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Bis(trifluoromethyl)phosphane and Bis(pentafluorophenyl)phosphane and Their Pentacarbonyl Tungsten Complexes: Improved Synthesis and an Experimental and Density Functional Study

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The use of Bu_3SnH and Me_3SnH in the synthesis of $HP(CF_3)_2$ and $HP(C_6F_5)_2$ from the corresponding bromides leads to a high-yield synthesis, which additionally provides these compounds in large quantities. The pentacarbonyl tungsten complexes $[W(CO)_5PH(CF_3)_2]$ and $[W(CO)_5PH(C_6F_5)_2]$ were synthesized reacting the corresponding phosphanes with $[W(CO)_5THF]$ and characterized by X-ray and elemental analysis as well as multinuclear NMR and mass spectroscopy. The vibrational analyses of $HP(CF_3)_2$ and $HP(C_6F_5)_2$ and their tungsten pentacarbonyl complexes were achieved in combination with hybrid DFT calculations. The optimized structures of $[W(CO)_5PH(CF_3)_2]$ and $[W(CO)_5PH(C_6F_5)_2]$ at the B3PW91 level of theory using a LanL2DZ basis and ECP at the tungsten atom and a 6-311G(3d,p) and 6-311G(d,p) basis set for the nonmetal atoms, respectively, yield an impressively good agreement between experimental and theoretical geometric parameters. An increased π-acidity of $HP(CF_3)_2$ in comparison with $HP(C_6F_5)_2$ and $HPPh_2$ is discussed in the context of vibrational analysis, X-ray structural investigations, and theoretical calculations.

Introduction

Bis(trifluoromethyl)phosphane, $HP(CF_3)_2$, and bis(pentafluorophenyl)phosphane, $HP(C_6F_5)_2$, are important compounds for the synthesis of nucleophilic bis(trifluoromethyl)phosphanide and bis(pentafluorophenyl)phosphanide synthons,[1] which are essential in the synthesis of chiral bidentate bis(perfluoroorganyl)phosphane ligands.

Trifluoromethylphosphanes have been known since 1953 and have been synthesized by an autoclave reaction of white phosphorus and CF_3I.[2] A more convenient access is based on the Ruppert procedure[3] which was improved for the synthesis of $Et_2NP(CF_3)_2$ by Röschenthaler and co-workers.[4] Several methods for the synthesis of bis(trifluoromethyl)phosphane have been published.[5] The reaction of $(CF_3)_2PI$ and elemental mercury in the presence of an excess of HI is suitable for the synthesis of small quantities of $HP(CF_3)_2$.[5] The reaction of $(CF_3)_2PI$ with an excess of Me_3SnH produces larger amounts of $HP(CF_3)_2$ but requires a fractional condensation of the very air sensitive mixture.[6]

The synthesis of pentafluorophenylphosphanes is based on the reaction of C_6F_5MgBr and phosphorus halides.[7,8] Bis(pentafluorophenyl)phosphane was first synthesized by reacting $(C_6F_5)_2PX$ (X = Cl, Br) with $LiAlH_4$[8] in Et_2O as a solvent, followed by aqueous workup.[9] A less practical reaction is based on the reduction of $(C_6F_5)_2PCl$ with PH_3 in a sealed glass tube.[10]

In this paper convenient, large-scale and high-yield syntheses for $HP(CF_3)_2$ and $HP(C_6F_5)_2$ are presented. Al-

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(1) (a) Hoge, B.; Thösen, C. *Inorg. Chem.* **2001**, *40*, 3113−3116. (b) Hoge, B.; Thösen, C.; Pantenburg I. *Inorg. Chem.* **2001**, *40*, 3084−3088. (c) Hoge, B.; Thösen, C.; Herrmann, T.; Pantenburg I. *Inorg. Chem.* **2002**, *41*, 2260−2265.

(2) Bennett, F. W.; Emeléus, H. J.; Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1565−1571.

(3) Ruppert, W.; Ruppert, I. *Tetrahedron Lett.* **1983**, *24*, 5509−5512.

(4) Kolomeitsev, A.; Görg, M.; Dieckbreder, U.; Lork, E.; Röschenthaler, G.-V. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *109*−*110*, 597−600.

(5) Cavell, R. G.; Dobbie, R. C. *J. Chem. Soc. A* **1967**, 1308−1310 and literature cited therein.

(6) Ansari, S.; Grobe, J. *Z. Naturforsch.* **1975**, *30b*, 651−652. Grobe, J.; Le Van, D.; Demuth, R. *J. Fluorine Chem.* **1988**, *39*, 385−395.

(7) Wall, L. A.; Donadio, R. E.; Pummer, W. J. *J. Am. Chem. Soc.* **1960**, *82*, 4846−4848. Fild, M.; Glemser, O.; Christoph, G. *Angew. Chem.* **1960**, *76*, 953. Cowley, A. H.; Pinnell R. P. *J. Am. Chem. Soc.* **1966**, *88*, 4533−4534.

(8) Fild, D.; Glemser, O.; Hollenberg, I. *Z. Naturforsch.* **1966**, *21B*, 920−923.

(9) Goerlich, J. R.; Plack, V.; Schmutzler, R. *J. Fluorine Chem.* **1996**, *76*, 29−35.

(10) Cooke, M.; Green, M.; Kirkpatrick, D. *J. Chem. Soc. A* **1968**, 1507−1510.

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though $HP(CF_3)_2$ and $HP(C_6F_5)_2$ have been known for a long time, no X-ray structural data of these compounds or their transition metal complexes have been reported. They are described here in order to gain insight into the coordination ability of these ligands.

Experimental Section

Materials and Apparatus. Chemicals were obtained from commercial sources and used without further purification. Bromobis(pentafluorophenyl)phosphane was synthesized by the reaction of C_6F_5MgBr and PBr_3 according to the literature procedure.[8] Bromobis(trifluoromethyl)phosphane was synthesized by treating neat $(CF_3)_2PNEt_2$[4] with gaseous HBr at −78 °C. ***CAUTION!*** The toxic compounds $(CF_3)_2PBr$ and $HP(CF_3)_2$ react violently with air. Solvents were purified by standard methods.[11] Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques.

Infrared spectra were recorded on a Nicolet-5PC−FT-IR spectrometer as KBr pellets or in a 10 cm gas cell. Raman spectra were measured on a Bruker FRA-106/s spectrometer with a Nd:YAG laser operating at $\lambda = 1064$ nm.

The NMR spectra were recorded on Bruker model AMX 300 (^{13}C, 75.47 MHz; ^{31}P, 121.50 MHz; ^{19}F, 282.35 MHz) and Bruker AC200 spectrometers (^{31}P, 81.01 MHz; ^{19}F 188.31 MHz; ^{13}C, 50.32 MHz; ^{1}H, 200.13 MHz) with positive shifts being downfield from the external standards 85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and TMS (^{13}C and ^{1}H). Calculations of NMR spectra were carried out with the program gNMR.[12] Quantum chemical hybrid density functional calculations were performed with the Gaussian 98 program package.[13]

Preparation of Bis(pentafluorophenyl)phosphane. Me_3SnH (1.98 g, 12.0 mmol) was condensed onto a solution of 4.33 g (9.7 mmol) of $(C_6F_5)_2PBr$ in 20 mL of hexane. The colorless solution was stirred for 30 min at room temperature. Removal of all volatile compounds in vacuo yielded 3.55 g (9.7 mmol, 100%) of $HP(C_6F_5)_2$ as a white powder (mp 49−51 °C). Elemental anal. (calcd for $C_{12}HF_{10}P$): H 0.35 (0.28); C 39.26 (39.37). NMR data ($CDCl_3$; rt): $\delta(^1H)$ 5.4 (d, quin) ppm; $\delta(^{31}P)$ −137.7 (d) ppm; $\delta(^{19}F_o)$ −128.3 ppm (m, 2F); $\delta(^{19}F_m)$ −159.6 ppm (m, 2F); $\delta(^{19}F_p)$ −149.3 ppm (m, 1F); $^4J(HF)$ 4.3 Hz; $^1J(PH)$ 236.5 Hz. Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 366 (98) $[HP(C_6F_5)_2{}^+]$; 198 (100) $[PC_6F_5{}^+]$.

