

# False Minima in X-ray Structure Solutions Associated with a “Partial Polar Ambiguity”: Single Crystal X-ray and Neutron Diffraction Studies on the Eight-Coordinate Tungsten Hydride Complexes, $W(PMe_3)_4H_2X_2$ ( $X = F, Cl, Br, I$ ) and $W(PMe_3)_4H_2F(FHF)$

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**Abstract:** The molecular structures of the eight-coordinate tungsten hydride complexes  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ) and  $W(PMe_3)_4H_2F(FHF)$  have been determined by single-crystal X-ray diffraction;  $W(PMe_3)_4H_2Cl_2$  and  $W(PMe_3)_4H_2F(FHF)$  have also been analyzed by single-crystal neutron diffraction, thereby accurately locating the positions of the hydride ligands. The structures of all of these complexes are similar and are based on a trigonal dodecahedron, with a distorted tetrahedral array of  $PMe_3$  ligands in which two of the  $PMe_3$  ligands are displaced over the halide substituents. However, the initial structures derived for both  $W(PMe_3)_4H_2Cl_2$  and  $W(PMe_3)_4H_2F(FHF)$  did not exhibit the aforementioned geometry, but were based on an arrangement in which the two *transoid*- $PMe_3$  ligands are displaced toward the two *cis*- $PMe_3$  groups, rather than tilted toward the chloride ligands. Interestingly, the unexpected structures for  $W(PMe_3)_4H_2Cl_2$  and  $W(PMe_3)_4H_2F(FHF)$  were discovered to be the result of an artifact due to the presence of a heavy atom in a polar space group, which allowed the X-ray structure solutions to refine into most deceptive false minima. Specifically, for the structures corresponding to the false minima, the *transoid*- $PMe_3$  ligands were incorrectly located in positions that are related to their true locations by reflection perpendicular to the polar axis. In effect, the incorrect molecular structures are a *composite* of the two possible true polar configurations which are related by a reflection perpendicular to the polar axis, i.e. a “partial polar ambiguity”. Of most importance, the solutions corresponding to the false minima are characterized by low *R* values and well-behaved displacement parameters, so that it is not apparent that the derived structures are incorrect. Thus, for space groups with a polar axis, it is necessary to establish that all of the atoms in the asymmetric unit belong to a single *true* polar configuration.

## Introduction

Although single-crystal X-ray diffraction is a most extensively used technique for the determination of molecular structure,<sup>1</sup> the derived results are not always unequivocal and may be influenced by a variety of factors.<sup>2</sup> For instance, it is well-documented that errors in space group assignment,<sup>3</sup> errors in atom assignment,<sup>4–6</sup> and the presence of disorder<sup>2d,7,8</sup> may each have a dramatic impact upon the accuracy of a structure determination. In contrast, it is not well-known that incorrect structures may be obtained as a consequence of the least-squares

refinement procedure converging to a *false minimum*.<sup>9</sup> Such a phenomenon clearly has serious implications with respect to the interpretation of X-ray diffraction data. In this paper, we

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(1) (a) Bürgi, H.-B.; Dunitz, J. D. *Helv. Chim. Acta* **1993**, *76*, 1115–1166. (b) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1–19. (c) *Accurate Molecular Structures: Their Determination and Importance*; Domenicano, A., Hargittai, I., Eds.; IUCr Monographs on Crystallography; Oxford University Press: New York, 1992. (d) Dunitz, J. D. *X-ray Analysis and the Structures of Organic Molecules*; VCH: New York, 1995.

(2) For reviews concerning problems interpreting X-ray diffraction data, see: (a) Ibers, J. A. *Critical Evaluation of Chemical and Physical Structural Information*; Lide, D. R., Paul, M. A., Eds.; National Academy of Sciences: Washington, DC, 1974; pp 186–198. (b) Donohue, J. *Critical Evaluation of Chemical and Physical Structural Information*; Lide, D. R., Paul, M. A., Eds.; National Academy of Sciences: Washington, DC, 1974; pp 199–218. (c) Jones, P. G. *Chem. Soc. Rev.* **1984**, *13*, 157–172. (d) Parkin, G. *Chem. Rev.* **1993**, *93*, 887–911. (e) Watkin, D. *Acta Crystallogr.* **1994**, *A50*, 411–437. (f) Harlow, R. L. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 327–339.

(3) For some leading references, see: (a) Marsh, R. E. *Acta Crystallogr.* **1995**, *B51*, 897–907. (b) Marsh, R. E. *Acta Crystallogr.* **1994**, *A50*, 450–455. (c) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1988**, *B44*, 77–78. (d) Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280–287. (e) Marsh, R. E.; Schomaker, V. *Inorg. Chem.* **1979**, *18*, 2331–2336. (f) Baur, W. H.; Tillmanns, E. *Acta Crystallogr.* **1986**, *B42*, 95–111.

(4) As a recent example, nickel(III) 1,4,7-triazacyclononane-*N,N',N'*-triacetate<sup>a</sup> has been shown to be the cobalt(III) derivative.<sup>b</sup> (a) van der Merwe, M. J.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489–3490. (b) Boeyens, J. C. A.; van der Merwe, M. J. *Inorg. Chem.* **1997**, *36*, 3779–3780.

(5) Problems in atom identity are not always restricted to pairs of atoms with similar atomic number and atoms that are quite disparate have been confused. For example, (i) the rather unusual four-coordinate colorless molybdenum complex  $Mo(PMe_3)_2Cl_2$ <sup>a</sup> has been subsequently determined to be, in fact, the zinc complex  $Zn(PMe_3)_2Cl_2$ <sup>b</sup> and (ii) the structures of both of the monocoordinate copper and silver aryl complexes,  $(2,4,6-Ph_3C_6H_2)Cu$  and  $(2,4,6-Ph_3C_6H_2)Ag$ <sup>c</sup> have been suggested to be that of partly, or entirely, the bromide compound  $(2,4,6-Ph_3C_6H_2)Br$ <sup>d</sup>. (a) Fromm, K.; Plaikner, M.; Hey-Hawkins, E. *Z. Naturforsch.* **1995**, *50B*, 894–898. (b) Cotton, F. A.; Schmid, G. *Polyhedron* **1996**, *15*, 4053–4059. (c) Lingnau, R.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 436. (d) Haaland, A.; Rypdal, K.; Verne, H. P.; Scherer, W.; Thiel, W. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2443–2445.

(6) (a) Marsh, R. E. *Acta Crystallogr.* **1990**, *C6*, 2497–2499. (b) Marsh, R. E. *Acta Crystallogr.* **1986**, *C42*, 1327–1328.

(7) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455–460.

describe some deceptive examples in which crystallographic models refine into false minima, the results of which are the generation of molecular structures that are characterized by well-behaved refinement and displacement parameters, but are grossly distorted from their true structures. Specifically, the ability to refine the crystallographic models described herein into false minima is a consequence of the presence of a heavy atom in a polar space group.

## Results and Discussion

Transition metal polyhydride complexes are an important class of molecules which have attracted considerable attention for a variety of reasons.<sup>10</sup> For example, their structure and bonding (e.g., dihydrogen complexes), reactivity (e.g., participation in many catalytic hydrogenation reactions), and spectroscopic properties (e.g., fluxionality on the NMR time scale) are some of the many issues that have been widely studied. One of our recent interests in this class of molecules has been concerned with obtaining details of the thermodynamics and kinetics of oxidative addition of H<sub>2</sub> to a transition metal center. In particular, we recently demonstrated that the oxidative addition of dihydrogen to 6-coordinate W(PMe<sub>3</sub>)<sub>4</sub>I<sub>2</sub> is characterized by an *inverse* equilibrium deuterium isotope effect.<sup>11,12</sup> As part of the course of these studies, we had reason to determine the structures of the entire series of 8-coordinate halide complexes W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> (X = F, Cl, Br, I), the results of which are described here.

(8) Disorder may influence X-ray structure determinations in rather dramatic ways. For example, (i) the structure of the unusual technetium oxo polymer [Cp\*<sub>2</sub>Tc(μ-O)<sub>3</sub>Tc]<sub>n</sub><sup>a</sup> has been reinterpreted as that of the monomeric rhenium complex, Cp\*Re(O)<sub>3</sub>, with the original misassignment having been due to a combination of disorder and twinning;<sup>b</sup> (ii) dinitrogen molecules of crystallization<sup>c,d</sup> have been reinterpreted as disordered dichloromethane solvent;<sup>e</sup> and (iii) a complex proposed to represent an intermediate species along the path of 1,2-trans-elimination of Cl<sub>2</sub> from a R<sub>2</sub>CCl-CCl<sub>3</sub> moiety,<sup>f</sup> is actually an artifact due to disorder.<sup>g</sup> (a) Kanellakopoulos, B.; Nuber, B.; Raptis, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1055. (b) Burrell, A. K.; Cotton, F. A.; Daniels, L. M.; Petricek, V. *Inorg. Chem.* **1995**, *34*, 4253–4255. (c) Balch, A. L.; Olmstead, M. M.; Safari, N. *Inorg. Chem.* **1993**, *32*, 291–296. (d) Wood, F. E.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 6332–6334. (e) Marsh, R. E.; Olmstead, M. M.; Schaefer, W. P.; Schomaker, V. *Inorg. Chem.* **1993**, *32*, 4658–4659. (f) Irving, A.; Irving, H. M. N. H. J. *Crystallogr. Spectrosc. Res.* **1988**, *18*, 439–446. (g) Kapon, M.; Herstein, F. H. *Acta Crystallogr.* **1995**, *B51*, 108–113.

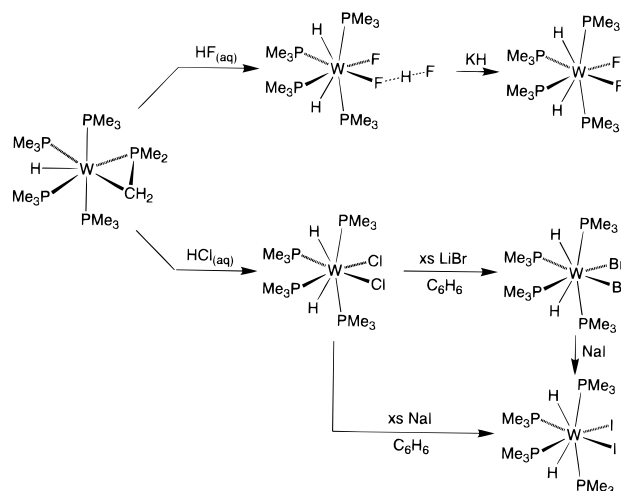
(9) The phrase “false minimum” is used in this paper to refer specifically to a refinement which yields the incorrect location of correctly assigned atoms in the correct space group. Thus, refinements which involve, for example, incorrect atom assignments or incorrect space groups are not false minima of the type discussed in this paper.

(10) (a) *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH Publishers: New York 1991. (b) *Transition Metal Hydrides*; Muettterties, E. L., Ed.; Marcel Dekker: New York, 1971. (c) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1–82. (d) Crabtree, R. H. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; 1994; Vol. 3, pp 1392–1400. (e) Also see the special volume: *Inorg. Chim. Acta* **1997**, 259, Nos 1 and 2.

(11) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 353–354.

(12) For other studies concerned with equilibrium deuterium isotope effects for oxidative addition of H<sub>2</sub> and related studies, see: (a) Abu-Hasanayn, F.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **1993**, *115*, 8019–8023. (b) Abu-Hasanayn, F.; Goldman, A. S.; Krogh-Jespersen, K. *Inorg. Chem.* **1994**, *22*, 5122–5130. (c) Wang, K.; Rosini, G. P.; Nolan, S. P.; Goldman, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 5082–5088. (d) Musaev, D. G.; Morokuma, K. *J. Organomet. Chem.* **1995**, *504*, 93–105. (e) Bakhtmutov, V. I.; Bertrán, J.; Esteruelas, M. A.; Lledós, A.; Maseras, F.; Modrego, J.; Oro, L. A.; Sola, E. *Chem. Eur. J.* **1996**, *2*, 815–825. (f) Hauger, B. E.; Gusev, D.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 208–214. (g) Gusev, D. G.; Bakhtmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115–120. (h) Hostetler, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7629–7636. (i) Lee, D. W.; Jensen, C. M. *Inorg. Chim. Acta* **1997**, *259*, 359–362. (j) Bender, B. R.; Kubas, G. J.; Jones, L. H.; Swanson, B. I.; Eckert, J.; Capps, K. B.; Hoff, C. D. *J. Am. Chem. Soc.* **1997**, *119*, 9179–9190.

## Scheme 1



**Syntheses of W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> (X = F, Cl, Br, I).** Although 8-coordinate hydride complexes of the composition W(PR<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> have been known since the early 1980s, only the fluoro and chloro derivatives have been previously reported. Specifically, the fluoro complex W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F<sub>2</sub> was synthesized by Green via reaction of W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H with HF(aq) followed by treatment with KH,<sup>13</sup> while the chloro analogue W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> was prepared by a variety of methods including (i) oxidative addition of H<sub>2</sub> to W(PMe<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>,<sup>14–17</sup> (ii) Na(Hg) reduction of W(PMe<sub>3</sub>)<sub>3</sub>Cl<sub>4</sub> in THF in the presence of excess PMe<sub>3</sub> under an atmosphere of H<sub>2</sub>,<sup>18</sup> and (iii) reaction of W(PMe<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> with methanol, in which case it was obtained as a mixture with W(PMe<sub>3</sub>)<sub>3</sub>(O)Cl<sub>2</sub>.<sup>18–20</sup> As an extension of Green's method,<sup>13</sup> we have found that W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> may also be prepared in high yield (ca. 80%) by the direct reaction of W(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H with aqueous hydrochloric acid (Scheme 1).<sup>21</sup> Importantly, W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> is a valuable synthetic precursor to the bromo and iodo analogues, W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Br<sub>2</sub> and W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>I<sub>2</sub>, via metathesis with excess LiBr or NaI, respectively.<sup>22</sup> W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>I<sub>2</sub> may also be obtained by treating

(13) (a) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1400–1402. (b) Green, M. L. H.; Parkin, G.; Chen, M.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1986**, 2227–2236.

(14) Sharp, P. R.; Frank, K. G. *Inorg. Chem.* **1985**, *24*, 1808–1813.

(15) W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> was first described in the Ph.D. Thesis of P. R. Sharp, Massachusetts Institute of Technology, 1980. We thank Professor R. R. Schrock for bringing this information to our attention.

(16) The 8-coordinate niobium and tantalum complexes M(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>-Cl<sub>2</sub> (M = Nb, Ta) have also been synthesized by a method involving oxidative addition of H<sub>2</sub> to 6-coordinate M(PMe<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>. See: (a) Luetkens, M. L., Jr.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 4474–4475. (b) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718–1726.

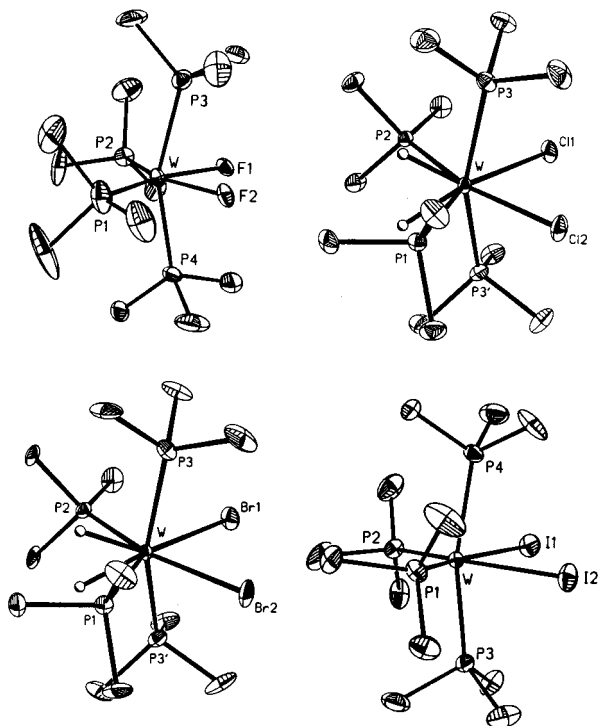
(17) W(PMe<sub>2</sub>Ph)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> may also be prepared by oxidative addition of H<sub>2</sub> to W(PMe<sub>2</sub>Ph)<sub>4</sub>Cl<sub>2</sub>.<sup>a</sup> In contrast, W(PMePh)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> is not obtained by the reaction of W(PMePh)<sub>4</sub>Cl<sub>2</sub> with H<sub>2</sub>.<sup>b</sup> (a) Rothfuss, H.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 2946–2953. (b) Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 8485–8491.

