. Santiago^a, Nihmal Sukran^a, Thomas R. Cundari^{b*} and Muhammed Yousufuddin^{a*}

^aUniversity of North Texas at Dallas, Life and Health Sciences Department

^bUniversity of North Texas, Department of Chemistry

Abstract

We present here the synthesis, crystal structures, and DFT calculations of tungsten (IV) and tungsten (VI) phosphino polyhydrides. We have used high quality X-ray diffraction at low temperature to assist in locating, for the first time, the hydrides in these complexes. The polyhydrides each contain four phosphine ligands with the general formula $P(RPh_2)_4$ (where $R = Me$ or Et) making very intriguing eight and nine-coordinate complexes. The eight-coordinate complexes [tungsten (IV)] resemble a slightly distorted dodecahedron while the nine-coordinate complex [tungsten (VI)] resembles a tricapped trigonal prism. Optimized DFT geometries showing the position of the hydrides for all three compounds that were crystallographically characterized have also been calculated. The combination of our results indicate that these compounds are best described as classical metal hydrides.

Synthesis of the Tungsten Tetrahydride Compound

The reaction scheme used to synthesize $WH_4(PPh_2Me)_4$.

The tungsten (IV) complex was synthesized via a sequential one-pot synthesis by reacting 4 moles of methyl diphenylphosphine (PPh_2Me) and 4 moles of lithium triethylborohydride ($Li[C_2H_5]_3BH$) with tungsten hexachloride (WCl_6) in air.^{1,2,3} Crystals were formed immediately after the reaction had completed. The hydrides were located using low temperature and high resolution X-ray diffraction data.^{4,5}

Other Tungsten Polyhydrides

Other tungsten polyhydrides were also synthesized. $WH_4(PPh_2Et)_4$ was synthesized using a similar method as described above but instead the PPh_2Et was used as the stabilizing ligand. $[WH_3(PPh_2Me)_4]^+$ was synthesized by adding HCl to $WH_4(PPh_2Me)_4$ to form the corresponding salt. For $WH_4(PPh_2Et)_4$ crystals formed immediately. For $[WH_3(PPh_2Me)_4]^+$ crystals were formed after storing the reaction vessel in a $-20^\circ C$ freezer for one week.

Our attempts to synthesize $WH_4[P(Me_2Ph)_4]$ the methods presented here were not successful. $P(Me_2Ph)$ is very air-sensitive and we believe that this ligand may have decomposed in our attempt to manipulate it in air. It should also be noted that our attempts to synthesize $WH_4(PPh_2)_4$ using a similar method to the formation of what we presume to be, $W(PPh_3)_4$ as no hydrogen atoms could be found around the metal via preliminary crystallographic analysis. However this compound was only investigated using X-ray diffraction so the formulation is tentative.

Tungsten Polyhydride Geometries

The X-ray structure of $WH_4(PPh_2Me)_4$ (left) with the core represented in the middle and right.

X-ray structure of $WH_4(PPh_2Et)_4$ (top left) and $[WH_3(PPh_2Me)_4]^+$ (top right). The core of $WH_4(PPh_2Et)_4$ is shown on the bottom left and the core of $[WH_3(PPh_2Me)_4]^+$ is shown on the bottom right.

Dodecahedron Geometries for Tetrahydrides

The core of $WH_4(PPh_2Me)_4$ (middle) and $WH_4(PPh_2Et)_4$ (right) showing slightly distorted dodecahedron geometries. Dodecahedron (left) taken with permission from Wiley.

Optimized Structures from DFT Calculations

Optimized structures for $WH_4(PPh_2Me)_4$ (left), $WH_4(PPh_2Et)_4$ (middle), and $[WH_3(PPh_2Me)_4]^+$ (right).⁶