Preparation of Pentacarbonylbis(pentafluorophenyl)phosphanetungsten, $[W(CO)_5PH(C_6F_5)_2]$.[14] To a freshly prepared, intensely red, solution of 6.00 g (15.1 mmol) $[W(CO)_5THF]$ in 200 mL of THF was added 5.03 g (13.7 mmol) of $HP(C_6F_5)_2$. After stirring for 10 h at room temperature, the red solution was concentrated in vacuo, giving a green oily residue, which was extracted with 200 mL of hexane. The pale green solution was concentrated in vacuo and stored at −20 °C for 1 day, yielding 6.44 g (9.3 mmol, 68%) of colorless crystals (mp 87 °C, dec at 90 °C in a molten glass capillary). Single crystals were obtained by sublimation at 65 °C in vacuo (5×10^{-4} mbar). Elemental anal. (calcd for $C_{17}HF_{10}O_5PW$): C 29.52 (29.59); H 0.25 (0.15). NMR data (THF; rt): $\delta(^{31}P)$ −100.1 ppm; $\delta(^{19}F_o)$ −131.2 ppm (m, 2F); $\delta(^{19}F_m)$ −160.3 ppm (m, 2F); $\delta(^{19}F_p)$ −148.5 ppm (m, 1F); $\delta(^{13}CO_{tr})$ 196.3 ppm (d); $\delta(^{13}CO_{cis})$ 194.0 ppm (d); $\delta(^{13}C_i)$ 103.6 ppm (m), $\delta(^{13}C_{o/m})$ 146.5 ppm (d; $^1J(FC)$ 251 Hz, m), respectively. 137.6 ppm (d; $^1J(FC)$ 258 Hz, m); $\delta(^{13}C_p)$ 143.6 ppm (d; $^1J(FC)$ 261 Hz, m); $\delta(^1H)$ 7.6 ppm; $^1J(PH)$ 380.5 Hz; $^1J(WP)$ 249.9 Hz; $^1J(W(^{13}CO)_{tr})$ 174.6 Hz; $^1J(W(^{13}CO)_{cis})$ 125.6 Hz; $^2J(P(^{13}CO)_{tr})$ 29.6 Hz; $^2J(P(^{13}CO)_{cis})$ 5.7 Hz. Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 690 (18) $[W(CO)_5PH(C_6F_5)_2]^+$; 662 (20) $[W(CO)_4PH(C_6F_5)_2]^+$; 634 (18) $[W(CO)_3PH(C_6F_5)_2]^+$; 606 (1) $[W(CO)_2PH(C_6F_5)_2]^+$; 578 (3) $[W(CO)PH(C_6F_5)_2]^+$; 550 (3) $[WPH(C_6F_5)_2]^+$; 532 (100) $[P(C_6F_5)_3]^+$; 365 (17) $[P(C_6F_5)_2]^+$; 198 (8) $[P(C_6F_5)]^+$.

Preparation of Bis(trifluoromethyl)phosphane. $(CF_3)_2PBr$ (7.33 g, 29.4 mmol) was condensed onto 9.90 g (34.0 mmol) of Bu_3SnH which was degassed in advance at room temperature in vacuo. After stirring for 45 min at 0 °C, the only volatile compound $HP(CF_3)_2$ was condensed into a stopcock vessel, yielding 4.984 g (29.3 mmol, 99.9%) of $HP(CF_3)_2$ as a colorless liquid. NMR data ($CDCl_3$; rt): $\delta(^1H)$ 5.3 (d, sep) ppm; $\delta(^{31}P)$ −48.0 (d, sep) ppm; $\delta(^{19}F)$ −47.3 ppm (d, d); $\delta(^{13}C)$ 128.5 ppm (q, mult); $^1J(CF)$ 317 Hz; $^1J(PH)$ 240.7 Hz; $^2J(PF)$ 60.6 Hz; $^3J(FH)$ 10.0 Hz.

Preparation of Pentacarbonyl[bis(trifluoromethyl)phosphane]tungsten, $[W(CO)_5PH(CF_3)_2]$.[15] $HP(CF_3)_2$ (2.55 g, 15.0 mmol) was condensed onto a freshly prepared, intensely red solution of 4.80 g (12.1 mmol) of $[W(CO)_5THF]$ in 200 mL of THF. After the mixture was stirred for 10 h at room temperature, the red solution was concentrated to 5 mL to give a green oil. The residue was extracted with 200 mL of hexane. The slight green solution was concentrated in vacuo and stored at −20 °C for 1 day, yielding 2.69 g (5.4 mmol, 45%) of colorless crystals. Single-crystals were obtained by sublimation at room temperature in a nitrogen atmosphere. Elemental anal. (calcd for $C_7HF_6O_5PW$): H 0.28 (0.20); C 17.13 (17.02). NMR data ($CDCl_3$): $\delta(^{31}P)$ 1.7 ppm (d, sep); $\delta(^{19}F)$ −54.9 ppm (d,d); $\delta(^{13}CO_{tr})$ 193.7 ppm (d); $\delta(^{13}CO_{cis})$ 191.4 ppm (d); $\delta(^{13}CF_3)$ 124.5 ppm (q,d,q); $\delta(^1H)$ 6.5 ppm; $^1J(PH)$ 359.5 Hz; $^1J(WP)$ 268.8 Hz; $^1J(FC)$ 319.1 Hz; $^1J(PC)$ 65.8 Hz; $^1J(W(^{13}CO)_{tr})$ not observed; $^1J(W(^{13}CO)_{cis})$ 124.5 Hz; $^2J(PF)$ 75.9 Hz; $^2J(P(^{13}CO)_{tr})$ 32.3 Hz; $^2J(P(^{13}CO)_{cis})$ 6.7 Hz; $^3J(FC)$ 3.5 Hz; $^3J(FH)$ 6.4 Hz. Mass spectrum (EI, 20 eV) {*m/z* (%) [assignment]}: 494 (100) $[W(CO)_5PH(CF_3)_2]^+$; 466 (8) $[W(CO)_4PH(CF_3)_2]^+$; 425 (6) $[W(CO)_5PH(CF_3)]^+$; 397 (7) $[W(CO)_4PH(CF_3)]^+$; 369 (5) $[W(CO)_3PH(CF_3)]^+$; 354 (16) $[WPH(CF_3)_2]^+$; 324 (12) $[W(CO)_5]^+$; 296 (24) $[W(CO)_4]^+$; 268 (22) $[W(CO)_3]^+$; 240 (4) $[W(CO)_2]^+$; 151 (15) $[HP(CF_3)CF_2]^+$; 131 (8) $[CF_3PCF]^+$; 113 (6) $[CF_3PCH]^+$; 69 (4) $[CF_3]^+$.

X-ray Crystallography. One suitable single crystal of each compound was carefully selected under a polarizing microscope and mounted in a glass capillary. The scattering intensities were collected by an imaging plate diffractometer (IPDSII, STOE & CIE) equipped with a normal focus, 1.75 kW, sealed tube X-ray source (Mo Kα, $\lambda = 71.073$ pm) operating at 50 kV and 40 mA. Intensity

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[11] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals;* Pergamon Press: Oxford, England, 1980.

[12] Budzelaar, P. H. M.; *gNMR*, version 4.1; Cherwell Scientific: Oxford, U.K., 1998.

[13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

[14] Green, M.; Taunton-Rigby, A.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 1875−1878.

[15] Grobe, J.; Le Van, D.; Meyring, W. *Z. Anorg. Allg. Chem.* **1990**, *586*, 149−158.

data for $HP(C_6F_5)_2$ were collected at room temperature by ω-scans in 100 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 20°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 10 min) in the 2θ range 2.3−59.5°. Intensity data for $[W(CO)_5PH(C_6F_5)_2]$ were collected at 170 K by ω-scans in 123 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 66°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 5 min) in the 2θ range 2.3−59.5°. The intensity data for $[W(CO)_5PH(CF_3)_2]$ were collected at 260 K by ω-scans in 120 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 60°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 2 min) in the 2θ range 2.3−59.5°. Cooling down to temperatures lower than 260 K caused damage of the crystal, probably due to a phase transition. Structure solutions and refinements were carried out using the programs SHELXS-97[16] and SHELXL-93.[17] The H atom positions were taken from the difference Fourier card at the end of the refinement. Due to the presence of heavy atoms in the crystal structures of $[W(CO)_5PH(C_6F_5)_2]$ and $[W(CO)_5PH(CF_3)_2]$, numerical absorption corrections were applied after optimization of the crystal shapes (X-RED[18] and X-SHAPE[19]). The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. Details of the refinements are given in Table 2.

Results and Discussion

Several attempts to synthesize $HP(C_6F_5)_2$ by reduction of $(C_6F_5)_2PCl$ or $(C_6F_5)_2PBr$ with $LiAlH_4$ gave $H_2PC_6F_5$ as a byproduct, even at −90 °C in THF solution. After filtration and evaporation of the solvent, it was possible to remove $H_2PC_6F_5$[20] in vacuo, yielding crude $HP(C_6F_5)_2$ contaminated with lithium and aluminum salts. To remove the salt contaminations, an aqueous workup was necessary as previously reported.[9] Our own experiments revealed $(C_6F_5)_2P(O)H$[21] and $(C_6F_5)_2P(O)OH$[21,22] as major impurities after aqueous workup. Therefore, we investigated the use of triorganylstannanes, R_3SnH, as reducing reagents. Due to its different volatility, Me_3SnH turned out to be the reagent of choice for the transformation of $(C_6F_5)_2PBr$ into $HP(C_6F_5)_2$. The treatment of $(C_6F_5)_2PBr$ with an excess of Me_3SnH in hexane solution at room temperature selectively yields $HP(C_6F_5)_2$. The product is obtained in a quantitative yield as an analytically pure white powder, after evaporation of all volatile compounds in vacuo.

$$Me_3SnH + (C_6F_5)_2PBr \xrightarrow[\text{hexane}]{\text{rt}} Me_3SnBr + HP(C_6F_5)_2$$

In comparison with $(C_6F_5)_2PBr$ or $(C_6F_5)_2PCl$, which both are liquids at room temperature, $HP(C_6F_5)_2$ melts at 49−51 °C (lit.[8] mp 52 °C). The higher melting point of this phosphane compared with those of the corresponding halogene phosphanes is striking. For example, Ph_2PH melts at −14 °C, 30 °C lower than Ph_2PCl. The boiling point of Ph_2PH is 40 °C lower than that of chlorodiphenylphosphane. To find out whether intermolecular fluorine···hydrogen bridges are responsible for the unexpected higher melting point of $HP(C_6F_5)_2$ a structural investigation was undertaken.