(18) Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803–810.

(19) For a further discussion of the reactions of W(PMe<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> and W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> with alcohols, see ref 17b.

(20) The formation of the dimethylphenylphosphine analogue W(PMe<sub>2</sub>-Ph)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> was observed as a side-product in the synthesis of the dinitrogen complex W(PMe<sub>2</sub>Ph)<sub>4</sub>(N<sub>2</sub>)<sub>2</sub>, by reduction of W(PMe<sub>2</sub>Ph)<sub>3</sub>Cl<sub>4</sub> with Mg under N<sub>2</sub> in the presence of PMe<sub>2</sub>Ph. See: Fakley, M. E.; Richards, R. L. *Transition Met. Chem.* **1982**, *7*, 1–2.

(21) Furthermore, the iron complexes Fe(PMe<sub>3</sub>)<sub>4</sub>(H)X (X = Cl, Br) have been obtained in an analogous fashion via the reaction of Fe(PMe<sub>3</sub>)<sub>3</sub>(η<sup>2</sup>-CH<sub>2</sub>PMe<sub>2</sub>)H with HX. See: Karsch, H. H. *Chem. Ber.* **1977**, *110*, 2222–2235.



**Figure 1.** Molecular structures of  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ).

$W(PMe_3)_4H_2Br_2$  with an excess of NaI.<sup>23,24</sup> However, since  $W(PMe_3)_4H_2I_2$  slowly loses dihydrogen to give *trans*- $W(PMe_3)_4I_2$ ,<sup>11</sup> its preparation is best performed under an atmosphere of  $H_2$ .

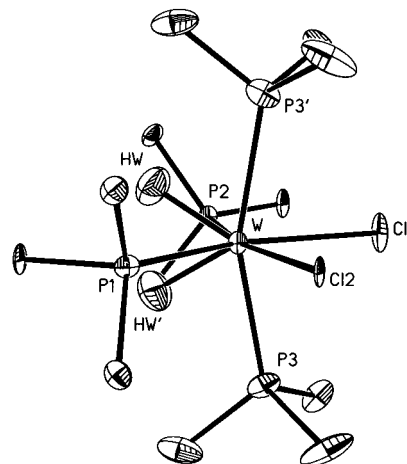
**Molecular Structures of  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ).** The molecular structures of  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ) have been determined by single crystal X-ray diffraction, as illustrated in Figure 1. The chloro derivative has also been studied by single crystal neutron diffraction (Figure 2), which accurately located the positions of the hydride ligands. As is evident from Figures 1 and 2, the molecular structures of  $W(PMe_3)_4H_2X_2$  are all similar, and are based on a trigonal dodecahedron,<sup>25</sup> with a distorted tetrahedral array of  $PMe_3$  ligands. Alternatively, the structures of  $W(PMe_3)_4H_2X_2$  may be considered to be derived from a distorted octahedral [ $W(PMe_3)_4X_2$ ] fragment, with the two *trans*- $PMe_3$  ligands displaced toward the *cis*- $X$  ligands and the hydride ligands capping the two triangular  $P_3$  faces. As such, the geometries of  $W(PMe_3)_4H_2X_2$  are similar to related complexes, e.g.,

(22) In contrast, it is noteworthy that NaI and KI have been reported to be incapable of converting  $W(PMe_2Ph)_4H_2Cl_2$  to  $W(PMe_2Ph)_4H_2I_2$ ; LiI, however, can achieve this transformation. See: Rothfuss, H.; Gusev, D. G.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 2894–2901.

(23) KBr and KI may also be used as reagents to prepare  $W(PMe_3)_4H_2X_2$  ( $X = Br, I$ ). However, attempts to synthesize  $W(PMe_3)_4H_2F_2$  by metathesis of  $W(PMe_3)_4H_2Cl_2$  with either LiF or AgF were unsuccessful.

(24) In addition to  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ), the mixed-halide complex  $W(PMe_3)_4H_2(Cl)(I)$  was observed (by  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectroscopy) to form rapidly upon mixing approximately equimolar solutions of  $W(PMe_3)_4H_2Cl_2$  and  $W(PMe_3)_4H_2I_2$ , the equilibrium mixture having the expected statistical distribution of species in the ratio 2:1:1, respectively.  $^{31}P\{^1H\}$  NMR spectroscopic data for  $W(PMe_3)_4H_2(Cl)I$  ( $C_6D_6$ ):  $\delta$  -22.2 [d,  $^2J_{P-P} = 62$ ; t,  $^2J_{P-P} = 17$ ,  $^1J_{W-P} = 185$ ; 1  $PMe_3$ ], -27.8 [t,  $^2J_{P-P} = 17$ ;  $^1J_{W-P} = 183$ ; 2  $PMe_3$ ], -36.0 [d,  $^2J_{P-P} = 62$ ; t,  $^2J_{P-P} = 17$ ;  $^1J_{W-P} = 155$ ; 1  $PMe_3$ ].

(25) For reviews on eight-coordination, see for example: (a) Lippard, S. J. *Prog. Inorg. Chem.* **1967**, *8*, 109–193. (b) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179–275. (c) Burdett, J. K.; Hoffmann, R.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2553–2568. (d) Keppert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 1, Chapter 2, pp 31–107.



**Figure 2.** Neutron diffraction structure of  $W(PMe_3)_4H_2Cl_2$ .

$Mo(PMe_2Ph)_4H_2Cl_2$ ,<sup>26</sup>  $W(PMe_2Ph)_4H_2Cl_2$ ,<sup>27</sup>  $[W(PMe_3)_4H_2Cl_2][BF_4] \cdot Cp_2Fe$ ,<sup>14</sup> and  $Ta(PMe_3)_4H_2Cl_2$ .<sup>16,28</sup>  $^1H$  and  $^{31}P$  NMR spectroscopic studies on the series of complexes  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ), as summarized in Table 1, are consistent with the solid-state structures also being maintained in solution. For example, with the exception of the fluoro complex which shows additional  $J_{F-H}$  coupling, the hydride signals of each of the complexes have the appearance of a doublet of doublet of triplets due to phosphorus coupling.<sup>29</sup> The structures are, therefore, as first noted by Sharp for the chloro derivative  $W(PMe_3)_4H_2Cl_2$ ,<sup>14</sup> static on the NMR time scale at room temperature. Caulton has noted that the analogue  $W(PMe_2Ph)_4H_2Cl_2$  is also stereochemically rigid on the NMR time scale at room temperature.<sup>17a</sup> More impressively, Caulton has also reported that the trihydride  $W(PMe_2Ph)_4H_3Cl$  is stereochemically rigid on the time scale of 1 day, as judged by the rate of isomerization of selectively deuterated  $W(PMe_2Ph)_4H_2DCl$ .<sup>17a</sup> Thus, the NMR spectroscopic properties of the halide derivatives  $W(PR_3)_4H_2X_2$  and  $W(PMe_2Ph)_4H_3Cl$  differ considerably from those of the fluxional tetrahydride complexes  $W(PR_3)_4H_4$ .<sup>30,31</sup> Selected bond lengths and angles for  $W(PMe_3)_4H_2X_2$  ( $X = F, Cl, Br, I$ ) are summarized in Table 2; as expected, the bond lengths obtained by the X-ray and neutron diffraction studies on  $W(PMe_3)_4H_2Cl_2$  are comparable. The principal variation in the structures upon progressing from the fluoro to iodo derivatives involves an expansion in (i) the  $X-W-X$  bond angles [increasing from  $76.3(3)^\circ$  to  $81.4(1)^\circ$ ] and (ii) the *trans*  $P-W-P$  angles [increasing from  $157.5(2)^\circ$  to  $166.2(1)^\circ$ ]. Such changes are consistent with those expected on the basis of the increase in size of the halide ligands from F to I.

The derived  $W-X$  bond lengths are similar to, but slightly longer than, the respective mean values for structurally characterized tungsten halide complexes listed in the Cambridge

(26) Lenenko, V. S.; Yanovskii, A. I.; Struchkov, Yu. T.; Shur, V. B.; Vol'pin, M. E. *Sov. J. Coord. Chem.* **1986**, *12*, 367–373.

(27) Dadkhah, H.; Kashaf, N.; Richards, R. L.; Hughes, D. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1983**, *255*, C1–C4.

(28) The crystal structure of  $Ta(PMe_3)_4H_2Cl_2$  was originally described (ref 16) in space group  $Cc$ , but it was later refined in the centrosymmetric space group  $C2/c$ . See: Marsh, R. E.; Slagle, K. M. *Inorg. Chem.* **1985**, *24*, 2114–2115.

(29) As has been noted by Caulton for  $W(PMe_2Ph)_4H_2Cl_2$ , the first-order appearance of a doublet of doublet of triplets pattern for the  $WH_2$  group is a deceptively simple pattern for a  $A_2MM'XX'$  spin system. See ref 17a.

(30) (a) Meakin, P.; Guggenberger, L. J.; Peet, W. G.; Muettteries, E. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 1467–1474. (b) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Abdul-Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1204–1211.

(31) For other accounts of fluxionality in eight-coordinate complexes, see ref 25b and: Muettteries, E. L. *Acc. Chem. Res.* **1970**, *3*, 266–273.

**Table 1.**  $^1\text{H}$  NMR Spectroscopic Data for the Hydride Signals of  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) in  $\text{C}_6\text{D}_6$ 

$\text{W}(\text{PMe}_3)_4\text{H}_2\text{F}_2^a$		$\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2^a$		$\text{W}(\text{PMe}_3)_4\text{H}_2\text{Br}_2$		$\text{W}(\text{PMe}_3)_4\text{H}_2\text{I}_2$	
$\delta$ (ppm)	m, J (Hz)	$\delta$ (ppm)	m, J (Hz)	$\delta$ (ppm)	m, J (Hz)	$\delta$ (ppm)	m, J (Hz)
-1.50	d, $^2J_{\text{P-H}} = 35$ d, $^2J_{\text{P-H}} = 37$ t, $^2J_{\text{P-H}} = 55$ t, $^2J_{\text{F-H}} = 8$	-3.44	d, $^2J_{\text{P-H}} = 37$ d, $^2J_{\text{P-H}} = 43$ t, $^2J_{\text{P-H}} = 61$	-4.57	d, $^2J_{\text{P-H}} = 38$ d, $^2J_{\text{P-H}} = 44$ t, $^2J_{\text{P-H}} = 61$	-6.20	d, $^2J_{\text{P-H}} = 38$ d, $^2J_{\text{P-H}} = 47$ t, $^2J_{\text{P-H}} = 62$

<sup>a</sup> Data for  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{F}_2$  and  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  reported here are within experimental error of the literature values.

**Table 2.** Selected bond lengths (Å) and angles (deg) for  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ )

	$\text{W}(\text{PMe}_3)_4\text{H}_2\text{F}_2$	$\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$			$\text{W}(\text{PMe}_3)_4\text{H}_2\text{Br}_2$	$\text{W}(\text{PMe}_3)_4\text{H}_2\text{I}_2$
		X-ray	neutron	X-ray false min.		
W-X(1)	2.083(7)	2.517(3)	2.518(10)	2.485(7)	2.672(3)	2.903(1)
W-X(2)	2.061(9)	2.557(3)	2.570(10)	2.548(6)	2.718(3)	2.922(1)
W-P(1)	2.449(5)	2.443(3)	2.468(12)	2.464(7)	2.445(7)	2.455(2)
W-P(2)	2.421(5)	2.456(2)	2.459(11)	2.467(5)	2.458(5)	2.454(3)
W-P(3)	2.483(6)	2.507(2)	2.504(6)	2.495(5)	2.515(4)	2.538(3)
W-P(4)	2.458(6)	2.507(2) <sup>a</sup>	2.504(6) <sup>a</sup>	2.495(5) <sup>a</sup>	2.515(4) <sup>a</sup>	2.536(3)
W-H		1.65(9)	1.709(12)			
H-W-H		67(6)	63.5(8)			
X(1)-W-X(2)	76.3(3)	78.5(1)	78.2(2)	79.4(3)	78.4(1)	81.4(1)
P(3,4)-W-X(1,2) <sub>av</sub>	81[2]	83[3]	83[3]	97[2]	83[3]	85[2]
P(1,2)-W-P(3,4) <sub>av</sub>	95[2]	96[1]	94[3]	86[2]	95[4]	93[2]
P(1)-W-P(2)	128.3(2)	122.3(1)	123.5(4)	120.9(3)	121.2(3)	120.1(1)
P(3)-W-P(4)	157.5(2)	160.1(1)	160.4(5)	162.0(3)	160.8(3)	166.2(1)

<sup>a</sup> P(4) is P(3'), the symmetry equivalent of P(3).

**Table 3.** W-X Bond Length Data

$\text{W}(\text{PMe}_3)_4\text{H}_2\text{X}_2$	$d(\text{W-X})_{\text{av}}/\text{Å}$	$d(\text{W-X})$		$r_{\text{cov}}(\text{X})/\text{Å}^c$	$[d(\text{W-X})_{\text{av}} - r_{\text{cov}}(\text{X})]/\text{Å}$
		CSD mean/ $\text{Å}^a$	CSD range/ $\text{Å}^b$		
W-F	2.072	1.922(119)	1.657-2.319 (273)	0.60	1.47
W-Cl	2.537	2.415(80)	2.221-2.861 (1702)	0.99	1.55
W-Br	2.696	2.600(60)	2.428-2.756 (256)	1.14	1.56
W-I	2.913	2.820(49)	2.665-3.004 (289)	1.33	1.58

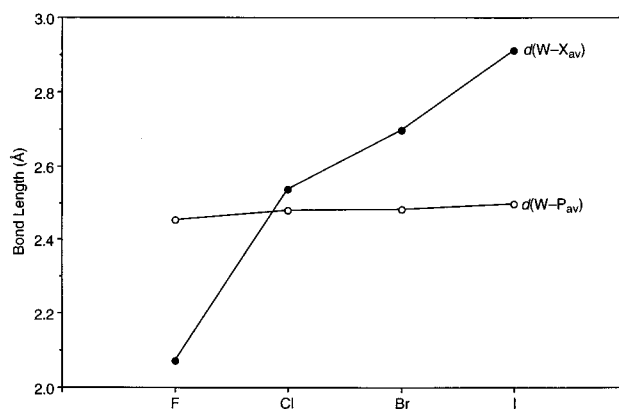
<sup>a</sup> The value in parentheses is the sample standard deviation. <sup>b</sup> The value in parentheses is the number of observations. <sup>c</sup> All data taken from Pauling (Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 224) with the exception for F which is taken from Robinson et al. (Robinson, E. A.; Johnson, S. A.; Tang, T.-H.; Gillespie, R. J. *Inorg. Chem.* **1997**, *36*, 3022-3030).

Structural Database (Table 3).<sup>32</sup> Presumably, the observation that the W-X bond lengths are consistently longer than the CSD mean is a reflection of the fact that the tungsten centers in these complexes are 18-electron and electronically saturated, so that the W-X bonds are not foreshortened by lone pair  $\pi$ -donation from X to W. In this regard, the ability of halogen lone pair  $\pi$ -donation to shorten a W-X bond length is clearly illustrated by the fact that the W-I bond lengths in  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{I}_2$  [2.903(1) and 2.922(1) Å] are considerably longer than the respective value in its six-coordinate counterpart,  $\text{W}(\text{PMe}_3)_4\text{I}_2$  [2.782(1) Å],<sup>11</sup> in which the tungsten center is electronically unsaturated in the absence of lone pair  $\pi$ -donation from I to W.<sup>33</sup> Furthermore, the W-Cl bond lengths in  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  [2.517(3) and 2.557(3) Å] are also longer than the corresponding values in 17-electron cationic  $[\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2]^+$  [2.436(6) and 2.439(6) Å].<sup>14</sup>

Since the W-X bond lengths in  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{X}_2$  are not foreshortened by dative  $\pi$ -donation from X to W, the complexes

(32) CSD Version 5.13: 3D Search and Research Using the Cambridge Structural Database, Allen, F. H.; Kennard, O. In *Chem. Design Automation News* **1993**, *8* (1), 1, 31-37.