Results

$WH_4(PPh_2Me)_4$			$WH_4(PPh_2Et)_4$			$[WH_3(PPh_2Me)_4]^+$		
Bond (W-H)	Distance (Å)	Computed (Å)	Bond (W-H)	Distance (Å)	Computed (Å)	Bond (W-H)	Distance (Å)	Computed (Å)
W1-H1a	1.68(3)	1.725	W1-H1a	1.75(3)	1.709	W1-H1w	1.53(4)	1.719
W1-H1a	1.72(2)	1.751	W1-H1a	1.56(4)	1.726	W1-H1w	1.61(6)	1.719
W1-H1a	1.63(3)	1.730	W1-H1a'	1.75(3)	1.709	W1-H1w	1.65(6)	1.706
W1-H1a	1.68(3)	1.731	W1-H1a'	1.56(4)	1.726	W1-H1w	1.65(5)	1.678
						W1-H1w	1.39(4)	1.707
W-H (Average)	1.67(2)	1.734(11)	W-H (Average)	1.65(3)	1.718(10)	W-H (Average)	1.56(5)	1.706(17)
Bond (W-P)	Distance (Å)	Computed (Å)	Bond (W-P)	Distance (Å)	Computed (Å)	Bond (W-P)	Distance (Å)	Computed (Å)
W1-P1	2.4729(7)	2.480	W1-P1	2.4684(12)	2.623	W1-P1	2.5289(12)	2.612
W1-P2	2.4315(7)	2.497	W1-P2	2.4677(11)	2.537	W1-P2	2.4973(12)	2.557
W1-P3	2.4920(7)	2.583	W1-P1a	2.4684(12)	2.623	W1-P3	2.5001(12)	2.555
W1-P4	2.4821(7)	2.513	W2-P2a	2.4677(11)	2.537	W1-P4	2.5325(13)	2.611
W-P (Average)	2.4696(7)	2.518(45)	W-P (Average)	2.4680(11)	2.580(50)	W-P (Average)	2.5147(12)	2.584(32)
Angles (P-W-P) (°)			Angles (P-W-P) (°)			Angles (P-W-P) (°)		
P1-W1-P2	93.31(2)	97.734	P2-W1-P2a	91.17(5)	94.96	P1-W1-P4	95.86(4)	91.132
P1-W1-P3	141.52(2)	134.151	P1-W1-P2a	136.39(2)	134.333	P1-W1-P3	129.72(4)	129.716
P1-W1-P4	93.86(2)	98.469	P2a-W1-P1a	98.61(4)	99.41	P1-W1-P2	90.15(4)	96.832
P2-W1-P3	94.40(2)	96.465	P2a-W1-P2	91.17(5)	94.96	P3-W1-P4	89.36(4)	91.218
P2-W1-P4	144.24(2)	139.913	P1a-W1-P2	136.39(2)	134.336	P2-W1-P4	131.26(4)	129.938
P3-W1-P4	101.37(2)	98.003	P1a-W1-P2a	98.61(4)	99.41	P2-W1-P3	122.44(4)	120.279
P-W-P (Average)	111.45(2)	110.789	P-W-P (Average)	108.72(4)	109.56	P-W-P (Average)	109.79(4)	109.852

The displayed data shows comparisons of bond lengths and angles between our compounds and computed values.

Conclusion

In summary, our group has successfully synthesized and determined the X-ray structure (complete with hydrogen atoms surrounding the metal) of three tungsten phosphino polyhydrides. This adds three more structures to the rare group of tungsten phosphino polyhydride structures that are currently known. These compounds each form fascinating high coordination complexes with equally fascinating geometries. Optimized geometries for all three compounds have also been computed with the lowest energy demonstrating classical metal hydrides. It is hoped that future studies into transition metal polyhydrides will contribute to the further understanding of the metal-hydrogen interaction. This may greatly assist in catalytic studies and formation of suitable hydrogen storage materials.

References

- [1] "Molybdenum and Tungsten Phosphine Polyhydrides" by G. G. Hlatky and R. H. Crabtree, Inorganic Synthesis Volume 22, Wiley (1990) 8-10;
- [2] "Improved synthesis of some molybdenum and tungsten tetrahydrides" by R. H. Crabtree and G. G. Hlatky, Inorg. Chem., 21 (1982) 1273-1275;
- [3] "The reaction of tetrahydridotetrakis(methyldiphenylphosphine)-molybdenum(IV) and -tungsten(IV) with acids" by E. Carmona-Guzman and G. Wilkinson, Dalton Trans., 18 (1977) 1716-1721;
- [4] X-ray diffraction Data was collected at the University of Texas at Arlington
- [5] (a) Bruker-AXS (2000); (b) Bruker-AXS (2006); (c) Bruker-AXS (2000); (d) Bruker-AXS (2006); (e) G. M. Sheldrick, Acta Cryst. C, 71 (2015) 3-8
- [6] Gaussian 16, Revision A.03, Frisch, M. J. *et al.* Gaussian, Inc., Wallingford CT, (2016)