Previous investigations showed that hybrid density functional theory B3PW91 is a reliable tool for structural as well as vibrational predictions for perfluoroorganyl phosphorus derivatives.[1a,c] The experimental IR and Raman spectroscopic data of $HP(C_6F_5)_2$ are listed in Table 1 and compared to theoretical data calculated at the B3PW91/6-311G(d,p) level of theory. It should be noted that no vibrational data of $HP(C_6F_5)_2$ have been previously published. The optimized structure of $HP(C_6F_5)_2$ exhibits a pyramidal arrangement around the central phosphorus atom with the sum of bond angles being 290.2°. The two C_6 planes of the C_6F_5 rings are twisted, as depicted in Figure 1, resulting in two rotational enantiomers of the $HP(C_6F_5)_2$ molecule. Depending on the spatial difference of the two C_6F_5 groups, the theoretical model predicts two sets of C_6F_5X fundamental vibrations. Depending on the minor spatial difference of the two C_6F_5 groups, the two sets of C_6F_5X fundamentals could not be completely resolved in the experimental spectra. To fit the theoretical vibrational frequencies to experimental infrared and Raman data, a scaling factor of 0.98 was used. After this operation theoretical and experimental frequencies agreed excellently, cf. Table 1. The P−H valence mode exhibits a difference of less than 40 cm^{-1} between the predicted mode of an isolated $HP(C_6F_5)_2$ molecule and the experimental frequency of polyatomic material, which might be interpreted in terms of only weak intermolecular interactions.

Bis(pentafluorophenyl)phosphane sublimes upon gentle warming (35 °C) on a water bath at a pressure of 5×10^{-4} mbar yielding colorless crystals. The X-ray structure analysis results in a monoclinic space group ($P2_1/c$) with four $HP(C_6F_5)_2$ molecules per unit cell, Table 2. The molecular structure of $HP(C_6F_5)_2$ is depicted in Figure 1, and selected bond lengths and angles are listed in Table 3. The experimental molecular dimensions of the $HP(C_6F_5)_2$ molecule are in good agreement with the optimized structure at the B3PW91/6-311G(d,p) level of theory, for example, [calculated]/X-ray d(PH) [141.5]/142(16) pm, d(PC) [184.9]/183.2(6) pm; [184.8]/183.5(6) pm, $d(CF)_{\varnothing}$ [133.1]/134.5 pm, $\angle$(CPC) [99.9]/100.1(3)°. Even the calculated and experimental CCPC dihedral angles, C21−P1−C11−C16 and C11−P1−C21−C22, Figure 1, which specify the torsion of the C_6F_5 groups, exhibit comparable values of [70.2]/66.2° and [63.2]/65.1°, respectively. As to be expected for a centrosymmetric space group, both rotational enantiomers are present in the unit cell.

The crystal structure of $HP(C_6F_5)_2$ exhibits intermolecular H···F interactions (H1−F13′, cf. Figures 1−3) of 251(2) pm, forming two sets of polymeric chains each with one rotational enantiomer along the crystallographic axis b, Figure 2. Figure 3 depicts the unit cell in the a, c plane, looking along the polymeric chains oriented on the b axis. The unit cell exhibits a very tight packing of the polymeric chains, which are

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(16) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Analysis*; University of Göttingen: Göttingen, 1998.

(17) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, 1993.

(18) *X-RED 1.22, STOE Data Reduction Program*; Darmstadt, 2001.

(19) *X-SHAPE 1.06, Crystal Optimization for Numerical Absorption Correction*; Darmstadt, 1999.

(20) Furin, G. G.; Krupoder, S. A.; Rezvukhin, A. I.; Kilina, T. M.; Yakobson, G. G. *J. Fluorine Chem.* **1983**, *22*, 345−376.

(21) A selective synthesis combined with experimental and spectroscopic data of $(C_6F_5)_2P(O)H$ and $(C_6F_5)_2P(O)OH$ will be published elsewhere.

(22) Oliver, K. W.; Rettig, S. J.; Thompson, R. C.; Trotter, J.; Xia, S. *J. Fluorine Chem.* **1997**, *83*, 47−50.

Table 1. Calculated Vibrational Frequencies and Observed Infrared and Raman Spectra of Solid $HP(C_6F_5)_2$ and the Data of the $HP(C_6F_5)_2$ Moiety in the Complex $[W(CO)_5PH(C_6F_5)_2]$[a]

	$HP(C_6F_5)_2$					$[W(CO)_5PH(C_6F_5)_2]$[a]				
	IR	RA	calc'd[b]	[IR][c]	(RA)[c]	IR	RA	calc'd[d]	[IR][c]	(RA)[c]
ν(PH)	2370 w	2368 (52)	2406.2	[2.0]	(100)	2400 w	2411 (4)	2441.9	[0.2]	(33.3)
ν(CC)	1643 m	1643 (54)	1647.0	[3.0]	(72.5)	1643 m	1644 (7)	1648.1	[1.9]	(31.5)
			1643.7	[7.6]	(30.1)			1645.6	[4.1]	(21.3)
	1630 w	1630 sh	1633.5	[0.4]	(6.4)			1634.6	[0.6]	(2.7)
			1632.4	[1.2]	(6.5)			1633.8	[0.4]	(2.0)
ν(CC)/ ν(CF)	1515 vs	1515 (3)	1520.9	[19.4]	(3.2)	1519 m		1525.1	[10.7]	(1.1)
			1517.8	[42.8]	(0.4)			1521.5	[17.0]	(0.2)
	1479 vs		1498.5	[100]	(0.6)	1484 s		1501.4	[31.3]	(0.1)
			1493.8	[14.2]	(0.5)			1495.1	[6.2]	(0.2)
	1401 w	1397 (22)	1403.3	[0.4]	(31.5)	1400 w		1402.3	[2.3]	(9.7)
	1388 m		1389.8	[7.0]	(6.4)	1386 w	1399 (3)	1389.8	[2.1]	(5.2)
	1294 m	1290 (6)	1316.9	[0.2]	(4.7)			1318.3	[0.0]	(0.6)
			1313.1	[0.5]	(1.8)			1315.3	[0.1]	(0.7)
	1289 sh	1280 (7)	1284.6	[2.1]	(1.6)	1295 w	1297 (2)	1290.5	[1.6]	(1.0)
			1281.2	[4.2]	(1.9)			1287.5	[2.4]	(1.1)
ν(CF)	1146 w	1142 (5)	1149.0	[1.2]	(0.6)	1144 vw	1148 (2)	1152.2	[1.1]	(0.4)
			1145.3	[0.3]	(0.9)			1148.6	[0.1]	(0.5)
	1092 s	1095 (8)	1097.0	[22.0]	(0.5)	1093 m		1101.2	[11.0]	(0.7)
			1091.0	[28.7]	(0.2)			1095.9	[12.8]	(0.1)
			1002.3	[5.4]	(0.4)			1003.0	[1.0]	(0.2)
	982 s	983 (2) br	991.1	[42.6]	(0.5)	986 m		997.1	[12.9]	(0.2)
δ(PH)	908 m	908 (9)	907.7	[3.8]	(6.5)	921 w	921 (2)	909.6	[2.3]	(2.2)
δ(PH)	854 m	854 (12)	846.6	[2.8]	(7.3)	892 w. br	895 (2)	890.1	[6.3]	(3.4)
ν(PC)	844 m	844 (8)	833.3	[3.3]	(3.6)	849 vw	848 (4)	837.6	[0.9]	(4.9)
ν(PC)	823 m	825 (16)	815.5	[3.0]	(10.8)			835.5	[0.3]	(4.7)
δ(CCF) in plane	724 w	726 (2)	741.2	[0.4]	(1.6)		749 (2)	742.8	[0.2]	(0.9)
	712 w	713 (4)	710.9	[1.2]	(3.0)			741.5	[0.5]	(0.6)
δ(CCC) out of plane			670.1	[1.5]	(0.6)			676.5	[0.8]	(0.7)
		654 (1)	660.3	[0.2]	(0.4)			667.2	[0.3]	(0.3)
			656.5	[0.0]	(0.1)			654.8	[0.0]	(0.1)
			650.1	[0.0]	(0.1)			652.5	[0.0]	(0.1)
	637 m	637 (2)	637.4	[0.8]	(0.7)	635 vw	635 (2)	639.0	[0.8]	(1.8)
		616 (2)	622.0	[0.1]	(1.3)		624 (1)	628.7	[0.4]	(0.7)
δ(CCC) in plane	586 vw	585 (64)	574.4	[0.1]	(8.3)		587 (6)	574.9	[0.0]	(4.1)
			572.5	[0.0]	(15.6)			573.7	[0.0]	(6.3)
	509 m	506 (100)	502.5	[0.9]	(3.7)	511 vw	510 (9)	505.7	[0.5]	(1.6)
			498.8	[0.3]	(21.2)			502.1	[1.4]	(8.4)
		444 (55)	437.9	[0.0]	(2.9)			439.8	[0.1]	(2.0)
			436.9	[0.0]	(7.2)			437.6	[0.1]	(3.0)
δ(CCF) out of plane	421 m	421 (21)	419.4	[1.9]	(3.3)	423 w		427.0	[3.4]	(4.6)
		393 (75)	398.8	[0.0]	(2.8)		391 (7)	395.7	[0.3]	(1.1)
			397.6	[0.0]	(3.1)			394.2	[0.1]	(0.8)
		367 (22)	380.8	[1.6]	(3.3)			383.7	[0.4]	(0.7)
		359 sh	362.2	[0.0]	(2.7)			370.3	[0.3]	(0.2)
			356.2	[0.1]	(0.5)		338 (4)	335.3	[1.4]	(1.8)
			313.4	[2.1]	(0.1)			321.7	[0.6]	(0.1)
			305.9	[0.2]	(0.0)			310.2	[0.1]	(0.1)
			305.4	[0.2]	(0.5)			306.5	[0.0]	(0.1)
		306 (20)	299.8	[0.3]	(1.9)			295.7	[0.2]	(0.3)
		279 (16)	271.2	[0.0]	(0.6)		279 (2)	273.8	[0.0]	(0.2)
			270.9	[0.0]	(0.3)			269.6	[0.0]	(0.2)
			268.2	[0.0]	(0.1)			267.6	[0.0]	(0.1)
			267.1	[0.0]	(0.1)			266.5	[0.0]	(0.0)
		228 (19)	222.3	[0.4]	(0.6)		233 (2)	226.3	[0.2]	(0.2)
			214.9	[0.2]	(0.1)			218.1	[0.1]	(0.0)
		208 (10)	201.4	[0.2]	(0.4)					
		180 (8)	166.7	[0.0]	(0.2)					
			160.7	[0.0]	(0.0)					
		136 (21)	130.9	[0.0]	(0.7)					
			127.9	[0.0]	(0.1)					
			127.4	[0.0]	(0.1)					
			103.8	[0.0]	(0.3)					
			77.6	[0.0]	(0.1)					
			24.7	[0.0]	(4.1)					
			22.1	[0.0]	(1.6)					
			17.1	[0.0]	(2.2)					