(33) As a further illustration of the ability of dative  $\pi$ -donation to shorten a metal-halide bond length, the Ti-Cl bond length in  $\text{TiCl}_4$  [2.170(2) Å]<sup>a</sup> is almost 0.2 Å shorter than that in either  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  [2.364(3) Å]<sup>b</sup> or  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OEt})$  [2.405(1) Å].<sup>c</sup> (a) Marino, Y.; Uehara, H. *J. Chem. Phys.* **1966**, *45*, 4543-4550. (b) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622-1629. (c) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009-3014.



**Figure 3.** Variation of W-X and W-P bond lengths in  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ).

would appear to furnish a useful series of data to demonstrate how the formally single bond lengths vary as a function of the halogen. For this reason, the variation of W-X bond lengths is illustrated graphically in Figure 3, and there is a good correlation with the covalent radii of the halogens.<sup>34</sup> For further comparison, the average W-P dative covalent bond lengths are essentially invariant across the series (see Figure

(34) It is worth noting that the value to be adopted for the covalent radius of fluorine has been a subject of much debate, due to the fact that all bonds to fluorine have considerable ionic character. See: Robinson, E. A.; Johnson, S. A.; Tang, T.-H.; Gillespie, R. J. *Inorg. Chem.* **1997**, *36*, 3022-3030.

**Table 4.** W–H and W–CH<sub>3</sub> Bond Length Data

	$d(\text{W}-\text{Y})_{\text{av}}/\text{\AA}^a$	$r_{\text{cov}}(\text{Y})/\text{\AA}^b$	$r_{\text{cov}}(\text{W})/\text{\AA}$
W–H	1.743[21] <sup>c</sup>	0.30	1.44
W–CH <sub>3</sub>	2.216[61]	0.77	1.45

<sup>a</sup> Mean W–Y (Y = H, CH<sub>3</sub>) bond lengths taken from the Cambridge Structural Database (Version 5.13). The value in brackets is the sample standard deviation. <sup>b</sup> Data taken from: Pauling L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; pp 224 and 227. <sup>c</sup> The mean W–H bond length is that of compounds determined by neutron diffraction. For comparison, the mean W–H bond lengths, including those compounds determined by X-ray diffraction, is 1.716[16] Å.

3).<sup>35,36</sup> In addition to establishing the variation of W–X bond length shown in Figure 3, it is also of interest to correlate the W–X bond lengths with the values predicted by the sum of covalent radii. Unfortunately, however, the covalent radius of tungsten is poorly defined, with values spanning the range 1.30–1.46 Å having been reported in the literature.<sup>37</sup> For this reason, we have independently evaluated the covalent radius of tungsten by consideration of the distribution of other W–Y bond lengths listed in the CSD. Specifically, we have focused attention on ligands that are incapable of  $\pi$ -donation and have well established covalent radii, namely hydride and methyl, so that the observed W–Y bond lengths should correspond closely to those of normal covalent bonds. By using the approximation  $r_{\text{cov}}(\text{W}) = d(\text{W}-\text{Y}) - r_{\text{cov}}(\text{Y})$ , the covalent radius of tungsten is estimated to be ca. 1.45 Å (see Table 4), although it should be recognized that this value represents a lower limit since these bond lengths may be potentially shortened by polar contributions to the bonding.<sup>38</sup> Such corrections are, however, likely to be small, and of the order 0.02–0.05 Å for W–H and W–CH<sub>3</sub> groups.<sup>38</sup> Thus, a value of 1.45 Å for the covalent radius of tungsten should provide a useful value for estimating W–X bond lengths in the absence of  $\pi$ -donation and polar effects; for example, the W–H bond length in W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> [1.71-(1) Å], as determined by neutron diffraction, is comparable to that predicted by the sum of the covalent radii [1.75 Å].<sup>39</sup> In contrast, however, the observed W–X (X = F, Cl, Br, I) bond lengths are *longer* (in the range 0.02–0.13 Å) than predicted

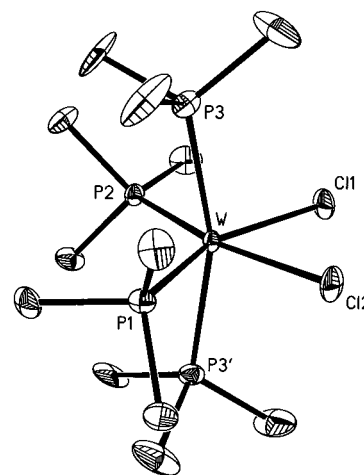
(35) Furthermore, the W–P bond length in W(PMe<sub>3</sub>)<sub>4</sub>I<sub>2</sub> [2.493(2) Å] (ref 11) is similar to the average value in W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>I<sub>2</sub> [2.496 Å].

(36) Since it is well-established that dative bonding is markedly influenced by charge effects, the observation that the average W–P bond lengths do not vary substantially across the series W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> (X = F, Cl, Br, I) suggests that the formal charges on the tungsten centers do not vary significantly. See: Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992–1007.

(37) Values of the covalent radius of tungsten that have been cited in the literature include the following: 1.30 Å,<sup>a,b,c</sup> 1.34 Å,<sup>d</sup> 1.37 Å,<sup>e,f</sup> 1.46 Å.<sup>g</sup> (a) Dean, J. A. *Lange's Handbook of Chemistry*, 13th ed.; New York, 1985; pp 3–126. (b) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford. (c) Moeller, T. *Inorganic Chemistry: An Advanced Textbook*; Wiley: New York; p 135. (d) Batsanov, S. S. *Russ. Chem. Bull.* **1995**, *44*, 2245–2251. (e) Moeller, T. *Inorganic Chemistry: A Modern Introduction*; Wiley: New York; p 71. (f) *Cambridge Structural Database System: Getting Started*; 1994; Appendix E. (g) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*, 2nd ed.; Academic Press: New York; Table 4.4.

(38) Polar contributions to a covalent bond result in bond lengths that are *shorter* than the sum of covalent radii. For example, the empirical Schomaker–Stevenson equation,  $d(\text{A}-\text{B}) = r(\text{A}) + r(\text{B}) - c|\chi(\text{A}) - \chi(\text{B})|$ ,<sup>4</sup> has been used to relate the shortening of a covalent A–B bond, with respect to the sum of covalent radii, to the difference in electronegativity of A and B. It should also be noted that the latter equation has been both modified and criticized by Pauling<sup>b,c,d</sup> (a) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37–40. (b) Pauling L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960. (c) Wells, A. F. *J. Chem. Soc.* **1949**, 55–67. (d) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: London, 1984; pp 287–291.

(39) It should be noted that Bau has also reported a value of 1.743(6) Å for the average terminal W–H bond length. See: Bau, R.; Drabnis, M. H. *Inorg. Chim. Acta* **1997**, *259*, 27–50.

**Figure 4.** Structure corresponding to a false minimum for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub>.

by the sum of covalent radii. One factor which may rationalize this lengthening of the W–X bonds is associated with the fact that the tungsten centers in W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> are 18-electron and electronically saturated. As such, filled–filled repulsions<sup>40</sup> between the halogen lone pairs and the electrons on the  $d^2$  tungsten center may serve to lengthen the W–X bonds.<sup>41</sup> By way of contrast, the W–H bond will obviously not be subject to such an effect (since H does not have any lone pair electrons), with the result that the observed W–H bond length is not longer than the sum of the modified covalent radii.

It is also worth commenting further upon the discrepancy between the most commonly cited literature value of 1.30 Å for the covalent radius of tungsten and the value suggested here, namely 1.45 Å. To understand the origin of this disagreement, it is necessary to discern the original source for the 1.30 Å value. Unfortunately, despite the fact that the covalent radius of tungsten is listed as 1.30 Å in several articles, this value is cited without attribution. The similarity, however, to Pauling's single bond *metallic radius*, namely 1.304 Å,<sup>42</sup> suggests that this may have been the apparent incorrect source of the cited value of 1.30 Å for the covalent radius.

**A False Minimum in the Structure of W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub>.** Of most interest, the structure shown in Figure 1 was *not* the original structure that was determined for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub>.<sup>43</sup> Specifically, the structure that was initially obtained was one in which the two *transoid*-PMe<sub>3</sub> ligands are displaced toward the two *cis*-PMe<sub>3</sub> groups, rather than tilted toward the chloride ligands (Figure 4). With all four PMe<sub>3</sub> ligands located in one hemisphere of the molecule, such an arrangement is unusual for eight-coordinate M(PR<sub>3</sub>)<sub>4</sub>X<sub>4</sub> complexes, which otherwise typically exhibit a *pseudotetrahedral* array of PR<sub>3</sub> groups.<sup>29</sup>

Although the ligand arrangement for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> shown in Figure 4 is uncommon, it was not regarded as chemically unreasonable since a similar structure had been reported previously for a related complex, namely [W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(OH<sub>2</sub>)]-[F].<sup>13,44</sup> Furthermore, (i) the *R* values ( $R_f = 0.0459$  [ $I > 2\sigma$  (*I*)], 0.0507 [all data]), (ii) the displacement parameters (see

(40) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25–41.

(41) It is also possible that steric interactions within the eight-coordinate complexes may result in longer bond lengths.

(42) The single bond metallic radii described by Pauling refer to "single covalent bonds for which the bond orbitals have the same hybrid character as in the metals themselves". See ref 38b, p 256.

(43) Murphy, V. J.; Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1995**, *117*, 9762–9763.

(44) Minqin, C.; Prout, K. *J. Struct. Chem.* **1986**, *5*, 23–27.

Figure 4), and (iii) the bond lengths about tungsten (see Table 2) were consistent with the derived structure being correct. However, even considering the structure of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  shown in Figure 4 to be acceptable, an issue that needed to be reconciled was why it was different from those of the fluoro, bromo, and iodo complexes. After much deliberation it was determined that the structure had actually refined into an extremely deceptive false minimum. Once the nature of the problem (vide infra) had been recognized, it was possible to adjust the structure and so refine it in the true minimum (Figure 1), characterized by lower  $R$  values ( $R_1 = 0.0234$  [ $I > 2\sigma(I)$ ], 0.0282 [all data]).

The ability to refine the X-ray diffraction data for  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  into a false minimum is a result of the molecule adopting a polar space group,<sup>45</sup> namely  $Cmc2_1$  (No. 36). In this regard, it is well-known that, for any molecule which crystallizes in a polar space group, two minima exist in a least-squares refinement procedure, corresponding to chemically identical structures which are related by a reflection perpendicular to the polar axis. The structures corresponding to the two polar configurations<sup>46</sup> typically, however, differ slightly in bond lengths as a consequence of the "polar dispersion error",<sup>47,48</sup> so that it is essential to establish that the correct polarity has been determined by refining both configurations.<sup>49</sup> For  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  in  $Cmc2_1$  with a polar  $z$  axis, the two polar configurations are related by reflection perpendicular to the  $z$  axis (i.e.,  $z_{\text{atom}} \rightarrow -z_{\text{atom}}$ ). However, it is important to emphasize that the relationship between the true (Figure 1) and false (Figure 4) structures of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  is *not* a simple reflection of *all* the atoms perpendicular to the  $z$  axis. Rather, the incorrect structure of the false minimum corresponds to the very unusual situation in which only the *transoid*- $\text{PMe}_3$  ligands of the true structure are reflected perpendicular to the  $z$  axis (with W located arbitrarily at  $z = 0$ ).<sup>50</sup> The specific relationship of the misplaced  $\text{PMe}_3$  ligand<sup>51</sup> to its true location is demonstrated by a comparison of their atomic coordinates, as summarized in Table 5. Thus, whereas the  $x$  and  $y$  coordinates of the respective atoms of the true and misplaced  $\text{PMe}_3$  ligands are comparable, the  $z$  coordinates are related by an approximate reflection through

(45) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525–541.

(46) We use the term "polar configuration", as opposed to "enantiomorph", because space group  $Cmc2_1$  (No. 36) is nonenantiomorphous (it contains both mirror and glide planes).

(47) Templeton was the first to describe this phenomenon, which was originally called the "polar dispersion shift".<sup>a</sup> (a) Zalkin, A.; Hopkins, T. E.; Templeton, D. H. *Inorg. Chem.* **1966**, *5*, 1767–1770. (b) Ueki, T.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr.* **1966**, *20*, 836–841. (c) Templeton, L. K.; Templeton, D. H.; Zalkin, A.; Ruben, H. W. *Acta Crystallogr.* **1982**, *B38*, 2155–2159.

(48) For other discussions of the polar dispersion error, see: (a) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 725–730. (b) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1784–1792. (c) *Anomalous Scattering*; Ramaseshan, S., Abrahams, S. C., Eds.; International Union of Crystallography, Munksgaard International Publishers: Penhagen, 1975. (d) Cruickshank, D. W. J.; McDonald, W. S. *Acta Crystallogr.* **1967**, *23*, 9–11.

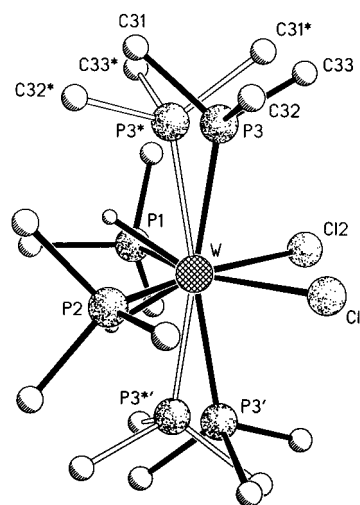
(49) Methods for determining the absolute structure involve refining either the Rogers  $\eta$  parameter<sup>a</sup> or the Flack  $x$  parameter.<sup>b–e</sup> The Flack  $x$  parameter has, however, been suggested to be the more reliable indicator of the correct absolute structure. Permissible values for  $x$  range from 0 for the correct absolute structure to 1 for the incorrect absolute structure; an intermediate value is indicative that the crystal is a racemic twin. (a) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734–741. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881. (c) Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1987**, *A43*, 75–78. (d) Bernardinelli, G.; Flack, H. D. *Acta Crystallogr.* **1985**, *A41*, 500–511. (e) Flack, H. D.; Schwarzenbach, D. *Acta Crystallogr.* **1988**, *A44*, 499–506.

(50) It should be noted that the relationship between the  $z$  coordinates of the true and false locations  $z(\text{true}) = -z(\text{false})$  is only true because W is arbitrarily situated at  $z = 0$ . More generally, the relationship would be  $z(\text{true}) = z(\text{W}) - z(\text{false})$ , if W were not to be located at  $z = 0$ .

(51) Note that only one of the *transoid*- $\text{PMe}_3$  ligands is crystallographically unique.