[a] The vibrational frequencies of the $W(CO)_5$ unit are summarized in Table 7. [b] B3PW91 functional and 6-311G(d,p) basis set, frequencies are scaled by a factor of $f = 0.98$. [c] Relative intensities are given. [d] B3PW91 functional and a LanL2DZ basis and ECP on tungsten and a 6-311G(d,p) basis set for the nonmetal atoms. The frequencies are scaled by a factor of $f = 0.98$.

geared by terminal C_6F_5 groups. The very good fit of the polymeric chains may be the reason for the unexpected high melting point of $HP(C_6F_5)_2$ rather than the very weak intermolecular H···F contacts. This is also supported by the

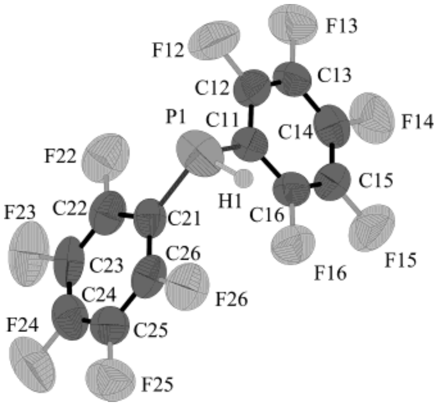

Figure 1. Molecular structure of $HP(C_6F_5)_2$ and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

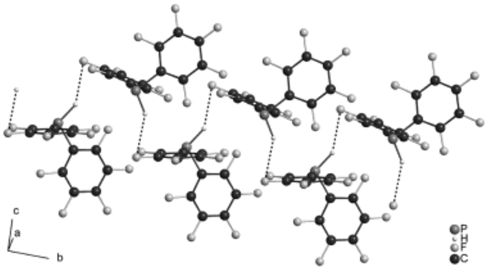

Figure 2. View showing a polymeric chain of $HP(C_6F_5)$ molecules, connected by H−F contacts.

Table 2. Crystal Data and Structure Refinement Parameters of $HP(C_6F_5)_2$ (**I**), $[W(CO)_5PH(C_6F_5)_2]$ (**II**), and $[W(CO)_5PH(CF_3)_2]$ (**III**)

	I	**II**	**III**
empirical formula	$HP(C_6F_5)_2$	$[W(CO)_5PH(C_6F_5)_2]$	$[W(CO)_5PH(CF_3)_2]$
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a [pm]	939.0(4)	1596.7(2)	661.3(2)
b [pm]	741.0(6)	747.8(1)	708.4(2)
c [pm]	1951.6(5)	1715.1(3)	1545.5(4)
α [deg]			77.22(2)
β [deg]	110.73(1)	107.36(1)	89.87(2)
γ [deg]			67.98(2)
vol [nm^3]	1.2700(13)	1.9544(5)	0.6519(3)
Z	4	4	2
formula mass	366.10	690.00	493.90
ρ_{calc} [g cm^{-3}]	1.915	2.345	2.516
μ [mm^{-1}]	0.335	6.116	9.069
abs correction	none	numerical	numerical
transm max/min	−/−	0.3942/0.6118	0.1175/0.4299
θ range [deg]	2.23−24.99	2.08−27.00	2.71−29.58
total data collected	5545	20001	7571
index range	$-13 \le h \le 12$ $-10 \le k \le 10$ $-27 \le l \le 26$	$-20 \le h \le 22$ $-8 \le k \le 10$ $-23 \le l \le 23$	$-9 \le h \le 9$ $-8 \le k \le 9$ $-21 \le l \le 21$
unique data	2199	4271	3492
obsd data	813	2789	1965
diffractometer	STOE image plate diffraction system		
radiation	Mo Kα (graphite monochromator, $\lambda = 71.073$ pm)		
temp [K]	298(2)	170(2)	260(2)
R_{merg}	0.1163	0.1000	0.0550
R indexes[a] [$I > 2\sigma(I)$]	R1 = 0.0612 wR2 = 0.1307	R1 = 0.0321 wR2 = 0.0411	R1 = 0.0356 wR2 = 0.0653
R indexes (all data)	R1 = 0.1711 wR2 = 0.1876	R1 = 0.0660 wR2 = 0.0453	R1 = 0.0832 wR2 = 0.0749
GOF (S_{obs})	1.163	0.945	0.949
GOF (S_{all})	0.876	0.825	0.799
no. of variables	213	312	186
F(000)	712	1288	452
largest diff map hole/peak [e 10^{-6} pm^{-3}]	−0.253/0.284	−1.177/0.974	−2.183/1.148

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$.

Table 3. Selected Bond Lengths (pm) and Angles (deg) of $HP(C_6F_5)_2$

P1	H1	142(16)	C11	P1	C21	100.1(3)	F15	C15	C16	120.9(6)
P1	C11	183.2(6)	C16	C11	C12	115.3(5)	F15	C15	C14	119.6(6)
P1	C21	183.5(6)	C16	C11	P1	122.6(5)	C16	C15	C14	119.5(6)
F12	C12	134.7(7)	C12	C11	P1	121.9(4)	C15	C16	F16	117.7(5)
F13	C13	133.9(7)	F12	C12	C13	117.7(6)	C15	C16	C11	123.5(6)
F14	C14	134.6(7)	F12	C12	C11	119.6(5)	F16	C16	C11	118.8(5)
F15	C15	134.9(7)	C13	C12	C11	122.7(6)	C26	C21	C22	114.2(6)
F16	C16	136.0(7)	F13	C13	C14	120.9(6)	C26	C21	P1	123.2(5)
F22	C22	135.1(7)	F13	C13	C12	120.5(6)	C22	C21	P1	122.5(6)
F23	C23	136.1(8)	C14	C13	C12	118.6(6)				
F24	C24	133.5(8)	F14	C14	C13	119.6(6)				
F25	C25	132.9(7)	F14	C14	C15	120.0(6)				
F26	C26	133.6(7)	C13	C14	C15	120.4(6)				

analysis of the vibrational data in comparison with quantum chemical calculations.

To exclude a probable influence of the intermolecular H···F interaction on geometric or vibrational data, a sterically demanding group, i.e., pentacarbonyl tungsten, was coordinated to $HP(C_6F_5)_2$.

Bis(pentafluorophenyl)phosphane reacts with a freshly prepared solution of $[W(CO)_5THF]$ in THF within 8 h at room temperature to give $[W(CO)_5PH(C_6F_5)_2]$.

$$[W(CO)_5THF] + HP(C_6F_5)_2 \xrightarrow[THF]{rt} THF + [W(CO)_5PH(C_6F_5)_2]$$

After removal of all volatiles and recrystallization from hexane, colorless crystals of $[W(CO)_5PH(C_6F_5)_2]$ were isolated in 70% yield, whereas the thermal reaction of $HP(C_6F_5)_2$ with $W(CO)_6$ gave the monosubstituted complex in only 34% yield.[14] The product, $[W(CO)_5PH(C_6F_5)_2]$, crystallizes in the monoclinic space group, $P2_1/n$, Table 2. The molecular structure of $[W(CO)_5PH(C_6F_5)_2]$ is depicted in Figure 4, and selected bond lengths and angles are summarized in Table 4. The packing of the unit cell in the *a*, *c* plane is shown in Figure 5. The crystal structure of $[W(CO)_5PH(C_6F_5)_2]$ exhibits no intermolecular H−F contacts below 300 pm. Geometric data of the $HP(C_6F_5)_2$ moiety in the complex $[W(CO)_5PH(C_6F_5)_2]$ are closely related to those of crystalline $HP(C_6F_5)_2$ and theoretical data of an isolated molecule. Only the P−H distance in the complex $[W(CO)_5PH(C_6F_5)_2]$ differs from the values for $HP(C_6F_5)_2$, but it overlaps within the error margin. Even the vibrational data of the $HP(C_6F_5)_2$ moiety in the complex $[W(CO)_5PH(C_6F_5)_2]$, Table 1, are nearly identical with those of $HP(C_6F_5)_2$ and prove that neither weak intermolecular H−F contacts in solid $HP(C_6F_5)_2$ nor the complexation by tungsten pentacarbonyl has a major influence on structural or vibrational data.

At first sight, the small difference between the P−H valence mode of the complex $[W(CO)_5PH(C_6F_5)_2]$ and solid $HP(C_6F_5)_2$ is surprising because the P−H valence mode of Ph_2PH is shifted by nearly 200 cm^{-1} to higher frequencies by complexation with pentacarbonyl tungsten.[23] Depending on the *σ*-donation of electron density from the phosphorus atom of Ph_2PH to the metal center, a more strongly polarized P−H bond results, indicated by a shift of the P−H valence

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[23] Smith, J. G.; Thompson, D. T. *J. Chem. Soc. A* **1967**, 1694−1697.

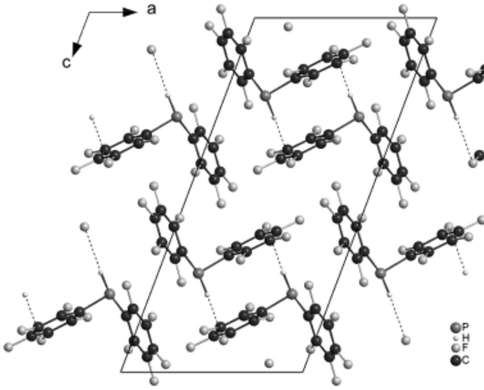

Figure 3. Unit cell packing of $HP(C_6F_5)_2$ in the *a*, *c* plane.

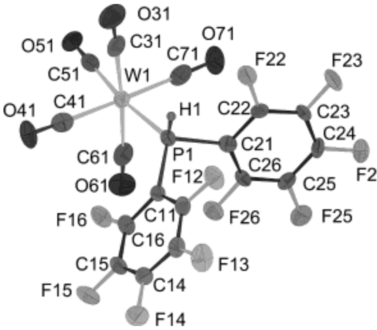

Figure 4. Molecular structure of $[W(CO)_5PH(C_6F_5)_2]$ and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Table 4. Selected Bond Lengths (pm) and Angles (deg) of $[W(CO)_5PH(C_6F_5)_2]$

P1	C21	182.7(6)	C21	P1	C11	100.4(2)	F16	C16	C11	120.1(5)
P1	C11	182.9(5)	C21	P1	W1	113.5(2)	C15	C16	C11	123.2(5)
P1	W1	247.7(1)	C11	P1	W1	127.8(2)	C51	W1	C31	89.5(2)
P1	H1	129(4)	C21	P1	H1	101(2)	C51	W1	C71	86.8(2)
W1	C51	201.1(6)	C11	P1	H1	94(2)	C31	W1	C71	91.6(3)
W1	C31	202.2(7)	W1	P1	H1	114(2)	C51	W1	C41	93.4(2)
W1	C71	202.3(7)	C16	C11	C12	115.2(5)	C31	W1	C41	86.8(3)
W1	C41	203.6(6)	C16	C11	P1	125.1(4)	C71	W1	C41	178.4(3)
W1	C61	205.1(7)	C12	C11	P1	119.7(4)	C51	W1	C61	90.1(2)
C31	O31	116.3(7)	F12	C12	C13	117.8(5)	C31	W1	C61	176.5(3)
C41	O41	115.7(6)	F12	C12	C11	119.3(5)	C71	W1	C61	91.8(3)
C51	O51	115.8(6)	C13	C12	C11	122.9(6)	C41	W1	C61	89.8(2)
C61	O61	113.6(7)	F13	C13	C14	120.9(5)	C51	W1	P1	173.1(2)
C71	O71	116.2(7)	F13	C13	C12	120.1(5)	C31	W1	P1	87.7(2)
C11	C16	138.7(7)	C14	C13	C12	119.0(5)	C71	W1	P1	86.9(2)
C11	C12	139.4(7)	F14	C14	C13	119.3(5)	C41	W1	P1	92.7(1)
C12	F12	134.4(6)	F14	C14	C15	119.9(5)	C61	W1	P1	93.1(2)
C12	C13	137.9(8)	C13	C14	C15	120.8(5)	O31	C31	W1	177.7(6)
C13	F13	134.0(6)	F15	C15	C16	120.9(5)	O41	C41	W1	178.1(5)
C13	C14	136.1(8)	F15	C15	C14	120.2(5)	O51	C51	W1	179.8(5)
C14	F14	134.5(6)	C16	C15	C14	118.9(5)	O61	C61	W1	176.7(6)
C14	C15	137.4(8)	F16	C16	C15	116.7(5)	O71	C71	W1	177.3(6)

mode to higher frequencies for the complex $[W(CO)_5PHPh_2]$. The π-back-bonding effect of Ph_2PH does not compensate the electron density transfer via the σ-donation. The increased π-acidity of perfluoroorganyl phosphanes compensates the electron transfer via the σ-donation from the phosphorus to the metal atom. As a consequence, complexation by pentacarbonyl group VI metals exhibits no significant influence on structural and vibrational data of perfluoroorganyl phosphanes.

The increased π-acidic character of $HP(C_6F_5)_2$ in comparison with Ph_2PH is also indicated by a shortening of the

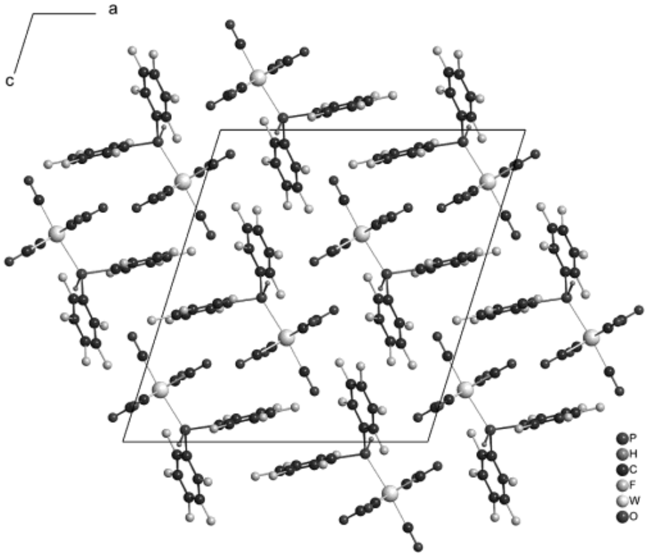

Figure 5. Unit cell packing of $[W(CO)_5PH(C_6F_5)_2]$ in the *a*, *c* plane.

W−P distance[24] by about 5 pm in the corresponding tungsten pentacarbonyl complexes and also is furthermore supported by a shift of the C−O valence modes to higher frequencies. The highest C−O valence mode of the complex $[W(CO)_5PH(C_6F_5)_2]$ at 2183 cm^{-1} is shifted by about 10 cm^{-1} to higher frequencies in comparison with $[W(CO)_5PHPh_2]$.[23]

Bis(trifluoromethyl)phosphane, commonly synthesized from halogeno bis(trifluoromethyl)phosphanes and trimethyltin hydride and isolated via fractional condensation, is conveniently prepared by substitution of the volatile Me_3SnH by the nonvolatile and commercially available Bu_3SnH. After the reaction of $(CF_3)_2PBr$ with a slight excess of Bu_3SnH at 0 °C without any solvent, pure $HP(CF_3)_2$ can be removed from the reaction mixture in vacuo as the only volatile compound in quantitative yield.

$$\mathrm{Bu_3SnH + (CF_3)_2PBr \xrightarrow[\text{neat}]{0\ ^{\circ}\text{C}} Bu_3SnBr + HP(CF_3)_2}$$

The experimental infrared and Raman data of $HP(CF_3)_2$ are identical with literature data[25,26] and in excellent agreement with theoretical data at the B3PW91/6-311G(3d,p) level of theory without using a scaling factor, Table 5. Only the calculated P−H valence mode deviates by about 80 cm^{-1} from the experimental value. The predicted geometric parameters of $HP(CF_3)_2$ with C_s symmetry are as follows: d(PH) 141.5 pm, d(PC) 188.8 pm, $d(\mathrm{CF})_{\varnothing}$ 134.0 pm, $\angle$(CPC) 99.3°, $\sum\angle$(P) 287.5°. The assignment and approximate mode description of the fundamental modes, as outlined in Table 5, are based on the calculated vibrational race and displacement vectors, respectively.

In analogy to bis(pentafluorophenyl)phosphane, bis(trifluoromethyl)phosphane reacts with a freshly prepared solu-

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(24) Reibenspies, J. H.; Darensborg, D.; Atnip, E. *Z. Kristallogr.* **1994**, *209*, 759−760.

(25) Bürger, H.; Cichon, J.; Grobe, J.; Demuth, R. *Spectrochim. Acta* **1973**, *29A*, 47−54.

(26) Dobbie, R. C.; Straughan, B. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2754−2756.