**Table 5.** Relationship between the Atomic Coordinates ( $\times 10^4$ ) for the True [P(3) and C(3X)] and Misplaced [P(3\*) and C(3X\*)]  $\text{PMe}_3$  ligands in  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$

atom	x	y	z
P(3)	−1819(1)	7567(1)	342(2)
P(3*)	−1815(3)	7543(2)	−310(5)
C(31)	−2672(7)	7526(7)	−763(10)
C(31*)	−2647(21)	7389(23)	856(28)
C(32)	−2284(6)	8650(6)	1064(8)
C(32*)	−2210(19)	8574(21)	−1176(24)
C(33)	−2309(7)	6575(7)	1180(9)
C(33*)	−2.302(24)	6504(17)	−1136(29)

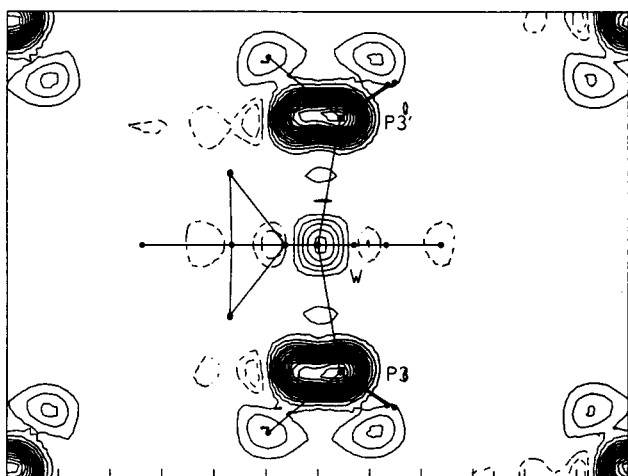


**Figure 5.** Superposition of the structures corresponding to the true (solid bonds) and false (open bonds) minima of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$ .

the origin, i.e.,  $z(\text{true}) = -z(\text{false})$ . The result of this selective transformation, as illustrated in Figure 5, is a displacement of the *transoid*- $\text{PMe}_3$  ligands by ca.  $19^\circ$  from their true locations. Since the incorrect structure is related to the true structure by a reflection perpendicular to the polar axis of only a *selection* of the atoms, we describe the effect as a result of a "partial polar ambiguity". We have introduced the latter term to emphasize the distinction with the well-known "polar dispersion error", an effect which is concerned with two structures that are related by a reflection perpendicular to the polar axis of *all* atoms.<sup>47–49</sup>

Adopting a polar space group is not the only requirement for the X-ray diffraction data for  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  to be refined into the well-behaved false minimum described above. In addition, it is the presence of a single heavy atom that allows the structure to refine so well into a false minimum. Such a situation arises because the tungsten atoms of the  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  molecules are arranged centrosymmetrically with respect to each other, even though the molecules themselves are not. *Pseudosymmetry* of this type involving heavy atoms which dominate the X-ray scattering is well-known to result in the generation of electron density maps which exhibit effective mirror symmetry perpendicular to the polar axis during the initial stages of refinement: essentially, the observed electron density difference maps correspond to a superposition of the two possible true polar configurations described above.<sup>52</sup> For example, an electron density difference map based only on the position of the tungsten atom exhibits rigorous mirror symmetry perpendicular to the polar  $z$  axis (Figure 6), corresponding to a composite of both possible true polar configurations. Upon incorporation of additional atoms in the model, the *pseudosym-*

Only W in position



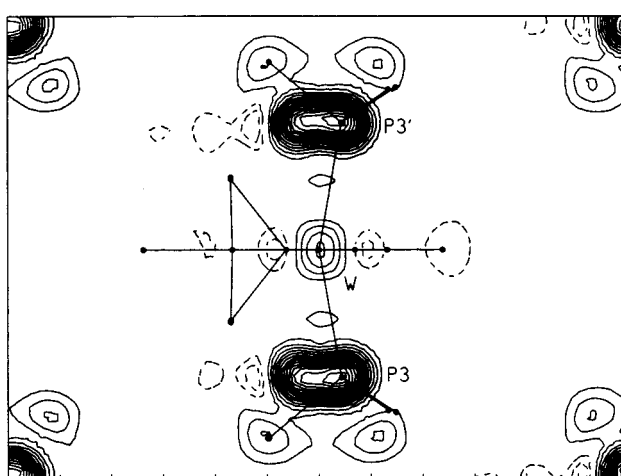
**Figure 6.** Electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower), with only W in position. Upper map contours are at  $-5, -3, -1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 \text{ e}\text{\AA}^{-3}$ ; lower map contours are at  $-1, -0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 \text{ e}\text{\AA}^{-3}$ .

metry is removed and the electron density difference map would consequently be expected to depart from mirror symmetry. However, as is evident from the electron density difference maps shown in Figures 6–12, which sequentially correspond to increasing the number of atoms in the model, effective mirror symmetry is observed at all stages of the refinement procedure. As a result, even in the final stages of refinement, it is possible to select the incorrect locations for a set of atoms, especially if such positions are not chemically unreasonable.<sup>53</sup> Perhaps even more surprising than locating atoms in incorrect positions is the fact that the subsequent model refines so well, in terms of

(52) In fact, the appearance of centrosymmetry can be so deceptive that truly noncentrosymmetric structures have been incorrectly assumed to be centrosymmetric. For example, (i)  $Cp^*TaCl_3(\eta^2-COSiMe_3)$ , originally described as a fully mirror-plane disordered centrosymmetric  $Pcam$ ,<sup>3</sup> is in fact ordered in noncentrosymmetric  $Pca2_1$ ,<sup>b</sup> while (ii)  $[TpBut]In$ , originally reported to be 2-fold disordered in  $Cmcm$ ,<sup>c</sup> is in fact ordered in noncentrosymmetric  $Cmc2_1$ .<sup>d</sup> (a) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149–164. (b) Rheingold, A. L. *Acta Crystallogr.* **1990**, *C46*, 2374–2377. (c) Dias, H. V. R.; Huai, L.; Jin, W.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1973–1974. (d) Kuchta, M. C.; Dias, H. V. R.; Bott, S. G.; Parkin, G. *Inorg. Chem.* **1996**, *35*, 943–948.

(53) Such a phenomenon is related to the concept of homometric structures, i.e., different structures with the same Patterson Map. See: *Patterson and Pattersons*; Glusker J. P., Patterson, B. K., Rossi, M., Eds.; Oxford University Press: New York, 1987.

W and P1 in position



**Figure 7.** Electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower), with W and P1 in position. Upper map contours are at  $-5, -3, -1, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 \text{ e}\text{\AA}^{-3}$ ; lower map contours are at  $-1, -0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 \text{ e}\text{\AA}^{-3}$ .

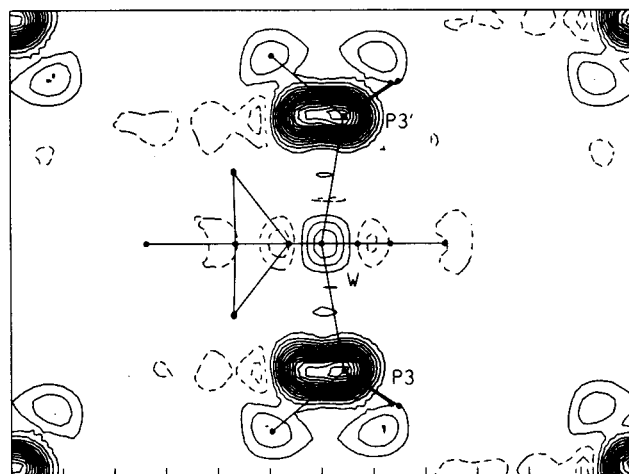
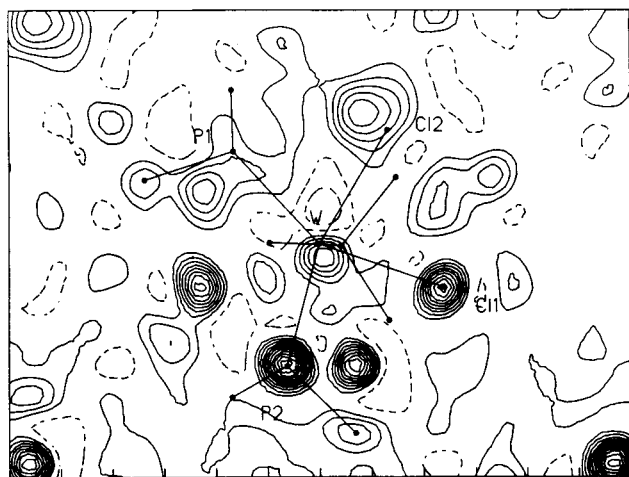
both  $R$  values and molecular parameters. For example, the bond lengths and angles associated with the *transoid*- $PMe_3$  ligands in both the correct and misplaced positions are summarized in Table 6, from which it is evident that, even though the values do differ slightly, the P–C bond lengths and C–P–C bond angles observed for the incorrect location are not anomalous and so on their own would not be a strong indication that the derived structure was incorrect. Likewise, there is nothing particularly untoward with the anisotropic displacement parameters (so-called “thermal parameters”), as judged by Figure 4, especially in view of the motion that is often seen for ligands such as  $PMe_3$ . Nevertheless, we have used PLATON<sup>54</sup> to assess in a quantitative manner the credibility of the displacement parameters of the structure corresponding to the false minimum.<sup>55</sup> Interestingly, PLATON identifies that the anisotropic displacement parameters of the carbon atoms of the misplaced  $PMe_3$  ligand are unusual, as judged by the magnitude of the ratio  $U_3/U_1$ .<sup>56,57</sup> However, it does *not* identify that the anisotropic displacement parameters of the misplaced phosphorus

(54) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(55) For a review covering quantitative aspects of the interpretation of anisotropic displacement parameters, see: Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880–895.

(56)  $U_1, U_2$ , and  $U_3$  are the three main axes components of the thermal ellipsoid.

W, P1 and Cl2 in position



**Figure 8.** Electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower), with W, P1, and Cl2 in position. Upper map contours are at  $-3, -1, 1.5, 2, 2.5, 3, 4, 5, 6, 7, 8, 9, 10, 11 \text{ e}\text{\AA}^{-3}$ ; lower map contours are at  $-1, -0.3, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 \text{ e}\text{\AA}^{-3}$ .

atom are unusual, with the ratios  $U_3/U_1$  for the three phosphorus atoms being similar.<sup>58</sup> As such, the criterion of unusual displacement parameters provides no indication that the misplaced phosphorus atom is incorrectly located. Furthermore, since it is widely recognized that anisotropic displacement parameters are influenced by a variety of factors (e.g., disorder and absorption corrections), it is not apparent that the unusual carbon anisotropic displacement parameters identified by PLATON would have necessarily been taken as evidence that the *entire*  $PMe_3$  ligand was misplaced. The validity of such a statement can be seen by noting that significantly worse anisotropic displacement parameters appear frequently in the literature.<sup>59</sup>

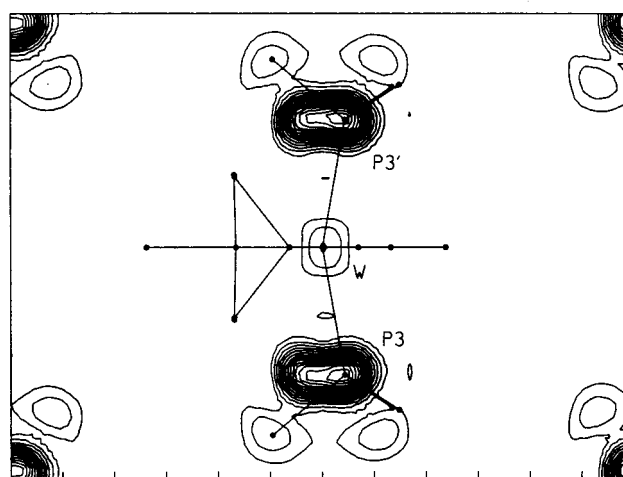
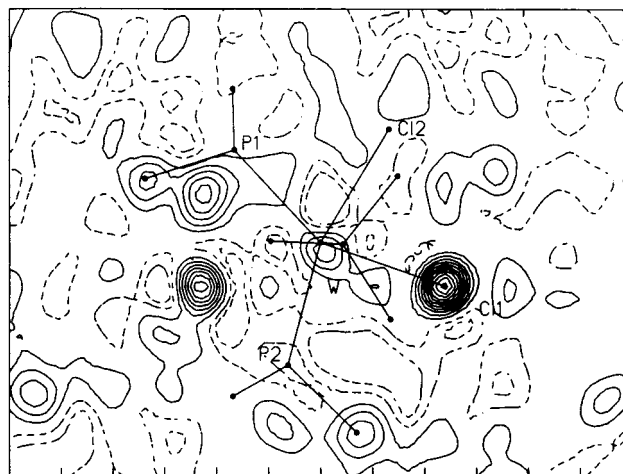
The magnitude of nonbonded intermolecular and intramolecular interactions may also be used to evaluate the validity of a structure. In this regard, PLATON has identified several nonbonded interactions in the incorrect structure that are absent

(57) Specifically, the ratios of  $U_3/U_1$  for C(31), C(32), and C(33) are 5.95, 20.84, and 6.82, respectively. For comparison, the ratios for other carbon atoms are in the range 3.05 to 4.06.

(58) The ratios of  $U_3/U_1$  for P(1), P(2), and P(3) are 1.91, 1.48, and 2.17, respectively.

(59) For example, Harlow's "ORTEP of the Year" award is an illustration of the fact that structures with unusual displacement parameters are frequently published. See ref 2f.

W, P1, P2 and Cl2 in position



**Figure 9.** Electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower), with W, P1, P2, and Cl2 in position. Upper map contours are at  $-1, -0.3, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 \text{ e}\text{\AA}^{-3}$ ; lower map contours are at  $1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 \text{ e}\text{\AA}^{-3}$ .

in the true structure.<sup>60</sup> However, since these interactions are between  $PMe_3$  hydrogen atoms in *calculated* positions, it is not clear to what extent this observation alone would have been able to indicate that the *entire*  $PMe_3$  ligand (and not just the methyl groups) was incorrectly located. Finally, with respect to other criteria for evaluating the credibility of a structure, it is important to note that the structure corresponding to the false minimum passed the Hirshfeld rigid bond test,<sup>61</sup> using PLATON at the  $2.5 \sigma$  level.<sup>62</sup>

It is important to emphasize that the principal issue is not so much one of distinguishing which of the  $W(PMe_3)_4H_2Cl_2$  structures shown in Figures 1 and 4 is correct, but rather, having arrived at the incorrect structure of Figure 4, is it obvious that it corresponds to a false minimum of the refinement procedure? It is our opinion, based on the above discussion, that it is not

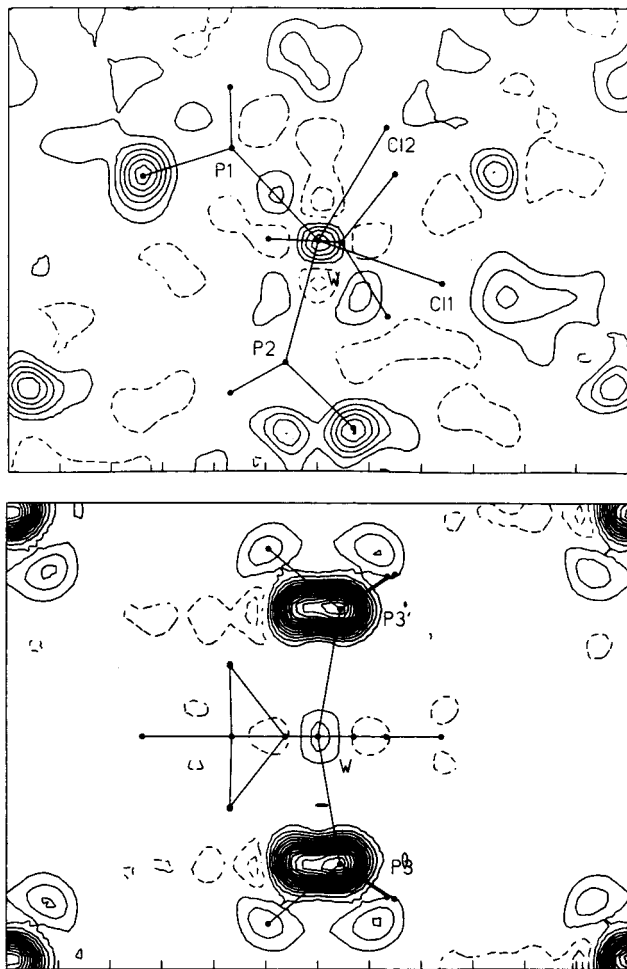
(60) The structure corresponding to the false minimum of  $W(PMe_3)_4H_2Cl_2$  is characterized by four intramolecular  $H\cdots H$  contacts more than  $0.25 \text{ \AA}$  less than the sum of the van der Waals radii (max =  $-1.28 \text{ \AA}$ ) and two intermolecular  $H\cdots H$  contacts more than  $0.25 \text{ \AA}$  less than the sum of the van der Waals radii (max =  $-0.44 \text{ \AA}$ ).

(61) Hirshfeld, F. L. *Acta Crystallogr.* **1976**, A32, 239–244.

(62) For other articles concerned with similar tests, see: (a) Rosenfield, R. E.; Trueblood, K. N.; Dunitz, J. D. *Acta Crystallogr.* **1978**, A34, 828–829. (b) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1968**, B24, 63–76.