Table 5. Calculated Vibrational Frequencies and Observed Infrared and Raman Spectra of $HP(CF_3)_2$ and the Data of the $HP(CF_3)_2$ Moiety in the Complex $[W(CO)_5PH(CF_3)_2]^a$

		$HP(CF_3)_2$					$[W(CO)_5PH(CF_3)_2]^a$				
assignmt	mode descript	IR	RA	calc'd^b	[IR]^c	(RA)^c	IR	RA	calc'd^d	[IR]^c	(RA)^c
$\nu_1(A')$	$\nu(PH)$	2351 m	2354 (80)	2440.3	[4.6]	(100)	2388 w	2386 (7)	2446.0	[1.4]	(69.2)
$\nu_2(A')$	$\nu(CF)$	1209 vs	1206 br	1207.9	[95.2]	(1.5)	1215 s		1207.2	[25.4]	(0.4)
$\nu_3(A')$		1178 vs		1176.1	[100]	(1.7)	1205 s		1187.1	[13.1]	(0.3)
$\nu_{14}(A'')$			1153 br.sh	1169.6	[7.1]	(0.7)	1162 m	1169 (1)	1172.3	[1.5]	(0.3)
$\nu_4(A')$		1141 m		1148.6	[11.8]	(0.9)	1152 m	1154 (1)	1161.2	[0.2]	(0.7)
$\nu_{15}(A'')$		1128 vs	1130 br.sh	1133.1	[61.3]	(2.1)	1137 s	1135 (2)	1141.9	[9.6]	(2.0)
$\nu_{16}(A'')$				1116.8	[81.9]	(1.0)	1123 s	1115 (2)	1131.4	[5.4]	(0.3)
$\nu_{17}(A'')$	$\delta(PH)$	855 vw	852 (10)	860.7	[5.3]	(5.3)	854 sh	855 sh	882.9	[8.3]	(6.5)
$\nu_5(A')$		809 w	809 (12)	815.2	[11.4]	(5.8)	868 m	867 (5)	865.6	[1.7]	(2.1)
$\nu_{18}(A'')$	$\delta_s(CF_3)$	755 m		747.9	[2.7]	(0.2)	749 w		750.9	[0.0]	(5.3)
$\nu_6(A')$			744 (100)	747.1	[0.5]	(9.8)		749 (6)	750.1	[0.4]	(0.3)
$\nu_7(A')$	$\delta_{as}(CF_3)$	560 vw	557 (3)	559.9	[1.7]	(0.8)	558 sh	559 (3)	558.8	[2.0]	(1.5)
$\nu_{19}(A'')$				525.2	[0.1]	(0.2)			541.4	[0.0]	(0.3)
$\nu_{20}(A'')$				523.4	[0.0]	(0.4)			537.2	[0.1]	(0.0)
$\nu_8(A')$		525 vw	524 (5)	520.6	[1.0]	(0.4)			522.6	[0.0]	(0.1)
$\nu_9(A')$	$\nu_s(PC_2)$	441 m	440 (60)	443.0	[4.5]	(4.5)	464 m	469 (4)	469.8	[2.9]	(1.7)
$\nu_{21}(A'')$	$\nu_{as}(PC_2)$			436.4	[4.1]	(2.9)	456 w		458.3	[1.2]	(0.2)
$\nu_{10}(A')$	$\tau(CF_2)$	303 m*		298.9	[0.2]	(0.2)					
$\nu_{11}(A')$	$\rho(CF)$		279 (55)	275.9	[0.0]	(3.2)		283 (4)	279.1	[0.0]	(0.8)
$\nu_{22}(A'')$		255 w*	252 (8)	248.6	[0.2]	(0.7)			252.0	[0.0]	(0.3)
$\nu_{23}(A'')$				229.5	[0.0]	(0.2)			229.6	[0.0]	(0.1)
$\nu_{12}(A')$	$\delta(PC_2)$		120 (6)	118.9	[0.3]	(0.2)			106.3	[0.0]	(0.2)
$\nu_{13}(A')$	$\tau(CF_3)$			61.8	[0.1]	(0.0)					
$\nu_{24}(A'')$				25.6	[0.0]	(0.0)			29.1	[0.0]	(0.0)

[a] The vibrational frequencies of the $W(CO)_5$ unit are summarized in Table 7. [b] B3PW91 functional and 6-311G(3d,p) basis set. [c] Relative intensities are given. [d] B3PW91 functional and a LanL2DZ basis and ECP on tungsten and a 6-311G(3d,p) basis set for the nonmetal atoms.

tion of $[W(CO)_5THF]$ in THF within 8 h at room temperature to $[W(CO)_5PH(CF_3)_2]$.

$$[W(CO)_5THF] + HP(CF_3)_2 \xrightarrow[THF]{rt} THF + [W(CO)_5PH(CF_3)_2]$$

Removal of all volatiles and recrystallization from hexane results in colorless crystals of $[W(CO)_5PH(CF_3)_2]$ in 45% yield. In contrast to neat $HP(CF_3)_2$, which reacts violently with air, $[W(CO)_5PH(CF_3)_2]$ exhibits no reaction upon short contact with air. In an earlier paper $[W(CO)_5PH(CF_3)_2]$ was described as a thermal sensitive oil.[15] However, no obvious decomposition of the solid material was apparent during a period of 2 weeks at room temperature. The erroneous notice, that $[W(CO)_5PH(CF_3)_2]$ decomposes at 40 °C in vacuo, may be attributed to the high sublimation pressure of the complex.

Colorless single crystals were obtained by room temperature sublimation. The X-ray structure analysis results in a triclinic space group, $P\bar{1}$, Table 2. The molecular structure of $[W(CO)_5PH(CF_3)_2]$ is shown in Figure 6, and selected bond lengths and angles are summarized in Table 6. The unit cell packing in the *a*, *c* plane is depicted in Figure 7. The complex molecules are oriented in such a manner that they form fluorous layers in the *a*, *b* plane, with intermolecular H···O contacts (H1−O18′, cf. Figures 6 and 7) of 249(3) pm.

The vibrational frequencies of the $HP(CF_3)_2$ moiety in the complex $[W(CO)_5PH(CF_3)_2]$ are comparable with those of noncomplexed $HP(CF_3)_2$, except for the P−H valence and one hydrogen deformation mode. The H−P−W deformation mode of approximately A′ symmetry involves a back and forth moving of the hydrogen atom to the tungsten atom, while the hydrogen deformation mode of approximately A″ symmetry involves a sidelong moving of the hydrogen atom to the tungsten atom and is therefore less influenced in comparison to noncomplexed $HP(CF_3)_2$. The PH valence mode of $HP(CF_3)_2$ is shifted by around 30 cm^{-1} to higher frequencies by complexation with tungsten pentacarbonyl. This comparably small shift may be attributed to the increased π-acidity of $HP(CF_3)_2$ as already discussed for the corresponding Ph_2PH and $HP(C_6F_5)_2$ complexes.

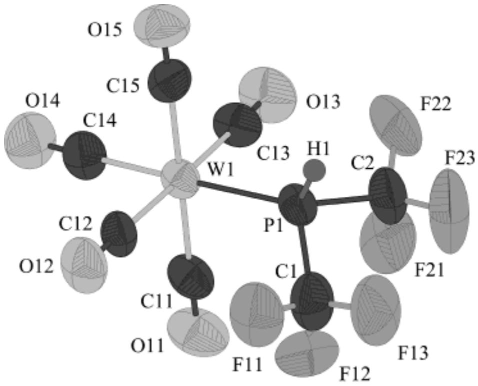

Figure 6. Molecular structure of $[W(CO)_5PH(CF_3)_2]$ and the atom-numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

The carbonyl stretching frequencies of $[W(CO)_5PH(C_6F_5)_2]$ and $[W(CO)_5PH(CF_3)_2]$ indicate a higher π-acidity of $HP(CF_3)_2$, as it is evaluated by an increased shift of the C−O valence modes to higher frequencies, Table 7. The W−P distances of $[W(CO)_5PH(C_6F_5)_2]$ and $[W(CO)_5PH(CF_3)_2]$, 247.7 and 242.3 pm, respectively, agree with the increased π-back-bonding effect for the $HP(CF_3)_2$ ligand.

The ^{31}P NMR resonances of $HP(C_6F_5)_2$ and $HP(CF_3)_2$ are shifted by about 37 and 50 ppm, respectively, to lower field by coordination to pentacarbonyl tungsten, while the $^1J(PH)$

Table 6. Selected Bond Lengths (pm) and Angles (deg) of $[W(CO)_5PH(CF_3)_2]$

W1	C14	200(1)	C14	W1	C11	90.2(4)	C2	P1	C1	99.4(5)
W1	C11	202(1)	C14	W1	C13	87.9(3)	C2	P1	W1	117.3(3)
W1	C13	203.0(7)	C11	W1	C13	89.2(3)	C1	P1	W1	118.8(3)
W1	C15	204(1)	C14	W1	C15	89.8(4)	C2	P1	H1	103(3)
W1	C12	204.9(7)	C11	W1	C15	179.3(3)	C1	P1	H1	92(3)
W1	P1	242.3(2)	C13	W1	C15	91.5(3)	W1	P1	H1	121(3)
C11	O11	115(1)	C14	W1	C12	89.7(3)	F13	C1	F12	109(1)
C12	O12	113.6(7)	C11	W1	C12	89.7(3)	F13	C1	F11	106.7(8)
C13	O13	113.4(8)	C13	W1	C12	177.3(4)	F12	C1	F11	106.7(9)
C14	O14	115(1)	C15	W1	C12	89.6(3)	F13	C1	P1	115.0(8)
C15	O15	114(1)	C14	W1	P1	178.9(3)	F12	C1	P1	110.6(6)
P1	C2	186.8(9)	C11	W1	P1	90.5(3)	F11	C1	P1	108.4(8)
P1	C1	188(1)	C13	W1	P1	91.3(3)	F21	C2	F22	108.2(9)
P1	H1	135(8)	C15	W1	P1	89.4(3)	F21	C2	F23	108(1)
C1	F13	130(1)	C12	W1	P1	91.1(2)	F22	C2	F23	105.6(9)
C1	F12	130(1)	O11	C11	W1	178.7(8)	F21	C2	P1	111.6(7)
C1	F11	133(1)	O12	C12	W1	178.9(7)	F22	C2	P1	109.1(8)
C2	F21	131(1)	O13	C13	W1	177.9(8)	F23	C2	P1	113.9(7)
C2	F22	131(1)	O14	C14	W1	178.6(7)				
C2	F23	131.4(1)	O15	C15	W1	178.7(8)				