## W, P1, P2, Cl1 and Cl2 in position

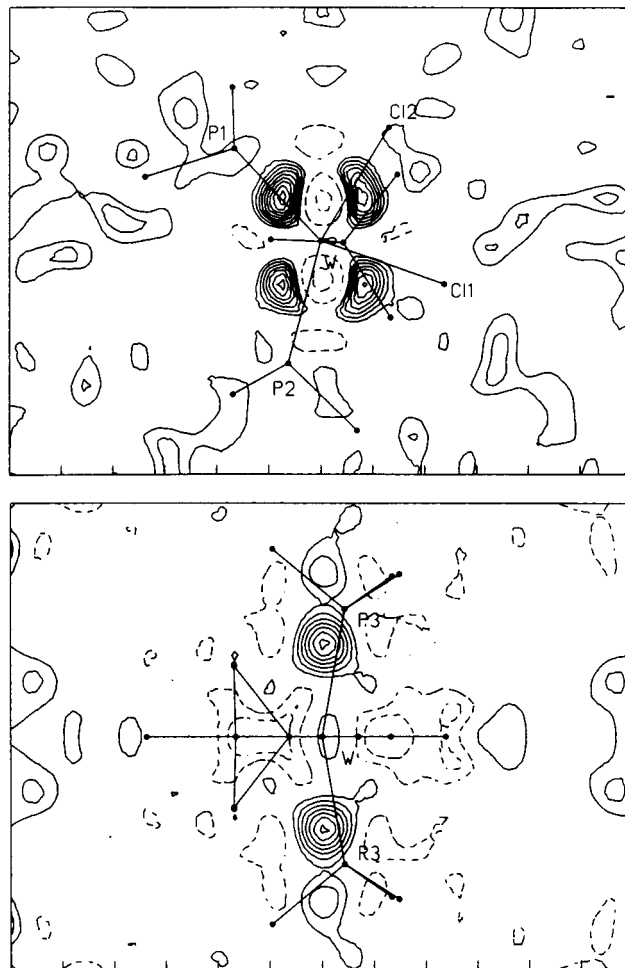


**Figure 10.** Electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower), with W, P1, P2, Cl1, and Cl2 in position. Upper map contours are at  $-1, -0.3, 0.5, 1, 1.5, 2, 2.5, 3 e\text{\AA}^{-3}$ ; lower map contours are at  $-1, -0.3, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 e\text{\AA}^{-3}$ .

obvious. It is also evident that the false minimum is quite deep, since the least-squares refinement calculations show no tendency to converge to the true minimum. Supporting this observation, Harlow has carried out a series of structure factor calculations correlating  $R$  with the position of the *transoid*- $PMe_3$  groups, as illustrated in Figure 13.<sup>2f,63</sup> Importantly, Harlow's correlation demonstrates that a least-squares refinement procedure would be incapable of converging from the false minimum to the true minimum for these complexes.

Undoubtedly, one of the reasons for the well-behaved refinement in the false minimum is a consequence of the fact that the scattering is dominated by a *single* heavy atom. It is, therefore, worth noting that problems associated with a false minimum in the structure solution of  $W(PMe_3)_4H_2Br_2$  (which also crystallizes in polar  $Cmc2_1$ ) were not as pronounced as observed for  $W(PMe_3)_4H_2Cl_2$ , presumably because, relative to chlorine, bromine provides a greater contribution to the total X-ray scattering.<sup>64</sup>

**Neutron Diffraction Refinement of  $W(PMe_3)_4H_2Cl_2$ .** Since neutron scattering factors do not vary with atomic number in the simple way that X-ray scattering factors do, neutron



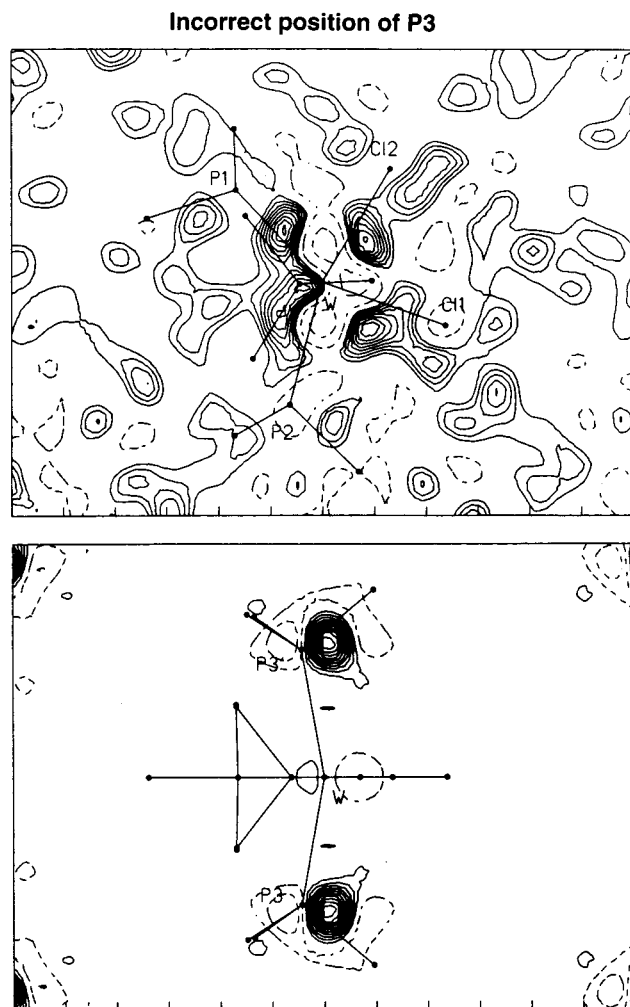
**Figure 11.** Final electron density difference maps for  $W(PMe_3)_4H_2Cl_2$  in the planes W–P1–P2–Cl1–Cl2 (upper) and W–P3–P3' (lower). Upper map contours are at  $-1, -0.3, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 e\text{\AA}^{-3}$ ; lower map contours are at  $-0.2, -0.1, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 e\text{\AA}^{-3}$ .

diffraction refinements are not subject to the problems that the presence of a single "heavy atom" presents in the refinement of X-ray diffraction data. As such, neutron diffraction offers the potential for providing a means of identifying problem structures of this type. For this reason, a neutron diffraction data set for  $W(PMe_3)_4H_2Cl_2$  was collected and, as expected, a difference Fourier map with the  $P(3)Me_3$  group removed unambiguously located the correct positions for the atoms of the missing ligand. Such behavior is in marked contrast to the corresponding difference map for the X-ray diffraction data (Figures 6–12), which shows little bias toward the true location of the missing  $PMe_3$  ligand.

Although the neutron diffraction data are capable of unambiguously determining the correct location for the atoms of the missing ligand from a difference map, it is important to note that the neutron diffraction data for  $W(PMe_3)_4H_2Cl_2$  can also be refined into a false minimum, albeit poorly. Thus, by using the non-hydrogen atoms of the structure corresponding to the false minimum as a starting point, the neutron diffraction structure maintained the incorrect conformation<sup>65</sup> upon refinement (see refinement #1 in Table 7), but the anisotropic displacement parameters were unreasonable.<sup>66</sup> Furthermore, refinement was also possible upon incorporation of all hydrogen atoms except those associated with  $P(3)$  (see refinement #2 in

(63) Borman, S. *Chem. Eng. News* **1995**, Oct 2, 27–29.

(64) False minima would not be expected to be observed for  $W(PMe_3)_4H_2F_2$  since the space group it adopts ( $P2_1/n$ ) is not polar.



**Figure 12.** Final electron density difference maps for the structure corresponding to the false minimum of  $W(PMe_3)_4H_2Cl_2$  in the planes  $W-P1-P2-C11-C12$  (upper) and  $W-P3-P3'$  (lower). Upper map contours are at  $-1.0, -0.3, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 e\text{\AA}^{-3}$ ; lower map contours are at  $-0.2, -0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 e\text{\AA}^{-3}$ .

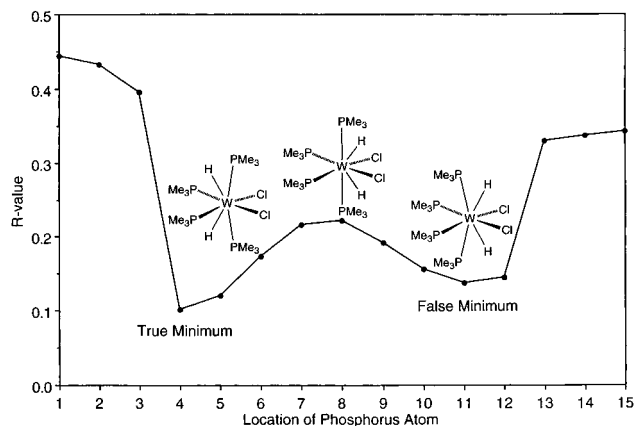
**Table 6.** Bond Lengths and Angles Associated with the True and Misplaced  $PMe_3$  Ligands in  $W(PMe_3)_4H_2Cl_2$

	true	misplaced
W-P(3)	2.507(2)	2.495(5)
P(3)-C(3)	1.81(1)	1.86(3)
P(3)-C(32)	1.825(8)	1.84(2)
P(3)-C(33)	1.823(8)	1.86(3)
C(31)-P(3)-C(32)	100.7(4)	112(2)
C(31)-P(3)-C(33)	100.9(5)	98(2)
C(32)-P(3)-C(33)	99.5(5)	97(1)
C(31)-P(3)-W	119.8(4)	118(1)
C(32)-P(3)-W	116.0(3)	112.4(8)
C(33)-P(3)-W	116.7(3)	116.0(1)

Table 7). For comparison, the refinement parameters for (i) the true structure incorporating all atoms except the hydrogen atoms associated with P(3) (refinement #3) and (ii) the true structure incorporating all atoms (refinement #4) are also listed in Table 7.

(65) For comparison, derived bond lengths for this refinement are as follows: W-P1 (2.458 Å), W-P2 (2.520 Å), W-P3 (2.480 Å), W-C11 (2.672 Å), W-C12 (2.591 Å), P1-C11 (1.786 Å), P1-C12 (1.768 Å), P2-C21 (1.637 Å), P2-C22 (1.893 Å), P3-C31 (1.779 Å), P3-C32 (1.788 Å), and P3-C33 (1.693 Å).

(66) For example, some of the isotropic thermal parameters refined to negative values and some were large.



**Figure 13.** Harlow's  $R$ -value calculations as a function of the positions of the *transoid* phosphorus atoms (the methyl groups and hydride ligands were not included in the calculation). The graph illustrates that once an incorrect position (locations 9–15) has been selected for the phosphorus atom, it refines to the false minimum (location 11), at which point it is trapped from refining to the true minimum (location 4). The figure is modified from that published in: Harlow, R. L. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 327–339.

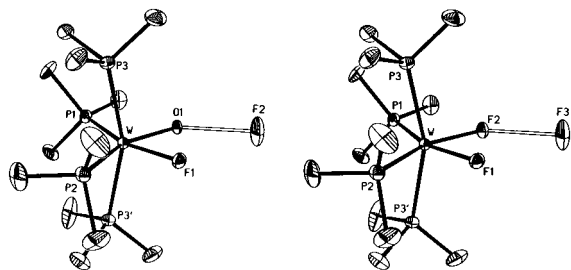
**Table 7.** Neutron Diffraction Refinement Data for Various Models

refinement <sup>a</sup>	$R^b$	$R_w^c$	GOF <sup>d</sup>
#1	0.679	0.749	10.95
#2	0.576	0.639	9.47
#3	0.384	0.473	7.01
#4	0.144	0.166	2.61

<sup>a</sup> Refinement #1 corresponds to that of the false minimum in which only the 13 non-hydrogen atoms are included in the model with isotropic displacement parameters. Refinement #2 corresponds to that of the false minimum in which all atoms, with the exception of the hydrogen atoms associated with the methyl groups of P3, are included in the model with isotropic displacement parameters. Refinement #3 corresponds to that of the true structure in which all atoms, with the exception of the hydrogen atoms associated with the methyl groups of P3, are included in the model with isotropic displacement parameters. Refinement #4 corresponds to that of the true structure in which all atoms are included in the model with all atoms except W refined anisotropically. <sup>b</sup>  $R = \sum[(F_o^2 - F_c^2)]/\sum(F_o^2)$ . <sup>c</sup>  $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ . <sup>d</sup>  $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - m)]^{1/2}$ .

Even though the neutron diffraction refinement corresponding to the false minimum is not acceptable by conventional standards, the observation that refinement was possible, without diverging, is relevant since neutron diffraction structures are commonly obtained by refining the atomic coordinates of the structure as determined by X-ray diffraction, rather than by solving the neutron diffraction data. Thus, in the event that a neutron diffraction structure were to be obtained by refining the incorrect coordinates corresponding to a false minimum of an X-ray diffraction study, it is possible that the ability to carry out a refinement could potentially be taken as an indication that the connectivity is correct, and that the poor refinement parameters are reflective of a poor quality crystal. For such a scenario, it is possible that neutron diffraction would not provide a decisive answer.

**Another Example of a False Minimum and Reformulation of  $[W(PMe_3)_4H_2F(OH_2)]F$ : A Bifluoride Complex,  $W(PMe_3)_4H_2F(FHF)$ .** The deceptive nature of the false minimum observed for  $W(PMe_3)_4H_2Cl_2$  suggests that other structures may also suffer from related problems of refinement into unrecognized false minima. One particular example that we thought may have been subject to such an effect was the aqua-fluoro complex  $[W(PMe_3)_4H_2F(OH_2)][F]$ ,<sup>13,44</sup> since this compound also exhibited a similar arrangement of  $PMe_3$  ligands to that



**Figure 14.** False minima structures for  $W(PMe_3)_4H_2F(FHF)$ . Left: Structure refined with the originally reported incorrect composition,  $[W(PMe_3)_4H_2F(OH_2)][F]$ . Right: Structure refined with correct composition,  $W(PMe_3)_4H_2F(FHF)$ .

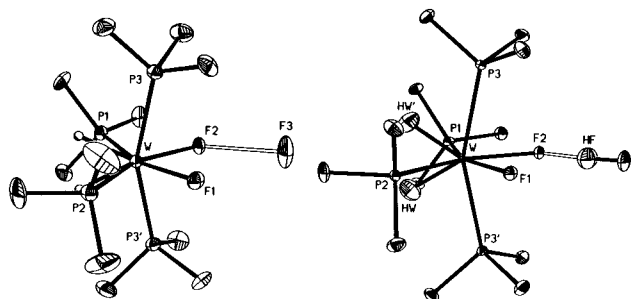
**Table 8.** Selected Bond Lengths (Å) and Angles (deg) for Various Refinements of  $W(PMe_3)_4H_2F(FHF)$

	X-ray		neutron (true min.)	$W(PMe_3)_4H_2F(OH_2)[F]^c$
	true min.	false min.		
W–F(1)	2.038(8)	2.024(13)	2.060(5)	2.028(13)
W–F(2)	2.100(7)	2.052(12)	2.117(5)	2.056(12) <sup>a</sup>
W–P(1)	2.457(3)	2.471(5)	2.431(5)	2.470(5)
W–P(2)	2.439(4)	2.463(7)	2.422(5)	2.467(7)
W–P(3)	2.495(2)	2.490(4)	2.468(2)	2.489(4)
W–H			1.702(5)	
H–W–H			63.7(3)	
F(1)–W–F(2)	75.7(3)	76.9(5)	75.2(2)	77.3(5)
P(3,3′)–W–X(1,2) <sub>av</sub> <sup>b</sup>	81[1]	98[1]	81[1]	98[2]
P(1,2)–W–P(3,3′) <sub>av</sub>	95[2]	85[2]	95[2]	85[2]
P(1)–W–P(2)	127.2(2)	125.7(4)	129.0(2)	125.6(4)
P(3)–W–P(3′)	157.6(2)	159.3(3)	157.3(2)	159.3(3)

<sup>a</sup> W–O(1) bond length. <sup>b</sup> X = F, O. <sup>c</sup> X-ray.

corresponding to the false minimum of  $W(PMe_3)_4H_2Cl_2$ , i.e., all the  $PMe_3$  ligands occupy positions in one hemisphere, rather than a distorted tetrahedral array about the metal center. Therefore, to investigate such a possibility, we recollected the diffraction data on proposed  $[W(PMe_3)_4H_2F(OH_2)][F]$ . After confirming that it does indeed refine well (e.g.,  $R_1 = 0.0500$ , GOF = 1.05) with the reported structure (Figure 14, Table 8), the atomic coordinates of the *transoid*- $PMe_3$  ligand were adjusted by reflection of their  $z$  coordinates (with W at  $z = 0$ ). Importantly, this adjustment, which resulted in the *transoid*- $PMe_3$  ligands being displaced by ca.  $21^\circ$  from their original positions, was accompanied by a significant improvement in the refinement parameters (e.g.,  $R_1 = 0.0364$ , GOF = 1.00), and even the tungsten hydride ligand could be located. It is, therefore, apparent that the original structure reported for  $[W(PMe_3)_4H_2F(OH_2)][F]$  corresponds to a false minimum in terms of its atom positions. However, even though the tungsten hydride ligand could be located, the hydrogen atoms associated with the proposed water molecule could not. While it was certainly possible that the second hydrogen of the proposed  $H_2O$  moiety could be disordered, neutron diffraction studies demonstrated conclusively that only a single hydrogen atom is present. Evidently, the atom proposed to be oxygen should be reassigned as fluorine, such that  $[W(PMe_3)_4H_2F(OH_2)][F]$  is better reformulated as the bifluoride complex  $W(PMe_3)_4H_2F(FHF)$ ,<sup>67</sup> the X-ray and neutron diffraction refinements corresponding to this structure are illustrated in Figure 15. In support of this proposed reformulation, elemental fluorine analysis is in accord with the latter formulation (calcd. F, 10.4%; found F, 10.5%).<sup>68</sup>

As described for  $W(PMe_3)_4H_2Cl_2$  above, we have also used PLATON to evaluate the credibility of the structure corresponding to the false minimum of  $W(PMe_3)_4H_2F(FHF)$ , with the



**Figure 15.** X-ray (left) and neutron (right) diffraction structures of  $W(PMe_3)_4H_2F(FHF)$ .

correct atom assignment, as shown in Figure 14. Interestingly, although Figure 14 illustrates that the anisotropic displacement parameters are well-behaved, PLATON identified that the anisotropic displacement parameters of three carbon atoms are unusual (as judged by the magnitude of the ratio  $U_3/U_1$ );<sup>69</sup> however, two of these atoms are associated with a  $PMe_3$  ligand that is correctly located. Furthermore, since PLATON also indicated that the anisotropic displacement parameters of two of the carbon atoms of the *true* structure are unusual,<sup>70</sup> it illustrates the difficulty of using this criterion to identify reliably atoms that are incorrectly located. Moreover, with the ratios  $U_3/U_1$  for the three crystallographically independent phosphorus atoms being similar,<sup>71</sup> PLATON did not identify the anisotropic displacement parameters of the misplaced phosphorus atom to be unusual. It is, therefore, apparent that, as with  $W(PMe_3)_4H_2Cl_2$ , the anisotropic displacement parameters corresponding to the structure of the false minimum of  $W(PMe_3)_4H_2F(FHF)$  do not provide a definitive indication that an entire  $PMe_3$  ligand has been misplaced.