coupling constant is increased by 144 and 119 Hz, respectively. The ^{31}P NMR spectrum of $[W(CO)_5PH(CF_3)_2]$ is shown in Figure 8 (upper trace), compared with a calculated spectrum in the lower trace, exhibiting a large doublet splitting caused by the $^1J(PH)$ coupling and a further septet splitting by the $^2J(PF)$ coupling by two CF_3 groups. Each septet is surrounded by a set of tungsten satellites as well as sets of ^{13}C satellites. The iteration of the experimental spectrum exhibits a ^{13}C isotopic shift of the phosphorus nuclei of $\Delta(\delta(P(^{12}C)_2 - \delta(P(^{12}C^{13}C)) = 0.01$ ppm to higher field. The ^{13}C NMR spectra of $[W(CO)_5PH(C_6F_5)_2]$ and $[W(CO)_5PH(CF_3)_2]$ exhibit each two resonances in the CO region. One resonance of one CO group trans oriented to the phosphorus containing ligand and a large trans $^2J(PC)$ coupling of about 30 Hz and one resonance for the four CO groups cis oriented, with a considerably smaller $^2J(PC)$ coupling of less than 10 Hz. The more intense ^{13}C NMR signals of the cis-oriented CO groups exhibit nearly equal $^1J(WC)$ coupling constants of 125.6 and 124.5 Hz of the C_6F_5 and CF_3 derivative, respectively.

To assign the experimental vibrational spectra of the pentacarbonyl tungsten complexes of $HP(C_6F_5)_2$ and $HP(CF_3)_2$ we optimized their structures at different DFT levels.

The pioneering comprehensive study of monometal carbonyls by Jonas and Thiel found the BP86 functional to be well suited for predictive purposes of vibrational and geometric parameters.[27] The BP86 functional tends to underestimate the C−O stretching modes rather uniformly by some 20−40 cm^{-1} while the M−C stretching modes were accurate to within 20 cm^{-1}.[28] A recent study also uses this method for mixed phosphane carbonyl group VI metal complexes.[29]

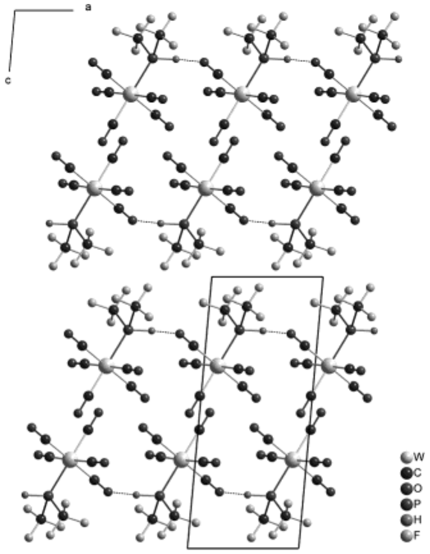

Figure 7. Unit cell packing of $[W(CO)_5PH(CF_3)_2]$ in the *a*, *c* plane indicating O−H contacts of 249(3) pm.

Structural optimizations and frequency analysis of the phosphane complexes $[W(CO)_5PH(C_6F_5)_2]$ and $[W(CO)_5PH(CF_3)_2]$ at the BP86 level of theory, using a LanL2DZ basis and ECP at the tungsten atom and a 6-311G(d,p) and a 6-311G(3d,p) basis set, respectively, for the ligand atoms, result in an unexpectedly good agreement between experimental and calculated harmonic frequencies for the $M(CO)_5$ moiety without the necessity of scaling factors, Table 7. On the other hand, the calculated vibrational frequencies of the phosphane ligands exhibit major deviations in comparison to experimental data. The underlying optimized structures overestimate the tungsten phosphorus and carbon phosphorus distances by means of 5 and 3 pm, respectively.

The use of a Becke's three-parameter functional with the nonlocal Perdew−Wang 91 correlation (B3PW91) gives a reasonably good agreement between experimental X-ray and theoretical structures, using the same basis functionals and ECP. The calculated bond lengths are slightly overestimated and agree within a range of less than 3 pm with the experimental value. The only exceptions are the P−H distances for which experimental values are naturally uncertain. The theoretical value of the P−H distance in $[W(CO)_5PH(CF_3)_2]$ of 141.2 pm compares with the experimental value of 135(8) pm within the error bars. Further geometric parameters of the optimized structure of $[W(CO)_5PH(CF_3)_2]$ with C_1 symmetry are as follows: [calculated]/X-ray $d(PW)$ [244.6]/242.3(2) pm, $d(PC)_{\varnothing}$ [189.4]/187.4 pm, $d(CF)_{\varnothing}$ [133.6]/131.1 pm, $d(WC_{tr})$ [202.5]/200(1) pm, $d(WC_{cis})_{\varnothing}$ [205.4]/203.4 pm, $d(CO)_{\varnothing}$ [114.1]/114.2 pm, $\angle(CPC)$ [100.0]/99.4(5)°, $\angle(CPW)$ [120.0]/118.8(3)°, and [119.8]/117.3(3)°. The calculated structure of $[W(CO)_5PH(C_6F_5)_2]$ with C_1 symmetry is described by the following data: [calculated]/X-ray $d(PH)$ [140.8]/129(4) pm, $d(PW)$ [250.5]/247.7(1) pm, $d(PC)_{\varnothing}$ [184.4]/182.8 pm, $d(CF)_{\varnothing}$ [132.9]/134.3 pm, $d(WC_{tr})$ [201.1]/201.1(6) pm, $d(WC_{cis})_{\varnothing}$ [204.8]/203.3 pm, $d(CO)_{\varnothing}$ [114.4]/115.5 pm, $\angle(CPC)$ [101.9]/100.4(2)°, $\angle(CPW)$ [124.8]/127.8(2)°, and [118.3]/113.5(2)°. The calculated values for the torsion of the C_6F_5 groups toward the C11P1C21 plane are specified by the dihedral angles C21−P1−C11−C12 and C11−P1−C21−C26. The

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(27) For example: Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474−8484. Jonas, V.; Thiel, W. *J. Chem. Phys.* **1996**, *105*, 3636−3648. Jonas, V.; Thiel, W. *Organometallics* **1998**, *17*, 353−360. Jonas, V.; Thiel, W. *J. Phys. Chem. A* **1999**, *103*, 1381−1393.

(28) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd ed.; Wiley-VCH: Weinheim, 2001; pp 130−136.

(29) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921−2930.

Table 7. Calculated Vibrational Frequencies on the BP86 and B3PW91 Levels of Theory and Observed Infrared and Raman Spectra of the $W(CO)_5$ Unit of the Complexes $[W(CO)_5PH(CF_3)_2]$ and $[W(CO)_5PH(C_6F_5)_2]$