In terms of nonbonded interactions, PLATON identified several close contacts between  $PMe_3$  hydrogen atoms, in *calculated* positions.<sup>72</sup> However, since short intramolecular  $H\cdots H$  contacts are also observed for the *true* structure,<sup>73</sup> it also illustrates the difficulty of using this criterion to suggest that an entire  $PMe_3$  ligand is misplaced. Finally, it is notable that

(67) In our original disclosure of the false minimum for  $[W(PMe_3)_4H_2F(H_2O)][F]$  (ref 43), we noted that since X-ray diffraction cannot distinguish definitively between O and F, and since the W–F and “W–OH<sub>2</sub>” bond lengths were similar, we felt that a better representation for  $[W(PMe_3)_4H_2F(H_2O)][F]$  was as isomeric  $W(PMe_3)_4H_2F_2(H_2O)$ . It was also recognized that the structure could be refined as a species of composition  $W(PMe_3)_4H_2F(FHF)$ . However, considering that we had no evidence that the composition as originally reported was incorrect, and since the difference in atom assignment had no effect on the nature of the false minimum, we did not at that point refine the structure as  $W(PMe_3)_4H_2F(FHF)$  for the purposes of our study.

(68) One of the possible reasons why  $W(PMe_3)_4H_2F(FHF)$  was originally mischaracterized is due to the fact that solutions dissociate HF yielding  $W(PMe_3)_4H_2F_2$ . The situation is, however, further complicated by a rapid exchange of fluorine atoms between  $W(PMe_3)_4H_2F_2$  and HF, which results in the hydride signal of  $W(PMe_3)_4H_2F_2$  losing coupling to fluorine. Full details describing the NMR spectroscopic features of  $W(PMe_3)_4H_2F(FHF)$  will be reported together with details on the molybdenum system.

(69) Specifically, the ratios of  $U_3/U_1$  for C(21), C(22), and C(32) are 5.80, 8.25, and 19.04, respectively. For comparison, the ratios for other carbon atoms are in the range 2.99 to 4.85.

(70) Specifically, the ratios of  $U_3/U_1$  for C(21) and C(22) are 6.62 and 9.78, respectively.

(71) The ratios of  $U_3/U_1$  for P(1), P(2), and P(3) are 1.57, 1.68, and 1.56, respectively.

(72) The structure corresponding to the false minimum of  $W(PMe_3)_4H_2F(FHF)$  is characterized by three intramolecular  $H\cdots H$  contacts more than 0.25 Å less than the sum of the van der Waals radii (max =  $-1.27$  Å) and two intermolecular  $H\cdots H$  contacts more than 0.25 Å less than the sum of the van der Waals radii (max =  $-0.28$  Å).

(73) The structure corresponding to the true minimum of  $W(PMe_3)_4H_2F(FHF)$  is characterized by two intramolecular  $H\cdots H$  contacts more than 0.25 Å less than the sum of the van der Waals radii (max =  $-0.33$  Å).

**Table 9.** Comparison of [MFHF] Metrical Data for Structurally Characterized Bifluoride Complexes

	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> F(FHF)		Mo(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> F-(FHF) <sup>a</sup> (X-ray)	Ru(dmpe) <sub>2</sub> (H)-(FHF) <sup>b</sup> (X-ray)
	neutron	X-ray		
M—FHF/Å	2.117(5)	2.100(7)	2.124(3)	2.284(5)
F··F/Å	2.389(6)	2.390(13)	2.351(8)	2.276(8)
MF—HF/Å	1.436(9)	not detd	1.27(11)	not detd
MFH—F/Å	0.961(9)	not detd	1.13(12)	not detd
F—H—F/deg	170.6(7)	not detd	157(8)	not detd
M—F··F/deg	131.2(2)	134.1(4)	ca. 134	129.9(3)

<sup>a</sup> Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428–7429. <sup>b</sup> Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1997**, 187–188.

the structure corresponding to the false minimum also passed the Hirshfeld rigid bond test<sup>61</sup> with use of PLATON at the 2.5  $\sigma$  level, providing yet a further indication that the structure is well-behaved.

**Structurally Characterized Transition Metal Bifluoride Complexes.** Although rare, transition metal complexes in which the bifluoride moiety is covalently bound to a metal center are preceded.<sup>74</sup> For example, the molybdenum analogue, Mo(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF), has been reported,<sup>75</sup> and Perutz has described the synthesis and structural characterization of *trans*-Ru(dmpe)<sub>2</sub>(H)(FHF).<sup>76–78</sup> For comparison, selected metrical data pertaining to the [MFHF] interaction in these complexes are compiled in Table 9. In each case, the [MFHF] interaction is not linear, with M—F··F angles in the range 129–134°. The F··F separations in each of these complexes are considerably less than twice the van der Waals radius of fluorine (1.4 Å),<sup>79</sup> a criterion by which the interactions may be viewed as comprising strong hydrogen bonds.<sup>80</sup>

Since W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) is the first transition metal complex with a [MFHF] interaction to be studied by neutron diffraction, the bond lengths and angles associated with location of the hydrogen atom are of considerable importance. In

(74) For reviews on bifluoride salts, see: (a) Tuck, D. G. *Progr. Inorg. Chem.* **1968**, *9*, 161–194. (b) Emsley, J. *Chem. Soc. Rev.* **1980**, *9*, 91–124. (c) Hibbert, F.; Emsley, J. *Adv. Phys. Org. Chem.* **1990**, *26*, 255–379. (d) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination*; W. A. Benjamin, Inc.: New York, 1968. (e) Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103–109. (f) Landrum, G. A.; Goldberg, N.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1997**, 3605–3613. (h) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*, Oxford University Press: New York, 1997.

(75) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428–7429.

(76) (a) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1997**, 187–188. (b) Whittlesey, M. K.; Perutz, R. N.; Moore, M. H. *J. Chem. Soc., Chem. Commun.* **1996**, 787–788. (c) Whittlesey, M. K.; Perutz, R. N. *Abstracts of 6th International Conference on the Chemistry of the Platinum Group Metals*, York, UK, July 21–26, 1996; poster 80.

(77) A complex with a bridging bifluoride moiety, [Cp\*NbF<sub>3</sub>( $\mu$ -FHF)]<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub>, has also been structurally characterized. See: Roesky, H. W.; Sotoodeh, M.; Xu, Y. M.; Schrupf, F.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *580*, 131–138.

(78) In addition to the aforementioned structurally characterized examples, bifluoride complexes have also been characterized in solution. For example, the platinum compound *trans*-Pt(PCy<sub>3</sub>)<sub>2</sub>(H)(FHF) has been generated in solution, but attempts to isolate it were unsuccessful. Evidently, dissociation of HF from *trans*-Pt(PCy<sub>3</sub>)<sub>2</sub>(H)(FHF) is facile since the <sup>1</sup>H NMR spectrum exhibits a doublet at  $\delta$  12.8 ppm (with a <sup>1</sup>J<sub>H-F</sub> coupling constant of 392 Hz), which is attributed to HF.<sup>3</sup> Furthermore, *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(Ph)(FHF) has also been spectroscopically characterized ( $\delta$  10.7 ppm).<sup>b</sup> (a) Hintermann, S.; Pregosin, P. S.; Rügger, H.; Clark, H. C. *J. Organomet. Chem.* **1992**, *435*, 225–234. (b) Coulson, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3111–3119.

(79) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(80) Strong hydrogen bonds are typically characterized by A··B separations that are  $\geq 0.25$  Å less than the sum of the van der Waals radii. See ref 74c.

particular, the present study demonstrates that the hydrogen bonding interaction is far from symmetric, with the hydrogen atom located much closer to the terminal fluorine [0.961(9) Å]<sup>81</sup> than to the tungsten-bound fluorine [1.436(9) Å]; the F—H—F interaction is close to linear with a bond angle of 170.6(7)°. For comparison, the hydrogen atom in bifluoride salts is symmetrically disposed with respect to the two fluorine atoms.<sup>74,82</sup> Evidently, the interaction in W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) may be considered to be close to an extreme that is best described as a hydrogen bonding interaction between W—F and H—F, i.e., [W—F···H—F].<sup>83,84</sup> Supporting such a notion, dissociation of HF from W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) occurs readily in solution,<sup>68</sup> as has also been noted for the molybdenum analogue.<sup>75</sup> In contrast, Perutz has reported that such dissociation does not occur for the ruthenium complex *trans*-Ru(dmpe)<sub>2</sub>(H)(FHF).<sup>85</sup> Perutz has also noted that the F··F separation [2.276(8) Å] in the latter complex is similar to that found in bifluoride salts (2.24–2.28 Å),<sup>86</sup> so that this complex is presumably closer to an extreme in [MFHF] interactions in which the hydrogen of the [FHF] moiety is more symmetrically displaced, and therefore representative of a stronger hydrogen bonding interaction, i.e., [Ru···F—H—F]. In support of this suggestion, the Ru—F bond length in *trans*-Ru(dmpe)<sub>2</sub>(H)(FHF) [2.284(5) Å] is cited as being longer than typical values (2.01–2.04 Å).<sup>87</sup>

**Other Examples of False Minima Associated with a “Partial Polar Ambiguity”.** X-ray structure refinements into a false minimum due to the presence of a polar axis are not restricted to the examples described in this paper. The earliest example of which we are aware is a report by Ibers in which it was described that the solution for [(Ph<sub>2</sub>MeP)<sub>3</sub>Ir(Cl)(N<sub>2</sub>Ph)][PF<sub>6</sub>] refined into a false minimum.<sup>88</sup> However, in contrast to the examples described here, it was readily recognized that the derived structure associated with the false minimum of [(Ph<sub>2</sub>MeP)<sub>3</sub>Ir(Cl)(N<sub>2</sub>Ph)][PF<sub>6</sub>] was incorrect since the Ph<sub>2</sub>MeP ligands exhibited unreasonable geometries (for example, a P—C—C angle of 136.5° rather than *ca.* 120°). Another example of this phenomenon that we have discovered is that it is possible to

(81) For comparison, the H—F bond length in HF is 0.918 Å. See ref 38b, p 226.

(82) Peterson, S. W.; Levy, H. A. *J. Phys. Chem.* **1952**, *56*, 704–707.

(83) For other examples in which M—F bonds participate in hydrogen-bonding interactions, see: (a) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221–250. (b) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. E. *Chem. Rev.* **1994**, *94*, 373–431. (c) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888–890. (d) Osterberg, C. E.; Arif, A. M.; Richmond, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 6903–6904. (e) Patel, B. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 13105–13106. (f) Ault, B. S. *Inorg. Chem.* **1991**, *30*, 2483–2487. (g) Herzog, A.; Roesky, H. W.; Jäger, F.; Steiner, A. *J. Chem. Soc., Chem. Commun.* **1996**, 29–30.

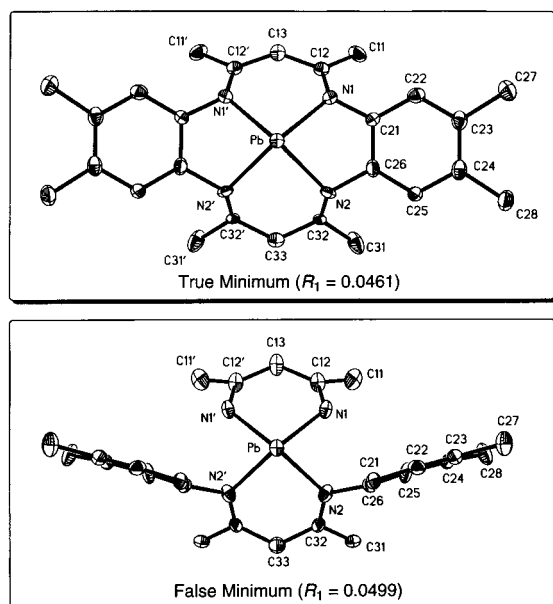
(84) W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F<sub>2</sub> is also a particularly good candidate for the W—F group to partake in hydrogen bonding interactions due to the existence of filled–filled repulsions between the d electrons on the metal center and the lone pairs on fluorine. In this regard, Caulton has suggested that the chloro ligand in the related complex W(PMe<sub>2</sub>Ph)<sub>4</sub>Cl<sub>2</sub>H<sub>2</sub> exhibits enhanced nucleophilicity. See refs 22 and 40.

(85) For example, the two fluorine nuclei of the bifluoride moiety exhibit a <sup>2</sup>J<sub>F-F</sub> coupling of 152 Hz. See ref 76a.

(86) (a) McDonald, T. R. *Acta Crystallogr.* **1960**, *13*, 113–124. (b) Frevel, L. K.; Rinn, H. W. *Acta Crystallogr.* **1962**, *15*, 286. (c) McGaw, B. L.; Ibers, J. A. *J. Chem. Phys.* **1963**, *39*, 2677–2684. (d) Ibers, J. *J. Chem. Phys.* **1964**, *40*, 402–404. (e) Williams, J. M.; Schneemeyer, L. F. *J. Am. Chem. Soc.* **1973**, *95*, 5780–5781. (f) Farnham, W. B.; Dixon, D. A.; Middleton, W. J.; Calabrese, J. C.; Harlow, R. L.; Whitney, J. F.; Jones, G. A.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1987**, *109*, 476–483.

(87) Furthermore, the bifluoride ligand in *trans*-Ru(dmpe)<sub>2</sub>(H)(FHF) is observed at 1690 cm<sup>-1</sup> in the IR spectrum, a value that is also indicative of a stronger [FHF] interaction than in Mo(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) (2682 cm<sup>-1</sup>) and W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) (2793 cm<sup>-1</sup>).

(88) Cowie, M.; Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 7608–7617.



**Figure 16.** True and false minima for  $[\eta^4\text{-Me}_8\text{taa}]\text{Pb}$ .

refine the macrocyclic lead complex  $[\eta^4\text{-Me}_8\text{taa}]\text{Pb}$  with a structure that is nonmacrocyclic (Figure 16).<sup>89</sup> Impressively, despite the dramatic difference in connectivity, the incorrect structure is nevertheless characterized by a low  $R$  value and well-behaved displacement parameters.