	$[W(CO)_5PH(CF_3)_2]$								$[W(CO)_5PH(C_6F_5)_2]$							
mode desrpt	Infrared	Raman	BP86[a]	[IR][b]	(RA)[b]	B3PW91[a]	[IR][b]	(RA)[b]	Infrared	Raman	BP86[c]	[IR][b]	(RA)[b]	B3PW91[c]	[IR][b]	(RA)[b]
ν(PH)	2388 w	2386 (7)	2364.4	[1.8]	(87.0)	2446.0	[1.4]	(69.2)	2400 w	2411 (4)	2406.8	[0.2]	(41.8)	2491.7	[0.2]	(33.3)
ν(CO)	2095 s	2092 (22)	2072.3	[14.2]	(44.5)	2171.3	[13.1]	(41.5)	2084 s	2082 (27)	2069.4	[19.3]	(47.8)	2169.9	[17.0]	(42.4)
		1996 (100)	1997.5	[1.9]	(100)	2094.2	[2.0]	(100)		1996 (100)	1993.3	[3.0]	(100)	2091.2	[3.4]	(100)
	1960 vs, br	1958 (13)	1983.9	[46.9]	(70.3)	2076.3	[48.4]	(66.7)	1957 vs,br	1960 (42)	1977.2	[53.2]	(94.5)	2069.7	[56.0]	(83.1)
			1972.7	[100]	(2.8)	2064.8	[100]	(3.0)			1967.7	[95.6]	(8.0)	2061.4	[94.3]	(9.3)
			1971.9	[99.1]	(2.8)	2063.8	[99.6]	(2.9)			1963.9	[100]	(3.0)	2057.0	[100]	(2.6)
δ(MCO)	593 m		595.0	[4.1]	(0.0)	615.2	[4.3]	(0.0)	585 s. br		605.0	[0.5]	(1.2)	628.9	[6.4]	(0.1)
	568 s		570.1	[2.9]	(0.1)	590.6	[3.0]	(0.0)			577.3	[3.8]	(0.2)	599.2	[3.9]	(0.0)
			568.8	[3.2]	(0.0)	589.1	[3.4]	(0.0)			577.0	[2.8]	(0.0)	598.8	[3.2]	(0.0)
ν(MC)		487 (1)	475.6	[0.0]	(0.3)	497.3	[0.0]	(0.2)		485 (2)	479.0	[0.0]	(0.2)	501.4	[0.0]	(0.1)
		435 (27)	433.6	[2.4]	(20.1)	443.7	[1.6]	(18.7)		443 (27)	430.5	[0.1]	(4.1)	443.1	[0.2]	(5.8)
		429 sh	426.4	[1.8]	(5.1)	433.2	[0.5]	(1.9)		417 sh	429.7	[0.0]	(5.5)	437.5	[1.4]	(1.8)
			424.3	[0.0]	(4.7)	431.0	[0.0]	(2.7)			416.3	[5.3]	(2.3)	435.7	[3.4]	(4.6)
			410.2	[1.3]	(0.9)	427.5	[2.0]	(2.1)			410.1	[1.9]	(0.3)	428.6	[1.4]	(0.3)
	414 w		395.2	[1.3]	(0.1)	408.0	[0.2]	(0.2)	412 vw		404.8	[0.8]	(0.3)	422.9	[0.5]	(0.3)
δ(MCO)		370 (2)	358.7	[0.0]	(0.0)	374.4	[0.0]	(0.0)		373 (5)	356.4	[0.4]	(1.0)	373.7	[0.2]	(1.8)
δ(PMC)			355.1	[0.3]	(0.2)	372.3	[0.4]	(0.2)			355.8	[0.0]	(3.1)	372.9	[0.1]	(1.6)
ν(PW)		210 (6)	195.9	[0.4]	(1.8)	204.7	[0.4]	(1.3)			121.2	[0.0]	(0.4)	127.0	[0.0]	(0.3)
δ(CMC)		106 (47)	101.7	[0.0]	(0.2)	106.3	[0.1]	(0.2)		103 (68) br	90.1	[0.0]	(0.7)	94.7	[0.0]	(0.4)
			85.2	[0.0]	(2.7)	88.5	[0.0]	(2.1)			86.6	[0.0]	(3.8)	90.6	[0.0]	(2.7)
			83.5	[0.0]	(3.5)	86.8	[0.0]	(2.8)			85.0	[0.0]	(4.5)	88.7	[0.0]	(3.5)
			82.9	[0.0]	(3.9)	86.0	[0.0]	(3.2)			81.4	[0.0]	(3.6)	85.3	[0.0]	(2.7)
			75.8	[0.0]	(0.6)	79.3	[0.0]	(0.5)			76.9	[0.0]	(1.5)	80.8	[0.0]	(1.4)

[a] LanL2DZ basis and ECP on tungsten and a 6-311G(3d,p) basis set for the nonmetal atoms. [b] Relative intensities are given. [c] LanL2DZ basis and ECP on tungsten and a 6-311G(d,p) basis set for the nonmetal atoms.

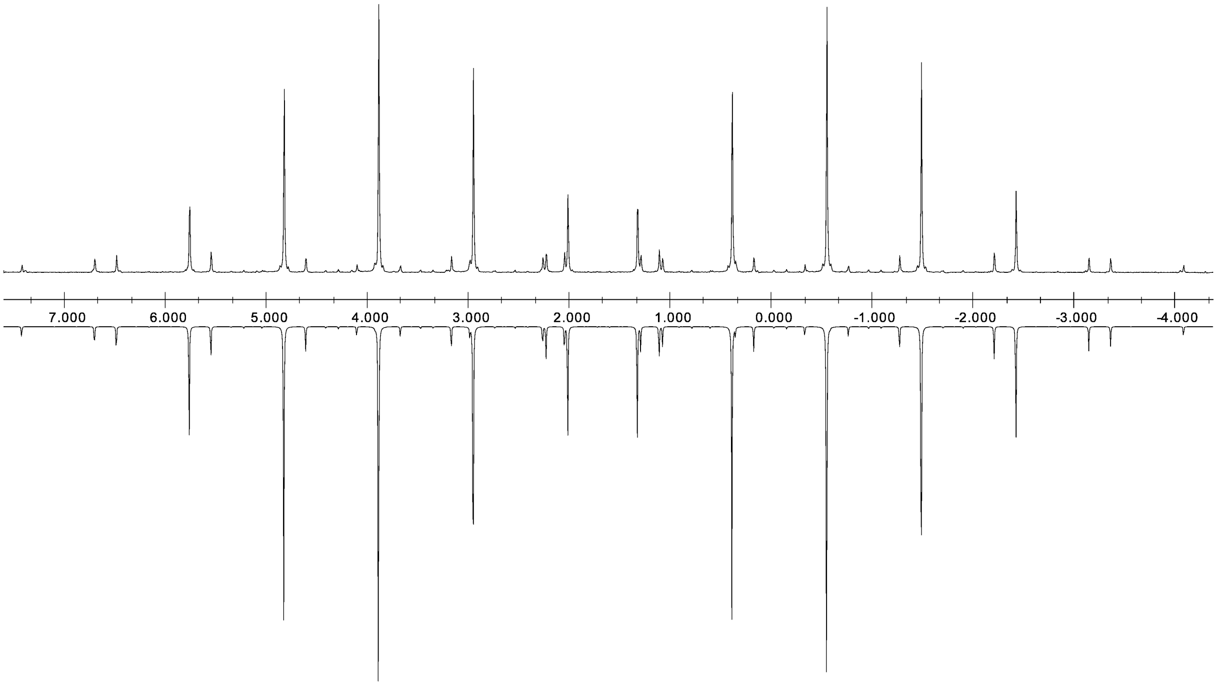

Figure 8. Experimental (a, upper trace) and simulated (b, lower trace) proton decoupled ^{31}P NMR spectrum of $[W(CO)_5PH(CF_3)_2]$.

comparison of the calculated values with experimental X-ray values exhibits significant deviations: [77.7]/60.45(1)° and [61.3]/57.91(1)°, respectively. This deviation is not surprising because the torsions of the C_6F_5 groups are strongly affected by packing effects.

If the B3PW91 functional is used, very good agreement between calculated and experimental vibrational frequencies of the phosphane ligands, and even the WC valence, the WCO deformation, and CWC deformation frequencies of the $W(CO)_5$ moiety, is achieved. The only exceptions are the CO valence modes, which are overestimated by 60−100 wavenumbers. Scott and Radom, 1996, investigated the performance of a variety of DFT functionals (BLYP, BP86, B3LYP, B3P86, and B3PW91) and developed a set of scaling factors for predicting vibrational frequencies. The use of Becke's one-parameter functionals BLYP and BP86 results in vibrational frequencies close to experimental data, i.e., scaling factors of 0.9945 and 0.9914, respectively, while the use of the Becke's three-parameter functionals, B3LYP, B3P86, and B3PW91, results in theoretical frequencies which have to be fitted by scaling factors of around $f = 0.95$.[30] Using the scaling factor of 0.9573 for the B3PW91 functional

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[30] Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.

with a 6-311G(d) basis, provided by Scott and Radom, we found a very good agreement between experimental and theoretical CO valence mode frequencies for the $W(CO)_5$ moiety, Table 7. The W−P valence mode of the complex $[W(CO)_5PH(CF_3)_2]$ could be assigned in the expected range[31] at 210 cm^{-1} in the Raman spectrum, while the comparable mode of the C_6F_5 derivative could not be assigned with absolute certainty.

To achieve a better comparability of the calculated frequencies of the phosphane ligands with the calculated modes of the noncomplexed molecules, the frequencies of the $HP(CF_3)_2$ ligand are listed as calculated in Table 5, while the frequencies of the $HP(C_6F_5)_2$ ligand are scaled by the same scaling factor already used for the noncomplexed molecule, Table 1. The theoretical vibrational modes of the complexed phosphanes are nearly identical with those calculated for the free molecules, as it is already observed for the experimental data. The unexpected weak influence on the P−H valence mode of $HP(CF_3)_2$ and $HP(C_6F_5)_2$ by complexation with tungsten pentacarbonyl is supported by theoretical calculations. Additionally, as a result of the increased π-acidity of $HP(CF_3)_2$ compared with $HP(C_6F_5)_2$, the calculated W−P distances of the pentacarbonyl tungsten complexes are shortened by 5.9 pm (B3PW91) for the $HP(CF_3)_2$ derivative, which is in impressively good agreement with the experimental value of 5.4 pm.

Acknowledgment. We are grateful to Prof. Dr. D. Naumann for his generous support and the Fonds der Chemischen Industrie for financial support. We thank Dr. W. Tyrra and Dr. K. Glinka for helpful discussions. Dr. L. Packschies is acknowledged for providing a Perl-script program, g98 frequency finder.[32]

Supporting Information Available: Crystallographic files in CIF format for the compounds $HP(C_6F_5)_2$, $[W(CO)_5PH(C_6F_5)_2]$, and $[W(CO)_5PH(CF_3)_2]$. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures of $HP(C_6F_5)_2$, $[W(CO)_5PH(C_6F_5)_2]$, and $[W(CO)_5PH(CF_3)_2]$ reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-200227, CCDC-200228, and CCDC-200229, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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[31] Guns, M. F.; Claeys, E. G.; van der Kelen, G. P. *J. Mol. Struct.* **1980**, *65*, 3−17.

[32] Program available at http://www.uni-koeln.de/themen/Chemie/software/g98ff/.