The false minima described in this paper correspond to an incorrect structural interpretation that may be considered to be intermediate between the examples of  $[(\text{Ph}_2\text{MeP})_3\text{Ir}(\text{Cl})(\text{N}_2\text{Ph})][\text{PF}_6]$  and  $[\eta^4\text{-Me}_8\text{taa}]\text{Pb}$  in terms of the severity of the effect. For example, the structure corresponding to the false minimum of  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  is sufficiently close to the expected structure (in contrast to the nonmacrocyclic structure for macrocyclic  $[\eta^4\text{-Me}_8\text{taa}]\text{Pb}$ ) and well-behaved (in contrast to the unreasonable geometries observed for the  $\text{Ph}_2\text{MeP}$  ligands in  $[(\text{Ph}_2\text{MeP})_3\text{Ir}(\text{Cl})(\text{N}_2\text{Ph})][\text{PF}_6]$ ), such that the derived incorrect result is plausible. Indeed, the fact that the compound now known to be  $\text{W}(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$  was originally reported with an incorrect configuration is testament to the deceptive nature of this phenomenon, and clearly demonstrates that structures which correspond to a false minimum of a refinement procedure may go unrecognized.

Finally, it is important to re-emphasize the distinction between the phenomenon described in this paper due to a “partial polar ambiguity” and that of the well-known “polar dispersion error”,<sup>47–49</sup> which describes the structural error introduced by refining a structure with the incorrect polarity, i.e., a structure in which the coordinates of *all* atoms should be reflected perpendicular to the polar axis to give the correct absolute structure.<sup>90,91</sup> Typically, the result of refining an incorrect absolute structure is manifested by a displacement (along the polar axis) of anomalous scatterers (heavy atoms) with respect to other atoms.<sup>92,93</sup> A principal consequence, therefore, of selecting the incorrect polarity is that derived bond lengths and

angles to heavy atoms may be incorrect, but the overall appearance of the molecule will not be influenced. The main distinction between the “polar dispersion error” and the “partial polar ambiguity” described here is that, for the latter, the incorrect structure is not related to the true structure by reflection of the coordinates of *all* atoms about the polar axis, but is rather related by reflection of *selected* atoms, i.e., *mixed* polarity. Consequently, the “partial polar ambiguity” results in a completely different geometric structure from the true structure.

## Conclusions

In summary, molecules which crystallize in polar space groups may suffer from structure solutions that refine into deceptive false minima. Significantly, for the examples described herein, the false structures are dramatically different from their true structures, but are nevertheless characterized by low  $R$  values and well-behaved displacement parameters. It needs to be emphasized that the important aspect of this issue is not concerned with identifying which of the solutions corresponding to the true and false minima is correct. Rather, the importance is concerned with recognizing that, once having refined into a false minimum, it may not be possible to detect that the derived structure is incorrect.

The ability for a well-behaved refinement to converge to a false minimum of this type will undoubtedly be most pronounced when the X-ray scattering is dominated by a single atom. Particular attention should, therefore, be given to “heavy atom” structures of this type in order to establish that the correct molecular geometry has been determined. Thus, further to the well-known requirement of selecting the correct sense of a polar axis, it is critical to ensure that all of the atoms in the asymmetric unit of a polar space group belong to a single *true* polar configuration.

To the extent that the incorrect structures described here are isomers of their true structures, it is worthwhile to compare the effect with that responsible for another example of isomerism which has been shown to be due to a crystallographic artifact, namely bond-stretch isomerism.<sup>2d,7,94,95</sup> Although the existence of bond-stretch isomers is phenomenologically more unusual than the existence of a pair of geometric “bond-bend” isomers, the ability to generate a pair of “bond-bend” isomers is perhaps

(91) For other comments on absolute structure, see: (a) Jones, P. G.; Meyer-Bäse, K. *Acta Crystallogr.* **1986**, *A43*, 79–80. (b) Jones, P. G. *Acta Crystallogr.* **1984**, *A40*, 663–668. (c) Jones, P. G. *Acta Crystallogr.* **1986**, *C42*, 924–925. (d) Jones, P. G.; Schelbach, R.; Schwarzmann, E.; Thöne, C. *Acta Crystallogr.* **1988**, *C44*, 1196–1198. (e) Rogers, D. *Acta Crystallogr.* **1979**, *B35*, 2823–2825.

(92) Cruickshank subsequently considered the effect further and derived an expression to indicate the magnitude of the error in atomic coordinates that could be expected upon neglect of  $\Delta f'$  and emphasized that the problem is not confined to the presence of heavy elements. See ref 48d.

(93) In addition to the polar dispersion error, Jones has noted that it is possible for the incorrect absolute configuration to give rise to “ghost peaks” in a difference map that may be subsequently refined well as an atom. Specifically, Jones described an example where it was possible to refine an additional oxygen atom (which was assumed to be water of crystallization) for the incorrect absolute structure. However, the  $U$  value for this oxygen atom became prohibitively high for the inverted structure, clearly indicating that its inclusion is erroneous. See ref 91d.

(94) For an additional discussion concerned with the complexity of the  $[\text{Mo}(\text{PR}_3)_2(\text{O})\text{Cl}_2]$  system, see: (a) Cotton, F. A.; Kohli, M.; Luck, R. L.; Silverton, J. V. *Inorg. Chem.* **1993**, *32*, 1868–1870. (b) Limberg, C.; Büchner, M.; Heinze, K.; Walter, O. *Inorg. Chem.* **1997**, *36*, 872–879.

(95) For examples of species that may be considered to be bond-stretch “isomers” if differences in counterion or solvent of crystallization are neglected, see: (a) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV *J. Chem. Soc., Chem. Commun.* **1997**, 421–422. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 10377–10381. (c) Köhn, R. D.; Seifert, G.; Kociok-Köhn, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2879–2881.

(89) Kuchta, M. C.; Parkin, G. *New J. Chem.* In press.

(90) The term “absolute structure” has been suggested by Jones as a general term to encompass situations which correspond to “determination of absolute configuration (or conformation), or of polar-axis direction or resolving the ambiguity of enantiomorphous pairs or of axis direction.”<sup>a</sup> Jones has also published an ambiguity table for noncentrosymmetric crystal classes, and has suggested that the expression “determination of polar-axis direction” should be replaced by “determination of the orientation of the structure with respect to the polar axis (axes)”.<sup>b</sup> (a) Jones, P. G. *Acta Crystallogr.* **1984**, *A40*, 660–662. (b) Jones, P. G. *Acta Crystallogr.* **1986**, *A42*, 57.

more dramatic since it requires *entire groups of atoms* being misplaced, rather than the apparent displacement of a single atom as observed in bond-stretch isomerism. A common feature of both these phenomena, however, is their deceptiveness. Thus, with respect to bond-stretch isomerism, even though it was well recognized that a chloride impurity would *apparently* increase the length of a metal–oxo bond,<sup>96</sup> it was not recognized that the long bond length for a pair of bond-stretch isomers was due to the presence of an impurity because the structures were so well-behaved. Likewise, crystallographers may be aware of the existence of false minima,<sup>97</sup> but this is normally because it is obvious that there are problems present with the solution at hand (e.g., high *R* values and poorly behaved anisotropic displacement parameters). However, in the present examples, the solutions refine sufficiently well that a false minimum would not normally be considered, as judged by the fact that the original structure  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$  unknowingly suffered from such a problem.

## Experimental Section

**General Considerations.** All manipulations were performed by using a combination of glovebox, high-vacuum, or Schlenk techniques.<sup>98</sup> Solvents were purified and degassed by standard procedures.  $W(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}^{13b}$  and  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2^{13b,99}$  were prepared by the literature methods. Solvents were purified and degassed by standard procedures. <sup>1</sup>H NMR spectra were recorded on Varian VXR-200 (200.057 MHz), VXR-300 (299.943 MHz), and VXR-400 (399.95 MHz) spectrometers. <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on the Varian VXR-300 spectrometer operating at 75.429 and 121.421 MHz, respectively. <sup>19</sup>F NMR spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 282.404 MHz. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  ( $\delta = 0$ ) and were referenced internally with respect to the protio solvent impurity ( $\delta = 7.15$  for  $\text{C}_6\text{D}_5\text{H}$ ) or the <sup>13</sup>C resonances ( $\delta = 128.0$  for  $\text{C}_6\text{D}_6$ ), respectively. <sup>31</sup>P chemical shifts are reported in ppm relative to 85%  $\text{H}_3\text{PO}_4$  ( $\delta = 0$ ) and were referenced with use of  $\text{P}(\text{OMe})_3$  ( $\delta = 141.0$ ) as an external standard. <sup>19</sup>F chemical shifts are reported in ppm relative to  $\text{CFCl}_3$  ( $\delta = 0$ ) and were referenced with use of  $\text{PhCF}_3$  ( $\delta = -63.72$  ppm) as an external standard.<sup>100</sup> All coupling constants are reported in Hertz. IR spectra were recorded as KBr pellets on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in  $\text{cm}^{-1}$ . Mass spectra were obtained on a Nermag R10–10 mass spectrometer with use of chemical ionization ( $\text{NH}_3$  or  $\text{CH}_4$ ) techniques. C, H, and N elemental analyses were measured with a Perkin-Elmer 2400 CHN elemental analyzer. Fluorine analyses were determined by Galbraith Laboratories, Inc. (Knoxville, TN).

**Synthesis of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$ .** A stirred solution of  $W(\text{PMe}_3)_4(\eta^2\text{-CH}_2\text{PMe}_2)\text{H}$  (3.38 g, 5.99 mmol) in pentane (50 mL) was treated

dropwise with aqueous hydrochloric acid (ca. 20 mL of a 4 M solution), resulting in the formation of a yellow precipitate; the addition was stopped at the point when the supernatant solution became a very pale yellow color. The precipitate was separated by filtration, washed with pentane ( $2 \times 15$  mL), and dried in vacuo. The product was extracted into  $\text{Et}_2\text{O}$  ( $2 \times 150$  mL) and filtered. The volume of the combined extracts was reduced to ca. 10 mL to afford yellow microcrystalline  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$ , which was isolated by filtration and dried under reduced pressure (2.78 g, 83%). Anal. Calcd for  $\text{C}_{12}\text{H}_{38}\text{Cl}_2\text{P}_4\text{W}$ : C, 25.7; H, 6.8. Found: C, 25.8; H, 6.3. IR data: 2971 (s), 2904 (vs), 2813 (w), 1933 (m) [ $\nu_{\text{W-H}}$ ], 1424 (s), 1296 (s), 1280 (s), 1269 (s), 938 (vs), 860 (s), 846 (s), 712 (vs), 665 (vs). MS:  $m/z = 561$  ( $\text{M}^+ - 1$ ). <sup>1</sup>H NMR data ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.39 [36 H, m, 4  $\text{PMe}_3$ ],  $-3.44$  [2 H; d,  $^2J_{\text{P-H}} = 37$ ; d,  $^2J_{\text{P-H}} = 43$ ; t,  $^2J_{\text{P-H}} = 61$ ].

**Synthesis of  $W(\text{PMe}_3)_4\text{H}_2\text{Br}_2$ .** A solution of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  (0.89 g, 1.59 mmol) in benzene (50 mL) was stirred with LiBr (3.19 g, 36.7 mmol) at room temperature for 1 day. The supernatant solution was filtered and stirred with another portion of LiBr (2.38 g, 27.4 mmol) for 15 h at room temperature. The solution was then filtered and the solvent removed under reduced pressure to give  $W(\text{PMe}_3)_4\text{H}_2\text{Br}_2$  as a bright yellow powder, which was washed with pentane (5 mL) and dried in vacuo (0.87 g, 84%). Anal. Calcd for  $\text{C}_{12}\text{H}_{38}\text{Br}_2\text{P}_4\text{W}$ : C, 22.2; H, 5.9. Found: C, 22.1; H, 5.3. IR data ( $\text{cm}^{-1}$ ): 2969 (m), 2909 (s), 1934 (w) [ $\nu_{\text{W-H}}$ ], 1418 (m), 1300 (m), 1278 (m), 945 (vs), 854 (m), 710 (m), 669 (m). MS:  $m/z = 651$  ( $\text{M}^+ + 1$ ). <sup>1</sup>H NMR data ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.42 [18 H, vt, " $J_{\text{P-H}}$ " = 4, 2  $\text{PMe}_3$ ], 1.48 [18 H, vt, " $J_{\text{P-H}}$ " = 3, 2  $\text{PMe}_3$ ],  $-4.57$  [2 H; s,  $^2J_{\text{P-H}} = 38$ ; d,  $^2J_{\text{P-H}} = 44$ ; t,  $^2J_{\text{P-H}} = 61$ ]. <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  21.1 [t,  $^1J_{\text{P-C}} = 13$ ; q,  $^1J_{\text{C-H}} = 129$ ; 2  $\text{PMe}_3$ ], 26.9 [t,  $^1J_{\text{P-C}} = 16$ ; q,  $^1J_{\text{C-H}} = 127$ ;  $^1J_{\text{W-C}} = 131$ ; 2  $\text{PMe}_3$ ]. <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-28.0$  [t,  $^2J_{\text{P-P}} = 16$ ;  $^1J_{\text{W-P}} = 174$ ; 2  $\text{PMe}_3$ ],  $-38.8$  [t,  $^2J_{\text{P-P}} = 16$ ;  $^1J_{\text{W-P}} = 186$ ; 2  $\text{PMe}_3$ ].

**Synthesis of  $W(\text{PMe}_3)_4\text{H}_2\text{I}_2$ .** A solution of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  (0.85 g, 1.51 mmol) in benzene (60 mL) was stirred with NaI (3.47 g, 23.2 mmol) under an atmosphere of  $\text{H}_2$  (ca. 2 atm) at room temperature for 1 day. The resulting orange solution was filtered and stirred with another portion of NaI (2.34 g, 15.6 mmol) under an atmosphere of  $\text{H}_2$  (ca. 2 atm) for 15 h at room temperature. The solution was then filtered and the solvent removed under reduced pressure to give  $W(\text{PMe}_3)_4\text{H}_2\text{I}_2$  as a pale orange powder, which was washed with pentane (10 mL) and dried in vacuo (1.09 g, 97%). Anal. Calcd for  $\text{C}_{12}\text{H}_{38}\text{I}_2\text{P}_4\text{W}$ : C, 19.4; H, 5.2. Found: C, 19.3; H, 4.6. IR data: 2970 (s), 2907 (s), 1961 (m) [ $\nu_{\text{W-H}}$ ], 1419 (s), 1300 (s), 1279 (vs), 938 (vs), 858 (s), 719 (s), 709 (s), 669 (s). MS:  $m/z = 668$  ( $\text{M}^+ - \{\text{PMe}_3\}$ ). <sup>1</sup>H NMR data ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.48 [18 H, vt, " $J_{\text{P-H}}$ " = 4, 2  $\text{PMe}_3$ ], 1.62 [18 H, vt, " $J_{\text{P-H}}$ " = 3, 2  $\text{PMe}_3$ ],  $-6.20$  [2 H; d,  $^2J_{\text{P-H}} = 38$ ; d,  $^2J_{\text{P-H}} = 47$ ; t,  $^2J_{\text{P-H}} = 62$ ]. <sup>13</sup>C NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  24.8 [t,  $^1J_{\text{P-C}} = 14$ ; q,  $^1J_{\text{C-H}} = 127$ ; 2  $\text{PMe}_3$ ], 27.8 [t,  $^1J_{\text{P-C}} = 16$ ; q,  $^1J_{\text{C-H}} = 126$ ;  $^1J_{\text{W-C}} = 132$ ; 2  $\text{PMe}_3$ ]. <sup>31</sup>P NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-39.3$  [t,  $^2J_{\text{P-P}} = 18$ ;  $^1J_{\text{W-P}} = 164$ ; 2  $\text{PMe}_3$ ],  $-57.2$  [t,  $^2J_{\text{P-P}} = 18$ ;  $^1J_{\text{W-P}} = 178$ ; 2  $\text{PMe}_3$ ].

**Synthesis of  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$ .**  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$  was prepared by the method described in the literature for  $[W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{OH}_2)]\text{[F]}$ . <sup>1</sup>H NMR data ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.18 [18 H, vt, " $J_{\text{P-H}}$ " = 3, 2  $\text{PMe}_3$ ], 1.29 [18 H, vt, " $J_{\text{P-H}}$ " = 4, 2  $\text{PMe}_3$ ],  $-1.73$  [2 H; t,  $^2J_{\text{P-H}} = 36$ ; t,  $^2J_{\text{P-H}} = 55$ ; 2 W–H], 11.5 [1H, d,  $^1J_{\text{F-H}} = 430$ , HF]. <sup>19</sup>F NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-237.3$  [s,  $\text{WF}_2$ ],  $-183.3$  [d,  $^1J_{\text{F-H}} = 430$ , HF]. IR data ( $\text{cm}^{-1}$ ): 2978 (w), 2910 (m), 2793 (w, br, W–HF), 1891 (w, br, W–H), 1421 (m), 1300 (m), 1284 (m), 1231 (w), 950 (s), 860 (m), 734 (m), 715 (m), 669 (m), 455 (m).

**X-ray Structure Determinations.** Crystal data, data collection, and refinement parameters for  $W(\text{PMe}_3)_4\text{H}_2\text{X}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) and  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$  are summarized in Table 10. A typical procedure is provided by the example of  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2$ . A single crystal of  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2$  was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected at room temperature with use of graphite monochromated  $\text{Mo K}\alpha$  X-radiation ( $\lambda = 0.71073$  Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. Systematic absences were consistent uniquely with  $P2_1/n$  (No. 14). The structure was solved with direct methods

(96) For an example of a report in which oxo-chloro disorder was described, but was not considered as a rationalization of bond-stretch isomerism, see: Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602.

(97) For example, false minima have been observed in the structure refinements of  $\text{Cr}_2(\text{OAc})_4(\text{H}_2\text{O})_2$ ,<sup>a</sup> adamantane,<sup>b</sup> and 4-(1-pyrrolidino)pyridinium propionate.<sup>c</sup> (a) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 688–692. (b) Donohue, J.; Goodman, S. H. *Acta Crystallogr.* **1967**, *22*, 352–354. (c) Wheeler, K. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 347–360.

(98) (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.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(99) <sup>1</sup>H NMR data ( $\text{C}_6\text{D}_6$ ) for  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2$ :  $\delta$  1.29 [18 H, vt, " $J_{\text{P-H}}$ " = 3, 2  $\text{PMe}_3$ ], 1.40 [18 H, vt, " $J_{\text{P-H}}$ " = 4, 2  $\text{PMe}_3$ ],  $-1.50$  [2 H, d,  $^2J_{\text{P-H}} = 35$ ; d,  $^2J_{\text{P-H}} = 37$ ; t,  $^2J_{\text{P-H}} = 55$ ; t,  $^2J_{\text{P-H}} = 8$ ].

(100) Evans, B. J.; Doi, J. T.; Musker, W. K. *J. Org. Chem.* **1990**, *55*, 2337–2344.

**Table 10.** Crystal, Intensity Collection, and Refinement Data for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>X<sub>2</sub> (X = F, Cl, Br, I)

	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> F <sub>2</sub>	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> Cl <sub>2</sub>	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> Br <sub>2</sub>	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> I <sub>2</sub>
lattice	monoclinic	orthorhombic	orthorhombic	monoclinic
formula	C <sub>12</sub> H <sub>38</sub> F <sub>2</sub> P <sub>4</sub> W	C <sub>12</sub> H <sub>38</sub> Cl <sub>2</sub> P <sub>4</sub> W	C <sub>12</sub> H <sub>38</sub> Br <sub>2</sub> P <sub>4</sub> W	C <sub>12</sub> H <sub>38</sub> I <sub>2</sub> P <sub>4</sub> W
formula wt	528.2	561.1	650.0	744.0
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)	<i>Cmc</i> 2 <sub>1</sub> (No. 36)	<i>Cmc</i> 2 <sub>1</sub> (No. 36)	<i>P</i> 2 <sub>1</sub> (No. 4)
<i>a</i> /Å	9.952(2)	13.577(2)	13.273(2)	9.041(3)
<i>b</i> /Å	13.967(3)	13.395(2)	13.656(2)	14.930(8)
<i>c</i> /Å	16.561(2)	12.598(3)	12.935(3)	9.764(4)
α/deg	90	90	90	90
β/deg	103.09(1)	90	90	114.98(3)
γ/deg	90	90	90	90
<i>V</i> /Å <sup>3</sup>	2242(1)	2292(1)	2345(1)	1194.7(8)
<i>Z</i>	4	4	4	2
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ(calcd), g cm <sup>-3</sup>	1.57	1.63	1.84	2.07
μ(Mo Kα), mm <sup>-1</sup>	5.44	5.54	8.59	7.99
2θ range, deg	3–50	3–55	3–50	3–55
no. of data	2569, 2054 [ <i>F</i> > 6σ( <i>F</i> )]	1436	1129	2850, 2753 [ <i>F</i> > 3σ( <i>F</i> )]
no. of parameters	173	110	110	172
<i>R</i>	0.0491 <sup>a</sup>	0.0234 <sup>b</sup>	0.0372 <sup>b</sup>	0.0241 <sup>a</sup>
<i>R</i> <sub>w</sub>	0.0512 <sup>a</sup>	0.0514 <sup>b</sup>	0.0806 <sup>b</sup>	0.0301 <sup>a</sup>
GOF	1.61	1.06	1.03	1.05

<sup>a</sup>  $R = \{\sum||F_o| - |F_c||\}/\sum|F_o|$ ;  $R_w = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$ . <sup>b</sup>  $R_1 = \{\sum||F_o| - |F_c||\}/\sum|F_o|$  for [*I* > 2σ(*I*)];  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$  for [*I* > 2σ(*I*)].

and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.<sup>101</sup> Hydrogen atoms on carbon were included in calculated positions.

Systematic absences for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> were consistent with *Cmcm* (No. 63), *Cmc*2<sub>1</sub> (No. 36), and *C2cm* (No. 40), of which a satisfactory solution was achieved with the choice *Cmc*2<sub>1</sub> (No. 36). The structure was solved with direct methods and standard difference map techniques and refined by full-matrix least-squares procedures on *F*<sup>2</sup> with SHELXTL (Version 5.03). Hydrogen atoms on carbon were included in calculated positions. The tungsten hydride ligand was located in a final difference map and refined isotropically. The weighting scheme used was  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $3P = (2F_c^2 + F_o^2)$  and the constants *a* and *b* were suggested by the program. Refinement data are summarized in Table 10.

Systematic absences for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Br<sub>2</sub> were consistent with *Cmcm* (No. 63), *Cmc*2<sub>1</sub> (No. 36), and *C2cm* (No. 40), of which a satisfactory solution was achieved with the choice *Cmc*2<sub>1</sub> (No. 36). The structure was solved with direct methods and standard difference map techniques and refined by full-matrix least-squares procedures on *F*<sup>2</sup> with SHELXTL (Version 5.03). Hydrogen atoms on carbon were included in calculated positions. The tungsten hydride ligand was located in a final difference map but was refined isotropically subject to the distance constraint  $d(W-H) = 1.70$  Å. The weighting scheme used was  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $3P = (2F_c^2 + F_o^2)$  and the constants *a* and *b* were suggested by the program. Refinement data are summarized in Table 10.

Systematic absences for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>I<sub>2</sub> were consistent with *P*2<sub>1</sub> (No. 4) and *P*2<sub>1</sub>/*m* (No. 11) of which a satisfactory solution was obtained in *P*2<sub>1</sub> (No. 4). The structure was solved with direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.<sup>101</sup> Hydrogen atoms on carbon were included in calculated positions and inversion of configuration established the correct absolute structure. Refinement data are summarized in Table 10.

Systematic absences for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF) were consistent with *Cmcm* (No. 63), *Cmc*2<sub>1</sub> (No. 36), and *C2cm* (No. 40), of which a satisfactory solution was achieved with the choice *Cmc*2<sub>1</sub> (No. 36). The structure was solved with direct methods and standard difference map techniques and refined by full-matrix least-squares procedures on *F*<sup>2</sup> with SHELXTL (Version 5.03). Hydrogen atoms on carbon were included in calculated positions. The tungsten hydride ligand was located in a final difference map and refined isotropically subject to the distance constraint  $d(W-H) = 1.70$  Å. The weighting scheme used

(101) 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.

**Table 11.** Crystal, Intensity Collection, and Refinement Data for W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>F(FHF)

	W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> F(FHF)		[W(PMe <sub>3</sub> ) <sub>4</sub> H <sub>2</sub> F-(OH <sub>2</sub> )] <sup>+</sup> [F] <sup>-</sup>
	true structure	false structure	
lattice	orthorhombic	orthorhombic	orthorhombic
formula	C <sub>12</sub> H <sub>39</sub> F <sub>3</sub> P <sub>4</sub> W	C <sub>12</sub> H <sub>39</sub> F <sub>3</sub> P <sub>4</sub> W	C <sub>12</sub> H <sub>40</sub> F <sub>2</sub> OP <sub>4</sub> W
formula wt	548.2	548.2	546.2
space group	<i>Cmc</i> 2 <sub>1</sub> (No. 36)	<i>Cmc</i> 2 <sub>1</sub> (No. 36)	<i>Cmc</i> 2 <sub>1</sub> (No. 36)
<i>a</i> /Å	14.246(3)	14.246(3)	14.246(3)
<i>b</i> /Å	12.917(2)	12.917(2)	12.917(2)
<i>c</i> /Å	12.358(2)	12.358(2)	12.358(2)
α/deg	90	90	90
β/deg	90	90	90
γ/deg	90	90	90
<i>V</i> /Å <sup>3</sup>	2274(1)	2274(1)	2274(1)
<i>Z</i>	4	4	4
radiation (λ, Å)	0.71073	0.71073	0.71073
ρ(calcd), g cm <sup>-3</sup>	1.60	1.60	1.60
μ(Mo Kα), mm <sup>-1</sup>	5.38	5.38	5.37
2θ range, deg	3–65	3–65	3–65
no. of data	2225	2225	2225
no. of parameters	116	112	112
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0364	0.0500	0.0500
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>b</sup>	0.0772	0.1292	0.1294
GOF	1.00	1.08	1.05

<sup>a</sup>  $R_1 = \{\sum||F_o| - |F_c||\}/\sum|F_o|$ , (b)  $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ .

was  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $3P = (2F_c^2 + F_o^2)$  and the constants *a* and *b* were suggested by the program. Refinement data are summarized in Table 11.

**Neutron Diffraction Structures.** A crystal of W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>Cl<sub>2</sub> (ca. 14.1 mm<sup>3</sup>) was mounted on an aluminum pin with halocarbon grease and sealed under a helium atmosphere inside an aluminum container. The container was placed in a closed-cycle helium refrigerator<sup>102</sup> and mounted on the four-circle diffractometer at port H6S of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by Ge (220) planes in transmission geometry, was of wavelength 1.16395(10) Å as calibrated against a KBr crystal (*a*<sub>0</sub> = 6.6000 Å at 295 K). The sample temperature was maintained at 15.0 ± 0.5 K during the experiment, and unit cell dimensions were determined by least-squares fit of sin<sup>2</sup> θ values for 32 reflections in the range 51° < 2θ < 60°. Intensity data were obtained over one octant of reciprocal space by means of ω–2θ scans. The intensities of two

(102) DISPLEX Model CS-202. APD Cryogenics, Inc.

**Table 12.** Crystal, Intensity Collection, and Refinement Data for Neutron Diffraction Structures of  $W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$  and  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$ 

	$W(\text{PMe}_3)_4\text{H}_2\text{Cl}_2$	$W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$
lattice	orthorhombic	orthorhombic
formula	$\text{C}_{12}\text{H}_{38}\text{Cl}_2\text{P}_4\text{W}$	$\text{C}_{12}\text{H}_{30}\text{F}_3\text{P}_4\text{W}$
formula wt	561.1	548.2
space group	$\text{Cmc}2_1$ (No. 36)	$\text{Cmc}2_1$ (No. 36)
$a/\text{\AA}$	13.489(4)	14.004(4)
$b/\text{\AA}$	13.287(5)	12.676(6)
$c/\text{\AA}$	12.426(3)	12.062(4)
$\alpha/\text{deg}$	90	90
$\beta/\text{deg}$	90	90
$\gamma/\text{deg}$	90	90
$V/\text{\AA}^3$	2227(2)	2141(2)
Z	4	4
temp/K	15	15
radiation ( $\lambda$ , $\text{\AA}$ )	1.16395(10)	1.0462(1)
$\rho(\text{calcd})$ , $\text{g cm}^{-3}$	1.6732	1.7003
$\mu$ , $\text{mm}^{-1}$	0.3116	0.3048
$2\theta$ range, deg	5–108	5–110
no. of data	1707	2335
data/parameters	6.3	8.3
$R^a$	0.14426	0.10496
$R_w^b$	0.16578	0.07427
GOF <sup>c</sup>	2.60822	1.02244

<sup>a</sup>  $R = \sum|(F_o^2 - F_c^2)|/\sum(F_o^2)$ . <sup>b</sup>  $R_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ .  
<sup>c</sup> GOF =  $[\sum[w(F_o^2 - F_c^2)^2]/(n - m)]^{1/2}$ .

reflections were monitored during the data collection and showed no systematic variations throughout. Integrated intensities  $I_o$  and variances  $\sigma^2(I_o)$  were derived from the scan profiles. Lorentz factors were applied, as well as an absorption correction.<sup>103</sup> Transmission factors were in the range 0.429–0.656. A total of 1707 independent reflections were collected. Further details are given in Table 12. Initial coordinates of non-hydrogen atoms were obtained from the X-ray structure determination and all hydrogen atoms were found by means of difference Fourier syntheses. Least-squares refinements were carried out by a full-matrix procedure,<sup>104</sup> minimizing  $\sum w[F_o^2 - (k^2 F_c^2)]^2$  by using all independent data. The final model included symmetry allowed positional and anisotropic displacement parameters  $\beta_{ij}$  for all 33 atoms, the scale factor  $k$ , and an isotropic type  $I$  extinction parameter<sup>105</sup> for a total of 271 variable parameters. The refinement converged with fit indices  $R(F_o^2) = 0.144$ ,  $R_w(F_o^2) = 0.166$ ,  $R_w(F_o) = 0.115$ , GOF = 2.61, based on all 1707 reflections. A final difference Fourier showed maximum positive residual density of 2.6% and negative residual density of 4.4% of the maximum density (Cl1). There were 37

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reflections with an extinction correction larger than 1.1; the maximum correction was 1.39 for (800). Bond lengths and angles are listed in Table 2.

A crystal of  $W(\text{PMe}_3)_4\text{H}_2\text{F}(\text{FHF})$  (ca. 10.5 mm<sup>3</sup>) was mounted on an aluminum pin with halocarbon grease and sealed under a helium atmosphere inside an aluminum container. The container was placed in a closed-cycle helium refrigerator<sup>102</sup> and mounted on the four-circle diffractometer at port H6M of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by Be (002) planes in transmission geometry, was of wavelength 1.0462(1)  $\text{\AA}$  as calibrated against a KBr crystal ( $a_0 = 6.6000 \text{\AA}$  at 295 K). The sample temperature was maintained at  $15.0 \pm 0.5 \text{ K}$  during the experiment, and unit cell dimensions were determined by least-squares fit of  $\sin^2 \theta$  values for 32 reflections in the range  $45^\circ < 2\theta < 58^\circ$ . Intensity data were obtained over one octant of reciprocal space by means of  $\omega$ - $2\theta$  scans. The intensities of two reflections were monitored during the data collection and showed no systematic variation throughout. Integrated intensities  $I_o$  and variances  $\sigma^2(I_o)$  were derived from the scan profiles. Lorentz factors were applied, as well as an absorption correction. Transmission factors were in the range 0.471–0.712. A total of 2335 independent reflections were collected. Further details are given in Table 12. Initial coordinates of non-hydrogen atoms were obtained from the X-ray structure determination, and all hydrogen atoms were found by means of difference Fourier syntheses. Least-squares refinements were carried out by a full-matrix procedure,<sup>104</sup> minimizing  $\sum w[F_o^2 - (k^2 F_c^2)]^2$  by using all independent data. The final model included symmetry-allowed positional and anisotropic displacement parameters  $\beta_{ij}$  for all 35 atoms, except W, which was treated isotropically, the scale factor  $k$ , and an isotropic type  $I$  extinction parameter<sup>105</sup> for a total of 280 variable parameters. The refinement converged with fit indices  $R(F_o^2) = 0.105$ ,  $R_w(F_o^2) = 0.074$ ,  $R_w(F_o) = 0.039$ , GOF = 1.02 based on 2335 reflections.

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**Supporting Information Available:** Tables of crystal structure data for  $W(\text{PMe}_3)_4\text{H}_2\text{X}_2$  ( $X = \text{Cl}, \text{Br}$ ) and  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2(\text{FHF})$  (53 pages, print/PDF). See any current masthead page for ordering information and Web access instructions. Crystal structure data for  $W(\text{PMe}_3)_4\text{H}_2\text{F}_2$  and  $W(\text{PMe}_3)_4\text{H}_2\text{I}_2$  are provided in the Supporting Information of refs 11 and 43, respectively.

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